Influence of coupled diffusion and viscous creep on the composition of metasomatic reaction bands

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We explore the feedback between reaction induced stress and component diffusion. Rim growth experiments in the system MgO-FeO-SiO$_2$, where orthopyroxene reaction rims were grown between olivine and quartz were made. Two different matrix-inclusion arrangements were used: In a single capsule vol. 10% of olivine grains (150 µm grain size) were immersed in a polycrystalline quartz matrix and, in a second compartemeent, the opposite matrix-inclusion arrangement was chosen using the same starting materials (San Carlos Olivine and synthetic quartz). The orthopyroxene rims that were formed around quartz inclusions in the olivine matrix were 11.6 µm after 80 hours run duration, in contrast, the orthopyroxene rims that formed around olivine inclusions in the quartz matrix were only 6.1 µm thick on average. Provided that run conditions and water fugacities were similar in both compartments of the assembly, this suggests mechanical feedback of the matrix with the rim growth reaction. We present a rate law for diffusion controlled reaction rim growth in spherical geometry and link it to the accommodation of the volume change of reaction by viscouse creep. For the experimental conditions of 1000°C, 1 GPa and a strain rate of $10^{-6}$ s$^{-1}$ we infer a transition from diffusion controlled growth to creep controlled growth for effective bulk viscosities on the order of $10^{16}$ to $10^{17}$ Pas. In the diffusion controlled regime, growth zoning with sharp compositional gradients within the reaction rim may develop due to local equilibrium constraints. If viscouse creep takes over rate control, compositional gradients across the growing rim tend to degrade and the original growth zoning may be obliterated. Pronounced growth zoning observed in many naturally formed reaction rims may thus be taken as an indication of diffusion controlled growth.

Transport, interface and rheological controls on the kinetics of mineral reactions

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We investigate three examples of reaction microstructures and textures using electron and ion beam techniques with high spatial resolution. In particular we are interested in the role of diffusion, interface energy and rheology during mineral reactions and their influence on microstructure and texture evolution. This is motivated by the notion that the latter determine geo-materials macroscopic properties.

First we discuss findings from natural and synthetic examples that corroborate fast diffusion along grain and phase boundaries. There diffusion may be enhanced by the presence of an amorphous phase even at homologous temperatures well below unity. In the context of reaction rim formation short circuit diffusion along grain and phase boundaries may lead to complex chemical patterns with equilibration domain sizes well below the grain size. In a second example we explore the potential of Cahn-Hilliard theory to describe mineral exsolution. We present numerical models of exsolution in ternary feldspar, which are compared with microstructures and chemical patterns from natural perthites. From this comparison we infer that fractionation of the anorthite component into albite-rich exsolution lamellae may be rate limiting during the coarsening stage, because of slow Al-Si interdiffusion in the silicate framework. The anorthite content of albite-rich lamellae appears to be a sensitive and robust monitor of the cooling history. Finally, we explore the feedback between reaction induced stress and component diffusion. Rim growth experiments in the system MgO-FeO-SiO$_2$ seem to indicate that, provided the materials involved are mechanically strong, reaction induced stress may slow down or even quench net transfer reactions. Our analysis indicates that the rheologies of polycrystalline quartz and olivine are well within the range of mechanical properties required for deformation by creep to take over reaction rate control.
Behavior of water during terrestrial planet formation

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Recent planetary formation theory suggests two stages of planetary accretion; the stage of runaway growth (e.g., Kokubo and Ida, 1998) followed by the stage of giant impacts (e.g., Chambers and Wetherill, 1998). Here, I discuss the behavior of water during terrestrial planets formation from theoretical points of view.

Usually, the solar nebula is thought to be too warm to form hydrous minerals at 1 AU from the Sun, so hydrated material is not available in planetesimals. However, recent theory suggests cool nebula, so that large amount of water can be trapped in planetesimals. Such water is lost during accretion, but substantial amount of water can be trapped in Mars-sized protoplanets formed during the stage of the runaway growth (Machida and Abe, 2007). Expected water content is size dependent; larger bodies retain water, but smaller bodies are dry. This may imply protoplanets are somewhat wetter than meteorites.

Accretion of water-bearing planetesimals results in many phenomena (Abe et al., 2000). Impact degassing would form a proto-atmosphere. A hydrous magma ocean can form in response to the thermal blanketing effect of an early proto-atmosphere. In addition, a large amount of hydrogen may be partitioned into metallic iron under high pressure, and delivered to the core.

In the stage of giant impacts, addition of material from large bodies beyond the orbit of Mars may transport water to the Earth region (e.g., Lunine et al., 2007). Giant impacts would remove some amount of water, but substantial amount survives them (Genda and Abe, 2003). Moreover, loss rate depends on the surface environment of protoplanets. On protoplanets with oceans, giant impacts result in relative enrichment of water against other gases, because gas species are efficiently blown away by the impact, while water ocean survives (Genda and Abe, 2005). Thus, planets those experienced giant impacts with oceans (Earth?) are likely enriched in water than those without oceans (Venus?) or those experienced no giant impacts (Mars?).

References

Li isotopes and Li/Ca measured in foraminifera via SIMS and MC-ICP-MS

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Lithium has a residence time within Earth’s oceans of ~1.5 Ma. Perturbations in the recorded Li isotope composition of seawater beyond this residence time likely reflect changes in competing fluxes of Li derived from continental silicate weathering and hydrothermal circulation. The importance of continental weathering in regulating global climate has led to great interest from several groups in ground-truthing and examining temporal records of lithium archived within foraminiferal tests. In this study we attempt to further our understanding of Li isotopes hosted within foraminiferal carbonate using a combination of in-situ SIMS and MC-ICP-MS analysis with which to measure Li/Ca and δ7Li. We find single specimens of G. truncatulinoides measured by SIMS show, in keeping with other more traditional trace metal concentrations, significant Li/Ca variation throughout the foraminiferal test that cannot be attributed to contaminant phases. Initial in situ lithium isotope ratios also allude to isotopic variation most likely reflecting depth migration during ontogenic stages of biomineralisation.

These observations can be put into context by our high precision MC-ICP-MS study of multiple specimens, sampled from five ocean basins. Deeper dwelling species record decreasing lithium isotope ratios with increasing depth of habitat. Although we document no variation in the lithium isotope composition of modern seawater we observe significant (~2 %) variation between surface dwelling Holocene G. sacculifer and G. ruber from several ocean basins. These lines of evidence are indicative of an environment control on the isotopic fractionation of lithium during biomineralisation, as previously proposed for Li/Ca incorporation.

This characterisation of lithium isotopes makes deconvolving variations in weathering intensity from variations in environmental forcing in Neogene records problematic. Using a multi-proxy approach however, down core variations in the lithium isotopic composition of foraminifera may yield valuable information on past weathering fluxes and climatic conditions.
Lead isotopes on lavas from the different evolution stages of Koolau Volcano—subaerial Makapuu stage, main shield stage lavas from the Koolau Scientific Drilling Project (KSDP) and Honolulu Volcanics (HV)—have identified three end member components in Pb isotope space: Makapuu, Kalihi, and a depleted component unique to the rejuvenated stage HV (Fekiacova et al., 2007). When plotted against SiO₂, the Pb isotope data define two trends consistent with a ternary mixing: a negative correlation defined by shield stage building lavas and a positive correlation defined by the post-erosional HV. Similarly, CaO/Al₂O₃ ratios, a proxy for pyroxene-to-garnet ratio in the source are negatively correlated with Pb isotope ratios and demonstrate the co-existence of peridotite and eclogite in the Koolau source.

The approach was extended to other Hawaiian volcanoes from the two geographic alignments Kea and Loa which have been shown to be compositionally distinct in Pb isotope space (Abouchami et al., 2005). CaO/Al₂O₃ and Pb isotope ratios display a negative correlation at the scale of the whole chain: most Kea-trend lavas cluster at high Ca/Al ratios (0.8) while Loa-trend lavas display a large range (0.6-0.7), overlapping Koolau data, with Makapuu lying at the extreme low end of the correlation. This coupled major-element-Pb isotope variability in Hawaii is interpreted in terms of mixing of pyroxenite and peridotite, in agreement with previous studies (Sobolev et al., 2005; Ren et al., 2005; Herzberg, 2006). Mixing calculations show that most Kea lavas are derived from a mantle peridotite source with small amounts of pyroxenite (10-20%) whereas Loa lavas contain up to 90% of the eclogitic (pyroxenite) component. In addition, the proportion of this component along the Loa track decreases with decreasing age of the volcano (~90% in Koolau to 50-70% in Mauna Loa). This feature might be related to a change in the thickness of the lithosphere along the Hawaiian chain. This suggestion is sustained by seismic data showing a thinning of the lithosphere from 100 km under Big Island to about 50-60 km under Kauai (Li et al., 2004), and also the observation that the amount of recycled component in mantle-derived melts is partly controlled by the thickness of the lithosphere (Sobolev et al., 2007). Alternatively, changes in potential mantle temperature across the Hawaiian plume might produce variations in the composition of the melts (Herzberg, 2006).

The major-element Pb isotope correlation demonstrates that the Pb isotope “bilateral asymmetry” (Abouchami et al., 2005) also extends to the ratio of peridotite to pyroxenite in the source of the Hawaiian mantle plume.

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Age and origin of Mars

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Mars may have formed via runaway growth within ~1 Myr or its accretion may have been more protracted and involved large impacts. Hf-W chronometry ought in principle to be able to distinguish between these two scenarios but reported Hf-W ages for Mars range from <1 Myr to ~12 Myr [1-4]. This range in ages is mainly due to different assumptions regarding the Hf/W ratio of the Martian mantle [5]. Th/W ratios of Martian meteorites are relatively constant and hence can be used to constrain the Hf/W ratio of the Martian mantle [5]. This approach requires knowledge of the Hf/Th ratio of the Martian mantle, which is generally assumed to be chondritic. The chondritic Hf/Th ratio however is not well constrained and potential variations in Hf/Th ratios among different chondrite groups have not been investigated. We developed analytical techniques for the precise determination of Hf/Th ratios by isotope dilution and present an improved determination of Hf/Th ratios in chondrites. This is used to better constrain the Hf/W ratio of the Martian mantle and the age of Mars. Our new Hf and Th concentration data reveal that carbonaceous chondrites have lower Hf/Th ratios than ordinary chondrites. The calculated Hf/W ratio of the Martian mantle therefore depends on assumptions regarding the bulk composition of Mars. For instance, using our new estimate for the Hf/W ratio of the Martian mantle, two-stage W model ages of ~7 Myr and ~4 Myr are calculated for an ordinary and carbonaceous chondrite-like composition of Mars, respectively. These ages change to ~15 Myr and ~13 Myr if one assumes that Mars accreted at an exponentially decreasing accretion rate and complete metal-silicate equilibration was always achieved. These ages would further increase if metal-silicate equilibration was incomplete. In spite of this model-dependence, Hf-W chronometry provides important constraints on the age and origin of Mars because the two-stage model age corresponds to the earliest time when core formation could have been completed [6]. Hence, based on our new estimate for the Hf/W ratio of the Martian mantle, it seems unlikely that Mars had entirely been accreted in less than ~1 Myr. This suggests that Mars is probably not a stranded planetary embryo and that its formation history was similar to that of the larger terrestrial planets.


Re-Os depth profile of the upper mantle beneath Central Europe

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Variations in Re and Os concentrations in upper mantle rocks from various geotectonic environments raise the question of whether they reflect primary or secondary processes. Recent studies have shown that Re can be metasomatically imported from subducting oceanic crust or by basaltic melt metasomatism. Osmium is a compatible element and its concentration mostly remains close to PUM estimates during various mantle processes, although addition of Os from subducting slabs can introduce radiogenic Os.

Rhenium and Os concentrations, and Os isotopic data were determined for a well-characterized suite of upper mantle xenoliths sampled from beneath the Kozákov volcano (5 Ma), of the Bohemian Massif (Czech Republic). This suite of mantle xenoliths represents the upper mantle profile composed of 3 different layers, from 33 to 70 km. The xenoliths underwent 7-15% partial melting and subsequent LILE enrichment by percolation of volatile-rich melt, which was not associated with recent volcanism. These processes were more intensive with increasing depth.

The samples have highly variable, but generally low Re and Os concentrations of 6–28 ppt and 0.2–2.1 ppb, respectively, and relatively uniform 187Os/188Os (0.1219–0.1276). Thus, they have Os isotopic compositions within the range of estimates of the modern convecting upper mantle. The Os concentrations and 187Re/188Os significantly vary with depth with the lowest Os and highest (but subchondritic) 187Re/188Os at the greatest depths (~70 km). Precise age of partial melting could not be determined because of evident perturbation of the Re-Os system. However, Lu-Os “ages” point to ~1.0 Ga depletion event, if the samples affected by perturbation are excluded.

The low Os concentrations and strongly subchondritic Re/Os ratios in some samples imply that Os was removed from the system at some stage of mantle evolution. We suggest that Os was removed during percolation of high-temperature sulphur-undersaturated melt causing sulfide breakdown and Os (and Re) removal. Our data suggest that such processes may affect large proportions of the upper mantle and could significantly modify the Os composition of the Earth’s subcontinental lithospheric mantle.
Antimony speciation in shooting ranges and its association with iron oxides

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Antimony compounds are known as environmental pollutants that may pose a serious threat to human health. The toxicity and bioavailability depends on the speciation of Sb. Antimony salts are known to be more toxic than other Sb compounds, and Sb$^{3+}$ is more toxic than Sb$^{5+}$. Sources of Sb contamination are smelters, emissions from the coal power plants, mining activities, vehicular traffic, and shooting activities. The bullets used for shooting practice contain Pb, Sb and Fe. In Switzerland alone, the estimated annual input of Sb into the environment by these activities is approximately 6 tons. Analyses of the soils at the shooting ranges revealed Sb concentrations of up to 5900 ppm, significantly above the estimated global average concentration in soils of 0.5 ppm (Reimann and De Carritat, 1998). Knowledge about secondary Sb-bearing phases formed during weathering of the bullets is crucial in order to assess the mobility and bioavailability of Sb in these environments.

Our results on weathering crusts around bullets show that various major Sb-bearing phases can be distinguished depending on the soil chemical conditions. Fe-rich phases always represent a major Sb host in the crust irrespective of the sampling site. Element distribution maps and quantitative analyses with an electron microprobe showed a correlation between Sb and Fe. X-ray diffraction analyses revealed that the crystalline Fe oxides are goethite and lepidocrocite. Raman spectroscopy of individual Fe-rich areas confirm the XRD results. The elevated background in the XRD patterns is attributed to ferrihydrite and organic material. In which way Sb is bound to these Fe oxides is not known to date and cannot be solved by the above mentioned techniques.

Knowledge about the geometry and binding behavior of sorbed Sb on different Fe oxide surfaces will help to evaluate the mobility of Sb in this system. Therefore, we collected Sb K edge EXAFS spectra of synthetic goethite, lepidocrocite, and ferrihydrite with different Sb surface loadings relevant to our field samples. The evaluation of these spectra will provide information about the Sb complexes on the surface of the iron oxide minerals. The comparison of these results with the spectra of the natural samples will then allow to describe the behavior of Sb associated with Fe oxides in the weathering crusts of the corroding bullets. The EXAFS studies are also important to numerous other sites polluted by Sb (e.g., acid mine drainage sites) where Fe oxides are known to act as scavengers of pollutants, for example Sb.

Reference

Using oxygen isotope and magnetism to reconstruct the paleotemperature framework of ancient travertine deposits in Death Valley, CA

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In the light of astrobiology research, studies of modern and ancient hydrothermal systems have illuminated our understanding of the origin and early evolution of the biosphere and highlighted the potential for life to develop in such environments on Mars and beyond. The recent discovery of iron oxides by Mars Rover Mission excited us for existence of water in the past, and possibility to find fossil life form in rocks. Oxygen isotope study may give us important information to interpret the geological history on Mars surface. Comparative studies of the sedimentology magnetism and geochemistry of modern and ancient analog systems are important with the particular goal of evaluating the paleotemperature regime and diagenesis. Such proxies allow better understanding of capture and retention of fossil biosignatures.

We developed a method to reconstruct a paleotemperature regime of fossil (Plio-Pleistocene) hydrothermal system in the Furnace Creek area of Death Valley, CA, USA.

To estimate the formation temperature for each fabric type, we applied the empirical equation of Kim and O’Neil (1997). Results showed that isotopic signatures of the Death Valley travertine sinters were correlated with paleotemperature environment and we show that the qualitative temperature relationships between fabric types were preserved. In addition the fabric type paleotemperature indicators are compared with magnetic paleotemperature indicators.
Ab initio molecular dynamics study of Ca\(^{2+}\) in water: Speciation as a function of P,T, and pH

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Ab initio molecular dynamics (AIMD) simulations of Ca\(^{2+}\) in water have been performed at \(\{T=300 \text{K}, P=0.3 \text{GPa}\}\), \(\{T=500 \text{K}, P=0.5 \text{GPa}\}\), and \(\{T=900 \text{K}, P=0.9 \text{GPa}\}\). The water coordination of the Ca\(^{2+}\) ion is found to increase from 6 at \(\{T=300 \text{K}, P=0.3 \text{GPa}\}\) to an average of 7 at \(\{T=900 \text{K}, P=0.9 \text{GPa}\}\). On the time scale of 20 ps no chemical changes such as the formation of Ca(OH)\(^+\) or Ca(OH)\(_2\) were observed for the periodic Ca\(^{2+}\) + 63 H\(_2\)O system. Coordination constrained AIMD simulations [1-3] have been carried out to determine the free energy barrier for dissociation of a H\(_2\)O molecule in the first solvation shell.

When CaO is introduced into a unit cell containing 62 H\(_2\)O molecules, Ca\(^{2+}\) and 2 OH\(^-\) are formed within femtoseconds. Subsequently, the two species are found to form transient Ca(OH)\(^+\) and Ca(OH)\(_2\) complexes. At \(\{T=500 \text{K}, P=0.5 \text{GPa}\}\) we predict the relative average concentrations 3%, 26%, and 71% for the species Ca\(^{2+}\), Ca(OH)\(^+\), and Ca(OH)\(_2\), respectively, while at \(\{T=900 \text{K}, P=0.9 \text{GPa}\}\) we obtain 4%, 35%, and 62%.

References

Combining CSIA with ground water dating: A first step toward the determination of in-situ PCE degradation rates

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Method and field site description
In order to predict the fate of organic pollutants in groundwater systems it is essential to know degradation rates. The combination of compound-specific stable isotope analysis (CSIA) with transient groundwater tracer techniques allows determining degradation rates in situ.

To demonstrate the feasibility of this concept, a former industrial site was investigated. Due to leakage of perchloroethene (PCE) solvent tanks, PCE as well as its transformation products trichloroethene, cis-dichloroethene and vinyl chloride were detected in ground water in concentrations up to 50 mg/L. We measured carbon stable isotopic signatures of these compounds and performed tracer-based ground water dating to determine the efficiency and typical biodegradation rates of these pollutants under natural conditions.

Principle findings and discussion
Along selected flow pathways, the isotopic signature \(\delta^{13}C\) of PCE changed from -24 \% up to -1 \% (vs. VPDB), which was a clear evidence for on-going degradation. Using a simple Rayleigh evaluation scheme and a set of isotopic enrichment factors deriving from literature, a range of degree PCE-biodegradation was calculated. However, since the published enrichment factors differ for more than an order of magnitude, the degree to which amount PCE was degraded could not reliably be determined. If the relevant enrichment factor of the site would be known, the biodegradation could be exactly quantified from isotopic data. Together with the determined local \(^{3}H-^{3}He\) ground water age differences of more than 20 years, PCE degradation rates can be obtained.

As \(^{13}C\) enrichment along with increasing water residence time was also observed in all the transformation products, the total dechlorination of PCE to non-toxic products was evident. However it remains open whether the degradation of the intermediates is complete.

Conclusions and outlook
In order to track and to quantify the degradation of chlorinated ethenes, the site-specific enrichment factor has to be determined. Such work is in progress and will allow us to obtain the effective degradation rates under the natural conditions being characteristic for our contaminated field site.
A noble gas record of groundwater recharge, paleoclimate, and mantle degassing in the North China Plain

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The North China Plain (NCP) is the largest alluvial plain in East Asia. It is one of the most densely populated areas of the world with great agricultural importance for China. The climate is continental semi-arid, with most of the about 600 mm/yr of precipitation falling during the East Asian monsoon season in summer. Intensive groundwater use for irrigation has led to strong drawdown of the potentiometric surface.

The study of the aquifer system in the NCP, in particular of groundwater recharge and its dependence on climate conditions, is therefore of vital interest. We present noble gas, stable isotope and radiocarbon data from 52 groundwater wells in the NCP that provide information on groundwater recharge in the piedmont plain, paleoclimate in the central plain, and mantle He degassing in the coastal plain.

In the unconfined aquifer of the piedmont area, tritium-bearing waters with 3H-3He ages younger than 40 yr are found down to depths of more than 10 000 m, indicating rapid vertical infiltration. The corresponding recharge rate of about 1 m/yr exceeds precipitation and can only be explained by recycling of groundwater pumped for irrigation. Effects of the anthropogenic modification of the recharge regime are also apparent in Ne excesses and stable isotopes.

Paleowaters with 14C ages up to nearly 40 kyr are found in the deep confined aquifers of the central plain. Noble gas temperatures indicate a glacial cooling of 4 - 5 °C relative to the holocene. However, the coldest period of the last glacial maximum is not represented in the record, presumably because recharge was limited during this extremely arid phase. Depletion of the stable isotopes in the paleowaters can be ascribed to cooling and increased monsoon intensity.

The deep groundwater from the coastal region is near the limit of 14C dating and exhibits the highest He excesses. While the excess He in the central plain has a radiogenic signature (3He/4He = 6·10^{-8}), the 3He/4He ratio increases in the coastal plain by an order of magnitude. This unusual feature clearly indicates the presence of a mantle He component, which can be attributed to known fault zones. Mantle He has also been observed in hydrocarbons from this area.

B isotope study on Tourmalines and Axinites in hydrothermal systems: Insights into fluid circulation

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Boron isotope compositions were determined in tourmalines and axinites from three different geological contexts in Western Anatolia, linked by the emplacement of granitic intrusion at crustal levels.

In Kadıkalesi (Bodrum), tourmalines in a Late Miocene monzodioritic pluton have low δ11B (-9‰), whereas tourmalines hosted in veins cutting the intrusion and in younger aplitic dikes show higher values of -6 ‰.

In Sinancilar, Menderes Massif, magmatic tourmalines of Early Miocene granitic-granodioritic body, and those belonging to late veinlets cutting the granite, have similar values (δ11B ≈ -4‰), whereas a progressive δ11B lowering is observed in tourmaline veins in host rocks away from the plutonic body (-7‰).

Thus, δ11B increasing in late hydrothermal tourmaline is observed in Bodrum, and the opposite is found in Menderes Massif. This different behavior between magmatic and late magmatic-hydrothermal tourmaline suggests that δ11B variations are mainly controlled by different proportion between magmatic and hydrothermal fluids, more than fluid-mineral isotopic fractionation.

In Maden Adası (Ayvalık), an Early-Middle Miocene volcano-sedimentary complex was subjected to extensive contact metamorphism. Axinites crystallized in Calcsilicate rocks of thermo-metamorphic aureola, from low-T to high-T rocks. The systematic variation of δ11B from -12.6‰ in the lower metamorphic degree samples to -7‰ in the higher temperature rocks, is mainly attributed to B isotope fractionation between circulating fluids and mineral.

Therefore, fluid-mineral boron isotope fractionation seems to play a major role when different B coordination occurs between fluids and crystallizing phases, like trigonal-B in fluids and tetragonal-B in axinites, whereas it is less important in the fluid-tourmaline (both trigonal-B) system.
Evolution of upper mantle in Southern Sanandaj – Sirjan zone of Iran

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In the Southern Sanandaj – Sirjan zone (Iran), there are several ultramafic complexes such as Kuhshah, Soghan and Abdasht. They have many evidences for belonging to the upper mantle and contain dunite, harzburgite and chromitite that in some parts, have been invaded by pyroxenitic intrusions. They show some evidences in various scales for evolution of upper mantle in this part of Iran. In the field, there are many pyroxenite veins and dykes that have been cut ultramafic sections and implies that upper mantle in this area have partially melted and then, resulting melts, have perculated in the other parts of the complexes and impregnated them. In microscopic scale, existence of second generation of orthopyroxene, clinopyroxene, olivine and euhedral chromespinels indicate strong percolation and melt/rock interaction in the upper mantle of the area. First generation minerals are large elongated and deform grains, while second ones have crystallized as small interstitial grains without any deformation. From mineral chemistry point of view, there are also two generation of minerals with different chemical composition. For example, first generation orthopyroxenes (Opx1) rich in compatible and depleted in incompatible elements relative to second generation ones, (NiO in Opx1=0.16 w% and NiO in Opx2=0.07 w%). In clinopyroxenes and olivines, there are similar properties too. Geochemical data on whole rocks indicate harzburgites are depleted mantle rocks that have partially melted and then invaded and impregnated by silicate ascending melts. REE patterns of these harzburgites show depletion relative to primitive mantle, but LREE enrichments relative to MREE are evident. This feature can be produced by entrance of more incompatible REE(LREE) from melts to the harzburgites. All of these evidences indicate upper mantle in Sanandaj-Sirjan zone, have been affected by partial melting and melt/rock interaction so there is strong heterogeneity in various scales in this part. The ultramafic complexes of Sanandaj-Sirjan have ascent and emplaced in the crust tectonically, and textural features show reequilibration in crustal conditions.

References

Geology, mineralogy, and genesis of the Iwami-Ginzan silver mine, Japan

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The Iwami-ginzan silver mine produced an enormous amount of silver following its discovery in 1309, and thus played a very important role as a major silver producing field, not only in Japan, but also at a global scale. The Iwami-ginzan silver deposit contains two types of ore bodies named the Fukuishi and Eikyu deposits: the former is disseminated type, and the latter vein-type. They are related to the dacite intrusion generated during the Pleistocene epoch of the Quaternary (Sakota et al. 2000).

The ore minerals of the Eikyu deposit are native silver, argentite, electrum, matildite, polybasite, stromeyerite, silver-bearing tetrahedrite, aikinite, Bi-bearing polybasite, wittichenite, tetrahedrite-tennantite, enargite, chalcopyrite, chalcocite, galena, sphalerite, and pyrite. The genetic temperature may be about 200°C. The disseminated Fukuishi deposit contained not only native silver, argentite and hematite but also jalpaite, mackinstyrite, pearceite, stromeyerite, and chlorargyrite. The genetic temperature of the Fukuishi deposit might be about 100°C.

There is a significant gravity anomaly in the Iwami-ginzan area, indicating existence of a cauldron, and the Iwami-ginzan is situated at the rim of the cauldron. During the Neogene, hydrothermal solutions are considered to have repeatedly infiltrated the faults and fractures in and around the cauldron. The hydrothermal solutions which produced the Iwami-ginzan silver mine also passed through these pre-existing faults and fractures. The very high ore grades in the Iwami-ginzan silver mine may have been caused by remobilization of earlier mineralization, and hence are the product of multiple episodes of ore genesis.

References
Sulphur isotopic composition of volcanic-hosted sulphide deposits at the Neoarchaean greenstone belts and the Belomorian mobile zone (Baltic Shield): A comparative study

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In the NE Baltic Shield the Late Archaean (2.81 – 2.76 Ga) greenstone belts and the Belomorian mobile zone (BMZ) comprise massive sulphide deposit associated with host volcanics. Sulphur isotopes in pyrite from the ores have been studied.

Generally the two types of Late Archaean greenstone belts are distinguished in the Baltic Shield: 1 – with prevalence of basic–ultrabasic metavolcanics; 2 – with predominance of felsic volcanic rocks. Within the BMZ the massive sulphide ore is associated with medium to felsic metavolcanics. In all the mentioned structures the sulphide ores constitute thick extensive bodies.

Discussion of results

Sulphur isotope composition in pyrite from the massive sulphide deposit of the 1- type greenstone belts resembles that of meteorite. In the latter $\delta^{34}S$ insignificantly varies within $-2 - +1^{\circ/o}$. In the massive sulphide deposit from the 2- type greenstone belts, dominated by felsic volcanics, the sulphur isotopes range more considerably $\delta^{34}S = -6 - +4^{\circ/o}$. The sulphide ore of the BMZ has even wider span of sulphur isotope composition $\delta^{34}S = -12 - +6^{\circ/o}$.

Conclusions

Pronounced variance of sulphur isotope compositions in the massive sulphide deposits associated with different volcanics of the Neoarchaean greenstone belts has been revealed. This may be explained by divergent depth of ore-producing magmatic chambers, which caused discrepant fractionation of sulphur isotopes.

In the BMZ the widest range of sulphur isotope compositions with evident trend to lighter isotope enrichment is caused by variable sulphur influx from both crustal and upper mantle sources in the spreading zone tectonic setting.

Ghost primordial He and Ne

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The canonical view of He isotope geochemistry holds that high $^3\text{He}/^4\text{He}$ and solar Ne in oceanic basalts fingerprint hidden undegassed mantle sources. Competing evidence of recycled material processed next to the Earth’s surface being present in the source of Hawaiian basalts is nevertheless very strong, whether it be carried by oxygen or Hf isotopes.

We here discuss the marble-cake paradigm in the light of Shuster et al.’s (2003) diffusion data on olivine. The closure temperature for diffusion of $^3\text{He}$ is $\sim 200^{\circ}C$ and the data show that He moves around remarkably fast, e.g., more than 1 km at 1500 $K$ and more than 5 km at 2000 $K$ within 1 Gy. Ever since the accretion of the Earth, He and Ne originally hosted in primordial material therefore pervaded all the lithologies coexisting on length-scales typical of a marble-cake mantle (1-100 m), and, in particular, contaminated U- and Th-poor refractory residues tightly folded in with streaks of primitive mantle. Dunite and harzburgite residues left by ridge activity, and their high-pressure equivalents, therefore act as long-term sinks for ‘ghost’ rare gases. Conversely, such restites also act as a source of primordial rare gases for whichever recycled material gets subsequently folded in during the rest of the Earth’s history, even long after most of the primordial material has been removed by processing at mid-ocean ridges. A numerical marble-cake diffusion model with suitable parameters can reproduce the uptake of primordial gases initially present in the primordial lower mantle by background refractory residues and its subsequent transfer to younger ‘layers’ of recycled pyroxenite. Both low- and high-$^3\text{He}/^4\text{He}$ hotspots may be produced by changing the duration of the diffusion process and the U and Th contents of refolded pyroxenite layers.

Upwelling beneath mid-ocean ridges happens much too fast (<100 My) for the refractory material to be flushed clean of primordial gases by diffusion. However, once back into the deep mantle, primitive-looking He and solar Ne from these refractory layers have plenty of time to permeate into all sorts of newly neighboring layers, whether recycled or primitive. Decoupling by diffusion certainly explains the lack of coherence between $^3\text{He}/^4\text{He}$ and lithophile isotopic tracers. Although rare gas isotopes require that the upper mantle is more outgassed than the lower mantle as a whole, neither He with high $^3\text{He}/^4\text{He}$ nor solar Ne in basalts are diagnostic of the presence of primordial material in the source itself. Likewise, the missing terrestrial $^{40}\text{Ar}$ is likely to be another ghost rare gas hosted largely by refractory residues, thus essentially voiding a widely used constraint on the proportion of undegassed solid mantle.

References

Biogeochemistry of plutonium and uranium in intertidal sediments

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Intertidal sediments of the NE Irish Sea basin contain elevated levels of transuranic and other nuclides derived from the authorised low level discharges to sea made by the Sellafield fuel reprocessing plant. The majority of the discharges occurred more than 25 years ago and the radionuclides have now become incorporated in offshore and intertidal sediments. These sediments provide a rare opportunity to explore the behaviour of artificial radionuclides in the natural environment. Microbially-driven redox cycling occurs in the sediments and this has been linked to seasonal variations observed in transuranic element solubilities.

Poised microcosm experiments were established using these sediments, and nitrate-, iron- and sulfate-reducing conditions developed. Radionuclide concentrations were measured by alpha spectrometry (234,238U; 238,239,240Pu) and high resolution ICPMS (235,236U). The microbial communities were characterised by DNA/RNA extraction and PCR amplification, followed by cloning and sequencing.

In the poised microcosms, plutonium solubility is enhanced approximately 6-fold in both nitrate- and iron-reducing conditions, with smaller changes in uranium solubility. Neither uranium nor plutonium are affected by sulfate-reducing conditions. 234U is more soluble than 238U, consistent with the establishment of disequilibrium, but this effect is even greater for the artificial isotope 236U, which can be used as an indicator for technogenic uranium.

The onset of nitrate-, iron- or sulfate-reducing conditions is accompanied by substantial shifts in microbial community structure, and both DNA- and RNA data give similar outcomes. In nitrate- and iron-reducing conditions, the communities are dominated by known nitrate- and iron-reducing organisms respectively. In the sulfate-reducing microcosms, known sulfate-reducers comprise only a small proportion of the community.

References

Solubility measurements of Neptunium-incorporated soddyite

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Spent nuclear fuel is likely to alter to uranyl minerals under the oxidizing conditions of a geological repository. Radionuclides, such as neptunium, may become incorporated into these secondary uranyl mineral structures, potentially altering the solubility of the phases and hence the mobilities of U and Np in the repository environment. Soddyte ((UO2)2(SiO4)(H2O)2) forms as an alteration product of spent nuclear fuel in laboratory settings (e.g., Finch et al., 1999), and significant concentrations of Np can be incorporated within soddyte (Klingensmith and Burns, 2007). The solubility and thermodynamic properties of pure soddyte have been studied (Gorman-Lewis et al., 2007). It is unclear, however, what effect Np(V) incorporation into the mineral structure of soddyte will have on the mineral solubility or on the extent to which Np is released from the phase.

We synthesized soddyte in the presence of 10 to 600 ppm aqueous Np(V) and measured the release of U, Np, and Si as a function of time under controlled pH conditions. XRD and FTIR analyses demonstrated that soddyte remained the only stable uranyl phase during the course of the experiments. We use the data to constrain the value of the apparent solubility product of soddyte as a function of Np concentration in the mineral. These values can be used to predict the extent of Np release from Np-bearing soddyte phases, and therefore are useful for modelling Np mobility under repository conditions.

References
Mineralogical, ore-microscopic and geochemical comparative study of Fe-Ni-ores of Lokris area (Central Greece)

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Nickeliferous iron ores (Fe-Ni-ores) located in the area of Lokris (Central Greece) is exploited by Larko A.G. Company. With an annual production of over than 18000 tons of nickel, Larko is ranked as one of the most important European nickel producers. In this study the Fe-Ni-ores of Agios Ioannis, Marmeiko and Tsouka deposits are compared according to their mineralogical, ore-microscopic and geochemical characteristics.

The examined Fe-Ni-ores, formed from lateritic weathering of ophiolithic complexes of the subpelagonian unit of Greece, to which the Lokris area belongs, are oolithe/pisolithe type. They consist of ooids, pisoids, peloids and abrasioliths (fragments of ooliths). Their major mineralogical constituents are hematite, goethite with minor quantities of kaolinite. Additionally in the Fe-Ni-ores chromite, Al-spinels are also present, while Ni-minerals (Nimite, Willemseite, Nepouite, Takovite) and Mn-minerals were found in minor quantities. The Fe-Ni-ores of Agios Ioannis and Marmeiko forms beds, which are placed on the karstificated limestones of Jurassic, while Tsouka ore deposit which also form beds, is placed on ultrabasic rocks. All three deposits are overlaid by transgressive sediments of the Cretaceous. The presence of fragments of ooids, clastics and abrasioliths, in the deposits of Agios Ioannis and Marmeiko, indicates redeposition of the Fe-Ni-ores. Both deposits are considered as secondary heterochthone formations. Contrary in the deposit of Tsouka the occurrence of a limited number of abrasioliths as well as the absence of inclusions of fragments of oolitis, indicates that a small transport and redeposition of the clastic components of the ooliths has occurred. The deposit of Tsouka is considered as a secondary pseudoautochthones deposit, having characteristic underlying laterite units. The correlation of the geochemical data of the deposits of Agios Ioannis and Tsouka showed that the ores formed from ultrabasic parent rocks. The relatively higher contents of Al and Ti as well as the occurrence of, Al-spinels, ilmenite with its replacement products (pseudorutile and leucoxene), anatase and magnetite, in the ores of Marmeiko, are signs for the fact that beside ultrabasic, also basic rocks were involved in the structure of the parent rocks.

Nd isotopes in Archean water masses: The importance of mantle- versus continentally-derived inputs

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The 2.9 Ga Pongola Supergroup (South Africa) contains shallow water banded iron-formation (IF) that possesses a primary seawater signature, and displays Nd isotope values indistinguishable from contemporaneous shale (εNd(t) between -2 and -4). The distinctly negative εNd(t) of the Pongola IF is atypical for many Archean IFs. Rare earth element distributions in the Pongola IFs vary as a function of relative water depth (as suggested by a transgressive-regressive cycle of IF deposition), and these observations indicate that shallow seawater along continental margins in the Archean was heavily influenced by inputs from continental weathering.

This scenario for the Pongola Supergroup is examined using data from contemporaneous IFs from the 2.9 Ga Pietersburg Greenstone Belt (South Africa). Whereas the Pongola IFs formed on a stable cratonic margin, the Pietersburg Greenstone Belt is not associated with pre-existing cratonic crust. Pietersburg IF samples display rare earth element distributions indistinguishable from older Isua IFs (3.8 Ga, Greenland) and younger Kuruman IFs (2.5 Ga, South Africa), and are consistent with primary seawater precipitates. Nd isotope signatures for the Pietersburg IFs are less negative (εNd(t) between -1 and 0) than contemporaneous shales and the coeval Pongola IFs. Therefore, it appears that Archean seawater was inhomogeneous with respect to Nd isotopes, similar to modern oceans. These data, and the contrasting depositional environments of the Pongola and Pietersburg IFs, suggests the presence of mantle-derived Nd in Archean open-ocean seawater, whereas coastal waters were dominated by continental Nd.
High-Precision Isotope Acquisition with the NanoSIMS 50L

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The in situ measurement of isotope ratios at high precision has always been a goal of secondary ion mass spectrometry (SIMS). The NanoSIMS 50L is a third-generation ion microprobe developed by Cameca and modified in collaboration with the Carnegie Institution of Washington. This instrument incorporates a number of design and functional improvements over the stock NS50, including precise stepper motor control over all slits, apertures and stage movements, a larger magnet, and a modified multicollector (6 moveable and 1 fixed) capable of holding both Faraday cups and miniature multi-dynelectron multipliers. The instrument is capable of attaining a minimum beam diameter of <50 nanometers with Cs and <200 nanometers with oxygen (O2), a factor of 5-10 improvement over the IMS6F/7F/1280 generation of instruments. The CIW instrument is also the first NanoSIMS to be fitted with multiple Faradays and associated high-precision electrometers.

One year’s experience with the NS50L has disposed of a number of incorrect perceptions with regard to its potential and capabilities for terrestrial geochemistry:

1) "Beam currents are too low to be useful": With Cs, a routine primary beam diameter of 100 nm is obtained with 2-3pA of current, sufficient to yield >1MHz of 32S from pyrite or 16O from silicate glass at >6000 MRP. 250pA of current yields a 350 nm beam that gives an H2O detection limit of 50 ppm on olivine.

2) "You’ll never get enough signal for Faradays": A 2.5 nA Cs beam with a diameter of 700 nm yields 90 pA of 32S from pyrite at >6000 MRP, sufficient to analyze 32S-33S-34S on Faraday cups and 36S in EM @ >10,000 cps. Similar results have been obtained for oxygen from Al2O3.

3) "The instrument is unproven at high precision": In multi-Faraday mode, spot-to-spot reproducibility is 0.4 permil (1sig) or better for 32-33-34S from pyrite, and for 28-29-30Si from a silicon wafer. Reproducibility as good as 0.15 permil (1sig) has been obtained for 32-33-34S from pyrite in different holes of a single sample holder. With multiple EMs, simultaneous measurements of Mg and Si isotopes in silicates achieves a reproducibility of ~1 permil (1sig) for all ratios from multiple craters. All of these measurements were obtained in raster craters at a spatial resolution of 5-10 μm.

Other high-precision and high-resolution applications of the instrument will be presented at the meeting.

Influence of reductive dissolution of iron oxides by S(II) on uranium mobility

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Transient redox conditions can influence the mobility of uranium by inducing changes in iron mineralogy with which uranium may be closely associated. Iron oxides play a critical role in uranium transport by providing reactive surfaces for sorption or by assisting in U(VI) reduction. Iron oxides reductively dissolve when exposed to S(II), produced by microbial sulfate reduction. This might lead to the mobilization of adsorbed U(VI). However, U(VI) might also remain solid-bound due to adsorption onto FeS or reduction by S(II) and precipitation as UO2. This study investigates the fate of sorbed U(VI) in response to reductive dissolution of iron oxides by S(II). In batch experiments, S(II) is incrementally added to a lepidocrocite suspension with preadsorbed U(VI). The S(II) concentration decreases with time due to oxidation by Fe(III), causing an increase in Fe(II) concentration. With every S(II) addition, an instantaneous increase in dissolved uranium concentration is observed. The concentration then gradually decreases for about one hour, but remains at a higher level than before sulfide amendment. This could be due to the competition between U(VI) and Fe(II) for surface sites, or to the transformation of lepidocrocite into FeS and lower affinity of FeS surfaces for U(VI) than lepidocrocite. Preliminary results regarding possible complexation of uranium with S(II) in solution, show that this process is negligible. XANES spectra imply a gradual but partial transformation of U(VI) into U(IV) during of the experiments. Results indicate that most likely the formation of FeS might be required for U reduction.
Maghemite lag: Formation and implication for mineral exploration

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Maghemite is the cubic form of Fe$_2$O$_3$ and isostructural with magnetite. It is a common mineral in weathered profiles in arid, semi-arid, subtropical and tropical environments but more rare in cooler humid regions (Eagleton, 1988).

The formation of maghemite has been attributed to aerial oxidation of magnetite, dehydration of lepidocrocite (-FeOOH) or goethite and transformation of goethite to maghemite under arid climatic conditions. It is concentrated in the course grains of bedrock remnants or grains formed at weathering profiles by accumulating surface material classified as lag. Lag” was defined by Bates and Jackson (1980) as a general term applied to coarse grained (> 2 mm), hard, but partially weathered rock fragments which concentrated at surface through attrition of finer materials. Studies show that ferruginized and maghematized lag can attract elements from subtle anomalies and reveal the metal sources with elevated contrast compared to ill nature soil and aeolian materials (Alipour et al., 1994 and 1995; Robertson, 1989 and 1995).

Therefore, its unique characteristics such as abundance in arid regions, covered deserts or cultivated lands, converts it to an excellent sampling media. Comparing geochemical behavior of maghematized and non-maghematized materials, maghematized lag can be sampled at first stage of regional exploration to delineate potential targets and non or weakly maghematized lag could be used in follow up stages to locate the source of the anomalies.

Fe-Ti oxide minerals geochemistry of Late Triassic Carpathian Keuper sandstones: Implications for provenance

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Selected Fe-Ti oxides minerals from the Carpathian Keuper sandstones at different localities from Slovakia were analyzed by JEOL-JXA-733 Super probe analyzer and identified as highly altered and fractured Fe-Ti oxide minerals. Iron oxides which form a large portion of the heavy minerals in the samples examined are represented mostly by ilmenite, titaniferous magnetite, leucoxene, and hematite. Chemical analysis of Fe-Ti oxides revealed that the total oxides generally are low and this may be related to the alteration on these grains. Most of Fe-Ti oxide minerals studied are polymineralic grains with mixture of two or more phases. The chemical composition of some grains indicates a coexisting mixture of ilmenite and titano-magnetite. The highly TiO₂ concentrations may indicate the metamorphic source rocks origin of the studied grains (Basu & Molinaroli 1989, 1991).

By comparing the present chemical results with that mentioned by aforementioned authors, it appears that Keuper ilmenites generally were derived from metamorphic and partly from igneous sources. Based on the mineralogical and geochemical indicators, the probable provenance of the Keuper sandstones was mainly the metamorphic and igneous rocks of the crystalline cores of the Western Carpathians and the foreland of the Bohemian Massif which were weathered and deposited in the continental mainly fluvial and littoral environments of deposition of the Keuper Formation.

References

Open system behaviour and early chronologies in the Solar System

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The problem of concordant ages between different chronometers in meteorite chronology is discussed since the earliest comparisons between the precise chronologies obtained by ⁸⁷Rb-⁹²Sr and ¹²⁹I-¹²⁹Xe were made. However in recent years the subject became again important since considerable analytical progress has been achieved and allowed one to use a variety of extinct radioactivities: ⁵⁶Al-⁵⁷Mg, ⁵³Mn-⁵⁴Cr, ¹⁸²Hf-¹⁸⁴W, ¹⁴⁶Sm-¹⁴⁴Nd and ¹²⁹I-¹²⁹Xe.

Most “apparent ages” obtained by different chronometers have been calibrated against the set of U-Pb ages obtained on chondritic phosphates (Göpel *et al.* 1994). The older age considered as an absolute reference corresponds to 4567 Myr and was obtained on refractory inclusions of the Allende meteorite by Manhès *et al.*, (1988) and later confirmed by Amelin *et al.* (2002).

When the whole set of apparent ages obtained by various chronometers is considered, no simple pattern is visible. Some chronometers compared to another chronometers may give older ages for a few objects, applied on other objects they result in younger.

These inconsistencies are observed by assuming that each chronometer behaves as a closed system and by using simple chronometric equations for each of them.

We developed a quantitative model in which meteorites behave as open systems. After their initial formation the system has been perturbed by shock events, reheating, metamorphism occurring on planetesimal or meteorite parent bodies. We can compute a model for continuous or episodic perturbations assuming that the perturbations generate a loss of radiogenic isotopes or a change in the parent-daughter ratios.

This model shows how ages obtained by two chronometers can be sometimes older, sometimes younger depending the age of perturbation event and its intensity. We also may obtain concordant ages between a long lived and short lived chronometer which however have no physical significance, concordancy being just an artefact.

We can interpret all the apparent ages obtained on meteorites with this model. The data are compatible with a model in which all primitive solid objects formed around 4567 Myr and were subsequently perturbed by events occurring from few hundred thousands years to 100 Myr.

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**In situ crystallisation processes in the Miocene PX1 pyroxenite intrusion (Fuerteventura)**

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The PX1 gabbro-pyroxenite intrusion of Fuerteventura (Canary Islands) displays a remarkable NNE-SSW trending vertical magmatic layering. This layering is strongly dependent on the regional tectonic regime and is expressed by alternating horizons of gabbros and pyroxenites, generated by successive magma injections into a progressively widening dyke system. Multi-scaled compositional variations span from olivine-rich pyroxenite, pure clinopyroxenite and plagioclase bearing pyroxenite to non-cumulative gabbro.

Whole-rock incompatible trace-element contents show large variations and poorly correlate with monotonous major element compositions, these features are typical of in situ crystallisation (Langmuir 1989) with variable amounts of interstitial liquid (L). La-ICPMS analyses of minerals and quantitative modelling based on Langmuir’s equation using REE concentrations in mineral phases show that these underwent re-equilibration with interstitial melts (Hermann et al. 2001).

Calculated REE patterns of mineral phases in samples are adjusted to fit the measured REE plots by playing with the degree of differentiation (F) and the proportion of interstitial liquid (L). L has a stronger influence than F on LREE for low degree of differentiation (F) and the proportion of interstitial adjusted to fit the measured REE plots by playing with the modal proportions of amphibole.

Dcpx were estimated using a predictive model (Wood & Blundy, 1997) on a sample selected for low whole-rock Zr, Nb and ZRE (24,33 ppm), and displaying a Eu/Eu* close to unity (0.96). The bulk rock partition coefficients have been estimated using modal contents of an olivine-gabbro sample.

The calculated amounts of L are 15 to 30% for plagio-pyroxenites and gabbros and correlate well with the proportion of interstitial amphibole in studied samples. The calculated amounts of fractionation (F) relative to a primary magma crystallisation experiment at 200 and 500 MPa. All experiments have been performed in an internally heated pressure vessel at intrinsic oxygen conditions using pure argon as a pressure medium. Three starting basaltic compositions have been chosen so that Ol, Plag or Cpx are crystallizing as a liquidus phase. The H2O concentrations in the glasses were obtained by infrared spectroscopy and Karl-Fischer-Titration.

As a result of the study we parameterized our experimental data in the form of simple equations describing the liquidus of Ol, Plag and Cpx as a function of dissolved H2O content. Finally, these simple equations have been incorporated into the algorithm of the COMAGMAT program [3].

Application of the refined COMAGMAT model is presented for basaltic lavas from the Mid-Atlantic Ridge (MAR) east of Ascension Island (7-11°S). To determine crystallization conditions of the given MORB suite two sets of equilibrium and fractional crystallization calculations have been performed. The results indicate that MORB-magmas beneath different segments of the MAR have crystallized over a wide range of pressures (100 to 900 MPa). Nearly isobaric crystallization conditions (100-300 MPa) were obtained for the geochemically enriched MORB, whereas N-MORB magmas are characterized by polybaric crystallization conditions (200-900 MPa). Our results demonstrate close to anhydrous crystallization conditions of N-MORBs, whereas geochemically enriched MORBs were successfully modeled in the presence of 0.4 to 1 wt % H2O in parentals melts. Our results are in agreement within ±200 MPa with previous approaches used to evaluate pressure estimates in MORB. In addition, our data illustrate that the effect of H2O on pressure estimates is within this uncertainty.

**The effect of minor H2O content on crystallization in MORB: Experiments, model, applications**

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The role of H2O on mineral cotectics and petrochemical trends in MORB systems has been thoroughly discussed in the literature (e.g. [1]). However, the quantitative knowledge on the effects of small amounts of H2O on the liquidus of olivine (Ol), plagioclase (Plag) and clinopyroxene (Cpx) is still limited by the lack of experimental data with well-constrained values of water activity. This, probably, results in considerable inconsistency between the available models [1-3] predicting the mineral liquidus depression as a function of the water dissolved in the melt.

To address the problem we conducted a set of crystallization experiments at 200 and 500 MPa. All experiments have been performed in an internally heated pressure vessel at intrinsic oxygen conditions using pure argon as a pressure medium. Three starting basaltic compositions have been chosen so that Ol, Plag or Cpx are crystallizing as a liquidus phase. The H2O concentrations in the glasses were obtained by infrared spectroscopy and Karl-Fischer-Titration.

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**References**

Stone decay in two-mica granite buildings of Northern Portugal

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The application of the natural stone as a building material catalyzes the deterioration process due to the reactivity between the rock minerals and industrial mortars and to the exposure to particular environmental conditions. Among the main factors in the origin of stone decay, the intrinsic characteristics of the rock are determinant in the behaviour of its constitutes. Three historical granite monuments from the Oporto region, largely affected by a diversity of stone deterioration types, have been selected in order to illustrate the combination of the intrinsic factors with weathering and environmental agents, responsible for the susceptibility of granite stones to deterioration: a millenarian Xth century Romanic church, a XVIIIth century Baroque church and a XIXth century neoclassical building. The granite the selected monuments are built with is classified as a medium- to coarse-grained leucogranite, syntectonic in relation with the third Hercynian deformation phase. This granite exhibits a non-porphyritic hydridomorphous granular texture and a mineral association of quartz, orthoclase, perthitic microcline, albite, muscovite and biotite. Apatite, zircon, monazite, ilmenite, and scarce tourmaline and garnet are accessory minerals. The granite is affected by late-to post-magmatic alteration as well as by weathering processes to various extents. In some outcrops the potassic feldspar is intensely kaolinized. The A/KCN molar ratio between 1.3 and 1.5 is an evidence of a strong peraluminous character due to the presence of primary muscovite. A U-Pb geochronological study on zircon and monazite indicates a minimum emplacement age of 318±2 Ma (Almeida, 2001). The granite stones applied in the selected monuments display different weathering degrees, as a consequence of different susceptibility to deterioration. Granular disintegration, plates, flakes, black crusts, thin black layers, efflorescences and biological colonization are the main deterioration types. Gypsum, halite, niter, glauberite, calcite, apatite, thomandite, anatase and mirabilite have been detected by X-ray diffraction and SEM analyses and play an important role in the stone decay (Silva, 2005). The main source of salts is rainwater, affected by the proximity with the Atlantic Ocean. Carbon and sulphur rich porous fly ashes and silicon and aluminium rich smooth fly ashes are also present, in the thin black films, produced by air pollution agents.

References


The CaCO₃ saturation state of Phanerozoic oceans

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Geochemical models suggest that perturbations of the global carbonate cycle in the geologic past resulted in large variations in the CaCO₃ saturation state (Ωₐ) of the ocean (Zeebe and Westbroek, 2003; Ridgwell, 2005). These variations may have influenced the evolution of biocalcifying organisms and global sedimentation patterns. To independently test these ideas, I deduce information on past oceanic Ωₐ from the geological record of calcified cyanobacteria and a numerical model of cyanobacterial mat calcification. A curve of threshold oceanic Ωₐ needed for cyanobacterial calcification is derived and compared to the Phanerozoic distribution of calcified cyanobacteria, providing some constraint on past oceanic Ωₐ levels. To this curve correspond threshold curves of pH and total alkalinity (TA). The emerging picture of considerable oceanic Ωₐ variation through time matches the long-term tectonic, geochemical and biological evolution of the Earth System: Ωₐ maxima at the base of the Cambrian (545 Ma; Ωₐ > 12), most of the Carboniferous (330-300 Ma; Ωₐ > 7), the mid Permian (280-260 Ma; Ωₐ > 9) and the late Triassic (210–200 Ma; Ωₐ > 7) correspond to periods of increased continental weathering or decreased neritic depositional space. A prominent drop in oceanic Ωₐ starting from an early Jurassic high (Ωₐ > 7) to a mid-Cretaceous low (Ωₐ < 3) records the advent of planktic calcifiers during the “mid-Mesozoic revolution”. Low and relatively stable oceanic Ωₐ after this event confirms the efficiency of the carbonate compensation mechanism in stabilising the global carbonate cycle. Both the “Cambrian Explosion” and key moments of the “mid-Mesozoic revolution” took place in highly supersaturated oceans, suggesting a link between these major evolutionary events and changes in ocean chemistry. Global biocalcification crises associated with Mesozoic oceanic anoxic events took place in poorly supersaturated oceans, when short-lived (< 1 Ma) perturbations of the global carbon cycle would have been most effective in inhibiting biocalcification.

References

Mineralization of organic matter in surface sediments of temporarily euxinic basins, Baltic Sea

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Organic matter is mineralized in marine sediments by microbial activity using predominantly oxygen, sulfate, and metal oxides as electron acceptors. Modern euxinic basins as found in the Baltic Sea or the Black Sea are of particular importance because they may serve as type systems for anoxia in Earth’s history.

We present here first results from biogeochemical investigations carried out in the Baltic deeps (Gotland Basin, Landsort Deep) during the first scientific cruise of the new German RV M.S. MERIAN in 2006. Short sediment cores were obtained with a multi-corer and analyzed for particulate and dissolved main, minor and trace elements besides stable carbon isotopes in dissolved inorganic carbon (DIC). Microsensors were applied to analyze steep gradients of oxygen, sulphide and sulphate. Pore water profiles were evaluated in terms of process rates and associated element fluxes. Gross and net anaerobic mineralization rates were additionally obtained from core incubations with \textsuperscript{35}S or bag incubations of sediment sections. Highest SRR were found in the top 5-10 cm. Element fluxes across the sediment-water interface were compared with re-evaluated literature data and show for the Baltic Sea a dependence from bottom water redox conditions, and sediment compositions and formation conditions (e.g., accumulation rates).

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Interaction of fluid flow, heat and mass transport, and chemical reactions in oceanic hydrothermal systems: New insights from fully coupled reactive transport simulations

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Circulation of seawater through the oceanic crust and the chemical reactions that occur along the flowpath control the composition of vent fluids. We use 1D and 2D fully coupled reactive transport models to explore the evolution of fluid flow, heat transport and chemical reactions in the oceanic crust and the implications for mineral alteration patterns and vent fluid composition.

Fully coupled models are required to assess the complex interaction between chemical alteration, fluid flow and thermal conditions in the oceanic crust. The recharge of seawater into the basaltic crust causes the precipitation of significant volumes of anhydrite and chlorite which reduces the porosity and thus the permeability of the recharge zone. Similarly, cooling of the hydrothermal fluid as it ascends to the seafloor below hydrothermal vents may lead to the precipitation of minerals such as quartz and a reduction in permeability. Alteration reactions in the high-temperature reaction zone also introduce some heterogeneity of the permeability distribution which are, however, somewhat less pronounced than the permeability reduction in the recharge and discharge zones due to lower thermal and/or compositional gradients and closer to equilibrium conditions. Therefore, over time chemical reactions have the potential to modify the flow field and the thermal conditions in oceanic hydrothermal systems which could lead to observable changes in discharge rate, temperature and/or chemical composition of seafloor hydrothermal vents.

It is interesting that, despite this potential for temporal evolution, the composition of vent fluids in oceanic hydrothermal systems (e.g. 21ºN, East Pacific Rise) are observed to remain constant on a decadal time scale. The fluid composition at these vents is consistent with rock buffering at greenschist metamorphic conditions. Our simulations are therefore aimed at incorporating this observational constraint and quantifying the magnitude, spatial distribution, time scales and rates of chemically induced permeability changes and the associated effect on flow and thermal conditions and the impact on the evolution of the vent fluid composition. Critical parameters and aspects that are explored in these simulations are water/rock ratios (which are dependent on the permeability and the reactivity) and the formulation of the porosity / permeability coupling used in the reactive transport code.
‘Geochemical’ research: Key building block for radwaste disposal safety cases in clayrocks

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Disposal of high-level radioactive waste in deep underground repositories has been chosen as the solution by several countries. Because of the special status that this type waste has in the public mind, national implementation programs typically mobilize massive R&D efforts, last decades and are subject to extremely detailed and critical social-political scrutiny. The culminating argument of each program is a ‘Safety Case’ for a specific disposal concept containing, among other elements, the results of performance assessment (PA) simulations whose object is to model the release of radionuclides (Rn) to the biosphere. Public and political confidence in PA results (which generally show that Rn release will always be at acceptable levels) is based on their confidence in the quality of the scientific understanding in the processes included in the PA model, in particular those governing radionuclide speciation and mass transport in the geological host formation. Geochemistry (obviously) constitutes a core area of research in this regard.

Clay-mineral rich formations are the targets of radwaste programs in several countries (France, Belgium, Switzerland…), principally because of their demonstrated capacities to adsorb many radionuclides and to limit (diffusion-dominated) mass transport. The corresponding key processes in PA models are radioelement chemistry (redox state, speciation, reactions determining Rn solid-solution partitioning) and diffusion-driven transport. These processes take place in solution-filled pore spaces, most of which are bounded by the surfaces (basal, interlayer, edge) of permanently charged clay minerals. In addition, natural rocks always contain other solid phases potentially capable of influencing radionuclide speciation (pyrite, organic matter…) as well as being physically and chemically heterogeneous at space scales ranging from sub-millimetric to hectometric.

In order to gain the detailed scientific understanding needed for constructing those parts of the Safety Case supporting how Rn transfer is represented in the PA model, a wide range of coordinated (and internationally collaborated) research has been carried out. The purpose of this presentation is to illustrate how research results in fields ranging from molecular dynamic calculations of ion distributions and mobility near clay surfaces, to clay surface-catalyzed transformations of the redox state of certain elements (Se…), to the effects of electrical double layers on the composition and ion transport properties of clayrocks, to measurement and model representation of micro-scale mineral-porosity relationships and the effects on diffusion, to use of geochemical modeling to estimate porewater composition, to use of high resolution detection methods to quantify diffusion at sub-millimeter scales…, have contributed to building convincing Radwaste Safety Cases.

Depleted uranium in the environment: A biogeochemical study

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Geochemical and microbial processes affecting the decomposition and dispersion of military depleted uranium (DU)/titanium alloy penetrators are being investigated. Since the behaviour is unique to this form of uranium, laboratory model systems are being used to define the effects of the chemical and microbial processes involved in decomposition. The effects of DU on bacterial communities are of particular interest and are being studied using both culturing and molecular methods, together with quantification of dissolved, colloidal and macro-particulate fractions of uranium decomposition products.

DU coupons with a mass of ca 8 g have been exposed to aqueous media containing appropriate terminal electron acceptors (TEA: oxygen, nitrate, Fe(III) or sulphate), and indigenous bacteria, either those present in various selected soils, or an inoculum cultured from an estuarine sediment and a loamy clay soil. The concentrations of the added TEA groups were monitored over time. Microcosms were supplied with excess electron donor and sacrificed once TEA reduction was complete. Abiotic control samples were also prepared for comparison.

There was greater degradation of DU by cultured aerobes, including ‘pitting’ of the surface when compared to anaerobes. An example of the pitting is shown in the photograph below taken after only one day of incubation at 15 °C.

The extent of DU corrosion under different conditions can be related to changes in solution geochemistry and microbial community structure.
Phanerozoic crustal growth constrained by zircon U-Pb age and Sr-Nd-Hf isotopic evidence from the granitoid rocks in Mongolia

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Mongolia is the largest segment of the Central Asian Orogenic Belt which is formed by accretion of island arcs and subdomain Precambrian microcontinents (Badarch et al., 2002). Here we report new U-Pb zircon ages and Sr-Nd-Hf isotopic data of granitoids from four representative areas along one transect from northwestern to southeastern Mongolia (Ider, Erdene, Akhar-Uul and Khanbogd). Zircon U-Pb age data show three distinct age ranges: ca. 538 Ma; 368-290 Ma; and 262–216 Ma, which reveal that: (1) Granitic magmatism in Mongolia was most active during the Carboniferous to Permian; (2) The Cambrian granitoids were emplaced in the Akhar-Uul area in the southern part of Mongolia, although previous studies assumed that the distribution of granitoids young towards the south; (3) The late Permian to Triassic granitoids are mainly located in the central part of the Mongolia (Erdene area). The widespread granitoids indicates accretion and collision processes took place continuously throughout the Phanerozoic. Isotopic data display significant differences along the transects. The Cambrian peraluminous granitoids in the Akhar-Uul area, in the passive continental margin terrane (Badarch et al., 2002) show high initial Sr isotopic compositions (0.7135 to 0.7244), and low εNd (-8.2 to -8.8) and εHf (-12 to -16). These features suggest that they were derived from sediment source and produced by erosion of old continental crust and were likely emplaced in a forearc environment. Granitoids in the Khanbogd area in an island arc terrane (368 to 290 Ma) show high εNd (+5.3 to +9.9) and εHf (+7.5 to +9.8) whereas those in Ider (350 to 290 Ma), Erdene and Akhar-Uul areas (282 to 213 Ma) that were emplaced in the Precambrian cratonic and Ordovician clastic basin terranes lower εNd (-2.7 to +4.7) and εHf (-4.1 to +5.5). The depleted isotopic character in the Khanbogd area corresponds to the upper mantle and lower crustal xenoliths included in Cenozoic volcanic rocks, suggesting these granitoids were formed by melting of mafic lower continental crust that was originally formed by mantle-derived magma. Whereas enriched isotopic signatures those in Ider, Erdene and Akhar-Uul areas may be explained by interactions with preexisting old crust where they were emplaced.

Reference

Tracer analyses as a tool to validate the effectiveness of pump-and-treat measures in the field.

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We show that the remediation of a contaminated site, by pump-and-treat, disturbed the groundwater dynamics and lead to mixing of different water components. The remediation impacts on groundwater mixing can be traced by the noble gases $^3$He and $^4$He, and by the transient tracers CFCs and SF$_6$. At the site, chlorinated ethenes as DNAPL lay at the bottom of an aquifer of fluvial sediments, that covers the top of a molassic rock of much older age. Before and after remediation the site was sampled for noble gases, CFCs and SF$_6$. All these bio-geological conservative tracers indicate a major change in groundwater dynamics although the contamination levels remain the same.

After the remediation, the observed $^3$He/$^4$He ratios of the local groundwater were lower then the atmospheric value (1.36*10$^{-6}$), whereas before the remediation the $^3$He/$^4$He ratios were considerably larger. Such distinct change of the He isotopic composition indicates the emanation of isotopically heavy He from the molassic hardrock, most probably through fractures. This let us assume that the DNAPL penetrated into the underlying bedrock, through those fractures that allowed the He to emanate. Such DNAPL impregnation of the bedrock may explain why the remediation measures failed, and would further imply that a DNAPL contamination can hardly be removed, under such conditions, by pump-and-treat methods. Moreover, the abrupt change in the $^3$He/$^4$He ratio of the local groundwater clearly prove that the remediation measures severely impacted the natural groundwater flow regime.

Other transient tracers, such as CFCs and SF$_6$, were found to be oversaturated both before and after the remediation. However, the observed change in concentration and relative abundance, again indicate that applied pump-and-treat schemes changed the local hydraulic situation, but did not remove significant amounts of the DNAPL contamination, because the contamination concentration did not decrease in response to the taken measures.

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Lu/Hf ratio and initial $^{176}\text{Hf}/^{177}\text{Hf}$ in the Solar System and the Earth

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The $^{176}\text{Lu}$-$^{176}\text{Hf}$ system is an invaluable tool for studying early differentiation in the Earth and other planets. An accurate knowledge of the initial condition of this isotopic system in the Earth remains elusive, despite the growing amount of Lu-Hf data on early Solar System materials. Determinations of $^{176}\text{Lu}$ decay constant by age comparison on terrestrial minerals and meteoritic phosphates yield consistent results, but two conflicts are still unresolved: 1) Slopes of Lu-Hf isochrons for bulk chondrites and achondrites, and some recently reported internal isochrons for eucrites and angrites are inconsistent with the “terrestrial” $^{176}\text{Lu}$ decay constant value, whereas other eucrite internal isochrons are consistent with it (e.g. Bouvier et al., MetSoc-2006, abstract #5348, Thrane et al., MetSoc-2006, abstract #5125); 2) Lu-Hf and Sm-Nd systems give different images of early mantle differentiation and proto-crust formation in the Earth, if we use the currently accepted $^{176}\text{Lu}$ decay constant value (e.g., Jacobsen (2003), Nature 421, 901-903).

There are several potential complications in determination of Lu/Hf ratio (and ratios of other refractory lithophile elements) from analysis of chondrites. First, Lu/Hf in chondrites can be heterogeneous, as a result of metamorphic phosphate growth, or uneven distribution of chondrules and CAIs. Second, Lu/Hf may vary between the classes of chondrites, and may not be representative of the Solar System value. Third, the bulk Solar System Lu/Hf value is not necessarily identical to the bulk Earth value.

There are several ways to address the first two complications, and to improve our knowledge of the bulk Solar System Lu/Hf. For example, one can study the Lu-Hf system in the least metamorphosed chondrites and chondritic matrices, and explore the correlation between Lu/Hf and the ratios of other refractory lithophile elements in various classes of chondrites and Solar photosphere. In addition, it may be possible to determine the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of the Solar System directly from analyses of minerals with low Lu/Hf from old, well preserved meteorites. An approach to the third problem – precise matching of the Lu/Hf ratio (and other geochemically significant elemental ratios) between the bulk Earth and the bulk Solar System, needs to be developed.

Biogeochemical interactions in soil – Ccontrols through aggregation?

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The microbial turnover of natural organic matter (OM) and anthropogenic contaminants in soils depends on both quality and accessibility of the substrates. Agglomeration of soil minerals with plant and microbial remains to soil aggregates of different sizes strongly affects this bioaccessibility. Applied pesticides, for instance, are first caught in-between or at the surface of aggregates. Sequestration occurs after movement into interior parts. Also natural OM turnover is restricted in inner-aggregate pore space, however, when aggregates are broken down by e.g. ploughing, (old) organic C and N sources are made available to microbial growth and can rapidly be degraded.

This keynote aims at elucidating the role of aggregate cycling for compound turnover and sequestration in soil. Case studies presented relate to the tracing of xenobiotics using mass spectrometry after sequential extraction, to the cycling and preservation of natural OM using compound-specific stable isotope techniques of biomarkers and amino acid racemisation assessment.

The results suggested that selective preservation of organic molecules in soil may become insignificant when bioaccessibility is not restricted at the surface of aggregates or after their break-down. In undisturbed and very small pore spaces the pollutants and natural organic nutrient sources are withdrawn from actual biogeochemical cycles for unknown periods of time. Racemization of amino acids indicates that the conserved molecules may even age for centuries, despite N deficiency frequently occurring in living terrestrial environments.
Archaea and Bacteria in an arsenic-rich shallow-sea hydrothermal system, Papua New Guinea

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The shallow-sea hydrothermal vents off Ambitle Island (Papua New Guinea) discharge hot (98 °C), slightly acidic (pH 6), AsIII-rich (~1,000 µg/L), chemically reduced fluids. Near the vent orifices, rocks and sediment are coated with AsV-rich (up to 7 wt. %) hydrous ferric oxides and green and orange biofilms. Shallow porewater chemistry changes rapidly with increasing lateral distance from the vents, approaching ambient seawater values within a few meters. Interestingly, porewater arsenic concentrations remain elevated even at 300 m lateral distance, predominantly as the oxidized AsV form (Price, R.E. et al., 2007. Appl. Geochem., in press).

Bulk genomic DNA was extracted from the biofilms and from near-surface sediment samples, amplified using standard bacterial and archaeal 16S ribosomal RNA primers, and sequenced. The archaeal communities in the orange and green biofilms consist entirely of uncultured, deeply-branching Crenarchaeota. The corresponding bacterial libraries were surprisingly sparse in thermophilic phyla (e.g., Thermus, Thermotogales, Aquificales), and dominated by several typically aquatic and sedimentary taxa. As an example, Bacteria in the green biofilm were nearly half alpha-Proteobacteria; strict phototrophs were not identified.

The archaeal libraries from sediment samples along a transect were also dominated by uncultured Crenarchaeota, but a few Euryarchaeota and Korarchaeota sequences were identified. Interestingly, a number of clones were >97% similar to Nitrosopumilus maritimus, the first chemolithoautotrophic nitrifying archaeon and the first mesophilic Crenarchaeote in pure culture (Köneke, M. et al., 2005. Nature 437, 543-546). Actinobacteria and gamma- and delta-Proteobacteria were ubiquitous along this same transect, and green sulfur and green non-sulfur Bacteria were found at 7.5 m and at 90 m from the vent, respectively.

In addition to gene surveys, several thermophiles were cultured from this site. Here, we report on a novel Bacterium isolated from the green biofilm on an anoxic, chemolithoautotrophic medium amended with 4,000 µg/L AsIII. The strain, PNG2, grows optimally at ~50 °C, but not above 60 °C. Based on the 16S gene sequence, PNG2 is an alpha-Proteobacterium, but with very low similarity (~90%) to any sequenced environmental clones or cultured strains.

Biogeochemistry of the Salton Sea, California

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The Salton Sea is a saline, closed basin lake 70 meters below sea level in the southern desert of California. It is the largest lake in California with a surface area of 945 km² and an annual inflow of 1,600 million m³. The Sea is hypereutrophic due to nutrient inputs from farm runoff, and the elevated sulfate concentration results in high rates of hydrogen sulfide production. The salinity of the Sea is 47 g/L and rising, with an annual salt load of 4 million metric tons. Construction of a salt repository is being considered to control the rising salinity, improve water quality, and maintain the Sea as a refuge for migratory birds. We estimate 700,000 metric tons of calcite are precipitating in the Sea each year, along with 7,000 tons of iron sulfide minerals. Hydrogen sulfide production rates, reoxidation rates in the water column, and atmospheric releases of H2S have been measured. In addition, we have measured dimethylsulfide concentrations >6 uM in the surface water, which are the highest ever reported. Hydrodynamic modelling of the proposed modified Sea indicates that persistent stratification could occur, with the potential for episodic releases of hydrogen sulfide during fall mixing.
The climatic and biotic thresholds on soil elemental cycling along an arid to hyperarid rainfall gradient

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Across much of the planet, soil properties and biogeochemical processes vary monotonically with changes in rainfall. The studies that provide these observations have generally been performed in landscapes supporting biota. In this study, we examined soils along a rainfall transition from arid (vegetated) to hyperarid (abiotic) in northern Chile, and find that key geophysical and biogeochemical processes exhibit a sharp non-monotonic response across the transition from biotic to nearly abiotic conditions. All sites are ~ the same age (late Pliocene) and have similar lithologies, so that any chemical differences are due primarily to rainfall. Here we focus on N and S: elements intimately involved in biological processes. Atmospheric deposition is the main input at all locations, but soil retention and in situ biogeochemical alteration is strongly dependent on rainfall and biota. At the arid (vegetated) site, soil N is predominantly organic and exceedingly low (0.03 kg m⁻²), while at the extreme hyperarid endmember, soil N is predominately NO₃⁻ and much higher than at the arid site (5.4 kg m⁻²). Sulfate retention increases with aridity, to 240 kg m⁻². In the driest soil, a large vertical variation in the SO₄ S and O isotope composition indicates inorganic isotope fractionation during dissolution/reprecipitation and downward transport of sulfate. In summary, the removal of water and biota essentially closes the common soil N and S cycles, resulting in soils that passively accumulate these elements as soluble inorganic ions. The long-term absence of biota strongly alters the behavior and fate of elements, highlighting the signature of life on Earth surface geochemistry.

References

Phosphorus, barium and boron in the deep-sea coral Desmophyllum dianthus: Preliminary calibrations

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We present new data for element/Ca ratios in modern samples of D. dianthus, with the goal of developing skeletal proxies for subsurface nutrient and carbonate system proxies. The samples were collected from Atlantic and Pacific regions (~350-1400m) representing a wide range of nutrient and carbonate system concentrations. Mean element/Ca ratios for each coral were obtained for lines along the exterior surfaces of septa using 193nm laser ablation HR-ICP-MS. To test the relationship to seawater chemistry, means for each sample were regressed against hydrographic data from nearby stations. The P/Ca values showed reasonable correlation with seawater phosphate (D-PO₄~1.0, where D=El/Ca-coral divided by El/Ca-seawater; R²~0.7). When a single high point is ignored, D-PO₄ decreases to ~0.3 and the correlation improves (R²~0.78), supporting the potential for a direct seawater nutrient proxy. However, this D value is far lower than the D-PO₄~7.0 reported by Montagna et al. (2006) for the same species, and more consistent with inorganic incorporation of an oxyanion. The Ba/Ca values are strongly correlated to seawater Ba/Ca (R²~0.95) with D~1.7, close to that of surface corals. Skeletal B/Ca values were examined for relationships to carbonate system variables. We found a positive correlation with seawater carbonate ion concentration (R²~0.77), and a weaker one with pH (R²~0.51). These new findings provide a preliminary context for exploring the potential for reconstruction of past nutrient and carbonate system distributions using deep-sea corals.

References
Fe isotopic composition of inner solar system materials: The fit of Martian basalts and minerals

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Currently, there is a debate about the Fe isotopic signature of inner solar system materials and whether Fe isotopes could be fractionated during planetary differentiation processes [1]. Large variations have been found among terrestrial mantle xenoliths, in sharp contrast to the homogeneous isotopic composition of terrestrial basalts. Previous Fe isotope work on lunar, Martian, HED and terrestrial basalts have shown that although the Fe isotopic compositions of these materials were relatively homogeneous for each planetary body, there were significant interplanetary differences [2]. This has been interpreted as a signature of the accretion history experienced by each planetary body. Martian mantle-derived samples, directly accessible for lab-based studies, are only available as Martian meteorites. They represent a variety of lithological types ranging from melt rocks to basaltic cumulates that formed during different episodes of Martian magmatic history. We present the most comprehensive bulk (>10) and major silicate minerals (>5) Fe isotope data from Martian basaltic rocks using a high-resolution MC-ICP-MS and compare our results with previously published data. At the level of precision obtained in our preliminary study (± 0.05‰ for δ57/54FeIRMM-14), all Martian meteorites and their dominant silicate phases appear to have an indistinguishable Fe isotopic composition. In addition, our data agree remarkably well with silicate phases appear to have an indistinguishable Fe isotopic composition compared to terrestrial and lunar igneous samples.

Rb-Sr and Sm-Nd isotope studies on the metabasalts of the Late Archean Hutti Greenstone Belt, Dharwar Craton, south India

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The Late Archean Hutti Greenstone Belt in the Eastern Dharwar Craton consists of predominantly tholeiites and felsic volcanic rocks and is surrounded by granitoid rocks. Based on distinctly different metamorphic mineral assemblages the belt can be divided into east-west and north-south trending arms.

Rb-Sr and Sm-Nd isotope studies were carried out on the metabasalts from both the arms of the Hutti Greenstone Belt. The samples of the N-S arm define a collinear array in the Rb-Sr isotope evolution diagram which corresponds to an age of 2674 ± 120 Ma (MSWD = 8). The samples of the E-W arm define a collinear array in the Sm-Nd isotope evolution diagram which corresponds to an age of 2664 ± 86 Ma (MSWD = 0.94). The above ages for the metabasalts are interpreted to represent time of metamorphism which occurred soon after formation of their igneous precursors. The granitoid intrusives and gneisses surrounding the belt with U-Pb titanite and zircon ages ranging from 2574 ± 8 Ma to 2531 ± 3 Ma are younger than the metabasalts.

Neither the E-W nor the N-S arm metabasalts show any correlation in εSr vs. εNd plot (Figure 1) and hence, it is inferred that their precursor magmas were not contaminated by continental crust. Based on the εNd values it is suggested that the E-W arm metabasalts were derived from a source relatively more Rb-depleted than that for the N-S arm metabasalts. The sources for the magmas represented by both the E-W and N-S arm metabasalts were depleted in LREE > 600 Ma ago before melting as they all have positive εNd values. Two felsic volcanics from the Hutti Schist Belt have both negative εNd and negative fSm/Nd values and they could have been derived from LREE enriched sources. The felsic volcanic from the E-W arm of the Hutti Schist Belt has negative εSr value indicating that its magma must have derived from Rb-depleted sources while the magma representing the felsic volcanic of N-S arm was either derived from sources or interacted with continental crust having high Rb/Sr ratio.

References

Figure 1: εSr vs. εNd plot for the Hutti metavolcanics calculated for an age of 2700 Ma
Influence of water - rock interaction on the chemistry of surface water in volcanic areas

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Natural water

River and spring water samples were collected from an andesitic volcano, Norikura, central Japan and a region covered in “Shirasu” ignimbrite on Kyushu Island. The statistical analysis showed that the water chemistry of those areas is only slightly influenced by hot springs or anthropogenic pollution, but is highly controlled by weathering of silicate rocks or ignimbrite. On the basis of the thermodynamic and stoichiometric calculation based on water–rock interaction, the water chemistry was successfully demonstrated by the following simple theoretical equation:

\[ [\text{Si}] = 2[\text{Na}^+] + (2[\text{K}^+]) + [\text{Mg}^{2+}] \]

Experiment of water-rock interaction

Rock dissolution experiments in a batch system were performed on andesite and “Shirasu” ignimbrite. The reactors were filled with 100 gram of rock powder and 2L of water, of which pH were adjusted with sulfuric acid and were left for over one year. The experimental results successfully demonstrated the above relations between silicon and cations.

![Graph showing measured and estimated silicon concentrations.](image)

**Figure 1:** Measured and estimated silicon concentrations. [Si] estimated is given by \((2[\text{Na}^+]+[\text{Mg}^{2+}])\). Open circles are the river water samples taken from Shirasu ignimbrite region, and solid squares are the experimental water samples of batch system.

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References


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A whiff of oxygen before the Great Oxidation Event?

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Many lines of evidence point to a rapid rise of atmospheric \(\text{O}_2(\text{P}_{\text{O}_2})\) between 2.45 - 2.22 Ga, a transition often referred to as the Great Oxidation Event (GOE). Before this time non-mass-dependent S isotope data (NMD-S) indicate that \(\text{P}_{\text{O}_2}\) was \(<10^{-5}\) times the present atmospheric level (PAL). The cause of the GOE is unknown. It could have been an immediate consequence of the evolution of oxygenic photosynthesis. Alternatively, \(\text{P}_{\text{O}_2}\) may have been controlled by a balance between oxidants and reductants at the Earth’s surface that crossed a critical threshold at that time. In the latter case, oxygenic photosynthesis could have evolved long before the GOE. This debate can be addressed by looking for evidence of trace \(\text{O}_2\) in the geologic record before 2.45 Ga.

The abundances of some redox-sensitive transition elements, such as Mo and Re, in ancient sediments can help address this problem because their weathering fluxes and global ocean budgets are sensitive to the availability of \(\text{O}_2\). The rates of weathering of sulfide minerals which are major carriers of these elements in igneous rocks are geologically rapid even when \(\text{P}_{\text{O}_2} \approx 10^{-5}\) PAL.

High-resolution chemostratigraphy in a newly-obtained late-Archean drill core reveals an episode of enrichment of these elements in the late Archean Mt. McRae Shale, Western Australia. Mo and Re concentrations in a pyritic black shale unit reach ~ 40 ppm and ~ 35 ppb, respectively. These enrichments are superimposed on a background of < 5 ppm and < 10 ppb, respectively, in underlying pyritic black shales. Re-Os geochronology demonstrates that the enrichment is a primary sedimentary feature dating to 2501 ± 8 Ma. Correlations with organic carbon indicate these metals were derived from contemporaneous seawater, providing convincing evidence that these metals were dissolved in late Archean oceans. The enrichment episode may record a change in local or global ocean Mo and Re inventories in response to changing \(\text{P}_{\text{O}_2}\). These findings point to the presence of small amounts of \(\text{O}_2\) in the environment > 50 Ma before the start of the GOE.
Sm-Nd and Lu-Hf garnet geochronology offers a quantitative link between isotopic ages and metamorphic conditions. Most commonly, the link is established on the basis of major element study of a peak metamorphic assemblage. Such an approach is valid only for low to medium grade metamorphism, where both major and trace elements preserve garnet growth conditions. At high temperatures major elements show diffusive profiles and hence are of very limited use for interpreting the dating results, which imposes a necessity for in situ studies of trace element distribution. In this study we present Sm-Nd and Lu-Hf garnet dating results along with laser ablation ICPMS trace element data obtained for high and ultra-high temperature rocks.

Migmatitic gneisses from N-Vietnam metamorphosed at ca. 800 °C show high quality Sm-Nd isochron ages spread between 50 and 30 Ma. Lu-Hf data obtained for the same samples failed to deliver tight age constraints but clearly point to much older dates. Both Sm and Nd tend to show decreasing from core to rim concentration gradient with decreasing crystal size, which is interpreted as reflecting variable degree of resetting. Indeed, the youngest Sm-Nd age was obtained for the sample with the smallest garnet crystals. Additionally, the youngest age is associated with the highest strain, which shows that not only temperature but also deformation is a significant factor facilitating resetting of the Sm-Nd, and potentially, Lu-Hf clocks in garnet. Lutetium in most analysed garnets shows Rayleigh-like patterns pointing to the preservation of prograde growth conditions. However, minor resetting of the heavy REE in the smallest crystals is observed.

In ultra high temperature granulites from the Bohemian Massif, Sm-Nd and Lu-Hf systems were decoupled and recorded distinct episodes separated in time by as much as 40 to 70 Ma. The oldest Lu-Hf age correlates with the steep Rayleigh-type Lu zonation profile, which indicates that under dry conditions, garnet can withstand temperature even in excess of 900 °C and preserve the time of prograde growth. In granulite which underwent hydration under amphibolite facies conditions, a younger Lu-Hf age correlates with the partially homogenized Lu zonation trend. In the case of Sm-Nd system in the studied UHT granulites, much younger ages do not reveal any obvious correlations with spatial distribution with these elements in garnet.

Weathering of rock minerals has great importance for the natural cycles of elements and other processes on the Earth surface. Lately, several isotopic systems have been employed to study rock weathering. The daughter 234U to the parent 238U ratio can be expressed as an activity ratio (234U/238U) equal to one at secular equilibrium. The (234U/238U) ratio often deviates from one due to recoil effects of 234U: it is either directly ejected (through 234Th) from a mineral or preferential leached from damaged mineral lattices. These effects result in natural waters mostly having (234U/238U) >1 whereas the outer rims of minerals have (234U/238U) <1, the latter depending on time, grain size and α-recoil distance. Thus, (234U/238U) should be a useful monitor to compare between physical or chemical weathering rates.

Two progressively flow-through laboratory leaching experiments on bulk crushed granite samples were conducted over 1200 hours. Input solutions were kept at pH 1 and output solutions were measured for their (234U/238U) and U concentrations. Both experiments show a similar three-step development:

1. 0-400 hours; (234U/238U) above 1 (1.00-1.15)
2. 400-700 hours; a gradual decrease in (234U/238U) reaching <1 (0.90-0.95)
3. 700-1200 hours; relative constant (234U/238U) at ~0.95

The initial U concentrations in the output solutions were of 800-400 ppt U with a continuous decrease in U concentration below <100 ppt after 1200 hours of leaching.

The observed behavior of (234U/238U) in the flow-through experiments suggests that continuous chemical weathering of a granite rock, yields waters with (234U/238U) >1 followed by (234U/238U) <1. As these experiments are short relative to the 238U decay rate, the initial high (234U/238U) cannot stem from in situ 238U decay and suggest that the excess 234U are released from damaged lattice sites due to preferential leaching. When the source of the excess 234U has been exhausted, direct dissolution of minerals from rim inwards starts to dominate the U signal and yields output solutions with a surprising 234U deficit. This suggests that under natural high chemical weathering rates, granitic rocks should yield natural waters with (234U/238U) <1. However this is rarely observed in nature and suggests that the release rates of (234U/238U) during natural chemical weathering, are not fast enough relative to the rates of physical denudation, thereby the 234U/238U system is useful in constraining the relative rates of the chemical and physical weathering.
**3500 Ma of crustal evolution in Fennoscandia as seen from Hf isotopes in zircons from granitoids**

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The Fennoscandian shield shows a generally younging trend from NE to SW, with regionally important crustal growth events in the late Archaean, late Palaeoproterozoic and early Mesoproterozoic. Zircons separated from granitoids (s.l.) ranging from Archaean to Permian age have been dated by U-Pb and analysed for their Hf isotope composition by laser ablation ICPMS. The crystallisation age of the oldest rock so far recognized is ca. 3.5 Ga, with $\varepsilon_{\text{Hf}} \leq +2$, but the rock contains ca. 3.7 Ga old inherited zircons with $\varepsilon_{\text{Hf}} < 0$, indicating a crustal prehistory up to >3.9 Ga. Both depleted mantle and Meso- to Palaeoarchaean crust contributed to crust-forming events at ca. 3.2, 2.9 and 2.7 Ga. At 1.86-1.67 Ga, the juvenile Palaeoproterozoic Svecofennian crust was remobilized at a large scale to form $>10^6$ km³ of Transscandinavian Igneous Belt (TIB) granitoids with relatively uniform $\varepsilon_{\text{Hf}} = +3\pm 3$. The TIB granites did not contain new mantle-derived material, and coeval mafic magmas must have acted mainly as a heat source. In the early Mesoproterozoic, the western margin of the shield grew along a long-lived subduction system. Hf isotopes indicate a significant juvenile input in the western, distal part of the continental arc system ($\varepsilon_{\text{Hf}} \approx +12$), and less so in the eastern, proximal part ($\varepsilon_{\text{Hf}} \approx +8$). At ca. 1.3 Ga and 1.22-1.21 Ga, the western part of the shield was underplated by depleted mantle material ($\varepsilon_{\text{Hf}} \approx +13$). This juvenile component contributed significantly to subsequent granitic magmatism, but its relative influence decreased with time. The late Palaeozoic alkaline magmas of the Oslo Rift are the youngest additions to the Fennoscandian crust. These seem to be mainly derived from a lithospheric mantle source with $\varepsilon_{\text{Hf}} = +2$ to +6, but with contributions from local Proterozoic crust.

**The alteration of zircon and its role in the remobilization of high field strength elements in the Georgeville granite, Nova Scotia**

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The structure and composition of metamict zircon from an epizonal A-type granite in the Antigonish highlands, Nova Scotia, was investigated using transmission electron microscopy (TEM), electron microprobe analysis (EMPA), laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS), and Raman micro-spectroscopy. Individual zircon crystals within the granite are variably altered and are comprised of up to four domains, designated A, B, C and D. Each domain is readily distinguished on the basis of texture and composition. Domain A consists of trace element-enriched zircon and zirconium oxide nanocrystals in an amorphous matrix. Coupled dissolution and reprecipitation of zircon A in proximity to microfractures produced a relatively trace element-poor zircon (domain B), and Th, U, Y, Yb-enriched inclusions (domain C). Domain D is composed of Hf-enriched, amorphous zirconium silicate that is depleted in Y, Yb, Th and U. Domain D occurs within microfractures together with lesser amounts of thorite and thorianite. Alteration of zircon, which is the dominant accessory phase in the Georgeville granite, resulted in preferential hydrothermal transport and precipitation of the lanthanides. Perturbation of the initial high field strength element and isotopic signature of zircon accounts, in part, for the anomalous chondrite normalized rare earth element patterns and Nd isotopic values reported previously for the Georgeville granite (Murphy and Nance, 2002).

**References**

Ti substitution in zircon

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A recently proposed geothermometer (Watson et al., 2006) assumes that the Ti content of zircon is buffered in equilibrium with rutile. However, Ti may substitute into either the Si or Zr site of zircon, and as a result, the concentration of Ti in zircon will change with pressure and with SiO₂ activity as well as temperature. Understanding how Ti partitions between the two sites is therefore crucial to developing this new geothermometer. Based on ionic radius arguments and recent experiments, it was suggested that substitution of Ti for Si dominates (Harrison et al., 2005; Ferry and Watson, 2006).

Gaining a more quantitative understanding of the energetics of Ti substitution in zircon requires the use of computational methods. Therefore, quantum mechanical calculations (CASTEP, Dmol, Crystal) were used as a basis for Monte-Carlo calculations to derive the enthalpy and free energy of mixing for the binary ZrSiO₄ – ZrTiO₄ (assuming that all compositions have the zircon structure) at various temperatures.

Similar calculations are being carried out for the binary ZrSiO₄ – TiSiO₄, again assuming a zircon structure. Preliminary quantum mechanical calculations suggest that substitution of Ti into the Zr site requires a similar amount of energy as substitution into the Si site for low Ti content (x=0.0625 in Zr(Si₁₋ₓTiₓ)O₄ compared with (Zr₁₋ₓTiₓ)SiO₄). Excess volume is also calculated for both solid solutions in order to estimate the effect of increasing pressure.

References

Understanding carbon isotope records from wetland plants: Implications for paleohydrology

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In contrast to terrestrial plants, carbon isotopic results from wetland plants, such as pond cypress, have a positive relationship with rainfall amount. One important plant in the greater Everglades ecosystems is sawgrass (Cladium jamaicense), which comprises an important part of the regional ecosystem. To calibrate and understand the isotopic changes that may potentially be related to changes in water level, which corresponds to hydroperiod in a temporal manner, mesocosm experiments were used to grow these plants at different water levels. 24 mesocosms were randomly assigned 4 different water treatments to simulate changes in hydroperiod and water depth, similar to the typical Everglades wet season and dry season cycle. Our initial results from this work show a strong correlation between variations in water depth and plant carbon isotope values in the shallow water treatments vs. the deeper water treatments (Fig.1). Further analyses are presently underway to compare assimilation with the collected carbon isotopic data. These results confirm the observations from the cypress work, and set the stage for using carbon isotopes from preserved OM and/or biomarkers to reconstruct changes in water level from wetland settings.

Figure 1: Carbon isotope values compared to water depth in young (A) and mature sawgrass leaves (B).
The sources of Nd isotopes in Arctic Ocean water

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The Arctic Ocean connects the Pacific and Atlantic Oceans and it also receives a significant freshwater input equivalent to 10% of the global river run-off. The most important exchange of Arctic Ocean water masses occurs through the Barents Sea and Fram Strait with the Nordic Seas (Norwegian, Greenland and Iceland Seas) and this exchange is crucial for the formation of North Atlantic Deep Water. The Nd isotopic composition, εNd(0), of the northern North Atlantic is well characterised but it is not clear how the signal is acquired and how it relates to the Arctic Ocean.

We have determined the Nd concentration, CNd, and εNd(0) of the major inflow areas to the Arctic Ocean through the Barents Sea and the Fram Strait, as well as the dominant Arctic outflow through the Fram Strait.

The Barents Sea inflow has a CNd of 15 pmol/kg and an εNd(0) of -10.7, which is similar to waters from the northeastern Nordic Seas and demonstrates that Nd from the Atlantic dominates the Arctic inflow. In contrast to the inflow, the Nd in the major Arctic Ocean outflow, the Fram Strait, is isotopically different with a higher εNd(0) of -9.8 throughout the entire water column, down to 1300m depth. This reflects addition of Nd derived from sources that include Pacific water, shelf sediments and rivers within the Arctic Ocean basin. River water inflow is a possible source for the added Nd to the surface waters, but it is also likely that Nd from Pacific waters modified by addition from shelf sediments in the Canada Basin is an important component in the Fram Strait surface outflow. The isotopic shift in the deeper water of the Fram Strait outflow is probably not directly related to river- or Pacific water input but rather to exchange with sediments along the shelf of the Canadian archipelago. It is likely that different sources contribute to the Nd at different depths in the water column. The influence of these sources on the isotopic composition of the northern North Atlantic will be discussed.

Reactivity of nitrates in the near field of type-B nuclear waste cells

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Introduction

B2-type nuclear waste consisting of a dry mixture of bitumen and a mineral phase (mainly NaNO₃ and BaSO₄ salts mixed with radionuclides) is proposed for deep geological storage. After closure the waste cell will progressively resaturate leading to the dissolution of soluble salts and the diffusion of dissolved species within the compartments of the storage cell (cement engineered barrier and argillite host rock in the French case). Chemical modifications, such as denitrification, catalysed by possibly existing bacterial activity, will affect the system equilibrium. This study is intended to gain a better comprehension of the redox reactions involving nitrates and bacteria and their possible impact on the long term evolution of the B2 waste cells.

Modelling concept

Denitrification processes are modelled with the Phreeqc code, which couples geochemical reactions with dispersive and diffusive transport. Calculations were performed on a 1D column with a nitrate source on one side followed by two major zones in which only diffusion of dissolved species (nitrates, organic matter...) is allowed.

A particular attention is paid to the role of nitrate as an electron acceptor in the presence of micro-organisms and different electron donors (i.e. iron, pyrite, organic matter or hydrogen gas). The consideration of these different redox reactions allows description of the overall denitrification process. The mathematical tool for estimation of the impact of bacterial activity on reaction kinetics proposed by Jin and Bethke (2005) has been implemented in Phreeqc to model microbial controlled kinetics in reactive chemical transport.

Discussion and conclusions

Different denitrification scenarios were modelled showing important nitrate reduction in the first centimeters within the cement barrier. Modifications of gas phase composition and mineralogical assemblages of cement and argillite barriers are also predicted. Results emphasize the lack of experimental data to constrain the model, but help to guide future laboratory experiments, to define the role played by the electron donors and to better estimate nitrate concentrations and microbial implications.

References

Trace element analysis and dating of monazite single grains by XRF milliprobe: Quick, cheap, simple

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Single grains (crystals) of monazite (Ce,La...)PO₄ are micro objects with size varying from 0.05 mm to 0.5 mm and mass from n-0.1 mkg to n-100 µg. Monazite are known as relatively stable in sedimentary environments and their detrital population could reflect the provenance. Such techniques as LA-ICP-MS, EMPA and SIMPS have good analytical characteristics (low detection limits, high precision and spatial resolution) and usually are applied. But they require expensive hardware and time-consuming sample preparation. This paper presents a new promising technique - XRF milliprobe of single grains (XRF MP/SG) for analysis of monazite trace elements (Sr, Y, Pb, Th, U), and chemical U-Th-Pb dating obtaining in a great number of such grains within a real time. It was designed with two thin X-Ray beams from two independent X-ray tubes, which irradiate the sample by turns. The beam of first tube (Mo anode) is monochromatic by cylindrical crystal-monochromator (LiF, plane 200) for MoKa line, the beam of second tube (Fe anode) is filtered by different changing filters. Both of beams are collimated to diameter 0.5 mm. Characteristic X-ray of a sample is detected by energy-dispersive spectrometer with Si(Li) detector cooled by liquid nitrogen. Detection limits in zircon, monazite for grains with masses 1-10 mg are as follows: Sr,Y – 5-10 ppm, Pb,Th,U – 10-20 ppm. The statistical uncertainty is defined by counting statistics in peak of element analytical line. In the fixed conditions of measurements it depends on weight of grain, concentration of the elements and analyses time.

Figure 1: Experimental statistic uncertainty of fluorescence intensity for monazite grain (mass 0.46 mkg, ball diameter 0.054 mm).

The systematic dependence between intensity of fluorescence being registered from the grain and mass, form of the grain is calculated.

The method is absolutely non-destructive, small grain can be repeatedly measured for improved statistics (and improved age precision), thus providing a possibility of analysis by other method.

Trees and weathering: Insights from root-mineral contacts

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Over geologic time scales atmospheric CO₂ levels are controlled by the feedbacks and processes of the long-term carbon cycle. One poorly understood aspect of this cycle is the impact of the evolution of large vascular plants (trees) and their role in accelerating silicate weathering. In particular, differences in weathering between gymnosperms (Paleozoic origin) and angiosperms (Mesozoic origin) still need to be unravelled as they may play a critical role in the regulation of atmospheric CO₂ over geologic time scales. Differences in nutritional requirements, seasonal shedding of biomass, extent of association with ectomycorrhizal fungi and associated microbial and terrestrial burrowing organisms are potentially responsible for these differences in weathering on soil and bedrock silicate minerals. However, the actual impact of the different trees and associated ecologies remains to be elucidated. Sensitivity analysis of the the GEOCARB model of Phanerozoic atmospheric CO₂ (Berner and Kothavala, 2001) indicates that even small differences in rates of weathering between the two tree types may have a significant impact on the evolution of Mesozoic CO₂.

To address this issue, this study focuses on soil cores collected along transects of small groves containing both angiosperms and gymnosperms in the Cascade Mountains of Washington State. These cores were carefully collected and preserved in epoxy with minimal disturbance to the samples. Root-mineral contacts and the spatial geometry of roots and soil particles were successfully captured in the epoxied core sections. Qualitative differences in these cores are observed both along the transect (corresponding to nearest tree type) and with depth in individual cores. Weathering intensity is greatest both near the surface (all cores), with soil particles coarsening with depth, and in proximity to the gymnosperms. Quantitative differences in the root-rock reaction zones will be directly evaluated using the electron microprobe to observe any mineral alteration near roots, as well as overall chemistry and petrology of the soils on a fine scale. This unique snapshot of the complex interactions between tree roots and their host soil mineralogy provides insight into the impacts of different tree types on silicate weathering.

References

Monazite single grain trace element analysis and dating by XRF milliprobe

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Monazite is stable in sedimentary environments and its detrital populations could reflect provenance. Such techniques as LA-ICP-MS, EMP and SIMS commonly are applied to study a monazite composition. They have good analytical characteristics but require expensive hardware and time-consuming sample preparation. Single-grain milliprobe XRF analysis (XRF-MP/SG) is a new promising technique for trace elements (Sr, Y, Pb, Th, U) determination and chemical U-Th-Pb dating of monazite. This technique was designed on a base of original XRF installation with two thin X-ray beams (collimated to 0.5 mm) from two independent X-ray tubes with Mo and Fe anodes and energy-dispersive spectrometer with Si(Li) detector. Detection limits for grains with masses 1-10 µg are: Sr, Y – 5-10, Pb, Th, U – 10-20 ppm. The fluorescence intensity of elements vs. shape and mass of grains as well as their matrix effect were calculated to calibrate the quantitative element analysis. The statistical uncertainty is defined by counting statistics in spectrum peaks. It depends on grain mass, element concentrations and measurement time (Fig. 1).

Figure 1: Experimental statistic uncertainty of fluorescence intensity for spherical monazite grain (m≈1.1 µg, Ø≈0.07 mm).

Up to then unknown ‘young’ stage of significant formation of monazite within the East European Platform has been discovered as a result of XRF-MP/SG application (Fig. 2).

Figure 2: Age spectra of detrital monazites from sediments sampled within the Ukrainian Shield.

Study of the copper reactivity in organic soils

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The accumulation of heavy metals in soils can cause adverse effects in natural systems due to their mobility and bioavailability. The study of heavy metals speciation in such systems can be controlled by the presence of different types of sorbent materials. Until now, several studies have deal with the interaction of heavy metals with isolated soil fractions such as natural organic matter which has been proved to bind strongly to metal cations. In the present work a comparative study was carried out between the copper binding on a peat sample and on a peat humic acid. A widely used model for describing the metal binding to humic substances is the NICA-Donnan. We have checked the possibility of using this model with the peat sample which is expected to exhibit a similar behaviour to that observed for humic substances in solution.

The effect of pH and ionic strength observed for the peat sample shows the same trend as in the peat humic acid. In both cases the copper binding is enhanced by an increase in pH or decrease in ionic strength. The main difference between both samples could be attributed to different binding sites content. The peat shows higher complexation capacity than its humic fraction.

An acceptable prediction of the experimental results for the peat sample was achieved with the NICA-Donnan model. The fitted parameters were quite similar to those obtained for the peat humic acid (Gondar et al., 2006) and also to the generic NICA-Donnan parameters for copper-humic acids binding published by other authors (Milne et al., 2003)

References
Geochemistry of microgranular enclaves and host granodiorite from Oledo, Central Portugal

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The Iberian massif corresponds to the southwestern extension of the European Variscan Belt. The Ordovician magmatism is rare in the Central Iberian Zone of this massif. A medium-grained biotite granodiorite from Lower Ordovician of 479-480 Ma crops out at the Oledo-Idanha-a-Nova pluton. It intruded the Cambrian schist-metagreywacke complex, is deformed and contains fine-grained biotite tonalitic and biotite granodioritic microgranular enclaves, which are darker and richer in mafic minerals than the host granodiorite. The microgranular enclaves show rounded or ovoid shapes, some of them irregular, having sharp, occasionally crenulated and diffuse contacts. Microgranular enclaves and host biotite granodiorite are peraluminous (A/CNK=1.00 to 1.13) and contain quartz, K-feldspar, albite-labradorite, amphibole, biotite, sphene, allanite, zircon, monazite, apatite, ilmenite and magnetite. Variation diagrams of the rocks and their biotite, sphene, allanite and ilmenite show trends of fractionation from tonalitic enclaves to host granodiorite. The rare earth element (REE) patterns are sub-parallel and show fractionation of REE from tonalitic enclaves to host biotite granodiorite. Biotite increases and anorthite content of plagioclase decreases from tonalitic enclaves towards the host granodiorite. Biotite composition shows fractionation with increase in deformation of host granodiorite. The least squares analysis of major elements and modelling of trace elements indicate that granodioritic enclaves and host biotite granodiorite were derived from the tonalitic magma by fractional crystallization of plagioclase, amphibole, biotite and ilmenite. The ($^{87}$Sr/$^{86}$Sr)$_{i}$ ratio (0.7050-0.7067), εNd$_{i}$ (1.56-3.46) and δ^{18}O (6.00-8.92‰) values indicate that they are I-type granitic rocks and contain a mantle component. The decrease in ($^{87}$Sr/$^{86}$Sr)$_{i}$, regular variation of εNd$_{i}$ and increase in δ^{18}O from tonalitic enclaves to host biotite granodiorite suggest that another mechanism has also occurred, probably mixing with other magmas or are related to deformation.

An integrated in-situ O, U-Pb and Hf isotope approach to decipher the petrogenetic evolution of granites

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The combination of in-situ O, U-Pb and Hf isotope analyses of zircon provides very powerful constraints on the sources, ages and evolution of granitoid magmas. This robust zircon record has been accessed at the intra- and inter-grain scale by combining SEM imaging with SIMS ($^{18}$O and U-Pb) and LA-MC-ICP-MS (Lu-Hf) micro-analysis. The combined information has been used to constrain crystallisation and crustal residence ages, magma sources and relative mantle and crustal contributions of late Caledonian ‘I-type’ granites of the Scottish Grampian Highlands, which were emplaced between 430 and 400 Ma following the c. 470 Ma Grampian Orogeny. These comprise two main suites based on whole-rock geochemical and isotopic data. This study focuses on granites and diorites of the 420 Ma Lochnagar and the 425-400 Ma Etive plutons (U-Pb ages), representing the Cairngorm and Argyll suites respectively. In both plutons high-precision SIMS oxygen isotope analyses have enabled us to recognise statistically distinct zircon populations (e.g. Lochnagar diorite: population 1: 6.6±0.4‰ (2σ), population 2: 7.4±0.4‰ (2σ)) that indicate the entrainment and mixing of distinct mafic and felsic lower crustal source components. The absence of pure mantle zircon populations ($^{18}$O (Zrc) = 5.3±0.3‰) indicates that none of the granites and diorites contain an identifiable unmodified mantle component.

In-situ Hf isotope data also show a large spread in both plutons (Lochnagar: εHf = +4 to -4; Etive: εHf = -2 to -8 (±0.7-1.0 εHf (2σ)). This variation is caused by mixing of several felsic crustal components of differing residence ages in the range ~1.2 – 2.0 Ga. Thus, this approach is able to distinguish several different mixing events and provides insights into the nature and ages of the sources involved. It also shows that formation of the 430-400 Ma Caledonian granites in Scotland is dominated by crustal recycling rather than crustal growth.
Very high exhumation rates in the central Swiss Alps, revealed by the (U-Th)/He and fission track analyses

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Apatite and zircon (U-Th)/He thermochronological data together with apatite fission track analyses from near the Lötschen valley and subsurface samples from the NEAT tunnel are used to constrain the exhumation and thermal history of the western part of the Aar crystalline massif in the central Swiss Alps. This region is undergoing active deformation as geodetic measurements indicate current uplift at a rate of 1 mm/a. Samples for this study have been collected over an overall elevation range of 3 km. Exhumation rates calculated from both age-elevation profiles and from cooling curves constructed using multiple systems agree with each other and suggest that a geothermal gradient of ~30°C/km has likely remained stable over the last 7 Ma. Zircon (U-Th)/He and apatite fission track data indicate that a period of relatively fast exhumation (~3 mm/a) occurred at 5.5-6.5 Ma. This episode of rapid exhumation, previously undetected in past studies, correlates well with a contemporaneous, high erosional flux in the internal parts of the Alps (Messinian salinity crisis). The rate of exhumation in the western Aar massif, although relatively high, is in agreement with Pliocene exhumation rates described recently from the nearby Mt. Blanc massif. Because of high spatial resolution and three dimensional sampling in this area we have identified a significant role of localized heat advection by hot fluid circulation in the crystalline rocks, postdating initial cooling registered by the applied methods. The northern part of our study area appears to have been severely affected, as evidenced by young apatite (U-Th)/He ages. Similarly, some zircon (U-Th)/He ages suggest considerable resetting in the lowest elevation, axial part of the valley. The average exhumation rate calculated for the period between closure to helium diffusion in apatite (U-Th)/He and the present day from the tunnel samples is ~0.3 mm/a while current surface uplift is 2-3 times faster. This discordance can be explained by either recent acceleration in uplift of the Aar massif or, more likely, by transient changes in the thermal structure within the massif due to fluid circulation and associated heat advection. Exhumation rates calculated with the reset ages represent minimum values. These results underscore the caution that must be taken when interpreting low temperature geochronological data from Alpine regions.

Magma generation and transport in subduction zones: Numerical simulations of chemical, thermal and mechanical coupling during magma ascent by porous flow

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Most subduction zones are characterized by significant magmatic activity responsible for building trench-parallel volcanic arcs above descending slabs. High magma production rates observed within the arcs result from infiltration of water-reach fluids released by slab dehydration. The released water triggers hydrous melting of hot mantle wedges located above the cold slabs. However, the process of magma transport from the melt generation region located above the hydrated slab surface at 100-300 km depth to the magma extraction zone at the volcanic arc surface, and its influence on mantle wedge deformation, are not well known. In particular, during basaltic liquid ascent through the mantle wedge, decreasing pressure and temperature changes are likely to induce significant compositional variations, especially in terms of dissolved water content. Relationships between melt transport and mantle wedge deformation are also not clearly understood. We present a numerical model of magma generation and transport in subduction zones, that simulates chemical, thermal, and mechanical interactions between fluids and solid rocks along the magma ascent pathway. Magma migration is modelled by a porous flow across a constant permeability matrix, while the solid downward current associated with subduction in the mantle wedge, is included. The heat advected by the percolating liquid phase as well as latent heat effect associated with melting will be included. Water exchanges between the molten rock and the solid matrix are computed as a function of pressure, temperature, and solubilities laws in melt. We will first present benchmark results to validate the porous flow modelling as well as the emnery equation resolution for a two-phase flow. The aqueous and magmatic fluid repartition within the mantle wedge will then be presented. Magma productivity rates, varying along the magma ascent pathway, will be discussed as a function of magma viscosity.
The Mo isotopic composition of rivers suggests complete euxinia in the Proterozoic ocean

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Quantifying the extent of past marine anoxia has become a key research goal in recent years [e.g. 1, 2]. Placing firm constraints on the oxygenation history of the ocean is essential for our understanding of the interaction between ocean and atmospheric chemistry, biological evolution, and nutrient controls on primary productivity. Recently, the isotopic record of the marine geochemistry of molybdenum has shown promise as such a palaeoredox indicator [1]. However the use of Mo isotopes in this way has been hampered by the fact that the isotopic composition of rivers, the dominant input of Mo to the oceans, is unknown and has been assumed to be that of average continental Mo isotopic composition.

We report here the isotopic composition of the dissolved Mo content from a selection of global rivers. In contrast to the expected value of 0‰ for the continental source to the oceans, the rivers sampled exhibit a range of Mo isotope compositions with δ97/95Mo always positive and ranging from 0.1 to 1.5‰. Further, there is a general relationship between δ97/95Mo and the reciprocal dissolved Mo concentration, defining an average δ97/95Mo input to the oceans of +0.7±0.2‰. Ancillary data, as well as published constraints on riverine Mo geochemistry, demonstrate that the mechanism for the observed isotopic fractionation is adsorption onto Fe-Mn oxides.

This process must occur wherever Mo exists as an oxidised aqueous species, therefore providing a mechanism for Mo isotopic fractionation in rivers since the onset of oxidative weathering on the continents ca. 2.2 billion years ago [3]. The estimated value for the δ97/95Mo input of Mo from rivers has profound implications for recent Mo isotope data from Mid-Proterozoic [1] and Mesozoic OAE [4] black shales [4]. Reported oceanic δ97/95Mo from these periods approach of the value we find in modern rivers suggesting perhaps a lower limit of riverine and oceanic δ97/95Mo after the onset of oxidative continental weathering and further implies near complete euxinia in the global ocean during these periods.

References

Long-term geochemical evolution of the near field repository: Insights from reactive transport modelling and experimental evidences

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The hydrogeochemical role played by clay-based barriers in a high-level nuclear waste (HLNW) repository is twofold: (1) the retardation of the groundwater inflow to the waste canisters, and (2) the retention of radionuclides in case of canister failure. The latter is especially relevant taking into account that parameters such as pH and redox state will control the solubility and sorption of radionuclides. The long-term evolution of the porewater chemistry of the barrier system depends mainly on the nature of the inflow groundwater and on the composition of clay material. On one hand, groundwater chemistry may undergo sharp changes due to the climatic evolution, mainly linked to glaciation / deglaciation cycles. On the other hand, the buffering response of barrier to these changes will intimately be associated with the composition and content of some accessory minerals in the clay (dissolution/precipitation of carbonate, sulphate and iron-bearing minerals).

In this work, the long term response of bentonite barrier due to the interaction with groundwater is evaluated by using reactive transport calculations. We considered a granitic groundwater and two commercial bentonites, MX-80 Wyoming-type and Deponit CA-N Milos-type. Moreover, a temperature gradient has also been considered.

The results indicate that the interaction of a granitic groundwater with the bentonite buffer has minor effects on the pH evolution of the system, buffered by carbonate minerals. The redox state seems to be controlled by the regional groundwater, in equilibrium with pyrite and siderite. Composition of the surface sites in montmorillonite in bentonite significantly change since an increase of calcium occupancy is predicted by the model, related to calcium sulphate dissolution.

Finally, temperature gradient caused by heat generation in the canister leads to a general decrease of pH. In addition, it affects the content and distribution of some accessory minerals such as gypsum or silica.

Recent experiments with high-density unsaturated bentonite performed in the frame of NF-PRO European project give support to the results obtained with the model.
Modelling the biospheric influence on the weathering rate of silicate rocks in an EMIC

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On geological time scales the main agent for removal of CO₂ from the atmosphere is the formation of carbonate rocks in the oceans. The rate of formation is dependent on the input of products of weathering of silicate rocks from river runoff [1]. Weathering rates depend on climatic conditions such as the strength of the hydrological cycle but also on biospheric processes such as soil genesis, which in turn depend on the climate [2]. These fluxes of the global carbon cycle are usually modelled with global geochemical box models on geological time scales. In order to get spatial scale resolutions of weathering rates a geochemical model can be combined with an Earth System Models of Intermediate Complexity (EMIC) as previously done in [3], by using the EMIC’s climatic output as input to the geochemical model. The study clearly illustrates the importance of spatial detail, which is not resolved in box models. In order to model weathering fluxes in a more direct way and quantify the importance of other spatially variable drivers, we develop a soil weathering module in connection with the SIMBA (SIMulation for Biospheric Aspects) vegetation model [4] for implementation into an EMIC. SIMBA simulates spatially explicit vegetation productivity and biomass as a function of temperature and soil moisture. With the soil module we simulate a) biospheric influence on soil water pH values through heterotrophic and root respiration of CO₂ [5] and b) potential soil water cation concentration by dissolution towards chemical equilibrium between soil water and generic silicate rock fragments corresponding to feldspars such as anorthite. The weathering or dissolution of cations from silicate rocks becomes a direct function of rainfall, runoff and soil water pH values and thus both directly and indirectly of biospheric productivity. In this talk we will present model results of spatial variability of pH and cation fluxes within the scope of long term climate variability.

References


Detecting core-mantle interactions with W

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Whether or not chemical interactions occur between the core and lowermost mantle has been a controversial issue. The unambiguous identification of core-mantle exchange yields major implications for constraining mantle circulation patterns, the timing of inner-core crystallization, conditions at the core-mantle boundary, and the existence of an early enriched reservoir at the base of the mantle. Recently, core-mantle interactions have been inferred on the basis of coupled 186Os-187Os enrichments and elevated Fe/Mn ratios in Hawaiian lavas (Brandon et al., EPSL 1999; Humayun et al., Sci 2004). Tungsten (W), however, provides a powerful, dual approach to the detection of core-mantle interactions through the use of both W isotopic signatures and concentration ratios.

We have analyzed a global suite of 86 mantle-derived lavas via LA-ICP-MS. The samples, which are primarily basaltic glasses representative of MORB, arc, and intraplate sources, show little variation in W/Ba (0.00136 ± 3, 2n). This value, which is concordant with previously published data for continental crust (Newsom et al., GCA 1996), is taken to represent the ratio of the silicate Earth. Assuming 6600 ± 1320 ng/g Ba in the silicate Earth, the abundance of W in this reservoir is 9.0 ± 5.8 ng/g. Accounting for the 1000 ± 300 ng/g W in the continental crust, the mean W concentration in the modern mantle is 4.1 ± 2.9 ng/g, with MORB and OIB representing more depleted and enriched source regions, respectively. Following mass balance, the core contains 516 ± 116 ng/g W. The relative abundance of W in the core and silicate Earth, coupled with the unique W isotopic signatures of these reservoirs (silicate Earth εW ≈ 0; core εW ~ 2.1), demonstrate that no core-mantle interaction is recorded in previously analyzed Hawaiian picrites (Schersten et al., Nat 2004), assuming a source of undifferentiated mantle.

As the W/Ba ratio of the core exceeds 10⁴, minor enrichments in W/Ba in plume-derived magmas provide a sensitive tracer of outer core additions to a deep mantle source. The restricted range of W/Ba in modern-mantle sources indicates that 1 wt% addition of outer core material to a model Hawaiian plume source (with ~9 ng/g W) would result in a detectable increase in W/Ba by > 50%, as compared to an ~ 10% change in Fe/Mn.
Mg-Fe\textsuperscript{2+}-Fe\textsuperscript{3+}-Al-Si-O phase relations at lower mantle conditions: Lack of evidence for Fe-disproportionation

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Experiment and theory show that the charge-coupled substitution Fe\textsuperscript{3+}Al\textsuperscript{3+} ↔ Mg\textsuperscript{2+}Si\textsuperscript{4+} is highly favored in Mg-perovskite, with Fe\textsuperscript{3+} on the large Mg-site and Al\textsuperscript{3+} on the smaller octahedral site [1-3]. This substitution is postulated to be so favourable that in the presence of (Mg,Al) perovskite, Fe\textsuperscript{3+} will form by the disproportionation reaction 3FeO ↔ Fe\textsubscript{2}O\textsubscript{3} + Fe\textsuperscript{0} [1]. This reaction would produce coexisting (Fe\textsuperscript{3+}, Al\textsuperscript{3+})-rich perovskite and iron metal in the lower mantle. If correct, FeO disproportionation provides a mechanism for the ‘self-oxidation’ of the mantle during core formation, and may help explain the siderophile element geochemistry of the mantle [1, 3]. Here, we investigate perovskite phase relations in the system Mg-Fe\textsuperscript{2+}-Fe\textsuperscript{3+}-Al-Si-O and report on laser-heated diamond anvil cell experiments at 30-100 GPa and 1500-2500 K. Run products were analyzed using synchrotron X-ray powder diffraction.

Experiments along the join MgSiO\textsubscript{3}-FeO\textsubscript{3} up to ~70 GPa show a considerable solubility (>25 mol\%) of Fe\textsuperscript{3+} into perovskite via the substitution 2Fe\textsuperscript{3+} ↔ MgSi, requiring that Fe\textsuperscript{3+} occupies the octahedral site in Al-free systems. Unit cell volumes increase slightly with increasing FeO, and the perovskite structure distorts mildly compared to distortion caused by Al\textsuperscript{3+} or coupled Fe\textsuperscript{3+}Al\textsuperscript{3+} substitution. New experiments along the join MgSiO\textsubscript{3}-FeAlO\textsubscript{3} show a maximum FeAl\textsubscript{2}O\textsubscript{4} solubility between 25 and 50 mol\% at 70 GPa.

We made compositions in which enough FeO was added on a molar basis to MgSiO\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} glasses for complete substitution via Fe\textsuperscript{3+}Al\textsuperscript{3+} ↔ MgSi should all the FeO disproportionate. Perovskite, ferropericlase and stishovite coexist in a composition with ~23 mol\% Fe\textsuperscript{3+}Al\textsuperscript{3+} at 35 – 60 GPa (~ 2000 K). In a composition with ~50 mol\% Fe\textsuperscript{3+}Al\textsuperscript{3+}, perovskite coexists with a ferrite-structured phase (± stish. or ferroper.) at similar P-T conditions. These results are explicable by quaternary phase relations in the reduced system MgO-FeO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}. In contrast, if iron disproportionation were occurring then a Fe\textsuperscript{3+}-Al\textsuperscript{3+}-rich perovskite would coexist with pure iron. Calculations show that even 1 mol\% iron metal should be detectable by diffraction, yet we see no clear evidence of metallic iron in any diffraction pattern. Our results indicate that above the maximum solubility of Fe\textsuperscript{3+} in aluminous perovskite, stishovite + ferropericlase are stabilised and phase relations remain quaternary.

References
**Black Sea shelf microbial reefs**

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**Introduction**  
Microbial reefs, fuelled by the anaerobic oxidation of methane, grow in anoxic waters at the Black Sea shelf (Figure a). The key methanotrophic microbes were identified, but little is known about the structures of reef-forming microbial communities.

In order to follow the reefs growth, we analysed sediment surrounding an active gas seepage (Figure b), a supposably initial reef stage (Figure c), as well as different parts of one reef (top, exterior and center) from the Danube Canyon by using molecular tools. Further reef samples from three different locations along the northwestern shelf (Metrol Cruise POS317/3: Danube Canyon, Northwestern Shelf and Paleo-Dnepr Area) were characterised to address the question whether the reefs are comparable structures.

**Figure:** Supposed stages of forming reefs

**Discussion of results**  
A major fraction of the reef-forming communities consisted of anaerobic methane oxidising archaea (ANME) of which either ANME-1 or ANME-2 dominated certain reef parts. Key bacterial players were members of the sulphate-reducing *Desulfosarcina* / *Desulfococcus*, as well as *Planctomycetes* and *Verrucomicrobia*. The reef’s top was characterised by the abundance of huge, apparently active ANME-2 aggregates whereas the center comprised mostly single, probably inactive cells. Most ANME-1 were found in the center, however including numerous dead cells. The exterior of the reef was highly heterogeneous with respect to ANME distribution and bacterial diversity. The comparison of reefs showed a high variability between activity and abundance of different groups, but most key players appeared in all samples.

**Conclusions**  
We hypothesize, that the most active microbial growth area of the reef is the top, whereas the center seems to be the oldest part. The reef’s exterior provides heterogeneous microniches and might grow more or less radially. Reefs along the northwestern shelf differed remarkably. Certain groups seem to represent typical reef-forming microbes, but the variable community structures suggest various environmental conditions or reef ages.

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**Scientific drilling in the Barberton Greenstone Belt**

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The Barberton Greenstone Belt in South Africa is a remarkable natural laboratory where conditions at the surface of the Archean Earth can be investigated. Shallow (100-1000m) diamond cores will be drilled in selected volcano-sedimentary successions in order to reconstruct the geodynamics of Archean sedimentation and volcanism, how these processes interacted at the interface between lithosphere-hydrosphere-atmosphere-biosphere, and the environments at the Earth’s surface where life first emerged and subsequently evolved.

Despite generally good outcrop, nowhere in the Barberton belt are complete sections preserved, and crucial features such as the contacts of lava flows and critical sedimentary rock sequences are not exposed. Drilling is needed to obtain such sections and relatively unaltered samples. Two main targets have been identified. (1) Sedimentary sequences will provide information about erosion and sedimentation on the early Earth, the composition and temperature of Archean seawater, and one site where life may have emerged and evolved. Tidal sequences will inform us about the dynamics of the Earth-Moon system, and spherule layers and impact debris provide information about the nature and magnitude of meteorite impacts. (2) Successions of ultramafic to felsic volcanic rocks will provide new insights into volcanic processes, mantle dynamics, and interaction between oceanic volcanic crust and the hydrosphere and biosphere. The sources of hydrothermal fluids on the ocean floor, driven by circulation of seawater through the volcanic pile, constitute a second habitat of early life.

The project is supported by scientists from 13 countries in five continents and by the mineral exploration industry. Planning meetings have been held in Johannesburg (Oct 2006), San Francisco (Dec 2006) and Berlin (March 2007). Proposals for funding have or will be submitted to agencies in Europe, America and Asia and to the ICDP.
Diagenesis in deep-seated Cretaceous black shales: Inverse modeling and transient model simulations

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A transport-reaction model was designed to identify the importance and specific rates of diagenetic processes operating in four sites drilled during ODP Leg 207 (Demerara Rise, Equatorial Atlantic). Model results reveal that almost 100 Ma after their deposition, deeply buried (200-500 mbsf) Cretaceous black shales still act as active bioreactors at great sediment depths. Methanogenesis in the black shales is identified as a key process, which dominates not only organic matter degradation but also the sulfate availability through the anaerobic oxidation of methane above the black shale sequences. The complete depletion of sulfate in the methane-rich black shale sequences promotes the dissolution of biogenic barites. The released barium reprecipitates as authigenic barite at the top of the sulfate depletion zone and serves as an indicator for the location of the sulfate-methane interface.

Reaction rate constants were determined by inverse modeling techniques. Due to the low metabolic activity in the deep biosphere, estimated rate constants are orders of magnitudes lower than those observed in the shallow subsurface. Model-determined methanogenic rate constants (1-3.5 10⁻⁹ a⁻¹) compare well with those estimated by the empirical power law (Middelburg, 1989). In addition, methanotrophic reaction rates (10⁻² μM a⁻¹) are similar to experimentally determined rates at other deep biosphere sites (ODP Leg 201). Transient model simulations indicate that the initial reactivity of the black shale organic matter must have been already low (ca. 1.1 10⁻⁸ a⁻¹) during its deposition 100 Ma ago. The decrease of organic matter reactivity and the associated decrease in methanogenic rates, as well as changing sedimentation rates lead to significant shifts of the sulfate methane interface over the past 100 Ma. The associated vertical migration of the barite precipitation zone is well recorded in the barite depth profile and supports our transient model results.

References

Phosphogenesis in recent upwelling areas: The importance of microbial communities indicated by lipid biomarkers

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The burial of phosphorus and the formation of phosphorites (phosphogenesis) in marine sediments represent an important sink in the global phosphorus cycle. Numerous basin-scale phosphorite deposits were formed in the geological past (e.g., Trappe 1998). Phosphogenesis is not only found in ancient settings, it is reported in recent sediments of upwelling regions as for example off Namibia, Peru, and Chile (Föllmi 1996).

These sediments contain dense populations of large nitrate-storing sulfate-oxidizing bacteria *Thiomargarita*, *Beggiaota*, and *Thioploca*, respectively. Due to metabolic activities of the thiophots generating sulfate, a close spatial connection to sulfate-reducing bacteria is established. Differences in the motility of the thiophots at the three study sites lead to different distributions of sulfate reducers in sediments off Namibia, Peru, and Chile. Profiles of lipid biomarkers attributed to sulfate reducers (10MeC₁₆:₀ fatty acid, ai-C₁₅:₀ fatty acid, and mono-O-alkyl glycerol ethers) document the close association to thiophots. Depth profiles of mono-O-alkyl glycerol ethers have been found to correlate best with the occurrence of large sulfur bacteria. This suggests a particularly close link between mono-O-alkyl glycerol ether-synthesizing sulfate reducers and thiophots. Lipid biomarker profiles indicate that the interaction between thiophots and sulfate-reducing bacteria favors phosphate enrichment, triggering phosphorite formation in upwelling areas.

Studying recent phosphogenic environments provides a basis to better understand microbial influence on phosphogenesis and to better constrain the role of microorganisms in the formation of ancient phosphorites.

References
**The role of cations versus anions in the dissolution of ionic crystals**

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In growth and dissolution of binary ionic crystals, a common assumption is that the cation plays a more fundamental kinetic role than the anion. This thinking derives from the recognition that a key step in ion transfer between solid and solution involves hydration (dissolution) or dehydration (crystallization). In the case of carbonate growth, the energetic penalty of removing water from the hydration shell may impose the limiting step, particularly if the metal involved is strongly hydrated (e.g., Fe²⁺, Mg²⁺). Surface complexation models [e.g., 1,2] are consistent with this thinking. However, to explore this process accurately requires knowledge of the interaction of these species with particular surface sites.

We can test these ideas with parameterized Monte Carlo calculations of dissolution reactions involving various carbonates. These models involve the full crystal lattice and are parameterized by ab initio and DFT calculations. This approach allows us to study the problem of how a given ion (Ca²⁺, CO₃²⁻) interacts at individual surface kink sites. In addition, we can investigate the role of specific metal inhibitors (Mn²⁺, Sr²⁺, Mg²⁺). We will present several examples, including (1) the influence of an impurity metal on dissolution in terms of dehydration versus carbonation reactions, and (2) differences in reaction pathway during anion versus cation attachment and detachment. The tested model generates a predictive tool for dissolution kinetics of carbonate minerals.

**References**


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**4⁰Ar/3⁹Ar geochronology and Sr-Pb isotopic evidence of post-collisional extensional volcanism of the eastern Pontide paleo-arc, NE Turkey**

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Tertiary aged post-collisional volcanics show stratigraphic, petrographic and age differences in the northern and southern zones of the eastern Pontides. The Eocene sequences in E-W direction are exposed as basin fillings in the southern zone and overlay the Upper Cretaceous and Paleocene aged units. The volcanic rocks in the Gümüşhane and Alucra areas are mainly basalt, basaltic andesite, andesite, trachyandesite and rare rhyolite-obsidien.

Petrochemically, the Gümüşhane area volcanics vary from basalt to dacite with low alkali tendency, whereas the Alucra area volcanics from basalt to basaltic-trachyandesite with high alkali tendency. The differences on the element variations of the tholeiitic-alkaline transition and calc-alkaline rocks can be explained by fractionation of clinopyroxene + hornblende + plagioclase ± magnetite ± apatite. The trace element variations show some similarities with enrichment of LILE and negative Nb, Ta and Ti anomalies. Particularly, the enrichments in LILE and a lesser extent in LREE, but the depletions in HFSE indicate that the rocks evolved from a parental magma derived from an enriched source formed by mixing of slab and asthenospheric melts. The chondrite-normalized-REE patterns of these volcanics resemble to each other and spoon-shaped with low to medium enrichment (LaN/LuN=2-35), indicating similar source area for the Gümüşhane and Alucra area volcanics.

The ⁴⁰Ar/³⁹Ar dating of the studied volcanics are between 37.7±0.2 and 44.5±0.2 Ma. The (⁶⁰Sr/⁸⁶Sr) values of the rocks are between 0.70457 and 0.70556, and their ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁴Pb/²⁰⁶Pb isotopic ratios range 18.59 to 18.73, 15.62 to 15.64 and 38.65 to 38.86, respectively. Pb- and Sr-isotopic ratios may imply that the rocks derived from a source region at the boundary of the mantle-crust, but the samples with low (⁶⁰Sr/⁸⁶Sr) values (<0.705) reflect the mantle source in their origin. The increasing values of SiO₂ (wt.%), Sr (ppm) ve (1/Sr)x10⁷ ppm⁻¹ versus (⁶⁰Sr/⁸⁶Sr) values suggest fractionational crystallisation (FC) rather than assimilation (AFC) in their evolution. Based on volcanic variety and distributions together with field and petrological data, volcanic activity in the Eocene time of the eastern Pontide is closely related to extensional tectonic regime with transtensional faults.
Post-collisional transition from orogenic to within-plate type volcanism in the Kulu-Haymana area (Central Anatolia, Türkiye)

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Introduction

Orogenic type calc-alkaline and continental within-plate type mildly alkaline volcanic rocks occur together in the Kulu-Haymana area (Central Anatolia, Türkiye). The former are represented by voluminous andesitic-dacitic lavas and their pyroclastites whereas the latter include alkali basalt, hawaiite, mugearite, bnenmoreite and trachydacite. Ar-Ar age data indicate that the volcanic activity was formed during Early Miocene (21.3-18.0 Ma) in the area. Also, a transition from the calc-alkaline to the mildly alkaline volcanism was formed in this period.

Geochemistry

The calc-alkaline volcanic rocks are medium-K in composition (K2O: 1.0-2.2 wt.%) and exhibit enrichment in large ion lithophile elements (LILE) and light rare earth elements (LREE) and depletion in high field strength elements (HFSE). 87Sr/86Sr(t) ratios and ε(Nd) values of the calc-alkaline rocks are 0.704452-0.705264 and 0.73-3.86 respectively.

In contrast, mildly alkaline volcanic rocks have a sodic tendency (Na2O/K2O: 1.5-3.2) and exhibit enrichment in LILEs, LREEs and HFSEs. The mildly alkaline rocks have relatively lower δ87Sr/86Sr ratios (0.703809-0.705159) and higher ε(Nd) values (2.32-4.50) than the calc-alkaline rocks.

Discussion and conclusions

According to geochemical features of the calcalkaline rocks, it can be deduced that the source of these rocks was a subduction-modified lithospheric mantle. High LILE contents and 87Sr/86Sr ratios (up to 0.705264) of the rocks raise possibility of crustal contamination. However, AFC modelling based on equations of De Paolo (1981) shows that the crustal contamination did not play an important role in the genesis of the calc-alkaline rocks (r: 0.2).

In contrast, alkali basalts show no evidence of subduction signature in their mantle source. The mantle source of the alkali basalts was heterogeneous. Two mantle sources were recognized for the alkali basalt samples: 1) depleted mantle (low 87Sr/86Sr and intermediate 143Nd/144Nd ratios) and 2) enriched mantle (high 87Sr/86Sr and low 143Nd/144Nd). Geochemical variations indicate that fractional crystallization played an important role in the evolution of evolved rocks.

The stratigraphic, petrologic and geohemical features of the volcanic rocks suggest the volcanism occurred in a post-collisional tectonic setting.

References


Evolution of kimberlite magmatic sources beneath Siberia

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Model for magmatic source and lithosphere structure

The kimberlite magma evolving at the lithosphere base form polybaric magmatic system chambers and melting regions in peridotites at 80 -60 kbar according to thermobarometry of minerals (Ashchepkov et al., 2006) from mineral separates and diamond inclusions (DI) (Logvinova and DI, 2006). At their top the magma-rich mantle diapir intrude the lithosphere. The evolved protokimberlite melts create a magma feeding system producing megacrystalline Ilm – Gar – Ol – CrDi aggregates up to 40 kbar (pyroxenite lens) or upper and heat the surrounding peridotite and eclogites followed by Ti–metasomatism. The submelting forms uprising polymeric musch column. Geotherms splits to hot and low-T branches. Relic subduction geotherms refer to dunite– harzburgites and Gar, Opx inclusions in diamonds. Several pulses of melt ascend from the basement beneath satellite pipes like for Ozernaya near Yubileynaya produce strong heating. Magmatic sources may shift to 40 kbar forming diamond- free kimberlites and carbonatites. Geochemical features of mantle peridotites are affected to melt-fluid flows from base and intermediate magma sources.

References

Heterogeneity in mid-ocean ridge sources
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This talk will review some theoretical considerations concerning the melting of heterogeneous sources and the implications for interpretation of melt inclusion data, particularly olivine-hosted inclusions from mid-ocean ridge environments. We have apparently adequate models that assume a locally or globally homogenous source and can explain major and trace element chemistry of basalts and correlations with physical variables like melt flux and axial depth. Such models are the basis of the consensus view of the average thermal and compositional state of the upper mantle and the range of their variability. However, a variety of data (most notably from melt inclusion diversity within samples and suites) and lines of reasoning (such as the need for recycling to maintain fertility of the source) require that heterogeneity exists within particular melting regimes as well as among them. We can classify heterogeneity by scale. There is some small scale (perhaps ~10 cm) below which the source melts as if it were effectively homogeneous and some large scale (perhaps ~ 1 km) above which the source components can be treated as chemically and thermally independent and their melts simply mixed; these scales may be different for different elements and lithologies. The challenge is to develop tools that predict behavior at intermediate scales where incomplete thermal and/or chemical interaction occur and hence standard mixing theory is confounded by complex feedbacks between composition and melting behavior and between melting and equilibration. Additional challenges center on the kinetics of interactions during melt migration through heterogeneous media.

I will review some of the reasons this problem defeats the current generation of melting models, the efforts that have been published by various authors, the theoretical progress that is needed, and the prospects for success.

Magmatism and the evolution of the Earth’s interior
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The flow of liquids relative to solids or other liquids is the only efficient mechanism for obtaining physical separation of chemical components of an initially homogenous material at high pressure. Hence the history of differentiation of the Earth’s interior is essentially the history of magmatic phenomena: core formation involving molten metal, formation and freezing of a silicate magma ocean, and ongoing partial melting of silicate solids. In early history much of this activity took place at very high pressure, in the lower mantle (plausibly, silicate magmatic activity continues today at the core-mantle boundary). In order to define possible evolutionary paths of the young Earth and to learn what evidence might remain today of such early processes we must build well-constrained models of igneous processes at appropriate pressures, temperatures, and compositions. This remains difficult because experimental study of lower mantle igneous petrology lies mostly beyond the pressure capability of multi-anvil devices and beyond the size and homogeneity capability of diamond anvil cells. We must rely on indirect tools: construction of phase diagrams and thermodynamic models from thermochemical and equation of state data contributed by mineral physics and the emerging field of high-pressure melt physics. There are roles in this enterprise for quantum and molecular dynamics computation, shock wave experiments, and a variety of in situ applications of synchrotron radiation. Once the major element phase equilibria are well-defined, then it is appropriate to turn to trace elements and the determination of partition coefficients at appropriate pressure, temperature, and major element compositions.

This plenary lecture will review the times and depths in Earth history where magmatic differentiation has determined planetary evolution, some basic thermodynamic tools for defining and understanding behavior in adiabatic environments like convecting mantles and magma oceans, progress in constructing appropriate phase diagrams, and areas of continuing uncertainty.
Petrography and geochemistry characteristics of the calc-alkaline Tertiary (?) tuffs in the Gumushane area, NE Turkey

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The study area is in the southern zone of the eastern Pontides, which is characterised by Liassic, Upper Cretaceous and Eocene volcanism [1]. Eocene volcanism consists of acidic, notr and basic volcanic and pyroclastic rocks in Gumushane and surrounding area [2]. In this study, mineralogical, petrographical and geochemical properties of the Gumushane region tuffs were investigated. These rocks are consisting of andesite, dacite, lapilli, vitric and silicification tuffs. Tuffs contain plagioclase (An 28-50), amphibole, glass shards, lesser pyroxene and K-feldspar, opaque oxides, secondary clay, sericite, calcite, chlorite, and devitrified glass. It is excessively weathering and silicification, and cut by dolerite.

Tuffs have a composition of contents 52-67% SiO₂, 0.55-0.74% TiO₂, 14-18% Al₂O₃, 0.5-6% FeO₄, 0.2-2.2% MgO, 1.5-2.9% Na₂O and 1.5-6% K₂O. Geochemically, these rocks change from andesite to dacite in composition and exhibit medium-high K calcalkaline characteristics. In variation diagrams show two different trends. Dacitic tuff is characterized high K₂O, Na₂O and Al₂O₃ and low CaO, Fe₂O₃, MgO and P₂O₅, but andesitic tuff is of inverse value. In addition, generally Na₂O, Fe₂O₃, Al₂O₃, CaO and MgO decrease whereas Zr, Ba, Rb, Th, U and Nb increase with increasing SiO₂. Rare earth element patterns pronounced Eu anomalies indicating plagioclase fractionation. All samples are characterised by significant flattening of REE patterns from Dy to Lu relative to the LREE. (Lu/La)N value is change from 3.3 to 7.7.

The investigated tuffs differ from the Eocene volcanics in the southern zone by their field, petrographical and geochemical characteristics. Probably these tuffs may be related to post Eocene volcanism.

References

Critical crater diameter and the impact response of asteroids

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Asteroid surface morphologies are expressions of the seismic properties of their interiors. They allow us to measure, to first order, how an asteroid responds to collisions and other high energy events through a quick examination of its largest craters.

The critical crater diameter Dcrit is defined as the minimum crater diameter on an asteroid whose formation disrupts, through distal shock and seismic effects, all previous craters ≤ Dcrit. This threshold is computed by applying crater scaling relations and peak particle velocity attenuation relations. If the largest distinct crater observed on an asteroid is typically at or near this threshold size, it follows from this analysis that small asteroids (e.g. 25143 Itokawa) can have no sizable craters, relative to their diameter, while large asteroids (e.g. 253 Mathilde) are likely to have hemisphere-spanning craters.

Because Dcrit can approach or even exceed the size of the target, the largest asteroids like Mathilde are likely to be saturated with hemisphere-spanning craters – up until the size that the asteroid is a geologically active and gravitationally relaxing planet. This is because craters smaller than Dcrit, however gigantic they might appear, do not broadcast globally.

Stress wave velocities on known asteroids, as parameterized by the model, are found to decay with the ~1.3 power of distance for most asteroids (circles plot the largest identified crater on each asteroid). This is much less attenuative than strong shocks. This is expected, because disturbances capable or destroying crater rims on asteroids are of very low particle velocity, and thus require stress waves lower in amplitude than typical lunar regolith cohesion. Models for asteroid catastrophic disruption, which rely upon stronger attenuation or upon hydrocodes tuned to energetic blast events, consequently over-estimate particle velocity attenuation and over-estimate the threshold for catastrophic disruption QD.
Interaction of gypsum with Pb-bearing aqueous solutions

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Sorption of heavy metals on mineral surfaces plays an important role in controlling both the dispersion and accumulation of these pollutants as well their geoavailability and bioavailability in near-surface environments. Among sedimentary rocks-forming minerals, gypsum arises as potentially useful to uptake a broad spectrum of dissolved metals because of the high reactivity of its surfaces and its abundance in nature.

With the aim of investigating the effectiveness of gypsum (CaSO4·2H2O) as a Pb-sequester, we have carried out macroscopic experiments in which 2 g of pure gypsum fragments (selenite variety) millimetre-sized (1.00-1.40 mm) were put in contact with 100 cm³ of Pb-bearing aqueous solutions. The initial concentrations of Pb in the solution were in the range between 10 and 1000 mg/l). Experiments were conducted at room temperature under atmospheric CO₂ pressure in a closed batch type experimental set-up. Independent experimental runs were carried out for each Pb(NO₃)₂ aqueous solution concentration. After specific reaction periods (ranging from 1 minute to a week), crystals were separated from the solution. The evolution of the aqueous solution composition was monitored using AAS, Ion Chromatography, and occasionally ICP-OES. Our experimental results show that the concentration of Pb²⁺ in the solution rapidly decreases during the first minutes of the interaction. The uptaking process takes place by the rapid dissolution of gypsum (pKsp = 4.58) and the simultaneous formation of an anglesite (PbSO₄, pKsp = 7.79) precipitate (identified by XRD and SEM-EDX) on the gypsum surface. Speciation calculations using PHREEQC (Parkhurst and Appelo, 2000) demonstrate that solutions tend to reach equilibrium with respect to both gypsum and anglesite phases after long interaction periods. The behaviour observed can be interpreted as a result of the coupling between gypsum dissolution and anglesite precipitation. The kinetics and effectiveness of this process is discussed. The macroscopic study is completed with some AFM observations.

References


Toxic metals in runoff from acid sulphate soils

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A massive supplier of toxic metals

A largely unrecognised geogenic source delivering massive amounts of toxic metals to the aquatic environment is presented. The source is a soil type – acid sulphate (a.s.) soil – that cover more than 17 million ha worldwide. This soil is located mainly on coastal plains and is developed when sulphide-rich sediments once formed under anoxic conditions in lakes or oceans are exposed to atmospheric oxygen. The pH of this soil is between 2 and 4.

The awareness of the problem

It is well known that from a.s. soils large amounts of acidity is leached, in particular during heavy rains or snow melting, causing severe acidification of downstream waters and inner estuaries. Associated fish kills have been reported from a variety of regions, including northern Europe, eastern Australia and south-east Asia. The metal problem associated with these soils is, however, largely unrecognised and unknown.

The mechanisms and extent of metal release

The behaviour of chemical elements, including potentially toxic trace metals, in a.s. soil landscapes has been sparsely studied. One exception is the largest a.s. soil occurrences in Europe, found on the coastal plains of western Finland, where a number of hydrogeochemical studies have been carried out. These have shown that the Finnish a.s. soils deliver to the aquatic environment large amounts of highly toxic metals such as Be, Tl and Cd, produces in low order streams concentrations of Al up to 300 mg/L and Mn 20 mg/L, and supplies much larger amounts of metals to the aquatic environment than the entire Finnish industry. Preliminary studies in Asia and others in Australia have indicated similar patterns in tropical and subtropical areas. The mechanisms and extent of the metal release from these nasty but also socioeconomically valuable soils are presented.
DIC concentration and $\delta^{13}$C in thermal springs of La Soufrière volcano (Guadeloupe, FWI): Implications for volcanic surveillance

Cyril Aubaud, Céline Dessert, Pierre Agrinier, Olivier Crisp, François Beauducel

La Soufrière volcano (Guadeloupe, FWI) is an arc volcano representing high risks of future eruptions. It is among the best surveyed volcano in the world, thermal springs and fumaroles being sampled and analyzed since 1979, providing a continuous data record over 28 yr [1]. The increase in seismic and fumarolic activity since 1992 and HCl degassing since 1998 prompted the observatory to intensify the surveillance of the volcano. Since CO$_2$ is the least soluble volatile species in magmas, it is the first to be degassed from a rising magma. As a consequence, carbon and its stable isotopes in fumaroles and magmas, it is the first to be degassed from a rising magma. It can be expected that future intrusions would result in an increase in DIC and $\delta^{13}$C-value in the springs. Therefore, DIC and $\delta^{13}$C may represent valuable tools for volcanic surveillance.

References


The role of fluid immiscibility in the formation of magmatic-hydrothermal ore deposits

Andreas Audétat, Thomas Pettke, Christoph A. Heinrich

Experimental studies suggest that large immiscibility gaps exist in H$_2$O-salt (±CO$_2$, CH$_4$) fluids at the P/T-conditions prevailing in subvolcanic to plutonic environments. Not surprisingly, therefore, samples recording the former coexistence of two types of fluids are rather common in the magmatic-hydrothermal systems. One major consequence of fluid immiscibility is chemical fractionation. PIXE, SXRF and LA-ICP-MS analyses of individual fluid inclusions have shown that Cu, Au, B, As, Sb and Li are often systematically enriched in vapor inclusions relative to coexisting brine inclusions (e.g., Williams-Jones and Heinrich, 2005). In the case of Cu and Au it is believed that this behavior is caused by the formation of stable sulfur complexes in the vapor phase, although definitive experimental proof is lacking so far. Another major consequence of fluid immiscibility is that differences in density and/or wetting properties lead to physical separation of the two fluid phases. This, together with chemical fractionation, can result in chemical zonations at various scales, e.g., the formation of epithermal gold deposits above porphyry-Cu deposits.

Fluid inclusion studies and experimental data suggest that intermediate to felsic magmas crystallizing at depths relevant for magmatic-hydrothermal ore deposits first exsolve a single-phase fluid of intermediate density and low salinity (2-10 wt% NaCl eq.) upon cooling (e.g., Audétat and Pettke, 2003). Fluid immiscibility commonly does not occur until the magma has approached its solidus, where pressure starts to change from lithostatic to hydrostatic. Due to the pressure decrease and the low salinity of the bulk fluid, the mass of vapor generated may often exceed that of the coexisting brine, such that the bulk fluid can be thought of a vapor plume at that stage. However, in view of the high metal content and relatively low mobility of brines it is nevertheless feasible that some deposits formed predominantly from brines rather than from vapors, and that the condensation of brine out of a low-density bulk fluid helped to concentrate the metals in a small rock volume. Element partitioning between coexisting fluid phases combined with quantitative fluid flow models will advance our understanding on how elements are separated, distributed and concentrated up to ore grade in magmatic-hydrothermal environments.

References

Provenance studies of sedimentary rocks can play an important role for palaeogeographic reconstructions. Such reconstructions are aided by varietal studies of detrital heavy minerals. In an ongoing varietal study of detrital zircons from sedimentary rocks of the Palaeozoic Gondwana margin of NW Argentina and N Chile, the detrital sources are traced. We will present the first morphology, zoning and U-Pb age data of zircon grains of the Middle Ordovician Lower Turbidite System of the Puna Turbidite Complex in NW Argentina (ca. 23°S, 66°30’W). The zircon analyses from two samples indicate a dominance of grains 100-150 µm in length that are euhedral or slightly abraded. Cathodoluminescence images reveal that most analysed zircons in the two samples are oscillatorily zoned, which is indicative of a magmatic origin. Less than 10 % of the grains are metamorphic. Zircons with only one visible growth phase are common. In situ U-Pb dating was applied to 50-60 grains from each of the two samples. The outer zoning was preferably dated in grains with several growth phases. Concordant preliminary U-Pb ages (uncorrected for common Pb) are mostly < 600 Ma. The morphology, zoning and U-Pb data make it probable that most analysed zircons in the two samples are of local origin, which also can be expected, because the Lower Turbidite System was deposited in a retroarc foreland basin position with a magmatic arc to the (present-day) west, and the Gondwana mainland to the east. The zircon age distribution make it possible that western sources dominated, but that also minor transport took place from the Gondwana mainland.

Proterozoic diamond formation at the Kaapvaal craton edge: Re-Os of Jagersfontein sulfide inclusions

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The mantle sampled by the ~90 Ma Jagersfontein kimberlite, near the southern edge of the Kaapvaal craton block in South Africa, is unusual as the diamonds contain asthenospheric, transition zone and a preponderance of eclogitic inclusions. This unusual depth range of diamond provenance may indicate that the multiple episodes of diamond formation seen in other Kaapvaal kimberlites (3.4 to 1 Ga; Richardson et al. 1993; Shirey et al. 2004) are distinct at Jagersfontein.

Sixteen diamonds, examined for N levels and aggregation states, hosted Fe-sulfide inclusions that were analyzed for composition and Re-Os isotopes. Eleven stones have low N contents (15 – 57 ppm) similar to, but not exclusive of, sublithospheric diamonds (Tappert et al. 2005), N contents in four stones range from 62 to 94 ppm, one stone contains 756 ppm. Based on N aggregation state, two diamond groups exist (<20 % vs. >33 % Ninal as B centers) suggesting different mantle residence temperatures and/or ages. The majority of the sulfide Re/Os ratios lie between >0.5-46, typical of eclogite with komatiitic to basaltic precursors.

Sulfides from crack-free diamonds fall on two arrays in the Re-Os isotope diagram: one with a 1.7 +/- 0.11 Ga age and a highly radiogenic initial 187Os/188Os (0.45 +/- 0.07), the other with an overlapping age of 1.42 +/- 0.40 Ga and a less radiogenic initial 187Os/188Os of 0.11 +/- 0.13. The former may indicate Proterozoic diamond growth by remobilisation of Archaean mafic components in the lithosphere, whilst the latter may represent growth from new fluids added to the lithosphere. N aggregation states and inferred temperature of provenance suggest diamond crystallization at multiple depths. In stark contrast to all other Kaapvaal eclogitic sulfide suites studied to date, Archaean ages are absent in the present suite. This result may relate to unique aspects of the Jagersfontein kimberlite, which has transported and preserved very deep diamonds, or be a consequence of its location on the craton edge.

References
Tracing metasomatic reactions using inert zircon coronas around ilmenite

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Thin (typically ≤ 10 µm wide) coronas of zircons are commonly found around Fe-Ti oxides in mafic granulites and gabbroic rocks (Bingen et al. 2001; Søderlund et al. 2004). The zircons may remain inert during subsequent metamorphic and metasomatic alteration and outline former grain boundaries allowing to quantify mass transfer and to constrain the mechanism of replacement reactions. We use microtextures and zircon coronas to obtain information on the metasomatic alteration related to scapolitization and albitization of two gabbros (Ødegården and Langoya gabbros) from Kragerø, Southern Norway. During scapolitization ilmenite is completely replaced by silicates and rutile. The scapolitized Ødegården gabbro contains trails of tiny zircons in talc (after enstatite) documenting a complete replacement of the Fe-Ti phase with a Mg-silicate (mg# = 0.95). In addition to Ca-rich scapolite and apatite, Mg-rich minerals phlogopite (mg# = 0.95) amphibole (mg# = 0.85) and sapphirine (mg# = 0.98) are formed during this alteration. The ilmenite in the scapolitized Langoya olivine gabbro is replaced by phlogopite and amphibole. Additional phases are prehnite and tourmaline. While Fe in both cases leaves the system, Ti remains as rutile in the scapolitized Ødegarden gabbro. However the rutile is located outside the zircon coronas suggesting local scale mobilization of Ti. The nearby Langoya magnetite mines are the likely sink for the leached Fe and indicate transport on the scale of km.

Trails of ca 10 µm sized zircons are also present in the albitite-rock of the Ødegården area. Here the zircons trails are located in albite spatially associated with rutile suggesting the albitite formed from an ilmenite bearing gabbro possibly via a stage of scapolitization.

References

Iron partitioning and the self-oxidation of the lower mantle

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Magnesium silicate perovskite (Mg,Fe)SiO3 (Mg-pv) and ferropericlase (Mg,Fe)O (fp) are the dominant phases in the lower-mantle. Their physical and chemical properties determine the dynamics of the deep Earth. It is thus of prime importance to constrain element partitioning at high pressure for improving the geochemical models of the Earth. We investigated iron partitioning between Mg-pv and fp synthetised under lower-mantle conditions (up to 115 GPa and 2200 K) in a laser heated diamond anvil cell (LH-DAC). Recovered samples were thinned to electron transparency by focussed ion beam (FIB) and characterized by analytical transmission electron microscopy (ATEM) and nanometer scale ion probe (nanoSIMS). Iron concentrations in both phases were obtained from EDX measurements and nanoSIMS. Our results are the first to show that recently reported transitions in the lower-mantle (Badro et al., 2003; Murakami et al., 2004) directly affect the evolution of Fe-Mg partitioning between both phases. Mg-pv is increasingly iron-depleted above 70-80 GPa possibly due to the high spin-low spin transition of iron in fp. Conversely, the perovskite to post-perovskite transition is accompanied by a strong iron enrichment of the silicate phase. Iron concentrations determined by ATEM and nanoSIMS are in excellent agreement. Nanoparticles of metallic iron were observed in the Mg-pv bearing runs (figure), suggesting the disproportionation of ferrous iron and the self-oxidation of the mantle, but were not observed when the post-perovskite (ppv) phase was present. Implications on the oxidation state of the Earth and core segregation will be discussed.

References
Metasomatism and melting in subduction–related volcanics: U-Th-Pa constraints from Vesuvius

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We argue that the highly undersaturated, incompatible element enriched lavas of southern Italy reflect the influence of a metasomatic component from subducted carbonate-rich sediments. Vesuvius in particular, provides a natural laboratory to study this process, located on an active margin where abundant clay-carbonate rich lithologies are currently subducting. Here we present new trace element and U-Th-Pa isotope data on historic potassic to ultrapotassic Vesuvius samples in order to constrain melting and metasomatic processes responsible for such petrologically distinctive rocks.

The samples display ubiquitous $^{238}$U excess (up to 27%) at relatively constant $^{230}$Th/$^{232}$Th. This combination of significant $^{238}$U excesses in enriched arc lavas is extremely unusual and we attribute this to the influence of carbonate component. In striking contrast to the $^{238}$U excess, our new $^{231}$Pa/$^{235}$U are among the highest reported for arc rocks. This further emphasises the decoupled U-Th and U-Pa systems on historic potassic to ultrapotassic Vesuvius samples in order to constrain melting and metasomatic processes responsible for such petrologically distinctive rocks.

More generally we try to relate the case study of Vesuvius to the array of highly alkalic Italian magmatism. We suggest two distinct episodes of melting and metasomatism occurring at different depths and timescales in the down-going slab beneath Vesuvius. Firstly, an episode of sediment melting below the solidus of carbonate phases at shallow depths which can generally explain the K-rich magmatism of the Italian volcanoes. Secondly, a recent episode of U-rich hydrous melts from carbonate- and clay-rich subducted metasediments, generated at the current depth of the slab beneath Vesuvius (>350km), can explain the observed $^{238}$U excesses.

Pyrite oxidation at seafloor conditions: Inorganic mechanisms

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Sulfide oxidation and weathering are important processes that govern the global iron and sulfur cycles both in terrestrial habitats, where sulfide oxidation gives rise to acid rock drainage (ARD), and at deep sea hydrothermal vents, where sulfide oxidation provides the necessary energy source to a large variety of biological processes. There have been many studies investigating the ARD related inorganic and biogenic mechanisms of sulfide oxidation and recently some studies also followed pyrite oxidation processes in deep sea environments. However, experimental studies of pyrite oxidation typically used changes in bulk solution chemistry normalized to the surface area of pyrite in equilibrium with the solution to evaluate the reaction kinetics and mechanisms. Yet the changes at the surface of the pyrite grains have so far been difficult to evaluate. We will present here for the first time rate and mechanism data for the inorganic oxidation of pyrite in synthetic hydrothermal vent fluid and in seawater from experiments that combined the bulk changes in solution chemistry with a quantitative 3D volume loss evaluation via vertical scanning interferometry (VSI). With this approach we could directly determine the mass of pyrite lost over the course of the reactions (mol/cm$^2$/min).

Single pyrite grains (~1mm$^2$) were reacted for 1 to 12 weeks with a synthetic hydrothermal vent fluid or a seawater solution, both under anaerobic conditions at ~25°C under gently stirred, dark conditions. The bulk chemical changes in the solution composition (e.g., SO$_4$, Fe$^{2+}$/Fe$^{3+}$) were evaluated using ion chromatography and spectrophotometric techniques, while volume loss was measured directly using VSI. For each pyrite grain, 3D surface topographic maps were obtained prior and after each time step, with a 1/3 or the pyrite grain being masked prior to the experiment in order to obtain a reference surface. After the experiment, the mask was removed and a second VSI scan obtained, which was subtracted from the original VSI scan of the unreacted pyrite surface. Using a specially developed Matlab code, the 3D volume loss during the reaction could be calculated from this direct measurement and this could be used to derive rates.

Preliminary VSI results yielded rates of 3x 10$^{-15}$ mol/cm$^2$/min in the vent fluid and 6x 10$^{-16}$ mol/cm$^2$/min in the seawater experiments. This data will be discussed and compared with previous literature data of bulk dissolution/oxidation of pyrite.
Petrographic and petrological characteristics of Dagbasi (Arakli-Trabzon) volcanites, NE Turkey

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Mineralogical, petrographical and geochemical characteristics of Liassic and Upper Cretaceous volcanic rocks in the Dagbasi area, which are situated in the northern zones of Eastern Pontides, are investigated.

Liassic volcanic rocks are basalt, andesite and pyroclastics (volcanic breccia, vitric and crystal tuff) in composition. Basalts contain labrador, augite and hornblende, while andesites contain oligoclase, biotite and hornblende. These volcanics are calc-alkaline to tholeitic transitional in character, and generally have low to high K2O contents. Major and trace element variation plots show that plagioclase, pyroxene, hornblende and Fe-Ti oxides played an important role in fractionation during evolution. The volcanic rocks are enriched in LILE (Sr, Ba, Th) and LREE, depleted in HFSE (Nb and Ti). (La/Lu)N values are between 4.6 and 9.8, show negative Eu anomalies (Eu/Eu*)=0.7-1.0. Based on trace element tectonic discriminations, all samples show volcanic arc signature.

Upper Cretaceous volcanites are dacite and rhyolite in composition. As phenocrysts, contain plagioclase, quartz, orthoclase, biotite and hornblende. This volcanics have calc-alkaline in character, and low-medium K2O contents. Increasing in SiO2 versus Fe2O3*, Al2O3, P2O5, MgO, TiO2, Y and Zr contents show negative correlation, suggesting significant plagioclase, hornblende, biotite and Fe-Ti oxide fractionation during the evolution of Upper Cretaceous volcanites. These volcanites enriched LIL elements and depleted HFS elements at the N-type MORB normalized trace element diagrams. Negative Nb and Ti anomalies indicate that subduction component and/or crustal contamination in their generation. (La/Lu)N values are between 3.20 and 6.75, show negative Eu anomalies (Eu/Eu*)=0.59-0.66. The concave REE patterns show hornblende fractional crystallizations.

Disequilibrium textures showing magma mixing such as oscillatory zoning, sieve textured and resorbed plagioclase phenocrysts, embayed quartz, breakdown of hornblendes and biotites are commonly observed in these rocks. In addition, basic enclaves observing in Upper Cretaceous dacites shows significant role of magma mingling during the evolution of Dagbasi Volcanics.

The whole data indicate that the Dagbasi (Trabzon) volcanics evolved by the fractional crystallization and magma mixing-contamination of a parental magma derived from lower crust and/or upper mantle, and the sources of those volcanics are enriched-MORB mantle in Liassic, and metasomatized MORB mantle in Upper Cretaceous.

Palaeonutrition of Prehistoric sites of Ghaleh Khan and Valeran: A case study

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Palaeodietary study of the prehistoric sites has been done for the first time in Iran. This study has supplied information about the nutritional habits of Prehistoric man. Chemical composition of bones and teeth gave some information about the nutrition of prehistoric people. These two sites which from ecological condition situated in two different places gave not only through the light on two different dietary system but different geological conditions provide different environments for the buried dead bodies.

In this paper we discuss result of spectroscopy obtained from XRF instrument and compare the result between these two sites.
Silica metasomatism of oceanic serpentinites

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Both dynamic and static recrystallization of serpentinite to soapstone have been reported from ultramafic masses in the oceans. While the development of talcous schists is common in detachment faults that are loci of large time-integrated fluid fluxes, static replacement of serpentinite by talc is more difficult to explain. We report on observations made in ODP drill core from Leg 209, Hole 1268, at the Mid-Atlantic Ridge (MAR) 15°N, where soapstone is abundant. Talc appears in blackwalls at the contact to small (<10 m) gabbroic units, but the majority of soapstone is not formed diffusively at mafic/ultramafic contacts. Static replacement of serpentinite by talc starts along anastomosing vein networks and continues to pervasive steatitization, during which the serpentinite hourglass texture is preserved. To transform magnesian serpentinite to talc (Mg/Si=0.75) massive removal of Mg or addition of Si is required. As the solubility of Mg is very low in fluids with pH>3, metasomatic enrichment of Mg or addition of Si is required. In fluids with pH>3 the majority of soapstone is not formed diffusively at mafic/ultramafic contacts. Static replacement of serpentinite by talc starts along anastomosing vein networks and continues to pervasive steatitization, during which the serpentinite hourglass texture is preserved. To transform magnesian serpentinite (Mg/Si=1.5) to talc (Mg/Si=0.75) massive removal of Mg or addition of Si is required. As the solubility of Mg is very low in fluids with pH>3, metasomatic enrichment of silica seems the most likely explanation. It appears that, except for obvious blackwalls, this metasomatism was facilitated by ingress of aqueous fluids. Serpentinite in Hole 1268 does not contain any brucite, suggesting that even the serpentinite has undergone silica metasomatism, as the precursor harzburgites and dunites had <15-20% orthopyroxene so that brucite would be expected to form during isochemical serpentinization. Gabbros in Hole 1268 do also show evidence for interactions with fluids with high silica activities since they are not rodingitized but instead show common greenschist alteration to chlorite, albite, and actinolite. This is unlike other drill holes in the MAR 15°N area and elsewhere, where brucite-bearing serpentinites host rodingitized gabbroic dikes.

We propose two possible explanations for the variability in aqueous fluid silica activity suggested by the phase assemblages of oceanic metaperidotites. (1) They are a result of the variable distribution of mafic units in a composite mafic/ultramafic crust, or (2) they are a consequence of the temperature-dependent reaction sequences taking place along the fluid flow path. To further explore the second possibility, we conducted isobaric (500 bar) geochemical model calculation. At temperatures >350°C, olivine is stable and hydration of pyroxenes imposes high silica activities to the fluids. Low aqueous silica activities can only develop at temperatures <350°C, in particular when fluid pH is high due to the hydrolysis of olivine. Brucite-bearing serpentinite as well as rodingite are expected to form under those conditions. Steatitization, in contrast, requires two conditions: high fluid flux and high silica activities. Sulfide assemblages in Hole 1268 suggest that oxygen and sulfur fugacities were high during silica metasomatism, which is consistent with our geochemical model predictions of coupled decreases in H₂ fugacity and pH with increasing fluid flux.

Hydrothermal systems in the eastern Manus Basin: Effects of phase separation and fluid mixing

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The number of factors affecting metal fluxes within hydrothermal systems is large and the evolution of magmatic-hydrothermal system is complex and often difficult to reconstruct from the fossil record. Studying active submarine hydrothermal systems has a tremendous advantage: one can directly link fluid chemistry with deposits composition and rock alteration. Hydrothermal vents in arc/backarc settings are particularly intriguing as these systems are considered modern analogues for VHMS deposits.

The eastern Manus Basin reveals variable basement composition, ranging from depleted mid-ocean ridge basalt to basaltic andesite to rhyodacite with pronounced island-arc geochemical affinity. In August 2006, hydrothermal activity in the eastern Manus Basin was investigated using a combination of mapping and sampling (using AUV ABE and ROV Jason2). Objectives included identifying geological settings, examining interactions of seawater with felsic rocks, and determining the extent of volatile magmatic inputs into these systems. At the PACMANUS area five previously discovered vent fields were mapped and sampled, and a new very active field, Fenway, was located. The core of the Fenway field is a 40 m diameter two-tiered mound with active black smokers. The mound features exposures of anhydrite-sulfide stockwork. At the DESMOS caldera and at North Su vent field within the SuSu Knolls area acidic, sulfate-rich sulfide stockwork. At the DESMOS caldera and at North Su vent field within the SuSu Knolls area acidic, sulfate-rich white smoker fluids were sampled. North Su also features black smoker activity with anhydrite stockwork. The abundance of massive anhydrite at Fenway and presence of anhydrite cement at North Su is consistent with significant local entrainment and heating of seawater.

Fluids sampled from felsic-hosted hydrothermal systems in the eastern Manus Basin exhibit great compositional variability within an individual vent field. Degassing of magmatic volatiles is evident in almost every vent field. Degassing of CO₂ is ubiquitous, while SO₂ degassing is obvious only in the Desmos and North Su hydrothermal fields. Excess fluorine in vent fluids is another indication of magma degassing. Evidence for past SO₄ degassing, in the form of native sulfur and advanced argillic rock alteration, exists in the South Su and PACMANUS areas. The majority of fluids exhibit salinities lower or higher than seawater, consistent with phase separation below the seafloor. Fluid boiling at the seafloor is evident in parts of the PACMANUS area (356°C, 1710 mbsl) and at North Su (325°C, 1180 mbsl).
Carbon dioxide sequestration based on alkaline residues

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Amongst various CO₂ sequestration scenarios, mineral trapping is regarded as one promising technique because it warrants a permanent and inherently safe storage of CO₂ (Lackner et al., 1995, Zevenhoven et al., 2006). The carbonation of Ca- and Mg-bound minerals is fairly simple in process even so fast reaction kinetics are required for a technical realization. The energy input for the technical process is dependend on different materials and therefore the net amount of CO₂ sequestered (Huijgen et al., 2006). Alkaline residues from combustion processes are favorable for CO₂-binding because they are cheap, highly reactive and are generated as byproduct from the process of power generation.

In the present work, the reaction of alkaline brown coal fly ashes with CO₂ was studied in aqueous suspension in order to 1) develop a technical process for carbonation that removes CO₂ from flue gas of a powerplant sufficiently fast and 2) to generate an alkalinity-containing solution ready for the injection into deep aquifers. Laboratory experiments were performed in an autoclave system to measure the CO₂ transfer as a function of solid-liquid ratios, CO₂ partial pressure and stirring rates. Mild process conditions (25-50° C, atmospheric gas pressures) were chosen in order to evaluate the storage capacity under low economic and energy costs.

We could achieve an uptake of more than 2 mol CO₂ per kg of the used fly ash. Considering the average amount of fly ash accumulated within combustion process this corresponds to a reduction of about 1 percent of the CO₂ emissions from a brown coal power plant.

In alkaline residues, such as steel slags or waste concrete, CaO and MgO are suspected to be the most important phases. In addition to the fly ash experiments we present first results of the CO₂ reaction with CaO and MgO in order to estimate the CO₂ binding potential of other feedstock materials and to get a more-detailed process understanding.

References


Effusive and subeffusive rocks in the area of rare-metal ore fields of Phanerozic and their petrogenetic significance

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Results of studying of composition and isotopic-geochemical data (Rb-Sr and Sm-Nd isotope systems) allow sharing out among effusive and subeffusive formations in the Transbaikalian region (Russia) three steady groups of rocks. These groups differ with time and place of separation of melt from uniform crustal source of magma: ongonites – surface F-rich extreme differentiations of granite magmas, on composition analogues of rare-metal granites; rhyolites, ongorhyolites, felsite-porphyries of potassium specializations - result of separation of melt from homogeneous still not differentiated hypabyssal magmatic sources; trachyrhyodacites and trachyrhyolites - have the common substratum of melting with granites, however removal at earlier stage at formation from the magma source. First two groups of rocks close age among themselves and rare-metal granites while formation of trachyrhyodacites can fix appreciable break in time with them. The geochemical relationship of all set of these rocks consists in enrichment lithophile rare elements, in the similar character of distribution of display rare elements that confirms representation about the common substratum of melting. Distinction is shown in levels of concentration of these elements, specialization and contents of volatile components (F, Cl, B), degrees mantel-crust interactions. Studying of melt inclusions has shown the magmatic nature of high potassium concentration in trachyrhyolite melt, its primary geochemical specialization on lithophile elements and chlorine. Concentration of chlorine attain here limiting saturation for haplogranitic system - 0,34 wt. % Cl.
Mineral chemistry and Os isotope systematics of Os-bearing alloys from the Guli massif (Russia): New data

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The Guli clinopyroxenite-dunite massif, like other clinopyroxenite-dunite massifs, e.g. Kondyor and Inagli, is situated at the periphery of the Siberian Craton (Russia). The unique features of the Au-PGE placers at Guli are (1) the dominance of Os-rich alloys over other platinum-group minerals (PGMs) and Au, and (2) the considerable predicted values of noble metals, particularly osmium (Malitch et al., 2002). This report presents for the first time results on mineral chemistry and Os isotope compositions of bedrock and detrital Os-rich alloy grains derived from three localities within southern part of the Guli massif. The Os isotope composition of PGMs was determined by laser ablation (LA) attached to multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) at All-Russia Geological Research Institute.

The PGM assemblage in chromitite is dominated by iridian osmium (5-100 microns in size); subordinate PGMs are laurite, osmian iridium, tetraferroplatinum, an unnamed RhNiAs and Ni-Ir sulphide. The majority of Os-rich nuggets from placer deposits (i.e. Ingaringda and Burlakovskiy), both single crystals and crystal aggregates, subdivided into six morphological types, are dominated by Os-rich alloys with considerable inter-nugget variation of Ir and Ru. Os-rich alloy nuggets are controlled by their chemical composition (type 1, 2, 5 and 6 correspond to osmium, with Os content > 80 at. %; type 3 and 4 are iridian osmium) and partly by the Os isotope composition. At Ingaringda, average $^{187}$Os/$^{188}$Os value for Os-rich alloys vary from 0.12443 ± 0.00010 (type 6) to 0.12475 ± 0.00053 (type 3), whereas at Burlakovskiy those are less pronounced. The Os isotope composition of type 3 and 4 nuggets slightly differs from that of other types. This variability supported by mineralogical evidence can be attributed to different source rocks (chromitite vs dunite).

The $^{187}$Os/$^{188}$Os values of the Os-rich alloys studied are close to those from a former N-TIMS study (Malitch, 2004), which showed mean value of 0.12463 ± 0.00034. The similar range of $^{187}$Os/$^{188}$Os values for Os-rich alloys, exemplified by both LA MC-ICP-MS and N-TIMS, is consistent with that for PGMs from Kondyor, and likely indicates a highly productive single-stage formation of PGMs in clinopyroxenite-dunite complexes. Finally, $^{187}$Os/$^{188}$Os model ages of osmium and iridium osmium constrain the age of ultramafic protoliths indicating that this event took place in Late Proterozoic, which corresponds to a stage of active tectonism in the development of the Siberian Craton.

Geo-electric investigation of Igbonla Geothermal Sources, South Western Nigeria

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Abstract

Twelve Schlumberger Vertical electrical Soundings were carried out Igbonla geothermal source, Epe, South Western Nigeria to investigate the geothermal source located within this area using current electrode separation (AB) of 1,500.0m. The interpreted result revealed a maximum of seven geo-electric layers composing of topsoil, sandy clay, clayey sand, clay, limestone and sand. The geothermal source was penetrated beneath three VES point at depth between 160 to 418m.

Introduction

Geothermal energy is produced from the heat of earth’s interior. Volcanoes, geysers, hot springs and boiling mud spot are visible evidence of great reservoir of heat that are located within and beneath the earth’s natural heat associated with active volcanoes or geologically young inactive volcanoes still giving off heat at depth. It has its origin in the molten core of the earth, where temperatures are 400°C. The geothermal field has been the subject of numerous geologic, geophysical and geo-chemical investigations by both the geothermal industries and various governmental organisations, therefore advances in this field will improve commercial development for economic reliability and commercial safety.

Several boreholes have been drilled in the past within the southwestern Nigeria, where this study was carried; and hot water has been located within the aquifer at a depth ranging from 600.0m with temperature ranging between 29°C to over 72°C where several attributes make geothermal energy a good source of energy. It can be exploited without burning fossil fuel (coal, gas or oil) and it produces only one-sixth of the carbon dioxide that a natural gas fuelled power plant or sulphur-bearing gases.

Conclusion

The geo-electric investigation carried out at Igbonla Epe South western Nigeria revealed the hot water reservoir to be characterized by low resistivity sand bed with resistivity varying from 6.5 to 30.0Ωm at depth of 160 to 418m. The boundaries of the geothermal field as obtained by the qualitative interpretation of the VES curves gave a reasonable result as inferred from the lithological data at Igbonla. On a general note, Abeokuta formation show geothermal activity from Igbonla eastwards to Ikeja and has derived its heat from the earth’s interior.
LA-ICP-MS geochronology of
detrital zircons in Late Paleozoic
sediment units of northern Chile:
Implications for terrane processes

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Late Devonian to Permian turbidite units are widely
exposed along the coast of northern Chile and represent parts
of an accretionary wedge at Gondwana’s Late Paleozoic active
margin in the present Central Andes. The units overstep the
boundary between the somewhat enigmatic Ordovician to
Devonian Chilenia terrane of alleged Laurentian origin in the
south and coeval autochthonous regions of Gondwana to the
north. Zircon populations of overstepping units deposited on
and derived from Chilenia should ideally demonstrate the
Laurentian heritage of the terrane by an absence of
geochronologic events typical of Gondwana and absent from
Laurentia, i.e. the Brasiliano orogenic cycle.

Using LA-ICP-MS we analysed populations of detrital
zircons in 6 samples, 2 each pertaining to the El Toco and Las
Tórtolas Formations in the northern, autochthonous part of the
study area, and 2 samples from the Huasco and Huentelauquen
Formations on Chilenia. Of each sample we analysed 140 to
145 grains. In this study we only considered grains falling
within 10% of concordia. This number of grains varies
between 99 and 118 between samples.

Concerning the Precambrian and Early Paleozoic, all
samples show essentially the same distribution of main events,
the “Grenvillian” orogenic cycle between 1400 and 900 Ma,
the Brasiliano cycle between 800 and 550, and the Early
Paleozoic Famatinian active margin cycle between 550 and
420 Ma. The younger, Late Carboniferous-Permian samples
also register a cluster of ages between 330 and 290 Ma
marking the re-initiation of subduction magmatism at this
margin after a period of magmatic, tectonic and metamorphic
quiescence in the Late Silurian and Devonian.

Considering the variable Late Paleozoic ages of the
studied samples we find that all record a very similar
distribution and succession of geochronologic events,
including evidence of the Gondwanan Brasiliano cycle in all
samples. Even though margin parallel sediment transport
could account for some of these grains, the size of Chilenia
(>1000 km N-S) should have kept this influence small. In
conclusion we find that our data cast doubt on a Laurentian
origin of the Chilenia terrane in northern and central Chile.

The effect of organic compounds on
the dissolution of amorphous silica-
Pyrochatechol, Salicylate, Hydrogen
Phthalate

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Silicon (Si) is one of the most common elements
constructing the earth’s crust and much of it is present in
different kinds of silica minerals (SiO\(_2\)). Information on the
mobility and transport of Si from minerals to water as silicic
acid (Si(OH)\(_4\)) is important to estimate the chemical
weathering of rocks. The dissolution of silica has been
investigated vigorously in inorganic salt solution included in
natural waters. On the other hand, a lot of organic
compounds (from simple organic compounds with low
molecular weight to polymer with high molecular weight) are
also present in natural waters. Only a few investigations
have been conducted on the effect of organic compounds on
the dissolution of silica and the interaction between silica and
organic compounds is still uncertain. In an oil field, the
groundwater with higher Si concentration than the solubility
of quartz was found and the Si concentration increased with
increasing the total organic carbon in the ground water,
suggesting that organic compounds may accelerate the
dissolution of quartz. A phenolic hydroxyl group and a
carboxyl group are often contained in main functional groups
in natural organic compounds such as humic acid.

In order to search functional groups that can strongly
interact with silica, in this study, we investigated the effect of
pyrochatechol with two hydroxyl groups, salicylate ion with
one hydroxyl group and one carboxyl group and phthalate ion
with two carboxyl groups on the dissolution of amorphous
silica. In conclusion, salicylate and phthalate ions inhibited
the dissolution of silica due to adsorption on the surface of
silica through hydrogen bonds, whereas pyrochatechol
accelerated the dissolution due to formation of silicic acid-
pyrochatechol complexes.

References
The freshwater pearl mussel: one species – several proxies
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Recently, bivalves became a powerful tool to supplement climate proxy data gathered from trees, stalagmites or lake sediments. Riverine bivalves provide an ideal junction between terrestrial, freshwater and marine proxy archives. Here, we studied shells of freshwater pearl mussels from Northern Sweden using a combination of sclerochronology (growth rate analyses) and isotope geochemistry (δ¹³C, δ¹⁸O). Valves were cut perpendicular to the direction of growth. After grinding and polishing, one of two “mirroring” thick sections was immersed in Mutvei’s solution. Sections were digitized and growth increment widths measured. Inherent age-related growth trends were extracted from the chronologies by estimating ontogenetic trends with cubic splines. Age trend removal was performed by dividing measured by predicted growth. Standardized growth records of different individuals were combined to a single master chronology and overall growth patterns and cycles were analyzed.

In addition, the remaining cross-sectioned shell portion was micromilled for stable carbon and oxygen isotope analyses. Following the shape of the growth increments, aragonite powder samples of annual resolution were milled. Oxygen isotope ratios of shell aragonite were used to calculate water temperatures. With increasing ontogenetic age stable carbon isotope values became shifted towards more positive values. After removal of age related trends, δ¹³C values exhibited a high degree of running similarity, permitting the construction of a δ¹³C master chronology.

Wavelet analyses of standardized shell growth and δ¹³C master chronologies revealed periodicities of 2-4 years, 6-7 years and 16 years. These oscillations closely resemble those well known from the North Atlantic Oscillation (NAO) and the tripole pattern in sea surface temperature anomalies.

Carbon in the peralkaline association: Footprints in the ashes
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Peralkaline felsic volcanism in the central Kenya rift, around Lake Naivasha, is well documented (age 0.4-0 Ma). Less known is the interspersed, contemporaneous mafic activity, comprising basaltic flows following initial effusion of tuffs and tuff cones. The latter include peperites with fresh basanitic glass lapilli enclosing abundant immiscible calcite globules (up to 45%): the enclosing matrix is largely comminuted lapilli, with a few accidental clasts. Some quench textures, and rare streaks of platy calcite, in the matrix indicate that this may have been still hot when erupted. Older volcanics (1.7 Ma) form the underlying rift floor. Carbonate sediments are absent from the area, and formation of calcite globules in glass by assimilation of any cold sedimentary limestone would impose impossible thermal requirements. No external source for the carbonate is known, and the carbonate globules enclosed in glass are an integral part of the eruption. Immiscible textures show all the forms expected from experimental studies for carbonate and silicate melts in equilibrium: these two melts must either have mingled or unmixed at high T. Primary carbonate is known in the phonolites and peralkaline trachytes of adjacent volcanoes; contemporaneous nephelinite-melilitite-carbonatite, as well as commercial CO₂ wells, are found along the rift, where this range of activity has prevailed for at least 23 Ma. Hence, these peperites are but a new form of carbonate volcanism, in intimate association with intensely peralkaline activity, spectacularly re-affirming the key role of CO₂ flux in rift magma genesis. Known natural samples of glass + carbonate are rare (five?), and basanite-calcite melt immiscibility has not been reported previously (the expected silicate phase from experiments is alkaline ultramafic/phonolitic, but 9 basanite + 1 calcite is equivalent to melilitite + CO₂). The P-T-X conditions for coexisting basanite-calcite melts remain to be defined, but the Kenyan peperites are not an isolated case (five others, from outside Africa, are currently under investigation). Although also from well-known provinces these too have gone unreported due to insufficient study being devoted to pyroclasts.

References
An attempt to use mean crystallite size of calcite for indicating metamorphic grade as exemplified by metamorphic carbonate rocks from NE-Hungary

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A great variety of low-T metasedimentary rocks are devoid of metamorphic facies indicating mineral assemblages. Instead, they contain common mineral assemblages that are stable over wide P-T fields. The structural and related chemical changes in certain phyllosilicates proved to be reliable empirical indicators for expressing differences in metamorphic grades (zones). Illite and chlorite “crystallinity” (called Küberl, etc.) indices have been widely used to determine diagenetic and metamorphic (anchi- and epi-) zones mostly in pelitic and marly lithologies.

The present study intends to reveal whether there is any relationship between the structural and chemical changes of carbonate minerals (mostly calcite) in metamorphic rocks and the increasing metamorphic grade (increasing temperature). For this purpose such metamorphosed (recrystallized) limestones and marbles were selected from NE-Hungary, the metamorphic zones of which and their intercalated metapelitic environments have been fairly well known by earlier phyllosilicate “crystallinity” studies (Szendrő Mts.: epizonal, Uppony Mts.: epi-anchizonal, Árkai, 1983, 1991).

Petrographic and cathodoluminescence microscopy and stable isotope measurements were used to characterize the textural and chemical features of carbonate metamorphic rocks. In addition, X-ray powder diffractometric single line (Voigt) profile analysis was also applied in order to determine changes in mean crystallite size of calcite (i.e., in average size of domains that scatter coherently the X-rays).

The mean crystallite size values of calcite range between 300 and 400 Å in the bulk rock samples. The crystallite size seems to be similar in the rocks originated from different (lagoon, reef and deep marine basin) sedimentary environments. Certain carbonate generations (lenses and after deformation), however, have lower (120 to 220 Å) crystallite size values (laguna, reef and deep marine basin) sedimentary environments. Certain carbonate generations (lenses and after deformation), however, have lower (120 to 220 Å)

References

High-precision $^{26}$Al-$^{26}$Mg dating of early Solar System processes

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The short-lived $^{26}$Al to $^{26}$Mg chronometer ($t_{1/2} = 0.73$ Myr) has been used to date Al-rich minerals in refractory inclusions and chondrules from chondritic meteorites, as well as feldspars from basaltic meteorites. Here, we explore the prospects of precisely and accurately resolving (and using) very small ($\leq 40$ ppm) excesses and deficits in the abundance of $^{26}$Mg in meteorites to date Al/Mg fractionation events associated with planetary differentiation in the first few Myr of the Solar System. Increases in Al/Mg ratios relative to chondritic (i.e., bulk planetesimal) values resulted from formation of basaltic magmas (Al/Mg = 1-3). Conversely, formation of essentially Al-free material resulted from olivine crystallization (pallasite olivine), formation of pyroxene cumulates (aubrites, diogenites) and partial melting (ureilites). The excesses and deficits that can be expected from these early Al/Mg fractionation events means it will be necessary to resolve $\delta^{26}$Mg* anomalies with precision and accuracy $< \pm 10$ ppm (2$\sigma$) to potentially utilize the $^{26}$Al-$^{26}$Mg chronometer to identify and date these processes.

Using a Nu Plasma MC-ICPMS, we have developed procedures that allow measurement of $\delta^{26}$Mg* anomalies (the offset of a sample's mass-bias-corrected $^{26}$Mg/$^{24}$Mg ratio compared to the mean of bracketing standards) in single analyses with precisions as low as $\pm 12$ ppm (2$\sigma$), which incorporates the uncertainties from the bracketing standards. Accuracy of data is verified by analysis of matrix-matched standards and, in some cases, by analysis of standards doped with $^{26}$Mg spike to create anomalies of known size. After anion and/or cation exchange chemistry, samples are analysed multiple times by MC-ICPMS in pseudo-high-resolution mode enabling resolution of molecular interferences (e.g., $^{12}$C$^{14}$N+) from Mg.

We have reanalyzed meteorites where small $\delta^{26}$Mg* excesses (angrites, eucrites) and deficits (pallasite olivines, ureilites, aubrites) have previously been reported, and used to constrain rapid timescales of planetesimal melting, differentiation and accretion in the young Solar System. These previous measurements were not made using high-resolution techniques and were characterized by somewhat larger analytical uncertainties than the present study. Further, we have also measured Mg isotopes in step-leaching fractions of C1 chondrites where large ($\epsilon$ to %) anomalies in neutron-rich isotopes of elements like Cr have been reported. Our new results place important constraints on the prospects of using high-precision Mg isotope measurements to date a wide range of meteoritic material and early Solar System processes.
Thallium isotope constraints on Earth’s accretion

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The extinct radionuclide $^{205}$Pb decays to $^{205}$Tl with a half-life of 15 Myr. The former presence of $^{205}$Pb in the solar system was recently inferred from a $^{205}$Pb/$^{204}$Pb isochron that was obtained for seven metal samples from the IAB iron meteorites Canyon Diablo and Toluna [1]. New Tl isotope data obtained for eight carbonaceous chondrites are in full accord with this isochron [2].

Several lines of evidence (based on I-Xe and Pd-Ag chronology; e.g., [3, 4]) indicate that the IAB parent body crystallised about 10 to 20 Myr after CAI’s. Based on this age, the IAB isochron yields an initial solar system $^{205}$Pb/$^{204}$Pb ratio of about $1.5 \times 10^{-4}$ and an initial Tl isotope composition of $\varepsilon^{205}$Tl$0 = -2.8 \pm 1.7$ [1]. The latter is unlikely to be greater than -2.5, given that the Earth’s mantle has a well-constrained age of >7 ppb for the bulk silicate Earth (BSE). This discrepancy can only be avoided if the Earth either experienced large-scale volatile loss at the time of the Giant Impact or accreted from volatile-depleted material characterised by a $^{204}$Pb/$^{204}$Pb ratio of $>2$. (2) If $\varepsilon^{205}$Tl$0$ is less than about -4.0, the present day $\varepsilon^{205}$Tl value of $-2.0 \pm 0.5$ [5, 6]. The available data thus indicates that the solar system was characterised by an initial $\varepsilon^{205}$Tl$0$ of between -2.5 and -4.5.

Two scenarios emerge if these values and recently determined metal-silicate and sulphide-silicate partition coefficients for Pb and Tl [7] are utilised to model the Earth’s accretion and core formation. (1) If $\varepsilon^{205}$Tl$0$ is greater than -3.5, then standard accretion models yield unrealistic Tl abundances of >7 ppb for the bulk silicate Earth (BSE). This discrepancy can only be avoided if the Earth either experienced large-scale volatile loss at the time of the Giant Impact or accreted from volatile-depleted material characterised by a $^{204}$Pb/$^{204}$Pb ratio of $>2$. (2) If $\varepsilon^{205}$Tl$0$ is less than about -4.0, the present day composition of the BSE can be readily reconciled with standard terrestrial accretion models, providing they feature late-stage segregation of sulphides from the mantle, as was recently proposed by Wood and Halliday [8].

The presently available Tl isotope data for meteorites do not permit a sufficiently precise definition of $\varepsilon^{205}$Tl$0$ to distinguish between these two scenarios. This indicates the importance of conducting further Pb-Tl isochron studies, which are able to provide a more precise estimate of $\varepsilon^{205}$Tl$0$.

References


Diffusion of fluids through quartz

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Bulk diffusion of fluids through quartz is a process that may change the properties of fluid inclusions. The estimation of diffusion coefficients is only based on a limited number of studies, which include large uncertainties (up to 80%). Diffusion depends on the solubility of a certain diffusing species in quartz, which defines, however, a second large uncertainty: what is the nature of the diffusing species? and what is its solubility? Moreover, most experimental work has only been done at higher temperatures, within the β-quartz stability field.

This study identifies, firstly, the types of dissolved and diffusing water-related species, of which interstitial impurities, i.e. mainly H$_2$O molecules positioned between regular lattice sides form the major group that is responsible for changes in fluid inclusions and diffusion in general. This defect cannot be detected after experimentation with IR spectroscopy or secondary ion MS that mainly detect substitutional impurities and small fluid inclusions themselves. Solubility of water in quartz in previous studies has been mainly defined as charge compensating Fe and Al impurities or replacing Si atoms.

A new mathematical diffusion model (according to Fick’s laws) is developed using SI conform units, i.e concentration (mol/L), fugacity (MPa), excluding terms like ppm or wt%, which can be applied to randomly located fluid inclusions in a quartz crystal. This model is directly applied to experimental studies with synthetic fluid inclusion to characterize leakage and re-filling. Hypothetical calculations of re-equilibration rates indicate nearly instantaneous alterations of fluid inclusions properties according to the solubility of water in quartz, using the parameter values obtained from previous studies. Diffusion from or to fluid inclusions can only take place if a concentration gradient is present in the quartz. Locally, these gradients may represent thermodynamic equilibrium conditions due to pressure gradients, and, consequently, diffusion will not occur.

The properties of fluid inclusions are excellent tools for new determination of diffusion coefficients and the nature of diffusing species through quartz. Gradients in chemical potential (or fugacity) between fluid inclusions and pore fluids is a driving force for re-equilibration. In addition, pressure gradients may provoke alterations (see also Bakker and Diamond, 2003). Combination of both driving forces are interpreted as crack-assistent diffusion. New experiments will be performed to estimate the mobility of H$_2$O, CO$_2$, H$_2$, O$_2$ and Ar through quartz crystals by characterizing the changing properties of known synthetic fluid inclusions.

References

Status and potential of exploration for PGE in India

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PGE Potential in India

Discovery of new platinum group of elements (PGE) deposits/mineralized zone is of great economic importance for any country. In India, till date only the i) Baula-Nuasahi layered Complex in Orissa, ii) mafic-ultramafic Hanmalapura Complex in Karnataka, and iii) the layered Sittampundi Anorthosite Complex in Tamil Nadu, are the three known promising PGE occurrences. Recent studies show that there is a tremendous potential for PGE-mineralisation in mafic-ultramafic complexes, ophiolite complexes and the fine grained sediments such as sulfide bearing black shales, occurring in different parts of our country.

Exploration Strategies

Determination of PGE at extremely low concentrations with the accuracy and precision and at high throughputs required for exploration studies needs optimization of critical steps such as selection of a representative sample and application of sensitive analytical techniques, etc. For identifying economically viable deposits and their mining, detailed geological, petrological and geochemical studies are essential on massive potential areas.

Geochemistry and mineralogy of Serov Ni lateritic deposit, N Urals

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Serov lateritic Ni deposit occurs within Kolsky massif in the northern part of the Serov-Magnitogorsk zone of the ultrabasites. The following zones are distinguished within the weathering profile (from the bottom to the top): serpentinites (1), leached serpentinites (2), saprolites (3) and laterites (4). The profile is covered by Early Jurassic to Late Tertiary sediments.

Ni mineralization is being studied by XRD, SEM and Microprobe in the laboratories of VSEGEI and NHM. In parent rock, Ni is distributed among the serpentine group minerals, olivine and pyroxene. For the leached serpentine zone, an increase of Ni content is typical in serpentines and appearance of “garnierite” veins, sometimes forming stockwork together with magnesite. The saprolite zone is characterized by broad variations of Ni content in serpentines – from low-common for lizardite and antigorite, to high, allowing them to be referred to as nepouite and pecoraite. Laterite is composed of goethite and haematite (< 1 % Ni), often with smectite admixture. Besides minerals listed, Ni was found in chamosite, talc, millerite and asbolane. XRD also recorded teophrastite Ni(OH)₂, honessit Ni₆Fe₂(SO₄)(OH)₁₆·4H₂O, willemseite (NiMg)₃Si₄O₁₀(OH)₂, nickeline – NiAs and maucherite Ni₁₁As₈.

Such mineral assemblage proves a long history of profile development: primary oxidized profile was partly reduced due to downward block movements evidently after covering the profile with lignites. The reduced parts of the cross section go down along the most permeable zones that connect with tectonic faults.

Later on the profile was oxidized again after recent uplifting. Such consequence of events has led to the redistribution of Ni and to the crystallization of sulphides, arsenides and chlorite.
Synthetic fluid inclusions in rutile: A new technique to study mantle fluids

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Experimental studies concerning the major and trace element composition of hydrous fluids migrating in the mantle or released from a subducted oceanic crust are technically challenging. Currently used methods include the weight-loss technique (e.g., Newton and Manning, 2002) and the diamond trap technique (e.g., Stalder et al. 2001; Kessel et al. 2005), which both have a number of advantages and disadvantages.

Here we follow a new approach by trapping fluids at mantle conditions in rutile, and analyze their major and trace element content by LA-ICP-MS. Rutile is a perfect mineral for this purpose because its solubility in aqueous fluid is relatively low (e.g.: Audétat & Keppler, 2005), but still high enough to allow crack-healing, and because it does not contain most of the elements of interest (except for HFSE). Major advantages of this method include: (i) it is applicable to a large range of P/T-conditions, (ii) there are no limitations regarding the complexity of starting materials that can be used, and (iii) identical batches of the same fluid can be sampled numerous times. Cubes of sintered rutile were loaded into Pt/Rh capsules, together with fine grained minerals (e.g., enstatite, olivine) and 15-25 µl aqueous solution containing 1000 ppm of Cs and Rb, the latter serving as internal standards for the LA-ICP-MS analyses. Experiments are carried out in 200 t piston cylinder apparatus, using pure salt assemblies and stepped graphite heaters. Run conditions are approached along a fluid isochoric path, and then held for two days. Resulting fluid inclusions are 20-40 µm in size, which is appropriate for LA-ICP-MS analyses.

The method is currently being tested on the system quartz-H2O and olivine-enstatite-H2O, for which reliable data are available from weight-loss experiments (Manning, 1994; Newton and Manning, 2002).

References

Seawater recycling into the deep mantle – And the source of 3He?

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Mantle-derived heavy noble gases (Ar, Kr, Xe) with isotopic components and elemental ratios similar to marine pore fluids have been unambiguously resolved in magmatic well gases and Mid Ocean Ridge ‘popping’ rock (MORB). This observation has been used to argue that recycling of marine pore fluids into the mantle dominates the non-radiogenic heavy noble gas inventory of the convecting mantle [1]. He and Ne isotopes in the mantle are unaffected because of their low concentration in marine pore fluids. This conclusion is further reinforced by the observation that slab-derived fluids trapped in the overlying mantle wedge have both halogen (Cl, Br, I) and heavy noble gas elemental compositions little different from marine pore fluids [2].

Numerical models of mantle convection provide further insight. In simulations that reproduce surface heatflow and plate motion, a seawater/Ar recycling flux into an initially degassed mantle, combined with internal radiogenic 40Ar ingrowth, can be determined that reproduces the best estimate of the mantle 40Ar/36Ar ratio of ~40,000 [1]. An independent outcome of the model, determined by the fluid dynamic control, is that the noble gas composition in the plume forming region at the core mantle boundary has a substantially lower 40Ar/36Ar, and is consistent with low plume 40Ar/36Ar observed maximum values.

A 3He flux (3He/4He=120Ra) into the same model from either D″ or the core determined to produce a convecting mantle with 3He/4He=8Ra, unsurprising, results in a plume forming region at the core mantle boundary with substantially higher 3He/4He ratios. A ‘deep’ 3He reservoir remains one explanation for plumes with high 3He/4He having low 40Ar/36Ar. The dual 40Ar/36Ar and 3He/4He result is not matched by models in which the high 3He/4He source is produced as a result of low 3He/U in the residue of shallow convecting mantle melting.

References
Intraplate volcanism due to small-scale convection – A 3D-numerical study

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Although most of the intraplate volcanism in ocean basins is expressed in linear chains, not all of those can be attributed to a stationary hotspot. Many ridges show erratic age-progressions (e.g. Musicians, Magellan seamounts) or span more than thousand kilometers in a couple of million years (e.g. Line Islands, Pukapuka ridges). Cracking of the lithosphere and small-scale convection have been invoked to account for this type of volcanism. The former presumes a partially molten asthenosphere, whereas the latter has not yet been tested and validated in a numerical model.

In the Earth’s uppermost mantle SSC is likely to develop due to instabilities of the thickened thermal boundary layer below mature oceanic lithosphere. It is characterized by convective rolls aligned by plate motion. Their onset is earlier (i.e. beneath younger and thinner lithosphere) for lower mantle viscosity (e.g. for hot or wet mantle) or adjacent to lateral inhomogeneities. In these cases, partial melt potentially emerges in the upwellings of SSC. This changes the compositional buoyancy owing to melt retention and additional depletion of the residue. Therefore, it promotes upwelling and allows for further melting. This self-energizing mechanism is able to sustain melt production in a once partially molten layer for a couple of million years.

In order to dynamically test the SSC hypothesis for intraplate volcanism, we take the step towards fully thermochemical 3D-numerical models of SSC. This is, we analyze a set of models at low mantle viscosities and varying temperatures, which provide insight into the interaction of SSC and melting. Therein, we explore the 3D-patterns of melt associated with SSC, the amounts and shapes of volcanism. We also incorporate small thermal anomalies that locally reduce the onset age of SSC.

Volcanism is predicted to evolve synchronously in a region of hundreds of kilometers after onset of SSC. Therefore, age progressions of ridges are not required to be monotonous anymore. The amount of volcanism is highly dependent on mantle viscosity. For ambient temperatures (1350 °C) viscosities have to be low (1.3·1019 Pa·s) and volcanism forms on 30 Ma old lithosphere. For elevated temperatures (1400 °C) viscosities can be higher (2·1019 Pa·s) and volcanism still forms on 50 Ma old lithosphere. Lateral thermal anomalies further increase viscosities required and are able to focus volcanism.

Stochastic modeling of surface roughness evolution during mineral dissolution

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Mineral dissolution rates are typically normalized by the surface area of the dissolving mineral. Any dissolution reaction, however, must cause the surface of the dissolving solid to change. It is, therefore, possible that surface area is a dynamic variable during mineral dissolution. In particular, surface roughness may evolve over time and, in order to interpret mineral dissolution rates, it is important to know whether a steady-state surface roughness exists and how this steady-state roughness might respond to variables that control dissolution rate such as dissolution reaction mechanism, solid defect density, and free energy of reaction (∆G_react).

Mineral dissolution and, by extension, surface evolution may be treated, theoretically, as a chemical kinetics phenomenon by parsing the surface into reactive sites. Unfortunately, the basic assumption of random collisions needed to formulate classical rate equations is inapplicable for surface evolution where site-site interactions are subject to geometric constraints. To address this problem, we have developed a 2-dimensional Ising model of dissolution and precipitation. In this model, the solid is represented by all spin-up lattice sites and reactions are represented by flipping the spin at a site with probability (per unit time) determined by the number of spin-up (or, occupied) nearest neighbors. By varying the functional relationship between reaction probability and the number occupied nearest neighbors, we simulated a variety of reaction mechanisms as well as the effects of ∆G_react. By introducing spatial heterogeneity into the reaction probabilities we simulated the effects of defects in the solid. Simulations were preformed with a variable time dynamic Monte-Carlo algorithm with reaction sites found with bisection of the surface.

Our simulations indicate that a unique steady-state surface roughness exists over a broad range of dissolution mechanisms. Carefully chosen defect structures were found to generate periodic surface roughness behavior which was, however, accompanied by periodicity in the net reaction rate indicating that the intrinsic reactivity of the surface was unaffected by defects. Surface roughness as a function of ∆G_react was found to be highly sensitive to the precipitation mechanism even when the net dissolution rate as a function of ∆G_react was relatively constant. Our results also shed insight into the existence of an inflection point in dissolution rate vs. ∆G_react. Results will be discussed in terms of relative step nucleation and retreat rates.
**EXAFS and XPS study of arsenate adsorption on manganite (γ-MnOOH) surfaces**

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**Introduction**

The introduction of toxic metalloid arsenic in the environment is of worldwide concern. Arsenic occurs in several oxidation states but in oxic environments the speciation is dominated by arsenate (As[V]), which is extremely reactive towards transition metal oxyhydroxide particles. The aim of this study is to characterize the structure and composition of arsenate species adsorbed on Mn oxyhydroxide surfaces as a function of pH and surface coverage.

**Experiment**

Batch experiments were conducted where arsenate was adsorbed onto manganite (γ-MnOOH) surfaces as a function of pH and surface coverage. A minimum of 72 hours equilibration time was allowed before the samples were centrifuged and the wet pastes were analyzed using EXAFS spectroscopy and cryogenic XPS techniques.

**Results and Discussion**

Arsenic K-edge EXAFS spectra were collected for manganite-arsenate samples over a wide range of pH and arsenate concentrations. The data reveal that there are no major differences in the spectra as a function of pH whereas minor differences are observed in the weak second shell features of the Fourier transforms. Data fitting indicates a first coordination shell of 4 oxygen atoms at the expected arsenate distances (ca. 1.7 Å) and a second shell caused by Mn backscattering together with multiple scattering within the first shell of As-O bonds. A complete quantitative evaluation of the EXAFS data is in progress.

Cryogenic XPS study on the same samples revealed that close proximity of the As 3d and Mn 3p lines makes it difficult to interpret the commonly used As 3d spectra, especially at low arsenic concentrations. In such cases, we found that the As 2p line is significantly more useful in order to understand the oxidation state, surface abundance and speciation of arsenic, as well as improving the detection limit for arsenic by a factor of 4 due to its high ionization cross-section. Consequently, we systematically analyzed the As 2p<sub>3/2</sub> binding energies and corresponding auger parameters of several arsenic oxide reference compounds (As<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>5</sub>, NaAsO<sub>2</sub> and Na<sub>2</sub>HAsO<sub>4</sub>) and calculated the atomic sensitivity factor. These data were subsequently used in the analysis of As 2p<sub>3/2</sub> spectra of the manganite-arsenate samples.

**Direct dating of archean microbial ichnofossils**

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A novel in situ laser ablation multi-collector-ICP-MS technique has enabled the first direct radiometric age determination of an Archean microbial ichnofossil. Direct in-situ U-Pb dating of titanite (CaTiSiO<sub>4</sub>) that infills tubular bioalteration textures in pillow basalt rims and hyaloclastites from the ~3.35 billion-year-old Euro basalt of the Pilbara craton, W. Australia (PWA) confirms their Archean Age [1]. A laser ablation spot size of ~40 µm was used to analyze titanite in the “root zones” at the centre of microtubule clusters. Thirteen analyzes in three thin sections gave a weighted average <sup>206</sup>Pb/<sup>238</sup>U age of 2921±110 Ma [1]. This late Archean age for titanite formation represents a minimum age estimate for the bioerosion. A pre-metamorphic age for the ichnofossils is consistent with chlorite overgrowths that cause their segmentation.

Multiple lines of evidence suggest that these tubular structures formed by microbial bioerosion of formerly glassy Archean lavas that were subsequently mineralized by titanite [2]. There are striking morphological similarities between Archean tubular structures from both the Pilbara and Barberton (BGB) cratons and microbial ichnofossils found in modern glasses. X-ray mapping shows carbon enriched along the margins of the tubular structures from both the BGB and PWA. Also, disseminated carbonates in the BGB pillow rims have C-isotopes depleted by as much as –16‰, which is consistent with microbial oxidation of organic matter.

**References**


**References**

Negative sulfate $^{17}$O anomalies as positive evidence for “Snowball Earth” hypothesis

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Since the discovery of a common occurrence of sulfate $^{17}$O anomaly in Earth’s continental deposits, a considerable amount of triple oxygen isotope data has been gathered for sulfate of diverse origins over the years. Without exception, until now all $\Delta^{17}$O values are positive, reaching as high as $+5.84$‰. It is known that the positive $^{17}$O anomalies are ultimately transferred from that of atmospheric ozone. This new parameter has proven to be powerful in sulfate source identification and quantification in geological, environmental, and atmospheric problems.

Here I present a large set of sulfate $\Delta^{17}$O data for marine evaporites and barites, which have had no direct link to atmospheric ozone chemistry. The data reveal variable negative $\Delta^{17}$O values among sulfates of different occurrences or ages. Specifically, sulfate $\Delta^{17}$O values lower than $-0.20$‰ are common in the lower Cambrian around the world (e.g., Siberia, Australia, and India) while none in the late Paleozoic or modern settings. Most remarkably, barites from the Marinoan cap carbonate sequences deposited ~635 million years ago possess a spike of extremely negative $\Delta^{17}$O values. Values lower than $-0.40$‰ are found in both northwestern Namibia and South China.

I propose that the triple oxygen isotope composition of shallow marine sulfate carries a portion of the tropospheric $\text{O}_2$ signal, which has had variable negative $\Delta^{17}$O values that were determined largely by stratospheric $\text{O}_3\text{-CO}_2\text{-O}_2$ chemistry. A quantitative relationship between atmospheric conditions and the $\Delta^{17}$O of atmospheric $\text{O}_2$ requires a comprehensive atmospheric model. If we assume that the $\Delta^{17}$O of air $\text{O}_2$ scales roughly linearly with $\text{pCO}_2$, as is supported by published glacial and interglacial data, the marine sulfate $\Delta^{17}$O data suggest that $\text{pCO}_2$ was much higher in Early Cambrian than in younger era, agreeing with previous modelling results. Most significantly, the negative sulfate $\Delta^{17}$O spike in the Marinoan cap carbonate sequences points to an extremely high $\text{pCO}_2$ at the immediate aftermath of a global deglaciation, supporting the Neoproterozoic ‘snowball’ Earth hypothesis. An on-going survey in South China is expected to yield a better picture of this negative “spike”.

Geochemical investigation of Kuhe - Dom Volcanic Rocks, central Iran

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The Urumieh-Dokhtar magmatic zone is a calc-alkaline magmatic arc of Eocene to Plio-Quaternary age. These magmatic arcs are linked to the subduction of the Neo-Tethys to the North below the Central Iranian Block. The Eocene volcano - sedimentary Rocks of Kuhe - Dom are located in Urmieh - Dokhtar magmatic belt in the northeast of Ardestan district, central Iran. The stratigraphic sequence is composed of lower Eocene Gorgab and Middle Eocene sahlab formations. The volcanic Rocks are olivine basalt, basalt, basaltic andesite, trachy basalt, trachy andesite, dacite, rhyodacite and rhyolite. The pyroclastics rocks are less common in this area and consist mainly of various types of crystal lithic tuffs and breccias, which crystals are essentially plagioclases and lithic fragments are mainly basaltic-andesites and trachy-basalt-andesites. On the basis of major, trace and REE element diagrams, the Kuhe – Dom rocks show characteristics of calcalkaline series typical of Urumieh-Dokhtar magmatic belt. Petrological and geochemical investigations demonstrate that the Kuhe – Dom Volcanic Rocks are high – K, Meta – aluminous and are consistent to continental arc environment.

References
Lu-Hf dating of sedimentary successions: Lessons learned

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It is notoriously difficult to obtain geochronological constraints for sedimentary formations with few or no biostratigraphic tracers and ash layers. The reasons for this are the necessity that the mineral phases chosen for dating 1) are truly authigenic, 2) remained closed systems since deposition and 3) do not include minor inherited phases such as clays at the time of analysis. Furthermore, the mineral must be rich in the radioactive parent isotope relative to the daughter product for the radiometric dating scheme. Phosphates, such as apatite and francolite, occur widely in sedimentary rocks as fossils and nodules, and are suitable candidates for sedimentary dating. In these phases, rare earth elements and uranium are favorably incorporated into the crystal lattice making them potentially suitable for dating by the lutetium-hafnium (Lu-Hf) and uranium-lead (U-Pb) systems. This talk presents a review of the results from sedimentary phosphates obtained to date, as well as the pro’s and con’s of the technique. Despite its limitations, dating of sedimentary phosphate by the Lu-Hf and U-Pb systems provides new age constraints for the sedimentary record that may lead the way for a better understanding of Earth history.

Sr isotope constraints on extent and character of fluid flow in EPR crust

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Crust formed at the super-fast-spreading southern East Pacific Rise ~3 my ago has been sampled at the north of the Easter microplate (22ºS) from two NW-SE striking escarpments at Pito Deep. The escarpments expose lavas, sheeted dikes and plutonics and provide a unique opportunity to investigate the lateral variations in hydrothermal alteration in the ocean crust. We use Sr isotope and trace element analyses integrated with petrographic indications of alteration to examine heterogeneity of fluid flow though the ocean crust.

The mobile metals Cu and Zn are variably depleted relative to magmatic concentrations but this depletion is decoupled from enrichments in 87Sr/86Sr. Strontium isotopic enrichment is also decoupled from Sr concentration suggesting that uptake of seawater Sr, for example into epidote, is not the principal control on the changing 87Sr/86Sr.

Two escarpments at Pito Deep allowed sampling of sheeted dykes over vertical extents of 700 m and 1000 m respectively. Sheeted dykes from two escarpments show 87Sr/86Sr of 0.70252-0.70364 and 0.70267-0.70466 respectively. Fresh MORB in this area has a 87Sr/86Sr of 0.70239. Localised (few to 10’s m) anomalously high 87Sr/86Sr (> 0.703) are associated with proximal faults. We interpret these data as indicating that these acted as conduits to channel fluid flow at high-temperatures. This provides compelling evidence for significant modification of rock and consequently fluid compositions during channelised flow.

In order to compare the extent of Sr-isotopic exchange between hydrothermal fluids and the crust at Pito Deep with the other two areas that have been studied in detail (Hess Deep and ODP Hole 504B) we have modelled the fluid flux through the system. We use the modelling approach developed by Bickle (1992) that assumes pervasive, kinetically hindered, isotopic exchange during one dimensional fluid flow. Although this does not appear to describe the hydrology of the system it allows quantitative estimates of the differences in fluid flux between these areas to be considered.

Modelling of Sr isotopic differences between the two escarpments at Pito Deep reveals spatial variability in fluid flux through the ocean crust formed in one location. Comparison with Hess Deep and ODP site 504B indicates that Pito Deep has experienced greater Sr isotopic exchange and consequently higher fluid flux. Interpretations will be discussed in the context of structural and thermal variations on regional and local scales.

References
The effect of sample matrix on the precision and accuracy of radiogenic isotope ratio measurements by MC-ICP-MS

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Introduction

Residual sample matrix is known to cause non-spectral matrix effects that adversely influence the accuracy of non-traditional stable isotope ratio determinations by MC-ICP-MS (e.g. Carlson et al., 2001). It is commonly assumed however, that matrix effects do not significantly influence the accuracy and precision of radiogenic isotope determinations by MC-ICP-MS (e.g. Nd, Hf, Pb). The external normalisation method (Tl) used to correct Pb data for instrumental mass bias means that Pb data are potentially susceptible to matrix effects if matrix causes different instrumental mass bias responses for Pb and Tl. We have therefore investigated the significance of matrix effects on the precision and accuracy of MC-ICP-MS radiogenic isotope data.

Observations and experiments

In the case of Hf, subtle differences have been observed between measured stable isotope ratio correlations (i.e. 178/177, 179/177, 180/177) for mafic and felsic sample material (Weis et al., 2007), raising the spectre that instrumental mass bias for samples may not follow the same empirical fractionation law as for standards. Preliminary experiments with Nd however, suggest that internal normalisation is effective in compensating for matrix effects.

In purified Pb samples, residual sample matrix decreases with increasing SiO2. Ca is the dominant matrix element, followed by Al, Fe and Mg; organics derived from ion exchange resin may also be present. This matrix causes changes in instrumental mass bias and signal enhancements of up to 80%. Experiments carried out on standards doped with Ca, Al, Fe and Mg, demonstrate that these four elements can account for Pb and Tl signal enhancements of up to ~50% and that enhancement of Tl > Pb. Pb and Tl instrumental mass biases also respond differently to matrix elements; both effects are greatest in the presence of Ca. Samples passed twice through chemistry show significant reduction in matrix effects and better reproducibility. Sample matrix must therefore be reduced to negligible levels for high precision and accuracy radiogenic isotope data.

References


Chlorine stable isotopes as a geochemical tracer along the Central American and the Izu-Bonin-Mariana arcs

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Chlorine stable isotope ratios of different potential sources of Cl to subduction zones (sediments (~ -2‰?), pore fluids (~8 to ~0.1‰), mantle (0‰), subducted oceanic crust, e.g., serpentinites (~1.8 to +0.5‰)) are distinct, thereby providing a geochemical tracer of the fluid source responsible for melts and arc volcanism. We have analyzed volcanic gases (collected in Giggenbach flasks), volcanic gas condensates, aqueous fluids from crater lakes, streams, geothermal wells, tephras, lavas, sediments from the subducting plate, backarc basalts, and clasts and muds from serpentinite seamounts to help identify the sources of Cl in the Central American (CA) and Izu-Bonin-Mariana (IBM) subduction zones.

δ37Cl values of volcanic gases from along the CA arc range from ~4 to +12‰. Gas samples from Poás (Costa Rica) have the most positive δ37Cl values (+5.2 to +12.1‰) of all volcanoes analyzed. However, the lake and streams in the Poás crater have near zero δ37Cl values with little to no variation over time. Gases from nearby, Turrialba and Irazú (Costa Rica) have negative δ37Cl values (averaging ~ ~2‰). Santa Ana (El Salvador) and Momotombo (S. Nicaragua) have δ37Cl values of +6.3 and +4.0‰, respectively. San Jacinto, San Cristobal, and Cerro Negro (N. Nicaragua) have negative δ37Cl values (averaging ~ ~2‰). Fuego (Guatemala) also is isotopically negative, ~0.6‰. Tephra and lava samples from six Nicaraguan volcanoes range from ~3.0 to +1.6‰.

δ37Cl values of volcanic gases from along the IBM arc are generally negative (averaging ~2.2 ± 1.2‰). Serpentinite clasts from the Conical and South Chamorro seamounts have bulk δ37Cl values of 0.33 and 0.31‰, respectively. Serpentine muds from both seamounts have bulk δ37Cl values of 0.12‰. Backarc basalts from the Guguan cross-chain also average 0.12‰. Sediments from ODP Leg 129 have negative bulk δ37Cl values, ranging from ~0.3 to ~1.2‰ (n = 3).

The consistently negative δ37Cl values of volcanic gas samples from along the IBM arc indicate that chlorine is likely sourced from subducting sediments, isotopically negative serpentinites, and/or pore fluids. Similar conclusions may be drawn from isotopically negative volcanic rocks from N. Nicaragua, Guatemala, and some volcanoes in Costa Rica. Additional ODP sediment samples from the Pacific plate will be analyzed to better define the δ37Cl value of the sediment source, which is not well known at present. The high δ37Cl values from Poás, Santa Ana, and Momotombo may be due to volatilization of acidic fluids at high temperatures, where extreme fractionations have been observed experimentally.
Highly siderophile elements in platinum-group element ore deposits
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We have studied the distribution of siderophile elements among base metal sulphides (BMS) and platinum-group minerals (PGM) found in platinum-group element (PGE) ore deposits. In order to address the question of which processes affect the formation of these deposits we have selected deposits that have undergone different cooling rates and degrees of metamorphism.

In sulfide droplets from the unmetamorphosed Noril’sk sills, which have undergone rapid cooling, almost all of the siderophile elements (except Pt and Au), occur in BMS. This suggests the model whereby a base metal sulfide liquid collects the PGE to form these deposits is correct. Platinum occurs as PGM exsolutions within the BMS. Possibly the Pt partitioned into the sulfide liquid, but it exsolved from the BMS during cooling.

In the PGE-reefs of unmetamorphosed layered intrusions (Busveld Complex and Great Dyke) ~30 to 60% of the siderophile elements (except Pt and Au) are present in BMS. The balance is found in PGM, which occur as exsolutions in the BMS or as grains at the contact with the BMS. The reason that a larger percentage of PGE are in the form of PGM is the slower cooling of the BMS in the layered intrusion, which would allow more time for exsolution of the PGE than in the case of the BMS from subvolcanic sills.

In the PGE-reefs from the metamorphosed layered intrusion (Penikat) the percentage of siderophile elements present in BMS covers a larger range, ~8 to 70 percent. There are many more PGM present and there has been extensive recrystallization of the BMS. Possibly the recrystallization of BMS during metamorphism facilitated the formation of a large number of PGM. The Pd-PGM are not always found associated with BMS. Three processes could have led to this: a) the BMS, which originally contained Pd, dissolved during metamorphism, leaving an insoluble Pd-PGM; b) the Pd could have been introduced to the PGE reef by metamorphic fluids; c) the Pd could have been locally remobilized into the silicates adjacent to the BMS.

The use of Campanian pumices in the Roman mortars of Messina area (Sicily) as indicator of technological tradition
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In this work we present the petrographic and geochemical characterization of pumices employed in the roman mortars sampled in the archeological sites of Messina area (Capo Peloro and Messina). The petrographic analysis shows the presence of two principal groups of mortars: i) cocciopesto bearing mortars; ii) pumices bearing mortars.

These data confirm the Romans’ knowledge of the property of pyroclasts and pottery fragments as raw material in the preparation of hydraulic binders with optimal physical and mechanical characteristics.

The archeologists, on the basis of the proximity, considered the pumice coming from the Aeolian Islands but no archeometric data exist till now supporting this hypothesis.

With the aim to establish the provenience of the pumice inclusions chemical analysis, carried out with SEM/EDS, were made on numerous mortars samples. The multivariate principal components diagram of the geochemical data (Fig.1) indicates the use of campanian pozzolana that was preferred to the Aeolian pumices because it guaranteed better hydraulic properties.

Fig.1
Geochemistry and tectonic setting of mafic rocks from the Othris Ophiolite, Greece

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The Othris Ophiolite in central Greece is a remnant of the Jurassic Neotethys Ocean, which existed between Eurasia and Gondwanaland. The mantle section of the Othris Ophiolite shows evidence for both mid-ocean ridge and supra-subduction zone tectonic settings (Barth et al., 2007). In this study geochemical analyses of minerals and whole rocks are presented for a suite of mafic rocks from the crustal section of the Othris Ophiolite. The mafic rocks form three chemically distinct groups.

Group 1 is characterized by N-MORB-type basalt and basaltic andesite with Na- and Ti-rich clinopyroxenes. These rocks show mild LREE depletion and no HFSE anomalies, consistent with moderate degrees (~15%) of anhydrous partial melting of depleted mantle followed by 30-50% crystal fractionation.

Group 2 is represented by E-MORB-type basalt with clinopyroxenes with higher Ti contents than Group 1 basalts. Group 2 basalts also have higher concentrations of incompatible trace elements with slightly lower HREE contents than Group 1 basalts. These chemical features can be explained by ~10% partial melting of an enriched mantle source.

Group 3 includes high MgO cumulates with Na- and Ti-poor clinopyroxene, forsteritic olivine, and Cr-rich spinel. The cumulates show strong depletion of HFSE, low HREE contents, and LREE enrichments. These rocks may have formed by olivine accumulation from boninitic magmas.

The petrogenesis of the Group 1 basalts is in excellent agreement with the melting conditions inferred from the MOR-type peridotites in Othris. Furthermore, the inferred parental magmas of the Group 3 cumulates are broadly complementary to the SSZ-type peridotites found in Othris. These results suggest that the crustal section may be genetically related to the mantle section.

In the Othris Ophiolite mafic rocks recording magmatic processes characteristic both of mid-ocean ridges and subduction zones occur within close spatial association. These observations are consistent with the formation of the Othris Ophiolite by intra-oceanic thrusting and forced subduction initiation at (or near) a mid-ocean ridge.

References

Nd model ages ($T_{DM}$) as an indicator of West Gondwanan suture in southeastern South America

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Available Nd ($T_{DM}$) ages for a roughly W–E transect across the units observed on both sides of the South Atlantic Ocean shows a conspicuous decrease in model ages eastwards; with the Damara Belt displaying the youngest values. There is a concentration of model ages around 2.0 Ga for the Supracrustal Schist Belt of the Dom Feliciano Belt, whereas for the Eastern Granite Belt the average falls to 1.3–1.6 Ga. For the Damara Belt (mainly its granitoids), the average also falls in the 1.3–1.6 Ga interval (McDermott and Hawkesworth 1990; Jung et al. 1998). This similarity, which may represent an affinity of the source areas for the Eastern Granite Belt and the African portion, can be explained by the participation of similar sources in the generation of these materials. Therefore, the isotopic differences between the Eastern Granite Belt and those further west, strengthen suggestions that the Major Gercino–Sierra Ballena lineament should be viewed as a Neoproterozoic Lithospheric suture (Basei et al. 2005). These results highlight the differences in the detrital zircon signatures across a proposed West Gondwanan suture, with those in the west being derived from distinctive South American basement sources and those in the east from distinctive African sources. An important gravimetric anomaly along the MGSB lineament also supports this interpretation (Hallinan and Mantovani 1993).

References
Any supernova $^{60}$Fe excess on Earth? Evidence from $^3$He in ferromanganese crust

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 Supernova (SN) explosions within 30 parsecs of Earth have the potential to affect the biosphere. Identifying SN debris on Earth allows models of SN frequency to be tested and assess their role in global environmental change. Identification of rare SN-produced isotopes in slow accumulating terrestrial archives is one method. The detection of $^{60}$Fe in 2.4-3 Ma layers in a ferromanganese crust from the deep Pacific Ocean (237KD) has been attributed a SN source [1]. However $^{60}$Fe is also produced by galactic cosmic-ray (GCR) interaction with Ni in extraterrrestrial material. Helium isotopes offer a way of testing the source of the $^{60}$Fe in 237KD. $^3$He is produced by GCR reactions and delivered to Earth in extraterrestrial dust, but SN-helium is not predicted to make it to the Earth. We have quantified the GCR-He contribution in 237KD, and, by comparing production rates in possible extraterrestrial material, we estimate the GCR-$^{60}$Fe from micrometeorites to test the SN hypothesis [2].

$^3$He/$^4$He (5.5 to 4440 R A) is a mixture of extraterrestrial He (implanted solar ions + GCR-He) and radiogenic He in terrestrial dust. Prior to 4-5 Ma $^3$He concentrations vary little and no $^3$He/$^4$He was higher than the solar wind value (290 R A). In the last 4 Myr average $^3$He increases significantly, six samples have $^3$He/$^4$He higher than solar wind and the average $^3$He/$^4$He (330 R A; n = 32) is higher than the average of the older samples (54 R A; n = 36). The statistical variability of $^3$He between replicates of < 4 Myr samples indicates that a small number of extremely GCR-He-rich micrometeorites have been incorporated. The $^3$He/$^4$Fe of 237KD (80-850) is comparable to the measured GCR $^3$He/$^4$Fe production rate ratio (400-500) in Ni-rich minerals in iron meteorites. The $^{60}$Fe in 237KD can be explained by a small number of FeNi-rich micrometeorites and rules out the need for SN debris.

To test whether the $^3$He in crusts reflect normal micrometeorite flux or ablation debris from entry melting of large meteorites we are analysing sections at the KT boundary from crusts with low $^{187}$Os/$^{188}$Os excursions that are temporally associated with enhanced meteoritic flux.

References

Fractionation of HSE during melt transport processes in supra-subduction mantle

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Highly siderophile elements (HSE) represent powerful tools for monitoring and dating mantle processes. Here we report a detail study of HSE and Re-Os isotopes of lithologies from the Voykar Ophiolite (Polar Urals) which formed in a subduction tectonic environment. The Voykar mantle rocks are extraordinary fresh and often free of serpentine. Even primary sulfides are preserved. This suggests that the original PGE distribution and the Re-Os isotope systematics have not disturbed by low temperature secondary alteration processes.

Our data suggest that old, more than 2 Ga old refractory harzburgite was percolated by suprasubduction melts about 0.6 Ga. These melts have formed dunite reaction channels and pyroxenite veins and locally redistributed the HSE in the surrounding harzburgite. In dunite channels and pyroxenite veins numerous sulfide globules transported by silicate melts have been observed. These sulfide globules make up the HSE budget of the pyroxenites and they are characterized by low concentration of Os, Ir and Ru compared to Pt, Pd and Re. High Re abundance in the pyroxenite (up to 2 ppb) suggest contribution from subduction slab.

HSE composition of dunites results from reaction between percolating melt and host peridotite. Close to the contact, residual peridotites become enriched in Pt, Pd and Re. But primary HSE features of the harzburgite, such as Pd, Pt, Re depletion relative to Ir, Os and Ru appear to be preserved in a distance of about 1 m away from the contact with dunite channel.

![Figure 1: HSE distribution through the dunite channel.](image-url)
Humic substances (HS) are natural organic polymers present in most environmental systems. They are redox-active and participate in microbiologically catalyzed redox reactions. Iron-reducing and many fermenting bacteria can use HS as an alternative electron acceptor in their metabolism. The reduced HS transfer electrons in a chemical reaction to electron acceptors like metal ions or organic pollutants, thus functioning as an electron shuttle between microorganisms and these terminal electron acceptors. So far the kinetics and thermodynamics of redox reactions of HS with iron(II) and iron(III) minerals as well as with microorganisms are poorly understood.

In order to tackle these knowledge gaps, the kinetics of microbial reduction of various HS by Fe(III)-reducing bacteria (Geobacter and Shewanella sp.) was quantified and compared to i) the direct microbial reduction of iron(III) minerals and ii) the reduction of iron(III) minerals by reduced HS. We determined the minimum concentration of HS necessary for observable electron shuttling.

The thermodynamics of redox reactions between HS and dissolved and solid iron(II) and iron(III) compounds was evaluated. Since O2 is the most important electron acceptor in nature, redox reactions of HS with iron compounds possessing different redox potentials were compared to HS oxidation by O2. We applied electron spin resonance (ESR) spectroscopy in order to quantify radical formation during HS redox reactions. As the contribution of HS-complexed iron to HS redox reactions is unclear, we extracted different iron fractions from HS by sequential extraction and quantified the redox properties of HS after each extraction step.

Our results showed that HS can react with several iron(II) and iron(III) minerals and efficiently catalyze biogeochemical processes in the environment. The fact that these processes a variety of reactive HS species such as semiquinone radicals are formed suggests that HS have the potential to be an important player in the redox cascade in natural environments.
Thermally altered early Silurian cyanobacterial mats: Biomarkers and $^{15}$N isotopic signatures

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Morphologically preserved cyanobacterial mats are rare in the fossil record due to destructive biological and diagenetic processes. Early Silurian black radiolarian cherts from the Holy Cross Mts. and Sudetes (Poland) contain abundant variously degraded remnants of benthic coccoid cyanobacterial mats. These cherts underwent thermal alteration with various intensity, which influenced the organic matter preservation.

Here we examined the organic matter of these cherts to investigate its origin and maturity. Aliphatic fractions of the extracted organic matter was dominated by n-alkanes in a range of 15 to 36 carbon atoms exhibiting unimodal distribution with a maximum between C$_{17}$ and C$_{19}$. The most immature cherts still contained hopanoids dominated by 22S-isomers attesting to the relative high maturity of the organic matter. The dominance of hopanoids over steranes and the isomers attesting to the relative high maturity of the organic matter. The dominance of hopanoids over steranes and the isomers attesting to the relative high maturity of the organic matter. The dominance of hopanoids over steranes and the isomers attesting to the relative high maturity of the organic matter. In contrast, the more mature sediments did not contain recognizable cyanobacterial biomarkers which are presumably lost during diagenesis. Thus, in spite of good morphological preservation, the biomarker signatures of the Silurian cyanobacteria, due to their thermal maturation, are no longer recognizable.

Nitrogen isotopic signatures of bulk organic matter in the studied cherts vary from -2.2 to +0.1‰ what is consistent with values observed for biological nitrogen fixation. Although it is known that diagenesis and bacterial degradation may alter the nitrogen isotopic composition, the rather low $\delta^{15}$N values from the studied cherts seem to reflect isotopic N signals not considerably changed by maturity and degradation.

Fingerprinting of a thin secondary mineral film on DU

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Depleted uranium (DU), a by-product in the production of nuclear fuel, is used for military purposes in projectiles for attacking armoured vehicles. Concerns about the ecological consequences following the use of DU as ammunition in wars in Iraq and in the former Yugoslavia have received much public attention. The long-term effect on groundwater and drinking water as a result of dispersed DU projectiles in soil is far from understood. In this study, the weathering of DU in conditions representing agricultural soil, rich in calcium and phosphate, was studied in laboratory experiments. Surface alteration products were identified by infrared spectroscopy (IR) and time-resolved laser-induced spectroscopy (TRLFS).

Discs of DU, 0.5 mm in thickness and 25 mm in diameter, obtained from a British pristine military tank shell were used in our experiments. One sample was placed in a solution containing $2.5 \cdot 10^{-3}$ M Ca(NO$_3$)$_2$ and $1.05 \cdot 10^{-3}$ M (NH$_4$)$_3$PO$_4$. After a contact time of 360 days the sample was taken out of the solution. IR- and TRLFS measurements were made on the surface of the sample, immediately after rinsing with deionised water and drying. The spectra obtained were compared with those of natural uranium minerals, formed under oxidising weathering conditions, provided by the Mineral Collection of the TU Bergakademie Freiberg. Comparison of the IR-spectra from the DU surface with those of the reference minerals revealed that the newly formed secondary mineral on DU is a uranium (VI) phosphate. Further identification of the respective uranium phosphate mineral was not possible with IR. However, a comparison between the TRLFS spectra of the newly formed unknown uranium phase on the DU disc with well-known TRLFS spectra of uranium reference compounds clearly showed the presence of meta-autunite. The hypothesis established in [1] was confirmed based on much better spectra with regard to signal-to-noise ratio and reproducibility. Agreement between TRLFS spectra from altered DU and the fingerprints was obtained not only in the position of the peak-maxima, but also in the life time of the fluorescence signals. TRLFS clearly shows the presence of a very thin layer of the newly formed uranium phosphate mineral on the DU disc, which is formed from the metallic uranium and the calcium phosphate solution, an alteration process that may well occur in agricultural soil.

References

Influences of the quartz host mineral on the Raman spectra of H₂O and aqueous salt bearing fluid inclusions

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Raman Spectroscopy offers a powerful tool for the investigations of aqueous phases in fluid inclusions and can provide insights of vibrational modes of different species. The water stretching vibrations between 2800 up to 3800 cm⁻¹ are the most informative signals for the investigation of fluids. This region shows one broad signal, which is a complex profile of overlapping bands. Dissolved electrolytes, which are present as simple ions are not Raman active but they can influence the characteristic Raman bands of the aqueous solution. The shape of the Raman contour shows a systematical change in dependence of the amount of dissolved anions and cations in the solution. The intensity in the front area of the water peak is decreasing to smaller values and a peakshift to higher wavenumbers could be observed. For this reason the Raman spectra of the stretching region of liquid water is often used to determine the salinity of fluid inclusions.

The Raman spectra of liquids were studied in synthetic H₂O and aqueous salt bearing fluid inclusions in quartz. The inclusions were synthesized at 600°C and various pressures in our laboratory. The Raman spectrum of H₂O is substantially different between a drop of water and a fluid inclusion. The spectrum of fluid phases in inclusions is not only defined by the fluid phase itself. The host mineral can influence the signal dramatically and modify the shape of the Raman bands due to polarization of the laser beam. In birefringent minerals such as quartz the spectra is strongly influenced by the crystallographic orientation of the host. Other modifications on the spectra are caused at the quartz- fluid inclusions interface depending on the angel of the surface of the inclusion wall. These phenomena may cause erroneous estimations of the salinity of fluid inclusions. We have qualified and quantified the variability of the Raman spectra due to these polarization effects in quartz.

Slow reaction rates, disequilibrium, and excess Argon: Teaching some bad dogs new tricks

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Geochemical, petrological, and geochronological interpretations about the evolving earth require assumptions about the poorly constrained rates of fundamental geologic processes. Among these processes are chemical reactions - whose rates determine whether systems reach equilibrium, and chemical transport mechanisms - whose rates control the lengthscale of equilibrium as well as important boundary conditions in models of isotopic closure. Here, I describe ways in which we can make use of otherwise problematic field situations where, 1) the equilibrium assumption, and 2) the standard model for isotopic closure, break down.

Models of reactive-transport within layered rock systems can be used to exploit fluid-rock disequilibrium to quantify reaction kinetics attending metamorphism. This method, involving Sr-isotopic diffusion and exchange is reviewed, as well as the fundamental result of its first application which suggests natural metamorphic reactions rates are many orders of magnitude slower than required for equilibrium to be maintained in most systems [1]. Such slow time-integrated reaction rates, corroborated by several other field based observations, mean that the petrologic evolution of the crust cannot a priori be assumed to follow equilibrium based predictions [2]. Quantification of reaction rates, coupled with equilibrium models, permits more accurate modeling of dynamic natural systems.

Excess argon, the result of a violation of the standard closure model, is a frequent annoyance in Ar/Ar thermochronology. Most important in the development of excess argon is the breakdown of the “zero-concentration boundary condition” assumption. Two system parameters ultimately control this: 1) the transmissive timescale, which is the time required for Ar-40 to escape from the local rock system, and 2) the total local sink capacity, which is the degree to which other local phases (minerals, fluids, and even grain boundaries [3]) may take in (i.e. partition) the Ar-40 relative to the mineral of thermochronologic interest. Numerical modeling of diffusive transport and exchange has yielded an empirical analytical equation which predicts the amount of excess argon in any phase in a system as a function of these two parameters [4]. With this quantitative model, it is possible to use this measureable quantity (excess Ar) as a tracer of transport, timescales, and cooling in its own right.

References
Focused pulses of regional metamorphism

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Growing evidence is emerging to support the idea that metamorphism, even in a regional context, may be punctuated – or dominated – by relatively short pulses of heating, fluid flow, and/or mineral growth. Here, we describe data from two Barrovian metamorphic terranes which test this idea.

In the Barrovian zones of Scotland, garnet Sm/Nd geochronology from the garnet and sillimanite zones yield the same peak metamorphic ages [1] (~465 Ma). The age is similar to the age of crystallization of large igneous bodies in the area. The contemporaneity of peak ages is explained by an efficient, advective component of heating, perhaps mediated by synchronous fluid flow [2]. The duration of this region-wide pulse of peak metamorphism is constrained by new Sr-in-apatite diffusion modeling. Apatite grains have detrital cores and metamorphic overgrowths and are included within porphyroblasts (e.g. garnet, staurolite). Modeling of intragrain diffusion of Sr constrains the duration of peak metamorphism to <250 kyr for garnet through staurolite zone samples. Garnet multi-component diffusion modeling from the sillimanite zone corroborates this brief pulse duration.

The Wepawaug Schist of Connecticut USA, also yields contemporaneous peak-T garnet Sm/Nd ages from different grades across the terrane (~380 Ma). This age matches a population of texturally young zircons associated with igneous intrusions in these rocks. Garnet cores from the kyanite zone, which have growth textures indicative of extremely rapid growth [3], have been dated by Sm/Nd at 388.6 Ma. This age is matched by another population of zircons also associated with igneous intrusions. This earlier prograde growth event may be related to another pulse of metamorphic growth, brought on by magmatic fluid and heat.

Brief pulses of metamorphic heating and mineral reactions, perhaps catalyzed by the introduction of fluids, may be superimposed on regional scale conductive heating at tectonic rates. Such short pulses could help explain the discrepancy between rapid lab-based reaction kinetics and much slower time-integrated field-based reaction kinetics [4].

References

U-Th stratigraphy of a cold seep carbonate crust

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Uranium and thorium concentrations and isotope compositions were measured on a set of 16 samples drilled across an authigenic carbonate pavement, providing the first stratigraphy for a cold seep carbonate crust. The 5.5-cm thick crust (NL7-CC2) was collected by submersible on the Nile deep-sea fan in an area of active fluid venting. U-Th analyses were corrected for initial Th using isochron methods.

Our calculated 230Th/U age-depth profile for NL7-CC2 provides evidence for continuous carbonate precipitation at the studied location over the last ~ 5000 years. Three distinct phases can be distinguished from top to bottom with average growth rates of ~ 0.4, 5.5 and 0.7 cm/kyr, respectively, corresponding to carbonate precipitation rates ranging from ~ 8 to 125 µmol/m²/h, consistent with previous estimates. High-resolution profiles for δ13C and major elements across NL7-CC2 show that those variations in carbonate precipitation rates were also accompanied by changes in carbonate mineralogy and composition of contemporaneous fluids.

We suggest that all those changes reflect primarily modification of the diagenetic environment, i.e. a progressive depletion of dissolved sulphate through anaerobic oxidation of methane, caused by carbonate crust formation. Overall, U-Th dating of cold seep carbonates offers a promising tool to bring new insights into biogeochemical processes at cold seeps and to assess the timing and duration of fluid venting on continental margins.
Spinel-lherzolite xenoliths from the Hoggar swell: Evidence for intracratonic asthenosphere upwelling and lithosphere rejuvenation

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The mantle xenoliths included in Quaternary alkaline volcanic rocks from the Manzaz-district (Central Hoggar) are proto-granular, anhydrous spinel lherzolites. Major and trace element analyses on bulk rocks and constituent mineral phases show that the primary compositions are widely overprinted by metasomatic processes, which however are not reflected by pyrometamorphic textures. Trace element modelling of the metasomatized clinopyroxenes allows the inference that the metasomatic agents that enriched the lithospheric mantle were highly alkaline carbonate-rich melts such as nephelinites/mellilitites (or as extreme silico-carbonatites). These metasomatic agents were characterized by a clear HIMU Sr-Nd-Pb isotopic signature, whereas there is no evidence of EM1 components recorded by the Hoggar Oligocene tholeiitic basalts. This can be interpreted as being due to replacement of the older cratonic lithospheric mantle, from which tholeiites generated, by asthenospheric upwelling dominated by the presence of a HIMU signature. Accordingly, this rejuvenated lithosphere (accreted asthenosphere without any EM influence), may represent an appropriate mantle section from which deep alkaline basic melts could have been generated and shallower mantle xenoliths sampled, respectively. The available data on lherzolite xenoliths and alkaline lavas (including He isotopes, Ra < 9) indicate that there is no requirement for a deep plume anchored in the lower mantle, and that sources in the upper mantle may satisfactorily account for all the geochemical/petrological/geophysical evidence that characterizes the Hoggar swell. Therefore the Hoggar volcanism, as well as other volcanic occurrences in the Saharan belt, are likely to be related to passive asthenospheric mantle upwelling and decompression melting linked to tensional stresses in the lithosphere during Cenozoic reactivation and rifting of the Pan-African basement. This can be considered a far-field foreland reaction of the Africa-Europe collisional system since the Eocene.

Lithosphere/asthenosphere interaction in a plume region: Evidence from Ethiopian mantle xenoliths

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Mantle xenoliths entrained in alkaline lavas from Injibara (Gojam) and Nekemte (Wollega) at the western border of the Ethiopia-Yemen basaltic plateau provide information on the lithospheric mantle evolution in an area where the existence of a deep mantle plume is widely accepted (Afar plume; Courtillot et al., 2003).

The studied xenoliths include prevalent spinel lherzolites and subordinate harzburgites (sometimes containing metasomatic amphibole) and olivin-websterites characterized by generally flat chondrite-normalized bulk-rock REE patterns, with only few enriched samples (La/Yb up to 5). Clinopyroxene (cpx) REE patterns are generally flat or LREE depleted (La/Yb down to 0.6). In a few samples a pristine Eu depletion is observed in garnet peridotite clinopyroxenes.

Sr-Nd isotopes on separated cpx mainly show compositions (87Sr/86Sr < 0.7030; 143Nd/144Nd > 0.5132) approaching the Depleted Mantle end-member, or displaced (87Sr/86Sr 0.7033-7034; 143Nd/144Nd 0.5129-0.5128) toward the Enriched Mantle components which also characterize the Ethiopian Oligocene plateau basalts.

These characteristics indicate that most xenoliths were variably affected by metasomatic processes, whose agents may be envisaged as mafic subalkaline melts that infiltrated and reacted at high melt/peridotite matrix ratio.

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The compositional evolution of the studied samples seems to reflect complex asthenosphere/lithosphere interactions occurring in a plume region where lithospheric bulging and thinning by the uprising asthenosphere is accompanied by pervasive refertilization due to reactive percolation of sublithospheric subalkaline melts. Therefore the studied mantle xenoliths may represent asthenosphere-derived mantle material entrained by the buoyancy flux of the Afar plume which equilibrated to shallower levels and accreted to the lithosphere.

References
Petrogenesis of the Ethiopian plateau basalts and their bearing on mantle plume components

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The Ethiopian-Yemen continental flood basalts represent an Oligocene Large Igneous Province where some typical features of deep mantle plume, including high ⁴He/³He ratios, have been documented (Afar plume; Courtillot et al., 2003). In the Ethiopian plateau large volumes (ca. 300000 Km³) of tholeiitic magmas, erupted in a short time span (31-28 Ma), appear to be zonally arranged with low-Ti basalts in the NW part of the province, and high-Ti basalts (and picrites) in the eastern sector neighbouring the Afar-Red Sea region (Pik et al. 1998).

An integrated petrogenetic model based on major element mass balance calculations, phase equilibria, and thermo-barometric evaluations indicates that primary basaltic magmas were generated by ca. 15-20% melting of mantle lherzolite at 1250-1300 °C / 13-16 Kb and ~1300-1350 °C / 14-19 Kb for low-Ti and high-Ti tholeites, respectively; high-Ti picrites by ~30% melting at ~1400-1450 °C / 20-30 Kb.

The calculated mantle sources invariably require hydrated lherzolite composition with up to 5% and 10% of amphibole for low-Ti and high-Ti magmas respectively, and a parallel increase of 2 – 17 times incompatible element abundances with respect to those observed in the Ethiopian mantle xenoliths. Further Ti-rich metasomatic phases (e.g. rutile, ilmenite, armalcolite) are required in the mantle sources, particularly for the generation of extremely high-Ti magmas (TiO₂ up to 5-6%). Therefore, low-Ti basalts may have been generated in the outer zone of the Afar-plume by partial melting of moderately metasomatized lithospheric mantle sources, in connection with the activation of the hotspot and related crustal bulging. High-Ti basalts/picrites could in turn be generated in the inner part of the Afar buoyancy flux from mantle sources significantly more enriched by plume components. These metasomatizing components may correspond to Na-alkali silicate mafic melts enriched in Ba, Th, Nb, Ti, Zr as well as light REE and show compositional analogies with the Ti-rich alkali silicate metasomatism documented in some mantle xenoliths from Kerguelen Islands (Grégoire et al., 2000).

References

Biogeochemistry of advective intertidal sediments

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Introduction
At tidal flat margins where the sediment surface slopes towards tidal creeks, deep advective pore water flow may be generated driven by the hydraulic gradient between sea water and pore water level at low tide (Billerbeck et al. 2006; Howes and Goehringer 1994; Wilson and Gardner 2006). Tidal and seasonal variation of trace metal and nutrient concentrations in deep pore waters of advective intertidal sediments have however remained largely unknown.

Results and Discussion
In-situ pore water sampling down to 5 m sediment depth in an intertidal sand flat in NW Germany revealed trace metal profiles similar to those observed in the upper centimetres of deep sea sediments. The pore water composition is strongly influenced by the location of the sampling site and its specific characteristics, like oxygen penetration depth and H₂S concentration.

At a location close to the main tidal creek tidal variations of trace metals, dissolved organic carbon (DOC), and nutrients were determined. Manganese concentrations e.g. increase by a factor of two from low to high tide in these depths, whereas uranium concentrations are decreasing to values half as high in the same time period. Pore water advection is shown to be most significant at 1 to 3 m depth. In these depth levels DOC and nutrients are enriched, whereas trace metals are enriched or depleted depending on their specific behavior under reducing conditions. Elemental species enriched in deep pore waters presumably represent an important source for the open water column when seeping out of the sediment. Release of manganese-enriched pore water supposedly explains tidal variations observed in the open water column of the study area. Seasonal pore water composition and temperature variations in depth profiles support the hypothesis that advection is significantly influencing the tidal flat system. The study of seasonal concentration patterns further evidences the interaction of trace metals like vanadium with DOC.

References
Geochemical tracing of core-mantle interaction: High-precision W isotopic data on komatiites using TIMS

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It has been suggested that coupled suprachondritic 187Os and 186Os in some plume-derived picrites and komatiites may be best explained by a small contribution (≤0.5-1%) of a component from the outer core in the mantle sources of these lavas. Tungsten is another siderophile element that might help tracing core-mantle interaction. The excess of 182W (from the decay of short-lived 182Hf during the first 60 Ma of solar system history) in the mantle relative to chondrites suggests that the core may have a deficit of 182W relative to the mantle (ε182W ≈ -2). A previous study of 182W systematics of Hawaiian picrites that show suprachondritic 187Os and 186Os did not reveal resolvable deficits in 182W at the 10-20 ppm level (Schersten et al. 2004). Because the effects of a 0.5-1% core contribution on 182W likely may be less than 30-40 ppm, external precisions better than 10 ppm (2σ) on 182W/184W or 183W/184W of lavas are required in order to resolve a core contribution. The goal of this project was to establish analytical protocols that allow the measurement of differences in the abundance of 182W in komatiites at the 5-10 ppm level by negative thermal ionization mass spectrometry using the Johnson Space Center TRITON TIMS. Komatiites show W abundance excesses (relative to similar incompatible elements such as Ce or Th) that remain unexplained and the association of some komatiites with plume/LIP provinces may hint at an origin of the source rocks in the deep mantle. Results over a 3 month period yielded in-run precisions (2σ) of individual W standard runs between 4 and 6 ppm for 182W/184W and 183W/184W, respectively, and external precision (2σ) of 7 and 9 ppm on 182W/184W and 183W/184W, respectively (n=10). After 3 months, it was observed that standard runs were systematically shifted to higher values by 10-15 ppm for both 182W/184W and 183W/184W. Two aliquots of a 2.7 Ga Belingwe komatiite yielded the best in-run precision (~6 ppm), and show values for 182W/184W that are within uncertainties of W standards run during the same time period. A single run for komatiite GOR 94-7 (Gorgona) shows an uncertainty of ±17 ppm (2σm) and a 182W/184W value overlapping with standard measurements. The main limitations on high-precision 182W measurements by N-TIMS are the influence of variable O isotopic compositions and minor Re oxide interferences on W oxide corrections. Normal W isotopic compositions and W abundance excess in these komatiites may reflect addition of crustal W during komatiite alteration.

Searching for selenium: In situ measurement in base metal sulfides

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To test the idea that most of the Se in rocks is located in base metal sulfide minerals (BMS), in situ Se concentrations in BMS would be useful. This is important for two reasons. Firstly, whole rock S/Se ratios have been used to model the formation of magmatic sulfide ore deposits. This approach is based on the idea that the whole rock analyze reflects the S/Se ratio of the BMS. Secondly, S and Se determination can be difficult and for Se, labor intensive. If Se could be determined in situ in BMS, then the whole rock Se would not be necessary.

Both whole rock Se and in-situ measurements of Se in BMS have been carried out on the BMS of the JM-reef of the Stillwater Complex and Merensky Reef of the Bushveld Complex.

In-situ Se is determined with a collision cell laser ablation (LA) ICP-MS (Thermo X7). Kinetic energy discrimination and a 50:50 mixture of H2:H2+He added to the collision cell minimize argide interferences. Sulfur is used as the ablation monitor. Detection limits range in the 1-5 • g/g Se (depending on laser beam), although quite high in terms of ICP-MS, it fits the purpose for Se determination in sulfide where Se ranges from 50 to 1000 • g/g Se. In order to better match the matrix, reference materials (RM) are Se-doped NiS beads (80-1000 • g/g Se) made from a technique similar to fire-assay preconcentration. Se is determined independently by preconcentration on thiol-cotton and INAA. RM homogeneity is tested with SEM imaging, microprobe determinations and LA-ICP-MS repeated determinations within a single bead. Reproducibility is in the range of 10 % RSD (at 2 •) for more than 30 Se determinations on different NiS beads.

Mass balance calculations show that within analytical uncertainties all, Se is hosted in BMS. Furthermore, our results compare favorably with previous PIXE determinations of Se in BMS of the Merensky Reef. These results suggest that assuming that all Se is hosted in BMS to interpret S/Se is valid.

In-situ Se concentrations of BMS indicate that most of the Se in rocks is located in BMS. This is important for two reasons. Firstly, whole rock S/Se ratios have been used to model the formation of magmatic sulfide ore deposits. This approach is based on the idea that the whole rock analyze reflects the S/Se ratio of the BMS. Secondly, S and Se determination can be difficult and for Se, labor intensive. If Se could be determined in situ in BMS, then the whole rock Se would not be necessary.

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Single-grain bulk Hf and in situ O isotopes as indicators of crustal recycling in magmas of the northern Arabian-Nubian Shield

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We present new in-situ (SIMS) oxygen isotopic ratios (δ₁⁸O(Zrc)) and bulk (MC-ICP-MS) ¹⁷⁶Hf/¹⁷⁷Hf (Hf(Zrc)) for single zircons from a series of basic to felsic plutons (n=12) of the Arabian-Nubian Shield (Sinai Peninsula, Egypt, and Southern Arabia) characterized by low δ¹⁸O(Zrc) and Hf(Zrc) measurements systematically were carried out on the same zircon grains, thus providing a robust set of combined δ¹⁸O(Zrc)-Hf(Zrc) data for these rocks.

In-situ δ¹⁸O(Zrc) values span the range from 3.8 to 14.2‰ (±0.1 to 0.25; 2σ) and generally compare well with previously determined bulk δ¹⁸O(Zrc) but in some cases identify the presence of different components within the zircon population analyzed here. Coupled with previously determined U-Pb ages, these are inferred to be xenocrysts (~770 Ma and ~900 Ma) characterized by low δ¹⁸O(Zrc) of 3.8-4.4‰ within two plutons of ~630 Ma and δ¹⁸O(Zrc)=5.5-6.6‰.

Hf(Zrc) shows a large spread of εHf(t) varying between +5.4 and +17.7. TDM model ages span the interval of 650-1200 Ma. Some of these model ages thus correspond to older reservoir ages than the so far accepted ~1000 Ma for this part of the ANS [1]. In general Hf(Zrc) correlates well with δ¹⁸O(Zrc) with lower but positive zircon εHf(t) matching higher δ¹⁸O(Zrc).

Three zircon O-Hf groups are identified: (a) moderately high to high δ¹⁸O(Zrc) with low (but positive) εHf(t); (b) mantle-like δ¹⁸O(Zrc) (5.3±0.6‰; 2σ [2]) with intermediate εHf(t); (c) very low δ¹⁸O(Zrc) (3.8-4.6‰) with high εHf(t).

These groups define three different components involved in the generation of the ANS post-collision calc-alkaline to within-plate alkaline-peralkaline magmatism. Group b reflects partial melting of lower crust material, while juvenile upper felsic crust assimilation is inferred for group a. The peculiar group c includes xenocrysts from two plutons and magmatic zircon from another two plutons and may reflect hydrothermally altered basaltic crust that was subducted and assimilated by some of the ANS magmas. It is interesting to note that the highest εHf(t) in this group correlate with TDM model ages close to the U-Pb ages, thus implying very rapid generation, subduction, and assimilation of the basaltic crust.

References

Sulfur saturation of Etna Basalt at 200 Mpa: Experimental setup and first results

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The amount and composition of volatile components in magmatic systems affect significantly magma degassing and control the partitioning of volatile components between melt and fluid phase on pressure release.

This study is focused on the solubility of S in natural Etna basalt at high temperatures (up to 1200 °C) and 200 MPa. Here we report the experimental setup for high temperature experiments and first results.

Sulfur is known to be a very aggressive component limiting the application of experimental approaches that use noble metal capsules, especially Pt and AuPd. Therefore, we applied two methods: experiments in gold capsules at 1050°C and in olivine capsules at T>1050°C. The olivine capsules are made of single crystal olivines (natural St. Carlos olivine) inserted into an outer Au₈₀Pd₂₀ capsule. Native S, palladium sulphide (PdS) and pyrrhotine (FeS) were used as sulfur sources in the experiments.

The experiments were conducted in internally heated pressure vessels at 200 MPa in a range of redox conditions from relatively reducing at quartz-fayalite-magnetite (QFM) oxygen buffer to oxidizing conditions (~QFM+4).

The experiments at 1050°C show that S concentration in hydrous (5 wt.% H₂O) basaltic melt at saturation with S-bearing mineral phase (anhedrite at oxidizing conditions and pyrrhotite at reducing conditions) decreases from ~6000 ppm to ~2000 ppm with decreasing fO₂. This dramatic 3-fold decrease in S content of the basalt is related to the change in S speciation from sulfate (SO₄) to sulfide (S²⁻) with reduction of the system. The transition of S⁰ to S²⁻ occurs in a very narrow range of fO₂ from QFM+2 to QFM+0.5.

Glasses obtained from experiments at 1200°C are in equilibrium with FeS and/or PdFeS phases and content 600 to 2000 ppm sulfur. Furthermore, these glasses are enriched in MgO due to reequilibration with MgO-rich olivine. Water concentrations of H₂O-presaturated basaltic glasses decreased from 5 wt.% to 2.8 wt.% indicating additional redox reactions inside the capsules, presumably interaction with host olivine. Further improvement of this experimental approach is required to better control the experimental conditions in the capsules.
Trace, REE and Sr isotopic investigation in the core top sediments from Bay of Bengal

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Trace and rare earth element (REE) data obtained using ICP-MS and Sr isotopic composition determined by TIMS was used for the detailed study of geochemistry and transport pathways of the sediments from Bay of Bengal. These terrigenous sediments are derived from: a) the Irrawaddy-Salween rivers b) Peninsular Indian rivers, c) Ganges-Brahmaputra (G-B) rivers, and d) erosional products from the Indo-Burman ranges. The objective of the present study is to understand the geochemistry of sediments and identify their provenance in Bay of Bengal using $^{87}\text{Sr}/^{86}\text{Sr}$ and trace elemental proxies. The results from core SK-157-27 (Lat:15°48.55′ N, Long:82°8′E, water-depth:1723m) show a high concentration of REE (~153 ppm) with high $^{87}\text{Sr}/^{86}\text{Sr}$ (~153 ppm) with high $^{87}\text{Sr}/^{86}\text{Sr}$ (0.72372±0.20), which may be due the source rock characteristics in the drainage basins of the Krishna and Godavari rivers. The core was retrieved from a region that represents mainly the terrigenous sediments of Godavari and Krishna rivers. The remaining three cores were collected from the northern part of the Ninetyeast Ridge. All these cores consist of fine grained sediments. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.713689 ±12) from core SK-157-14 (Lat:5°11.56′N, Long:90°5.97′E, water depth: 3306 m) suggest that the main source at this location is Irrawaddy-derived sediments with minor contributions from the Ganges-Brahmaputra rivers. High Ba and high Th/Ta ratio characterize the sediments from this core. The other two cores SK-157-15 (Lat: 7°48.55′N, Long: 90°15.92′E, water depth: 2870 m) and SK-157-16 (Lat: 8°46.86′N, Long: 90°18.42′E, water depth: 2920m) from the northern part of the Ninetyeast Ridge have relatively higher $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.716995±12 and 0.716670±24) suggesting a greater contribution from the Ganges-Brahmaputra sediments. Sediments from these two cores have high Sr, high Ba and relatively low concentration of redox sensitive elements. The decrease in the redox sensitive elements is attributed to the oxic deep-water environment. Our results clearly suggest that the $^{87}\text{Sr}/^{86}\text{Sr}$, REE and trace elemental characteristics in the Bay of Bengal sediments are highly variable and depend on the source and pathways of sediments.

References

Interrelations between Fe(II)/Fe(III) and U(IV)/U(VI) redox couples

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The mobility of uranium in natural environments is strongly affected by changes in its redox state. Reduction of U(VI) to U(IV) typically leads to an immobilization of uranium due to the low solubility of U(IV) minerals such as uraninite. Hence, initiating uranium reduction by stimulating microbial iron reduction has been proposed as a remediation strategy for aquifers contaminated with U(VI). Indications for U(VI) reduction concomitant to dissipative iron reduction have been obtained in several studies. Uranium might become directly reduced by iron reducing bacteria or indirectly by microbially produced Fe(II). It has been demonstrated that Fe(II) containing iron minerals such as magnetite and green-rust or Fe(II) adsorbed onto iron oxide surface can act as reductants for U(VI). However, also the oxidation of U(IV) by iron oxides has been reported. Consequently, it seems that both, uranium reduction and oxidation, can be coupled to Fe(II)/Fe(III) redox transformations. Here we want to discuss possible reasons for these apparently contradictory observations. Thermodynamic considerations show that the energetically favourable direction of a coupled U-Fe redox reaction depends on U and Fe concentrations and their speciation in the system. In addition to the speciation in solution, the thermodynamic stabilities of the solid phases, which are involved in the reactions, are of great importance. In particular, reduction of U(VI) becomes less favourable if the U$^{4+}$ activity is not controlled by the solubility of crystalline uraninite but by an U(IV) phase with higher solubility.

In a series of biotic and abiotic incubation experiments involving the metal reducing organism *Shewanella putrefaciens* and nanoparticulate hematite occurrence and extent of uranium reduction was investigated. Results from X-ray absorption spectroscopy reveal that, in the presence of hematite, U(VI) was not or only partially reduced. We propose that formation of crystalline uraninite is hindered in the experiments and by this complete reduction of U(VI) is inhibited. This hypothesis is supported by extended X-ray absorption fine structure (EXAFS) analyses which indicate that uraninite is not the primary product of microbial U(VI) reduction. Microbially produced U(IV) is either bound in an amorphous precipitate or remains adsorbed at the bacterial cell wall. It was further found that reoxidation of “labile” U(IV) by addition of hematite is possible. Occurrence or inhibition of uraninite formation might therefore explain the contradictory observations regarding the coupling of U and Fe redox reactions. That is, oxidation of U(IV) by iron oxides is feasible and only partial reduction of U(VI) can be achieved when uraninite formation is inhibited.
Argon and water diffusion in water-poor silicate glasses

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Knowledge on volatile diffusion is crucial for understanding the degassing behaviour of silicate melts as well as for understanding corrosion of glasses. H₂O is commonly the most abundant volatile in magmatic systems but it plays an important role in glass manufacturing as well. Argon diffusion is of particular interest because the diffusivity of argon is similar to that of molecular CO₂. Comparison of argon and water diffusion gives insights into the diffusion mechanisms of volatiles in general. At low concentrations H₂O dissolves as OH groups in silicate melts/glasses while argon acts as an inert species.

Here we report new experimental studies on Ar and H₂O diffusion in silicate and aluminosilicate glasses. The major objective of the work was to evaluate compositional effects on diffusion. Experiments were performed in cold seal gas pressure vessel using argon as the pressure medium. Polished glass wafers of water-poor, air-melted glasses (typical size 4 x 3 x 2 mm) were wrapped into Au foil so that the samples were directly exposed to the pressure medium. Water is usually present as impurity in the gas at per mill concentration. Thus during the experiment both H₂O and Ar diffuse into the samples. After the experiment, a section was cut perpendicular to the polished surface. Ar profiles were measured on the polished section by electron microprobe, H₂O profiles were analyzed using IR microspectroscopy. Surface concentrations in aluminosilicate glass are typically 0.13 -0.20 wt% Ar and 0.1 – 0.2 wt% H₂O at 200 MPa. Ar profiles are always described well with an error function while some of the H₂O profiles show a slightly convex shape. Deviation from ideal diffusion profiles in case of H₂O may be due to temporary changes in water content in the pressure medium and/or to increasing water diffusivity with increasing water content.

In silica glasses Ar diffusivity (D_Ar in m²/s) decreases by a factor of 1.5 from water-rich Suprasil (450 ppmwt H₂O) to water-poor Infrasil (<10 ppmwt% H₂O) emphasizing the role of dissolved water on noble gas diffusion. In alkali aluminosilicate glasses Arg diffusion is typically faster than in silica glass, but the diffusivity depends strongly on Al/(Na + K) ratio (ASI). For example at 705°C, 200 MPa log D_Ar increases from -14.1 for ASI=0.5 over -13.5 for ASI=1.0 to -13.1 for ASI=1.5. Incorporation of alkaline earth elements in aluminosilicate glasses reduces strongly the mobility of argon. At 620°C, 200 MPa D_Ar is two orders of magnitude smaller in an Ca:Mg bearing aluminosilicate (andesite) than in a pure alkali aluminosilicate (rhyolite). Water diffusion in alkali aluminosilicate glasses is one order of magnitude slower than argon diffusion at 500°C but due to lower activation energy only 0.2 log units slower at 800°C.
Li isotope studies of mantle-derived olivine by SIMS

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We report Li isotope variations analyzed by SIMS in olivine from terrestrial mantle xenoliths and mantle-derived magmas. The dependence of the δLi measured by SIMS on olivine composition was calibrated for compositions between Fo94 and Fo74 and amounts to 1.3 ‰ per Fo unit. Separated olivine grains were analyzed in epoxy mounts on the Cameca IMS-3f and IMS-6f SIMS at ASU. Precision of individual analyses including sample and standard uncertainties is typically ~1.5 - 3‰ (2σ).

Samples include spinel- and garnet-peridotites from Archean and Proterozoic mantle, pyroxenites, olivine megacrusts from kimberlites, and olivine phenocrysts in Hawaiian basalts. Samples display varying degrees of isotopic heterogeneity, from homogeneous δLi compositions with or without minor variations at grain margins, to large internal variations up to 16‰ within individual xenoliths. Significant variability may also occur among petrologically related samples that appear internally homogeneous.

Southern African low-temperature garnet peridotites display a range in δLi = -0.8 to +8.9 ‰. An orthopyroxenite has δLi at the high end of this range. The majority of Archean peridotites from Siberia display a relatively restricted range (mean δLi = 2.9 ± 3‰, 2σ, n=9) with minor internal heterogeneity, but exceptional xenoliths are isotopically heterogeneous with grains, or portions of grains extending to ~14‰. Fertile spinel lherzolites from SW USA including hydrous xenoliths from the Colorado Plateau appear relatively homogenous in δLi, with minor intra-grain isotopic zonation. In contrast, refractory peridotites from San Carlos, AZ display excursions up to +27‰, with strong intra-mineral zonation. Megacrusts from South African kimberlites, interpreted as melt-rock reaction products, have internal variations up to 10‰. Hawaiian phenocryst olivines and dunite xenoliths display internal heterogeneity up to ~6‰.

3Li/4Li fractionation during magmatic and metasomatic processes limits the use of Li isotopes as a tracer of crustal components in mantle-derived samples. However, with appropriate calibration of 3Li and 4Li diffusivities, the spatial and inter-mineral distribution of Li isotope variations can provide quantitative constraints on the kinetics of mantle and magmatic processes.

Experimental shock decomposition of siderite and the origin of magnetite in Martian Meteorite ALH84001

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Methods

Shock recovery experiments to determine whether magnetite could be produced by the decomposition of iron-carbonate were initiated. Naturally occurring siderite was first characterized by electron microprobe, transmission electron microscopy (TEM), Mossbauer spectroscopy, and magnetic susceptibility measurements to be sure that the starting material did not contain detectable magnetite. Samples were shocked in tungsten-alloy holders (W=90%, Ni=6%, Cu=4%) to further insure that any iron phases in the shock products were contributed by the siderite rather than the sample holder. Each sample was shocked to a specific pressure between 30 to 49 GPa.

Discussion of results

Transformation of siderite to magnetite as characterized by TEM was found in the 49 GPa shock experiment. Compositions of most magnetites are > 50% Fe2+ in the octahedral site of the inverse spinel structure. Magnetites produced in shock experiments display the same range of single-domain, superparamagnetic sizes (~50 to 100nm), compositions (100% magnetite to 80% magnetite - 20% magnesioferrite), and morphologies (equant, elongated, euhedral to subhedral) as magnetites synthesized by Golden et al. (2001) or magnetites grown naturally by MV1 magnetotactic bacteria, and as the magnetites in Martian meteorite ALH84001. Fritz et al. (2005) previously concluded that ALH84001 experienced ~32 GPa pressure and a resultant thermal pulse of ~100-110°C. However, ALH84001 contains evidence of local temperature excursions high enough to melt feldspar, pyroxene, and a silica-rich phase.

Conclusions

This 49 GPa experiment demonstrates that magnetite can be produced by the shock decomposition of siderite as a result of local heating to > 470°C. Therefore, magnetite in the rims of carbonates in Martian meteorite ALH84001 could be a product of shock devolatilization of siderite as well.

References

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A new metallophore for the nitrogen fixing bacteria *Azotobacter vinelandii*

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Nitrogen fixation, which is responsible for the natural input of new nitrogen into ecosystems, is performed by *N₂*-fixing bacteria using the enzyme nitrogenase. The Mo-nitrogenase is the most common and efficient form of the enzyme, but a V and a Fe-only nitrogenases, that are expressed when Mo is unavailable, have also been reported. The acquisition of Fe, Mo and V is thus essential for diazotrophic growth. The nitrogen fixing soil bacteria *A. vinelandii* excretes small organic ligands (siderophores) that bind Fe and increase its bioavailability [2-3]. Recently we reported that azotochelin, a bis(catechol) siderophore produced by *A. vinelandii* binds V(V) with a high affinity [1].

Here, we show that diazotrophic cultures of *A. vinelandii* use azotochelin as a vanadium carrier ("vanadophore") when Mo is limiting. Larger amounts of azatochelin (compared to other catechol compounds) are excreted in the growth medium when V is used for *N₂* fixation. The V-azotochelin complex is taken up by the bacteria via a specific transport system that doesn’t recognize other V-complexes (see Figure). Further, azatochelin can remove V from an unavailable DFB complex, resulting in an increase of uptake (see Figure). The transporter for V-azotochelin is regulated and shuts down at high (toxic) V concentrations.

Vanadium is the one of the first oxoanions, and the only transition metal with iron and copper, shown to have a high affinity uptake system involving a metallophore.

![Graph showing short term uptake of V](image)

Short term uptake of V (4 \(10^{-8}\) M V₅, 3.10⁻⁴M DFB (desferrioxamine B)) by *A. vinelandii* (CA 11.70). 10⁻⁴M azotochelin were added after 31 minutes.

References


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Mantle rocks of Voykar ophiolites could be subdivided into residual harzburgites (age over 2 Ga), dunites representing channels for migrating melts (Kelemen et al, 1995) and pyroxenite veins (age 0.6 Ga). Clinopyroxene (CPX) presents in all these rocks and it’s trace element composition could give an information about migrating melt composition (represented by interstitial CPX in dunites), degree of melting and subsequent modification by percolating melts of residual harzburgite (CPX in harzburgites). Also CPX composition may shed light on the mechanism of pyroxenite veins formation.

We have analyzed CPX from 9 harzburgites, 13 dunites and 13 pyroxenites using LA ICP MS at Max Plank Institute for Chemistry. The most uniform compositions are displayed by CPX from pyroxenites yielding subparallel patterns of incompatible elements at primitive mantle normalized spider diagram. They show clear supra subduction zone signatures - HFSE (e.g. Nb and Zr) depletion and relative LILE (e.g. Sr) enrichment, representing therefore late stage supra-subductional melts and/or fluids. Such conclusion is confirmed by presence of magmatic amphibole in several samples of pyroxenites testifying presence of magmatic water. The better estimates of melt compositions thus require measuring of water contents in those amphiboles due to severe influence of water on crystal-melt partitioning coefficients (Sobolev et al, 1996, Wood et al, 2002).

CPX from harzburgites also display subparallel trends in MREE-HREE part of spectrum, but their LREE concentrations display different degrees of modification by percolating melts (e.g. Batanova et al, 1998). CPX from dunites have the widest ranges of LREE/HREE ratios representing melts ranging from N-MORB-like melts to highly depleted in LREE melts which experienced reaction with large volume of residual rocks.

Data on olivine compositions still has to be evaluated.

References


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Nickel sorption on chalk and calcite
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Heavy metal retention in aquifers is controlled by sorption on aquifer material. Processes such as precipitation, incorporation and solution complexation also influence retardation, but in all cases, sorption plays a role. At natural or slightly polluted levels, it may be the predominant immobilization process. In several countries, such as those bordering the North Sea, drinking water comes from chalk (>90% calcite, CaCO₃). Nickel contamination can arise from industrial spills, waste disposal leaching, and in some cases [1], from the weathering of pyrite, where Ni is present in solid solution. However, little is known about sorption of Ni or other heavy metals onto chalk as an aquifer material.

We examined sorption on two types of natural chalk and compared it to the behaviour of synthetic calcite. Our purpose was to produce data for safety assessment and more effective remediation strategies. Batch experiments were performed at 25°C with atmospheric CO₂ partial pressure, in calcite equilibrated solutions, in the pH range 7.6 to 8.8.

Nickel sorption on calcite as well as chalk followed the same pattern observed for other divalent cations, namely:
1. At constant pH, Ni sorption was well-described by a Freundlich-type isotherm.
2. Adsorption increases with higher pH in the equilibrium suspension, higher surface area and decreasing adsorbate concentration. This is more consistent with Ni²⁺ exchange on surface sites than with coprecipitation.

Experimentally determined chalk Kd values (L/kg) correlate linearly with pH (as log Kd). Variability over about one order of magnitude disappears when surface area (L/m²) is taken into account: log Kd = (1.55 ± 0.17) pH – (14.2 ± 1.3). Such behaviour confirms the similarity of sorption properties for chalks and calcite, which is its main constituent.

Kd values can be related to migration velocity (i.e. relative to pore water flow) by the retardation factor R. With this new Kd, a Ni retardation factor for chalk was determined to be R = 130 and 9 at pH 8 and 7, respectively. This means that sorption onto chalk can significantly decrease Ni mobility, even in aquifers with low clay and organic matter content. Only at pH below 6, where calcite is dissolving, does Ni move substantially in chalk aquifers.

Reference

New evidences for existence of early Archaean terrains within Enderby Land, Antarctica
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Enderby Land is known as the oldest terrain of the Earth with age estimations ≥4 Ga (Sobotovich et al., 1974). Further study of different geological objects at the Enderby Land proved, from one hand, the unique age of this crust segment (DePaolo et al., 1982; Black et al., 1986) and, from the other hand, the unique thermodynamic conditions of accompanying evolution of these rocks (>1000°C) (Sheraton et al., 1987; Harley, Motoyoshi, 2000). As it had been demonstrated in the first studies of zircons from orthogneiss of Sones Mountain (Williams et al., 1984), in such cases we may face very local heterogeneity of zircon grains. It could be caused by their age and complicated reaction of zircon crystalline structure to the condition of ultra-high temperature metamorphism, which is marked twice during the existence of Napier Complex and disturbed all other isotope systems (McCulluch, Black, 1984; Black, 1988). This results in obtaining discordant ages in a rather wide range along U-Pb concordia which may not reflect the real geological events (Harley, Black, 1997).

Zircons from charnockite-enderbite rocks (Aker Peaks, Napier Mountains), which we have dated by SHRIMP-II, were analyzed earlier by conventional multigrain U-Pb ID-TIMS method (Belyatsky et al., 1990), but did not reveal age concordancy and colinearity. Our study demonstrates that the most optimal way to evaluate geologic events is the preliminary complex examination of zircons (CL, BSE, REE composition) and outline of cogenetic groups which allow to use traditional approach to age estimation through discordia construction. This approach has resulted in obtaining, at the first time, the reliable age of magmatic crystallization for enderbites – 3620±30 Ma and the age of primary enderbite’s protolith origin – 3950–3970 Ma. While some previously estimated younger ages of 2850–3050 Ma, which are considered as main metamorphic events of granulite facies for the whole Enderby Land (Harley, Black, 1997; Kelly, Harley, 2005), are absent in the studied zircons. At the same time in all dated zircons the metamorphic event of 2450–2480 Ma ago is clearly recorded and it is in agreement with the granulite facies metamorphism described by many authors. It is necessary to note, that zircons also are free of 1000–1200 Ma record in spite the extensive Proterozoic metamorphism dated by Harley, Black, 1988). These conclusions coinside with Sm-Nd isotope systematics of the enderbites: whole-rock (n=12) isochron corresponds to the age 3660±170 Ma and ε≥+0.7, with mineral isochrons show age of metamorphic event – 2440–2490 Ma. In general, it evidences to cratonization of the Napier Complex at about 2450–2480 Ma ago.

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Jetting and frictional melting in impactites

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The almost instantaneously pressure drop that occurs in the atmosphere following an impact leaves a vesicular rock of variable strength and considerably overpressure (> $10^5$ bar).
This pressure may potentially rupture the rock completely, but in a situation where part of the rock possess sufficiently strength the gas will flow from vesicle to vesicle, rupturing the vesicle walls and creating orifices. The gas flow may reach a jet-like condition with e.g. unstable flow and friction may partially remelt the vesicle walls.

Frictional melting may also occur by movement of the impactite body in the impact cloud causing the formation of melts on the exterior surfaces of the impactite.

In this study we demonstrate similarities and differences between the two types of glasses from SEM studies.

Modelling metal speciation in aquatic systems

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Nowadays, environmental problems related to aquatic pollution with heavy metals are numerous, therefore, it is important to understand metals behaviour in aquatic environments and to appreciate their transfer to the biota. The fate of the metals in the environment and especially their bioavailability is closely related to their interactions with the major reactive compartments (organic matter, iron and manganese oxides, clays). The objective of this work is to develop an approach based on the combination of several model to study metal ion speciation in different environmental systems. Models used to describe the interactions of metals with the main reactive phases in aquatic systems are CD-MUSIC (amorphous and crystallized iron oxides), NICA-Donnan (organic matter and manganese oxides), cationic ion exchange model (clays). First, this work implies the definition of generic parameters to describe the interactions of the studied metals with specific fractions of natural organic matter (i.e. exopolymers, alginic acids), iron and manganese oxides, a part of this information is missing in the literature. Then, after the validation of the approach by comparison with analytical results, this multi-surface model is applied to test sites corresponding to riverine environments.

These new models give good predictions of the behaviour of major and trace metal ions (Ca, Fe, U...) even in heterogeneous systems characteristic of the natural environment. The measured free metal concentrations in the solution are in agreement with those obtained from model calculations. In the case of bioavailability test experiments, the results are predicted with the natural organic matter constituents characteristics and and in fairly reasonable agreement with the experimental data.
Surface complexation and proton promoted dissolution in aqueous apatite systems

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Apatites (Ca$_5$(PO$_4$)$_3$F,Cl,OH) are the most abundant phosphorus-bearing minerals in nature and they are very important in agriculture as phosphorus containing fertilisers, as well as in medicine as main constituents of mammalian bones and teeth enamel.

The surface chemistry, in terms of surface complexation models, of these minerals is very much unexplored, and the dissolution mechanism is still debated. The objectives with our apatite studies are to characterize possible surface phase transformations and to clarify surface acid/base properties, ion exchange and readsorption reactions involving phosphate and calcium. Furthermore, ligand complexation reactions of these apatites with different organic polycarboxylic acids are also being studied. Studies are being made in pH ranges with/without extensive dissolution.

The strategy in modelling surface complexation and dissolution of apatite is to yield information provided by different macroscopic techniques: i) potentiometric pH and pF measurements; ii) dissolution characterization with respect to soluble fractions of calcium, phosphate and fluoride; iii) readsorption studies of phosphate, fluoride and calcium, as well as iv) surface charge measurements. Furthermore, this information is combined with surface spectroscopic characterizations using FTIR and XPS methods.

Crust-mantle dynamics in the early Earth: The 142-143Nd and 176Hf isotopic perspective

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New high precision isotopic data for 3.6 Ga to 3.87 Ga rocks from southwest Greenland and Western Australia show $^{142}$Nd excesses (formed by the decay of now extinct $^{146}$Sm [$t_{1/2}=103$ myr]) of 4 to 20 ppm compared to modern terrestrial compositions and 22-38 ppm with respect to primitive meteorites [e.g. 1]. Combined data from the same samples for the short-lived [146Sm-142Nd] and long-lived [147Sm-143Nd] decay schemes directly date the formation of chemically distinct silicate reservoirs during the first 30-50 myr of Earth history, near the time of core segregation. Differences in 142Nd signatures from coeval rocks from the two most extensive early Archean cratons reveal large-scale chemical dichotomies in the Earth’s mantle that persisted for at least the first billion years of Earth history. Temporal variations in $^{142}$Nd signatures track the subsequent incomplete remixing of these very early-formed mantle chemical domains.

Initial Hf isotopic compositions from zircons from the same samples yielding positive $^{142}$Nd anomalies are all within error of chondritic values (using $\lambda$ = 1.867 x 10$^{-11}$yr$^{-1}$). The $^{142-143}$Nd and initial $^{176}$Hf isotopic compositions of Archean rocks define the time-averaged Lu/Hf and Sm/Nd of their mantle source regions. Generation of positive $^{142}$Nd anomalies as well as $\varepsilon^{143}$Nd $\approx +3$ in 3.85 Ga samples, requires an early formed high Sm/Nd reservoir. In contrast, the near chondritic initial $^{176}$Hf/$^{177}$Hf compositions from the same early Archean samples indicate a source with a long-term chondritic Lu/Hf ratio. Thus the trace element pattern of the pre-3.85 Ga depleted mantle differs from the MORB source mantle, which is characterized by both supra-chondritic Lu/Hf and Sm/Nd. Significantly this suggests that typical continental crust with low Lu/Hf and Sm/Nd ratios is not the primary complimentary enriched reservoir to the early depleted mantle. Rather these observations support models for very early (30-60 myr after T$_0$) silicate differentiation of the Earth [e.g. 2] unrelated to early continental crust formation. Although >4.0 Ga zircons, including those from the Jack Hills, Western Australia, provide evidence that some Hadean continental crust was present, it may have been of only limited extent.

References
Thermochronological evidence for long-term elevated geothermal gradients in Ribeira Belt, SE Brazil

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This study addresses petrological/thermochronological relations in the São Fidelis-Santo António de Pádua (SFSAP - N Rio de Janeiro State, Brazil) sector of the central segment of the Neoproterozoic collisional Ribeira Belt. SFSAP mainly comprises granitoid (orthogneissic) rocks, migmatites and granulites/charnockites. Following the earlier collisional stage at 630-600 Ma, main (thrusting) regional deformation was coeval with peak metamorphism (850 ± 50º C, 8.0 ± 1.0 kbar), lower crustal melting and widespread charnockite development at 565 ± 8.0 Ma (U/Pb-zircon); further high-grade metamorphism evolved (at P ≥ 4 kbar) to ~ 600º C, being followed by decompression and retrogradation (~ 350º C) during long-term transpressional shearing at the late stages of the Braziliano Orogeny (Biotite-WR Rb/Sr age = 455 ± 4.0 Ma). The overall average cooling rate was low (< 5º C / Ma from 850 to 350º C), but distinct cooling paths indicate differential uplift and complex mechanical/kinematics interactions among the distinct lithotypes. Although migmatites show a globally stable 3º C / Ma cooling rate, most charnockites remained at T > 650º C until 510 - 470 Ma (Garnet-WR Sm/Nd), being then rapidly exhumed/cooled (~ 30º C / Ma) during post-orogenic granite emplacement in the area at 491 ± 7.1 Ma (U/Pb-zircon). Both charnockite thermal evolution and extensive production of granitoid melts imply that high geothermal gradients must have been sustained for a long period of time (50 – 100 Ma) in the studied area. Crustal geotherms are sensitive to both mantle heat-flux input and the amount/distribution of heat producing elements (HPE). Collisional active mountain building should have been followed by gravitational collapse of the orogen, induced by thermal erosion and progressive thinning of the lithosphere. The timing for the onset of the resulting thermal anomaly seems to have started at ca. 570 - 550 Ma and reflect initial upwelling of asthenospheric mantle and magma underplating along the main axis of the Ribeira orogenic belt. This, coupled with long-term generation of (high-HPE) granitoids, should have sustained elevated crustal geotherms (relative to the pre-granite conductive geothermal regime) for almost 100 Ma, promoting widespread charnockitization at middle to lower crustal levels.

From planetesimals to planetary embryos

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We investigate the collisional growth of planetesimals by means of numerical simulations using an orbit-averaged Monte Carlo approach (Nyffenegger 2005) originally proposed by Hénon for the study of stellar clusters. Such an approach is situated between explicit N-body and statistical methods. Similar to statistical treatments, we assume an overall potential to determine the general motion of the bodies. Perturbations to this motion are then caused by local interactions between the bodies (collisions, close encounters, etc.) which account for the stochastic nature of the system. In this respect, the Monte Carlo technique resembles the N-body method but it allows the use of a much large number of bodies. In addition and again similarly to N-body simulations, the tracking of individual bodies over time is easily done. Therefore, the entire collisional history of planetary embryos can be reconstructed.

After presenting some tests of the method, we shall focus on the collisional evolution of a swarm of planetesimals in the terrestrial planet region. We derive some important characteristics of this evolution such as the typical formation time, collision frequency, impactor mass, etc. We then discuss the implications of these quantities focusing in particular on planetary differentiation and the constraints placed by the extra-solar planets.

References


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Microbial biomineralization and redox transformation of As and Fe in an acid mine drainage

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Bulk chemical and mineralogical data (bulk XANES, EXAFS and XRD) showed that indigenous bacteria living in the As-rich Carnoules Acid Mine Drainage ([As] = up to 350 mg.l-1) play an important role in the nature and composition of the solid phases that sequester arsenic at the site: some bacteria oxidize Fe(II) but not As(III) and promote the precipitation of a rare ferric arsenite sulfate oxy-hydroxide mineral, called tooeleite (Morin et al. 2006), while other bacterial species catalyze As(III) to As(V) oxidation leading to the formation of amorphous As(V) rich ferric oxy-hydroxides (Morin and Calas 2006).

In order to better document the interactions between microbes and Fe and As redox processes in the Carnoules AMD, we combined Scanning Transmission X-ray Microscopy (STXM) and Transmission Electron Microscopy (TEM) to collect near-edge x-ray absorption fine structure spectra (NEXAFS) at high spatial and energy resolution and to perform high resolution imaging at the submicrometer scale, following procedures described previously (Benzerara et al., 2006). Spectromicroscopy was performed at the C K-edge, Fe L2,3-edge, and As L2,3-edge offering the possibility to locate living and/or mineralized bacterial cells and to characterize Fe and As oxidation states in the vicinity of those cells. Many precipitates were found associated with extracellular organic polymers. Moreover, some As-Fe precipitate show a vesicular appearance that we interpret as microbial cell’s products. TEM was used to image the same areas, providing higher resolution images and complementary crystallographic and chemical information through electron diffraction and EDX analysis. This approach offers a unique opportunity to assess at the submicrometer scale the various and heterogeneous geochemical activities of complex microbial communities in acidic environments.

References


Sedimentary phosphorus speciation and its relation to the CNS and bottom water in an estuary influenced by anthropic activities

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Phosphorus element plays a key role on the biogeochemical cycles in estuaries. Phosphorus is one of principal nutrients to the organic matter production in the aquatic system and its excess contribute to eutrophization process. This study focus on the sedimentary phosphorus speciation in the Santos Estuary, a strongly impacted coastal area located at São Paulo State – Brazil, where accommodates the largest harbour of Latin America with an important industrial pole which include 5 fertilizer industries, urbain poles with represenative domestic wastes and some mangrove vegetation along the system. During the summer period, the tourism activities contribute to the nutrient inputs to the aquatic environment. In this study, the sedimentary concentrations of bioavailable-P (P-bio) varied from 1.78 to 9.36 µmol g⁻¹, iron oxyhydroxides-P (P-Fe), from 1.09 to 37.68 µmol g⁻¹, authigenic-P (P-auth), from 0.37 to 10.64 µmol g⁻¹, fluorapatite-P (P-FAP) varied from 0.94 to 7.21 µmol g⁻¹ and organic-P (P org) varied from 0.37 to 10.50 µmol g⁻¹. The organic carbon (Corg) varied from 0.14 to 6.26 %, total nitrogen (TN) varied from 0.01 to 0.55 %, total sulfur (TS) varied from 0.01 to 2.11 % with high concentrations in the internal part of the port channel decreasing in direction to the Santos’ Bay. The TN and TS were highly correlated with C org and P org (r > 0.87, p<0.01), indicating that S org is the second pool of reduced S in the sediments, after S content associated to pyrite. Organic speciation of C, N, S and P were higher during the winter, while the inorganic ones were higher during the summer, due to the different intensities of mineralization process in these two marked seasonal periods at this region. In general, the sedimentary parameters show high positive correlations with the bottom hydrochemical characteristics as observed for dissolved inorganic phosphorus (DIP) (r > 0.77, p<0.01). There was negative correlations with dissolved oxygen (r = -0.69, p <0.01) in relation to sedimentary parameters. The sedimentary sulphur concentration increased when the water reduced conditions were present in the environment as occurred during the summer, facilitating the phosphorus liberation. On the other hand, there were significative percentages of P-Fe (around 40-53 %) in relation to total P and this is correlated to the C/N and C/S. The C/N (>6) and C/S (> 10) molar ratios showed that the continental organic matter input probably had high content of humic substances that could be sequestrate iron oxyhydroxides bound phosphorus.
Archaean evolution of the Okhotsk terrane by U/Pb zircon chronology

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Okhotsk terrane (NE Russia) is a most aged segment of the Pacific mobile belt. The Kukhtuy domain, the largest (45x120 km) part of this terrane, mainly consists of polymetamorphic basalt-dacite series and metasediments, covered by Riphean and Paleozoic sediments.

For revealing the succession of geological processes we studied accessory zircons from four typical rock units: hypersthene-plagioclase granulite schist (HPS), garnet-hypersthene-plagioclase granulite schist (GHPS) – from Maymecha area and garnet-biotite gneiss (GBG), wall-rock for biotite granite-gneiss (BGG) – from Khorundzha area. Before U/Pb SIMS SHRIMP dating, zircons were subdivided into morphotype groups. The U/Pb ages are in Table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zircon group</th>
<th>Ma ± 2α</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPS</td>
<td>1. Cores + volcanic FI, MI</td>
<td>3634±11</td>
</tr>
<tr>
<td></td>
<td>2. Cores and rims + MI</td>
<td>3568±12</td>
</tr>
<tr>
<td></td>
<td>3. Metamorphic grains + CO₂FI</td>
<td>3461±17</td>
</tr>
<tr>
<td></td>
<td>4. Metasomatic zircons</td>
<td>2777-1372</td>
</tr>
<tr>
<td>GHPS</td>
<td>1. Cores + volcanic MI</td>
<td>3651±18</td>
</tr>
<tr>
<td></td>
<td>2. Altered cores + volcanic MI</td>
<td>3507±17</td>
</tr>
<tr>
<td></td>
<td>3. Rims on 1 &amp; 2 + FI, MI</td>
<td>3446±52</td>
</tr>
<tr>
<td></td>
<td>4. Rims + H₂O FI</td>
<td>2086±23</td>
</tr>
<tr>
<td>GBG</td>
<td>1. Zoned cores</td>
<td>3284±18</td>
</tr>
<tr>
<td></td>
<td>2. Altered cores and rims</td>
<td>Discordia</td>
</tr>
<tr>
<td></td>
<td>3. Altered zoned grains</td>
<td>3245±23-2025±53</td>
</tr>
<tr>
<td>BGG</td>
<td>1. Cores+MI,FI and sector zoning</td>
<td>3330±20</td>
</tr>
<tr>
<td></td>
<td>2. Rims + FI</td>
<td>2718±13</td>
</tr>
</tbody>
</table>

The following evolutionary succession is proposed for the Kukhtuy domain, Okhotsk terrane, based on U/Pb age data, zircon REE pattern, geochemistry, fluid (FI) and melt (MI) inclusion study.

I. Initial mafic volcanism 3.7-3.65 Ga ago. Hf data for the same zircons: (\(^{187}\text{Hf}/^{187}\text{Hf}) = 0.280575 ± 0.00005, ε\(^{187}\text{Hf}(t) = +3.4\) show non-depleted magma source and 3.7-Ga protolith-mantle separation. II. First granite facies metamorphic (ultrametamorphic) event, 3.58-3.52 Ga ago. III. Second granite metamorphic event (3.48-3.46 Ga). IV. Third granite ultra-

Combining in situ isotope dating, petrology, and tectonic observations to infer rates of regional metamorphism

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The determination of metamorphic rates demands high precision dating of samples for which the physical conditions of formation are well constrained. For such rates to be meaningful, the tectonic evolution of the sampled units needs to be established. We derive rates of metamorphism from in-situ dating of structurally controlled REE minerals combined with field observations in the Central Alps to gain insight into geodynamic rates.

In metamorphites, the sequence of REE minerals reveals a series of irreversible reactions among silicates and phosphates. At diagenetic and low metamorphic conditions, detrital and newly formed monazite grains occur. Around 450°C, monazite disappears to form allanite, which is oriented in the main foliation. At temperatures >570°C, allanite is replaced by monazite, which grows after the development of the main foliation Sₘₜ. Garnet also overgrows Sₘₜ but predates monazite. These observations hold information on different processes: (1) collision and tectonic thickening, (2) regional heating, and (3) post-collisional folding. Th-Pb and U-Pb dating of allanite and monazite yields ages of 31.5±1.3 Ma and 18.0±0.1 Ma, respectively. Considering that the difference of 13.5 Ma between the two ages represents the T-interval from 450°C to 570°C, the average heating rate is 8-10°/Ma.

This rate may relate to a combination of processes, involving at first substantial tectonic transport (advecive heating dominant). This stage is followed by a period of minor tectonic transport, post nappe folding and thermal relaxation, when conductive heat transport dominates.

Tectono-thermal modeling (2D FEM) yields similar heating rates for units in front of the nappe stack, which is being exhumed owing to erosion and tectonic unroofing. Late orogenic heating during decompression lead to the thermal maximum in this external portion of the orogen 18-15 Ma ago, at a later stage than in the internal segment of the Central Alps (~30-22 Ma ago just north of the Insubric Line). In the latter part of the orogen, the metamorphic rates are largely dominated by advection due to tectonic extrusion of thrust sheets, i.e. units previously subducted. In the external parts of the Leptontine dome, the thermal field and metamorphic patterns evolved later, and rates reflect the heating followed by rapid cooling during orogenic exhumation.
Mass-dependent and mass-independent fractionation of Hg isotopes in aquatic systems

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Mercury is a globally distributed and highly toxic pollutant, the mobility and bioaccumulation of which is dependent on its redox cycling. Hg isotope analysis by MC-ICPMS is an important new tool for identifying Hg sources and tracking Hg transformations in the environment (Smith et al., 2005; Jackson et al., 2006; Bergquist et al., 2006; Kritee et al., 2007), with most measured natural samples displaying mass-dependent isotope fractionation (MDF). A small body of data suggests that natural samples also display mass-independent isotope fractionation (MIF) of the odd Hg isotopes (Jackson et al., 2006; Bergquist et al., 2006).

Reduction of Hg species to Hg(0) vapor is an important pathway for removal of Hg from aqueous systems into the atmosphere and occurs by abiotic and biotic mechanisms. In laboratory experiments, we find that photochemical reduction of both Hg$^{2+}$ and CH$_3$Hg$^+$ by natural sunlight leads to large MIF of the odd isotopes (\(^{201}\text{Hg}, \ ^{199}\text{Hg}\)) and preferential retention of the odd isotopes in the reactant (soluble) phase. Also, the relationship between MIF for the two odd isotopes of Hg is significantly different for the two photo-reduction pathways (Hg$^{2+}$ to Hg$^0$ versus CH$_3$Hg$^+$ to Hg$^0$). In contrast, both biological reduction (Kritee et al., 2006) and dark abiotic organically-mediated reduction follow MDF.

Natural samples from aquatic ecosystems preserve both MDF and MIF. In fish, MDF increases with the size and Hg concentration of the fish suggesting MDF may be useful in understanding Hg bioaccumulation (similar to $\delta^{15}$N). Fish also display a large range in MIF (4‰) with MIF always having positive values. Additionally, the relationship between MIF of the two odd isotopes in fish has a similar slope to the slope found for photo-reduction of CH$_3$Hg$^+$. Since fish bioaccumulate CH$_3$Hg$^+$, fish may be recording the extent to which CH$_3$Hg$^+$ is lost via photochemical reduction in an aquatic ecosystem. Fish populations from different locations have different MIF values, but mostly display similar MIF within a location. This suggests that MIF is preserved in the food web and could be used to quantify photo-reduction of CH$_3$Hg$^+$ of an ecosystem. Both MDF and MIF of Hg isotopes hold promise for quantifying and understanding Hg pathways and bioaccumulation in the environment.

CO$_2$-bearing fluid inclusions in upper mantle xenoliths from Tihany (western Hungary): Minimum trapping pressures and trace element compositions

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Analytical Techniques
In this study, microthermometry, Raman microspectroscopy and LA-ICP-MS analysis of dense CO$_2$-rich fluid inclusions hosted in orthopyroxenes from spinel peridotite xenoliths of the subcontinental lithospheric mantle from Tihany (western Hungary) were carried out.

Discussion
Petrographically two types of fluid inclusions are distinguished. Based on microthermometry, two different density ranges were observed. The CO$_2$-densities, together with the geothermometry of the peridotites based on orthopyroxene/clinopyroxene equilibrium, suggest that the studied xenoliths represent two, physically distinct domains in the lithospheric mantle, one shallow and one deeper. Raman microspectroscopy confirms that the fluid inclusions consist mostly of pure CO$_2$, but rarely H$_2$S is also observed. For multi-element analysis in situ LA-ICP-MS was used to identify elements associated with the CO$_2$ fluid inclusions in orthopyroxene. LIL elements such as K, Ba and Rb which are incompatible to the host orthopyroxene, were found to be concentrated at the CO$_2$ inclusions.

Conclusion
Since a precise geobarometer for the spinel peridotite stability field is not available yet, the minimum trapping pressure estimation from CO$_2$ fluid inclusions provides the best method available for pressure estimation in these mantle rocks. The CO$_2$ fluid inclusions in the studied peridotites suggest ~12°C/km temperature gradient for the upper mantle 8 million years ago when the xenoliths were brought to the surface by the host basalt.

The results of LA-ICP-MS analysis suggest that the orthopyroxenes and the enclosed fluids have very different trace element compositions. These results also suggest that the CO$_2$-rich fluids are important agents for transporting incompatible trace elements in the lithospheric mantle.
Reduction of FeO-rich chondrules in Kakangari and enstatite chondrites

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Kakangari (K) is a unique chondrite [1] whose bulk chemical composition is similar to enstatite (EC) and ordinary chondrites (OC). However, its high matrix abundance is more comparable to carbonaceous chondrites (CC). K chondrules have oxygen isotopic compositions indistinguishable from EC chondrules [1], suggesting that there might be a genetic relationship between the chondrules in these two chondrite groups.

We studied a suite of Kakangari chondrules [2] and noticed that they are similar to EC3 chondrules [3,4] in the following aspects: (a) no typical FeO-rich type II chondrules are present, (b) most chondrules are pyroxene-rich and (c) many chondrules contain SiO2. These characteristics make K and EC chondrules more similar to each other than to OC and CC chondrules. However, there are also major differences [e.g. 5] which imply that EC chondrules formed in a more reducing environment. For example, most chondrule silicates are more Mg-rich in EC (0.1<Fa<2.8, 0.4<Fs<2.2 [3]) than in Kakangari (2.5<Fa<5.5, 3<Fs<16 [2]) and their sulfide mineralogy is different (Mg-, Mn-,Ca-bearing sulfides in EC chondrules vs. troilite only in K chondrules).

Even though no typical FeO-rich type II chondrules are present, ubiquitous FeO-rich silicates have been observed in EC chondrules [e.g. 6-8]. Their characteristics and chemical compositions are very similar to FeO-rich pyroxenes and olivines in K chondrules [2]. In both K and EC chondrules, FeO-rich silicates show clear evidence that they have undergone solid-state reduction (e.g. reverse zoning, Ni-poor metal and troilite blebs, presence of SiO2 [2,6-8]). This reduction must post-date the first chondrule forming event.

[7] proposed a multi-stage model for EC chondrules that contain FeO-rich pyroxenes. These chondrules were originally formed in an oxidizing environment and then underwent solid-state reduction in a more reducing nebular environment. Furthermore, [8] showed that oxygen isotopic compositions of FeO-rich and FeO-poor silicates in an EH3 chondrite have the same oxygen isotopic groups.

We suggest that FeO-rich K chondrules originated from similar FeO-rich precursor material and underwent a similar, but less extensive reduction event. Subsequently, the evolutionary paths of FeO-rich K and EC chondrules diverged.

References

In situ characterizing the structural and chemical evolution of biopolymers during advanced fossilization: From Nature to experiments

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The Biogenic origin of fossil organic matter (OM) contained in metamorphic rocks is usually not easy to assess. Diagenetic and metamorphic processes are indeed responsible for the transformation of primary biogenic OM, leading to the loss of original chemical and structural information. However, it has been observed that morphological, textural and chemical bi-signatures might be preserved in some contexts [1]. To understand the conditions leading to such preservation, we have investigated the evolution of reference carbonaceous biocompounds (e.g. sporopollenin, lignin and cellulose) during pyrolysis using Raman and near edge x-ray absorption fine structure (NEXAFS) spectroscopy at the µm down to the nm scale. We hence describe and constitute a reference dataset for the differential evolutions of these precursors during carbonification and graphitization. Using the same techniques, we have in situ characterized, at multiple length scales, fern-related spores and vascular tissues within diageneric rocks from Alsace (France) and within high grade metamorphic rocks of the same Triassic age (230 Ma) from the western Alps (France)1. Biogenic OM as well as associated various carbonates minerals were mapped at the micrometer scale using Raman imaging. Ultrathin sections were prepared by Focused Ion Beam milling for further structural and chemical imaging of OM/minerals down to the nanometer scale with Transmission Electron Microscopy and Scanning Transmission X-ray Microscopy. In particular, the chemical nature of the carbon functional groups composing these OM and their spatial distribution were documented at a submicrometer scale using high spatial (~25 nm) and energy (~0.1 eV) resolution NEXAFS spectroscopy. Altogether, by combining microscopic and spectroscopic imaging techniques, we evidence in these samples systematic textural, chemical and mineralogical heterogeneities which are interpreted as remnants from primary biological structures. Such a multiscale characterization approach sheds new light on the fossilization processes of biogenic OM during advanced diagenesis and metamorphism, and allows for reconstructing their biological heritage which is of particular interest for the study of soft bodied fossils.

References
Aragonite: Crystallographically oriented fibres in eclogite-facies garnet from Corsica

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Aragonite, the high-pressure polymorph of calcite, occurs as a metamorphic index mineral in the lowest-grade low-temperature, high-pressure metamorphic terranes. The rapid kinetics of its back-reaction to calcite upon decompression makes its preservation an indicator of decompression under quite low temperatures, implying either anti-clockwise P-T paths or at least continuous cooling during decompression. There are indeed extremely few records of aragonite relics in relatively high-grade rocks, then as tiny inclusions in a rigid host mineral, which prevents expansion and transformation of the high-pressure carbonate polymorph, in the same way as it does for coesite or microdiamond.

We record here the occurrence and preservation of aragonite in eclogitic blueschists of eastern Corsica, showing a most uncommon microtexture. Aragonite exclusively (?) occurs as oriented rods in garnet crystals of a black calcite marble that immediately overlies serpentinite bodies of the meta-ophiolitic unit. The crystallographic control imparts to the garnet the appearance of a sector zoning, and the whole texture is very reminiscent of the crystallographically oriented intergrowths of either quartz or organic material ('graphite') already described in garnet of a few amphibolite-facies metamorphic terranes (Norway [1], Ireland). These observations and their significance will be discussed in the light of a detailed petrological description of these rocks, Raman imaging of the calcite/aragonite polymorphs in the sections and of Raman investigation of the abundant carbonaceous material of the samples. The bearing on the significance of other crystallographically oriented inclusions in (high-pressure?) garnet will be discussed as well.

References

The effect of paleozoic land plant evolution on atmospheric CO2 and O2

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Modeling, field and experimental studies, and proxy measurements support the idea that the rise and evolution of large vascular land plants, especially trees, during the mid-to-late Paleozoic had a profound effect on the biogeochemical carbon cycle. The development of extensive root systems brought about increased Ca and Mg silicate weathering and increased transfer of atmospheric CO2 to dissolved bicarbonate and ultimately to marine carbonates. Atmospheric CO2 was also removed as a result of increased burial of plant-derived organic remains, especially in the form of microbially resistant lignin. Increased weathering and organic burial led to a large drop in CO2, helping, via the atmospheric greenhouse effect, to set the stage for the vast Permo-Carboniferous glaciation.

Increased organic burial also resulted in the increased production of O2. This led to a Permo-Carboniferous maximum in atmospheric O2 at levels possibly as high as 30%. This elevated O2 likely contributed to an increase in the size of organisms, such as insects and amphibians, which breathe via various diffusive-like processes. During an approximately 20 million year period across the Permian-Triassic boundary, due to a decline in large land plant production that resulted in decreased terrestrially-derived organic burial, O2 production declined and brought about a large drop in O2. This drop must have been a contributing factor to the Permo-Triassic extinction.
New Ir data from K-T sections in the Paraiba Basin, NE Brazil

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New drill cores and outcrops across the K-T transition in the Paraiba Basin (Poty Quarry near Recife) of NE Brazil were collected in order to evaluate the environmental changes and evidence of the Chicxulub impact. Here we report on the sedimentology, stratigraphy and Ir concentrations, with an emphasis on the stratigraphic position of the Ir anomaly, which is of crucial importance in the ongoing Chicxulub impact debate.

The K-T transition is marked by a 40-50 cm thick conglomerate, which is present in the Poty well and outcrops, as well as in another two wells drilled over a distance of 75 km. The origin of this conglomerate is still under debate. It has been variously interpreted as impact-generated tsunami deposit, storm deposit, tectonic breccia or mass flow associated with a sea level lowstand. Our study shows that the conglomerate consists mainly of phosphate and glauconite pebbles, occasionally graded, and floating in a micrite matrix. No impact spherules were detected.

The age of deposition of this conglomerate is still in question. Although previous studies have placed it at or below the K-T boundary, the presence of Danian planktic foraminifera Parvularugoglobigerina eugubina indicates an early Danian zone P1a age, as also observed by Koutsoukos (2006).

At the base of the conglomerate and 15 cm above it we detected two Ir anomalies with concentrations of 0.5 and 0.6 µg/kg, respectively. At 5 cm and 15 cm above the conglomerate are two thin dark clay layers interbedded in marls of early Danian zone P1a age. In the upper clay layer, Albertao et al. (1994) reported Ir concentrations of 0.6 µg/kg. At 15 cm above the conglomerate and 15 cm above the conglomerate are two thin dark clay layers interbedded in marls of early Danian zone P1a age. In the upper clay layer, Albertao et al. (1994) reported Ir concentrations of 0.6 µg/kg. Thus, our results indicate multiple Ir anomalies, though all appear to be within the early Danian. This can be explained in two ways: 1) The Ir anomalies are derived from reworked ejecta material that was deposited at or prior to the K-T boundary, or 2) The Ir anomalies reflect an early Danian impact with subsequent reworking.

The speciation of metals in natural fluid inclusions at temperatures up to 700°C

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The speciation (oxidation state and coordination environment) of metals in fluids is key to understanding their transport in hydrothermal systems. For example, in the formation of porphyry and related epithermal ore deposits the type and stability of metal complexes will control partitioning between melt, brine, and vapour, and the mechanism of ore deposition.

Fluids trapped as inclusions in quartz can be heated, allowing in situ XANES and EXAFS studies of metal speciation. The ideal inclusions are 10s of µm in size, have metal concentrations in excess of 100s of ppm, contain no insoluble phases, and can survive heating to magmatic temperatures.

XAS spectra were recorded at beamline 13-ID-C (GSECARS) of the Advanced Photon Source from individual fluid inclusions in miarolitic quartz from the Omsukchan granite, Russia (Kamenetsky et al. 2004). The quartz sections were mounted in a windowless Linkam 1500 heating stage and the temperature of an inclusion determined by a thermocouple on the top surface of the sample. The inclusions are primitive, polyphase, have salinities in excess of 35 wt%, homogenise completely on heating to temperatures up to 700 °C, and contain 100s of ppm of Cu and wt% amounts of Fe, Mn, and Zn.

Two generations of magmatic polyphase inclusions with markedly different metal ratios were studied. In both cases Cu was found to occur exclusively as the linear species [CuCl2]− from 200 °C to at least 700 °C. Despite the high salinities there is no evidence for higher order coordination. Preliminary speciation results for Fe, Mn, and Zn at 700 °C will also be reported.

References

Evaluation of the CO₂-sequestration capacity of sandstone aquifers in the Campine Basin (NE-Belgium) based on autoclave experiments and numerical modelling

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The Campine Basin in NE-Belgium houses important CO₂-emitting industries. Injection of CO₂ in sandstone aquifers in this sedimentary basin could significantly reduce emissions towards the atmosphere.

An integrated study was set up to evaluate the effects of CO₂-water-rock interactions on the reservoir properties of 3 sandstone aquifers in the basin, i.e. the fluvial sandstones of the Westphalian C, Westphalian D and the Lower Triassic (Buntsandstein). A number of representative samples, from boreholes, of each reservoir were characterised by means of a broad spectrum of petrographical, geochemical and petrophysical methods. Five samples of each reservoir were exposed for a period of 6 months to the conditions prevailing in the reservoirs during and after CO₂ injection, in high temperature - high pressure autoclaves. CO₂-water-rock interactions were inferred from the evolution of the chemical composition of the brine in the autoclaves and comparison of the treated and untreated samples after the experiments.

Data from the detailed characterisation of the experimentally treated samples was used to construct a reaction model in PHREEQC. Reaction kinetics of 17 rockforming minerals are based on user-defined rate laws and parameters. CO₂-water-rock interactions inferred from the experiments were used to adjust reaction progress.

Numerical modelling confirms that the sequestration capacity of the studied reservoirs will be greatly enhanced by CO₂-water-rock interactions. During injection carbonate dissolution can enhance permeability of the reservoirs. In the first 15 years after injection alteration of Al-silicates (feldspars and clays) to kaolinite and illite buffers the pH-drop caused by CO₂-injection. Higher pH and release of K and Na promote ionic trapping, i.e. sequestration as dissolved bicarbonate species. Slow release of Fe and Mg from altering Al-silicates offers some potential for mineral trapping, i.e. sequestration of CO₂ as carbonate minerals. Dissolution of hematite and pyrite causes reduction of Fe³⁺ and precipitation of siderite. Substantial siderite precipitation occurs after more than 25 years and is initiated when a certain pH is reached due to Al-silicate reactions.

These numerical simulations illustrate that the sequestration capacity offered by CO₂-water-rock interactions is highly variable, depending on the reservoir mineralogy. The sequestration capacity of the studied reservoirs ranges from approximately 100-500 gCO₂/kgw.

40Ar/39Ar ages of the sill complex of the Karoo large igneous province: Implications for the Pliensbachian-Toarcian climate change.

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Reliable geochronological results gathered (n=76) so far have considerably constrained the timing of the emplacement of the Karoo large igneous province. Yet strikingly missing from this dating effort is the huge sill complex cropping out in the >0.6x10⁶ km² main Karoo sedimentary basin. We present sixteen new ⁴⁰Ar/³⁹Ar analyses carried out on fresh plagioclase and biotite separates from fifteen sill samples collected along a N-S trend in the eastern part of the basin. The results show a large range of plateau and mini-plateau ages (176.2 ± 1.3 to 183.8 ± 2.4 Ma) with most dates suggesting a ~3 Ma (181-184 Ma) duration for the main sill events and confirming the relatively long emplacement duration of the main volume of the province. The youngest plateau age at 176.2 ± 1.3 Ma obtained on a sill and two plateau ages at ~176 Ma obtained by [1] on the neighbouring Uderberg dyke swarm, unambiguously define a young “hot line” extending from the eastern Lesotho to the coast. This possibly illustrates important and late stress constraints related to the continental breakup near the future rifted margin.

The available age database of the Karoo province allows to correlate the Karoo CFB emplacement with the Pliensbachian-Toarcian second order biotic extinction and associated global warming and with the Toarcian anoxic event (providing that adequate calibration between the ⁴⁰K and ²³⁸U decay constant is made). The mass extinction and the isotopic excursions recorded at the base of the Toarcian appear to be synchronous with both the increase of magmatic production rate of the Karoo province and the emplacement of the sills. Field evidences and ⁴⁰Ar/³⁹Ar ages suggest that the sills intruding carbon-rich sedimentary layers filling the souther Africa Karoo basins might be one of the main culprits of the global warming and oceanic anoxic conditions recorded at this time. However, the long duration of the igneous activity is not easily reconcilable with the shorter time scales required by recent climate models derived from sill-sediment interaction [2,3]. We propose that the relatively low eruption rate of the Karoo province is one of the main reasons explaining why its impact on the biosphere is relatively low contrary to e.g. the CAMP (Triassic-Jurassic) and Siberia (Permo-Triassic) provinces.

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Hydrogeochemistry of the Mutnovsky volcano (South Kamchatka)
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The Mutnovsky volcano (52°21'N, 158°16'E, 2323 m) is located 75 km southward from the town of Petropavlovsk Kamchatsky. In terms of explosive activity and heat discharge, this volcano is presently among the most active volcanoes of the Kamchatka volcanic belt. In 2003 and 2005, we sampled springs, pools, and mud pots of the Donnoe fumarolic field. Sampling of aqueous solutions was accompanied by in situ measurement of pH, Eh, and Cl- and F- contents. The springs studied in the Mutnovsky volcano crater have diverse composition, but most of them belong to acid waters (pH ~ 2.5-3.5). The solutions have high contents of Al, Ca, Mg, Na, Mn, Fe, As, Cu, Ti, Co, Cr, and P. The highest contents of these elements previously known from the Kuril-Kamchatka volcanic arc at Kunashir Island are one to three orders of magnitude lower. The solution is also characterized by high concentrations of Au, Mo, and Zr, which are not usual for hydrothermal springs in areas of basaltic andesite volcanoes, and extremely high contents of B and Sr. Modeling was conducted with the method of using a Selector Win program in continuous reactor modification [1]. Large-scale extraction of components from basalts requires the presence of oxidized high-temperature gases, which could be formed in the upper part of the volcanic-hydrothermal system via mixing of magmatic fluids with overheated vapors of oxygen-enriched surface water. High-temperature mixed gases (surface water vapor and magmatogenic acid gases) are formed along the external boundary of condensation. The newly formed aggressive gas can leach most elements from host basalts. The gas is partially condensed to mix with magmatic fluid, while solutions are diluted and cooled in the course of their ascent. The next geochemical barrier (the second boiling zone) is characterized by the exsolution of some components (primarily, water vapor and small amount of acid gases) into the gas phase, while the remaining portion is enriched in some elements (Cr, Ni, V, Ti, and others) up to the required level. Thus, we assume that the hydrothermal spring in the Donnoe field is related to the zone of enriched brines arising at the secondary boiling boundary. This assumption is confirmed by thermodynamic calculations.

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References

Archaean enriched mantle reservoir beneath east Indian Shield
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Prograde hornblende-bearing mafic granulite xenoliths, associated with massif-type charnockite, is a significant feature of the collisional Eastern Ghats orogen (Kar, 2003). These mafic xenoliths have geochemical signature of arc-derived basalts (Fig. 1). No correlation in Sr-Nd isotopic compositions is observed and hence mixing of different mantle components can not be envisaged. But present day low 143Nd/144Nd values and high 87Sr/86Sr values indicate an enriched mantle reservoir as the source of these mafic xenoliths (Fig. 2). The 1.8 Ga Rb-Sr isochron represents the isotopic homogenization during granulite event in a collisional setting. Nd-model dates, calculated after Milisenda et al., 1994, ca 2.7 Ga (2688 to 2784 Ma), represents the time of extraction from the mantle. Also the enriched mantle reservoir in this segment of the east Indian Shield might have resulted from a previous crust-mantle interaction or crustal recycling (Shan Gao, 2004), during ca 3.0 Ga granulite event in the Eastern Ghats belt (Bhattacharya, 2001).

References
Sm-Nd isochron ages from Southern Granulite Terrain, South India: Age of protolith and metamorphism

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Temporal correlation of metamorphism and deformation in the poly-metamorphic and poly-deformed Southern Granulite Terrain (SGT) in south India is of primary importance to understand the evolution of continental lithosphere and tectonics. However, because of intensive overprinting of successive metamorphic and deformation events the time correlation could not be unambiguously achieved for SGT. We used an approach of analysing the carefully selected whole rock samples and mineral-separates for Rb-Sr and Sm-Nd systems to retrieve and resolve different tectono-metamorphic events experienced by these samples. A sample from the eastern part of the SGT and north of Cauvery Shear Zone, near Namakkal town yielded a good seven point Sm-Nd mineral isochron, for minerals garnet-1, garnet-2, diopside, ortho-pyroxene, plagioclase, biotite and whole-rock with an age of 879 ± 9 Ma (MSWD = 1.6). We have interpreted this to be an age of granulate facies metamorphism. Whereas, a regression line for the same minerals in Rb-Sr isotope evolution diagram corresponds to an age of ~ 524 ± 80 Ma. Furthermore, pairs of whole-rock – biotite and biotite-plagioclase yielded identical Rb-Sr ages of 540 ± 21 Ma and 543±21 Ma respectively with initial 87Sr/86Sr ratio of ~ 0.7023. We, therefore interpret this sample of granulate has experienced two tectono-thermal events. The older event at ~ 880 Ma completely re-equilibrated all the minerals for Sm-Nd system and therefore, has provided time of granulitization. Another younger event did not disturb the Sm-Nd system but reset the minerals for Rb-Sr system to variable extent at ~ 540 Ma. The four point Sm-Nd isochron for the whole-rock samples of granulites from the same region yielded isochron age of 2208 ± 130 Ma with MSWD 1.6. The Nd T CHUR model ages for the granulite samples from this region range from 2369 to 2935 Ma. This indicates that the formation of protolith of these granulites completed by ~2208 Ma ago which had undergone granulate facies metamorphism at ~ 880 Ma ago when the Sm-Nd radio-chronometer remained un-affected as the equilibration took place only at mineral scale.

The above results provide important time constraints for the protolith formation and two subsequent tectono-thermal events. The older at 880 Ma corresponds to Rodinia supercontinent period which caused the granulate facies metamorphism and younger at 540 Ma could be related to intensive regional deformation during Pan-African assembly of Gondwanaland.

REE pattern and Oxygen isotopes in zircons from different rocks (the Fennoscandian and Ukrainian Shields) as indicators of their genesis

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There are different views on the role of REE distribution in zircons as indicator of the rock genesis. Recent studies have shown deviations from the crystallochemical REE pattern typical for zircons of magmatic genesis: in high-pressure rocks (eclogites) -deficiency in HREE, and in so called “hydrothermal” zircons [1] –enrichment in LREE. The role of oxygen isotopes in zircons has been discussed in many publications.

We have studied the distribution of REE and oxygen isotope composition in zircons from Archaean sanukitoids (Karelia, the Fennoscandian Shield) and from ancient enderbites (Dniestr-Bug region, the Ukrainian Shield). The REE distribution was determined on a Cameca 4F SIMS instrument in Yaroslavl, the oxygen isotope composition on a Cameca 1270 SIMS instrument in Stockholm.

A detailed study of Karelian sanukitoids is given in [2]. Sanukitoid zircons which have been dated to 2740 Ma are enriched in LREE with (Yb/Sm)N=10-50, (Yb) N=1200-2700. Sanukitoid zircons which have been dated to 2740 Ma are enriched in LREE with (Yb/Sm)N=10-50, (Yb) N=1200-2700. This deficiency is not as pronounced as in eclogitic zircons, but still it indicates “granulitic” zircon generation has much lower concentration of REE elements with deficiency in HREE, and in so called “hydrothermal zircons” [1]. We have connected the genesis of sanukitoids with subduction processes that involve fluids or melts from a subducted slab in a mantle wedge [2].

Enderbites from the Dniestr-Bug region are the oldest rocks of Ukrainian Shield. They contain two zircon generations. The first one of magmatic genesis is as old as 3.65 Ga, the second, metamorphic generation is about 2.85 Ga old and was grown during granulitic metamorphism overprint on magmatic tonalities [3]. The distribution of REE elements in the early zircon generation is typical for magmatic zircons having chondrite-normalized REE pattern with positive slope from La to Lu and positive Ce and negative Eu anomalies. The second, “granulitic” zircon generation has much lower concentration of REE elements with deficiency in HREE (Yb/Gd)N=2-8, (Yb)N=300-400. This deficiency is not as pronounced as in eclogitic zircons, but still it indicates crystallization of zircon during metamorphism along with garnet enriched in heavy REE.

Our study has confirmed the indicator role of REE and oxygen isotopes in zircons in establishing the mineral genesis highly important for geochronological studies.

References
Metagenomics of deeply buried marine sediments

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Deeply buried marine sediments make up a vast potential biosphere and contain up to one-third of all microorganisms [1]. Sediments collected on Ocean Drilling Program Leg 201, which visited the Peru Margin in 2002, have been examined by many different methods. Using different molecular and biogeochemical procedures, two vastly different views of the subsurface microbial world have emerged. Based on intact polar lipids, RNA and FISH counts, there is evidence for a dominant and active archaeal community in sediments on the Peru Margin [2, 3]. Using different techniques on similar samples, evidence also exists that the subsurface microbial population is mostly bacterial [4, 5, 6]. Our recent study tried to address the discrepancies between experiments to resolve the understanding of subsurface microbial communities.

We have obtained 61.9 Megabases of metagenomic sequence from 4 separate horizons at ODP Site 1229 on the Peru Margin. Analysis of this metagenome shows that based on small subunit ribosomal RNA in-silico biomarkers, the subsurface community is dominated by Archaea at depth, reaching 88% of the microbial community at 50 meters below seafloor. We have also analyzed the gene content of the metagenome and over 85% of the genetic sequence does not have a closely related homolog in the public databases, suggesting that the deeply buried sediments hold a vast amount of genetic diversity. In addition to this metagenomic study, we have analyzed nucleic acid retrieved from this sediment environment by quantitative polymerase chain reaction and confirm that at depth, there is an archaeal dominance of the sediment microbial populations.

The subsurface sediment of the Peru Margin is extremely unique in that it holds a vast amount of archaean microorganisms, more than any environment previously studied. This has now been determined by both measurements of active cells and total genetic material.

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Hexachlorocyclohexanes trace pathways and processes in the Canadian archipelago


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Hexachlorocyclohexane (HCH) is the most abundant organochlorine pesticide in the Arctic Ocean. Most of the HCH loadings took place by atmospheric deposition until ~1980, and by ocean current transport thereafter. The α-HCH concentrations in surface water on the North American side of the Arctic Ocean are 2-4 times higher than on the Eurasian side. Measurements made on the Swedish Tundra Northwest 1999 expedition in the Canadian Archipelago showed that surface water concentrations of the HCH isomers varied by about 2-fold, with higher concentrations near the Beaufort Sea to the west and lower ones in Baffin Bay – Davis Strait at the east end. Enantiomer fractions of α-HCH, EF = (+)/[(+)+(−)], were less than the racemic value of 0.500 and ranged from 0.436 in the Beaufort Sea to 0.454 in Baffin Bay, indicating preferential microbial degradation of (+)α-HCH. HCH distributions in the eastern Archipelago were consistent with mixing of three water bodies with characteristic end member concentrations and EFs. Levels of α-HCH in air of the central Archipelago were 37 ± 9 pg m−3 and 53 ± 5 pg m−3 before and after the mid-July ice breakup, a significant (p <0.001) increase of 30%. The concentration increase was accompanied by a reduction in the EF in air after ice breakup, from 0.495 ± 0.003 to 0.482 ± 0.010, indicating sea-to-air transfer. It is suggested that enantiomers of α-HCH in air can provide a sensitive indication of ice cover loss in the Arctic.
Soil-air exchange of legacy organochlorine pesticides


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Of the dozen persistent organic pollutants (POPs) to be eliminated under the Stockholm Convention, eight are organochlorine pesticides (OCPs: DDT, aldrin, dieldrin, endrin, heptachlor, chlordane, mirex and toxaphene). Residues of OCPs remain in agricultural soils and are continually emitted into the atmosphere, thereby buffering atmospheric concentrations and slowing rates of decline. OCPs also contaminate background soils, presumably as a result of atmospheric deposition. "Chemical markers" for identifying sources and tracing soil-air exchange include pesticide isomers, parent/metabolite pairs and enantiomers of chiral compounds. Elevated concentrations of OCPs in air over agricultural soils confirm their emissions and, when coupled with micrometeorological techniques, such measurements can determine fluxes. The relative volatilities of soil residue components can be used to reliably predict their proportions in air. Campaigns in southern Mexico show much higher concentrations of DDT in air compared to temperate North America, yet proportions of DDT/DDE in air of the Great Lakes region implicate emissions from regional soils rather than transport from Mexico. Profiles of toxaphene constituents in soil and air of the southern U.S.A. and Mexico show characteristic depletion of certain labile congeners. These congeners are also depleted in surface water samples from the Atlantic Ocean during the 1990s, however sample profiles from the 1980s more closely resemble technical toxaphene. Enantiomers of two chiral components of technical chlordane, trans- and cis-chlordane, are in nonracemic ratios in present-day ambient air samples, but were racemic in atmospheric deposition samples from Sweden in the early 1970s. Background soils contain residues of DDT which vary over four orders of magnitude and are poorly correlated with latitude or percent soil organic matter. Residues of chiral OCPs in these soils show much more variability in enantiomer composition than do the same compounds in ambient air. These observations indicate the dual role of soils in supplying OCPs to and receiving them from the atmosphere, the changing role of agricultural application vs. soil emission sources and postdepositional diagenesis of OCPs in background soils.

Experimental investigation of the behaviour of CO₂ droplets rising in seawater under hydrate forming conditions

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We present comprehensive experimental results on the upward motion of CO₂-droplets in simulated deep-sea environments. A cooled high pressure tank was used to establish conditions along a natural oceanic hydrotherm. At pressures and temperatures well inside the CO₂ hydrate stability field, observed rise rates were in accordance with predictions based on empirical equations developed to match momentum of hydrate-covered, deformed droplets. In contrast, droplets rising at P,T conditions closer to the phase boundary deviated from model predictions in numerous instances. This was related to a partially incomplete or missing hydrate skin due to insufficient thermodynamic forcing. To support this relationship, additional experiments outside the field of hydrate stability were carried out and compared to the erratic data. The results confirm expectations and show that non-hydrated droplets have a markedly different rising behaviour and rise rates of up to 40% higher than equally buoyant droplets with a hydrate skin. This might have a significant impact on the vertical distribution of dissolved CO₂ in the ocean and has to be taken into account when assessing CO₂ sequestration at mid water depth.
Complementary methods for characterization of stream sediments as an aid in assessment of sediment quality

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Introduction

The European water framework directive (WFD) has not come yet up with environmental quality standards for sediments. It is still open which sediment monitoring approaches will be used.

The aim of the present work is to demonstrate on selected stream sediments what type of characterization can be obtained when using interdisciplinary approach.

Methods

Complementary methods were: X-ray diffraction (XRD), inductive coupled plasma – mass spectroscopy (ICP-MS), X-ray fluorescence (XRF), solid state 27Al MAS NMR, 29Si MAS NMR, grain size analysis and Mössbauer spectroscopy.

Results, discussion and conclusion

Advantages and disadvantages of each method were discussed. Solely ICP-MS method requires chemical decomposition. It is the most useful for microelement analysis (51 element), which data can be used in geostatistical analysis and detection of anomalies. Other techniques are non destructive and require simple physical sample preparation. XRD method can give with certainty class and group of minerals. Determination of clay minerals, when present <5%, is less certain. XRF method is suitable for determination of major elements, particularly of Si and limited number of trace elements. However, Mg and Na cannot be detected. The particle size distribution was determined in fraction <63 µm. It was found that the amount of clays (fraction <4 µm) was in the range 7.4 – 12.6%. Mössbauer spectra taken at room temperature and at 70 K in a mixture of several minerals are difficult to interpret. Valuable information concerning the valence and site populations of iron in poorly crystallized minerals can be obtained. Solid state 29Si MAS NMR can give structural information, like the number of different SiO4, Si(Al)O3 units. 27Al MAS NMR gives the presence and number of tetrahedral and octahedral Al sites and their ratio. Grain size analysis and surface area of particles is a fundamental property of sediments and is important in pollution research. All of the studied methods are recommended in future sediment analysis.

Oxygen isotope heterogeneity and disequilibria of olivine phenocrysts in large volume basalts: Case of Iceland

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Olivine phenocrysts in the largest volume Holocene fissure basalts from Iceland’s eastern rift zone are moderately to severely out of oxygen isotope equilibrium with their host magma. We present a set of laser fluorination analysis of >70 individual and bulk crystals of olivine and plagioclase, and their host glasses with average precision of better than 0.07‰. We also report ion microprobe analyses of cores and rims of 61 olivine crystals from 13 samples with precision on single spots of 0.10-0.35‰ (1stdev). Within each sample studied, we find that basaltic glass is relatively homogeneous, plagioclase phenocrysts exhibit δ18O variability, while individual olivines are more variable and span from mantle values of 5.2‰ down three permil below, in equilibrium with their low-δ18O glass. The famous Laki basalt studied here still holds the record for Holocene volcanism.

Discussion

The famous Laki basalt studied here still holds the record for Holocene volcanism. In addition, we have found subtle disequilibrium in this and other Icelandic basalts. As discussed in the Introduction, this disequilibrium is not accurately predicted by the usual U-series model of mantle melting. lattice disequilibria are most likely produced by variations in the degree of hydration and/or assimilation of host rocks. We find that basaltic glass is relatively homogeneous, plagioclase phenocrysts exhibit δ18O variability, while individual olivines are more variable and span from mantle values of 5.2‰ down three permil below, in equilibrium with their low-δ18O glass.

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Advantages and disadvantages of each method were discussed. Solely ICP-MS method requires chemical decomposition. It is the most useful for microelement analysis (51 element), which data can be used in geostatistical analysis and detection of anomalies. Other techniques are non destructive and require simple physical sample preparation. XRD method can give with certainty class and group of minerals. Determination of clay minerals, when present <5%, is less certain. XRF method is suitable for determination of major elements, particularly of Si and limited number of trace elements. However, Mg and Na cannot be detected. The particle size distribution was determined in fraction <63 µm. It was found that the amount of clays (fraction <4 µm) was in the range 7.4 – 12.6%. Mössbauer spectra taken at room temperature and at 70 K in a mixture of several minerals are difficult to interpret. Valuable information concerning the valence and site populations of iron in poorly crystallized minerals can be obtained. Solid state 29Si MAS NMR can give structural information, like the number of different SiO4, Si(Al)O3 units. 27Al MAS NMR gives the presence and number of tetrahedral and octahedral Al sites and their ratio. Grain size analysis and surface area of particles is a fundamental property of sediments and is important in pollution research. All of the studied methods are recommended in future sediment analysis.

References

The speciation of sulfur in magmatic-hydrothermal fluids

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Sulfur compounds are major constituents of volcanic gases and magmatic-hydrothermal fluids. They are responsible for the climatic effect of major volcanic eruptions as well as for the transport and precipitation of metals during the formation of magmatic-hydrothermal ore deposits. Up to now, it was usually assumed that SO\textsubscript{2} and H\textsubscript{2}S are the only important sulfur species occurring in high-temperature magmatic fluids.

The speciation and oxidation state of sulfur in aqueous fluids was studied using synthetic fluid inclusions in quartz cores generated in rapid-quench autoclaves under controlled oxygen fugacity and variable pressures and temperatures (500 – 950 °C; 500 – 3000 bar). Run durations lasted up to several weeks. The sulfur speciation in the fluid inclusions was determined by Raman spectroscopy. Raman spectra were calibrated against standard solutions.

At Ni-NiO buffer conditions, H\textsubscript{2}S was the dominant sulfur species in the fluid, coexisting with small amounts of SO\textsubscript{2}. At Re-ReO\textsubscript{2} buffer conditions, the quenched fluid contained a mixture of SO\textsubscript{2}, SO\textsubscript{4}\textsuperscript{2-} and HSO\textsubscript{4}\textsuperscript{-}. Our data therefore suggest that under oxidizing conditions as they may prevail in many magmatic systems in subduction zone settings, aqueous fluids contain abundant species of hexavalent sulfur (see Fig. 1).

Figure 1: Experimentally determined sulfur speciation in aqueous fluids. Shown are the conditions under which the molar fraction of SO\textsubscript{2} equals that of H\textsubscript{2}S and under which SO\textsubscript{2} is equally abundant as species of hexavalent sulfur (“SO\textsubscript{3}”).

REE enrichment in authigenic and biologically mediated minerals of phosphate rocks

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The geochemical behavior of the REE under the influence of chemical and microbial activity is still insufficiently explored issue. REE significant bioaccumulation and fractionations was recently reported by many authors in plant organs (Ding et al., 2005) and with microbial activity (Bishay, 2005).

The REE are accommodated in minute authigenic minerals in the phosphate rocks which reach to about 12.65% \Sigma REEs. The NASC normalized REE pattern of these minerals are nearly flat with occasional distinct -ve Eu anomaly suggesting fluctuations in the redox environment during their formation (Fig.1). The mobilization and enrichment of the REE is evidenced by both abiotic and biotic laboratory experiments. It is indicated that under controlled boundary conditions, some organic acids as well as biological mediation of the phosphate rocks influence the redistribution and enrichment of REE.

Fig.(1): NASC REE diagram of some authigenic minerals showing Eu anomaly.

References

Doping-induced structural phenomena in Pb-based relaxors

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Perovskite-type relaxor ferroelectrics are among the key materials in modern solid-state science due to their outstanding dielectric, electro-optic, and electro-elastic properties, which are the basis of a number of technological applications including information storage and processing. The unique physical properties of relaxors are related to their local structure, which strongly deviates from the global, average structure. Here we report on the relationship between the observed phonon anomalies and the local atomic arrangements in Pb-based perovskite-type relaxors studied by synchrotron X-ray diffraction and polarized Raman spectroscopy of representative lead scandium tantalate/niobate single-crystal compounds. It is shown that the development of ferroic species and ferroelectric state on cooling can be followed by analysing quantitatively the intensity ratios of the Raman scattering arising from the corresponding local structural distortions \cite{1}. The degree of B-site doping can control the size of ferroelectric domains. Different types of local structural changes occur upon A-site doping, depending on the ionic radius of doping element, its valence and affinity to form stereochemically active lone-pair electrons.

References


Variation in natural mercury isotopic ratios of coal formations

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High precision mercury (Hg) stable isotope measurements of coal offer a new tool to investigate inputs of Hg to the atmosphere from coal combustion. Mercury was quantitatively isolated from coal by combustion and trapping in a KMnO\textsubscript{4} solution. Mercury isotopic measurements were determined by cold vapor multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). Instrumental mass bias was corrected using an internal thallium standard and concentration-matched sample-standard bracketing. Mercury isotopic variations are reported here in delta notation (\[^{202}\text{Hg}/^{198}\text{Hg}\]) and referenced to the NIST SRM 3133 Hg standard. Sample and standard replicates had an external 2\% standard deviation of \(<\pm0.2\\%\) for \[^{202}\text{Hg}\] (Blum and Bergquist, 2007).

Coal samples were analyzed from across the USA that ranged in rank from lignite to bituminous and in age from Eocene (~55 Ma) to Pennsylvanian (~300 Ma). The \[^{202}\text{Hg}\] of these samples ranged from -0.98 to -2.27 \%. A positive correlation was observed between calorific value of coal (BTU lb\textsuperscript{-1}) and \[^{202}\text{Hg}\] values for coals (\(p < 0.05, R^2 = 0.89\)) (Figure 1). One interpretation of this trend is that the Hg isotopic composition of coal shifts towards isotopically heavier values with increased metamorphism due to preferential volatilization of isotopically lighter Hg.

We also observed mass independent fractionation (MIF) in these coal samples with \(^{200}\text{Hg}\) and \(^{198}\text{Hg}\) (Blum and Bergquist, 2007) ranging from -0.1 to -0.3 \%, which we suggest may be caused by photochemical reduction of Hg prior to deposition in coal. Analyses of Hg ores and refined Hg do not show MIF and thus may be isotopically distinguishable from coals (Smith \textit{et al.}, 2005). Our results suggest that Hg isotopic ratios of coal formations could aid in source apportionment of coal combustion emissions of Hg and lead to a better understanding of the global Hg cycle.

References


Evidence for a late $^{60}$Fe injection into the protoplanetary disk

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Understanding the origin of short-lived isotopes in meteorites can constrain the astrophysical setting of Solar System formation and the earliest evolution of the protoplanetary disk and proto-Sun. Whereas early Solar System abundances of short-lived isotopes with relatively long half-lives like $^{53}$Mn and $^{182}$Hf broadly reflect input from stellar sources over the history of our Galaxy, the inferred levels of $^{41}$Ca, $^{26}$Al and $^{60}$Fe are too high to uniquely derive from Galactic production. Some of the $^{41}$Ca and $^{26}$Al may have formed by particle irradiation near the proto-Sun. In contrast, the exclusive stellar origin of $^{60}$Fe requires that it was synthesized in a nearby star and injected into the nascent Solar System. Here, we show that meteorites with highly-variable Fe/Ni ratios originating from differentiated planetesimals that accreted within 1 Myr of Solar System formation record identical deficits of ~25 ppm in $^{60}$Ni (the daughter product of $^{60}$Fe) compared to samples from Earth, Mars and chondrite meteorites. With clear evidence for live $^{60}$Fe when the chondrite and eucrite parent bodies formed, our study requires that $^{60}$Fe was injected into the protoplanetary disk ~1 Myr after Solar System formation, at a time when $^{26}$Al was homogeneously distributed. This decoupling of the first appearance of $^{26}$Al and $^{60}$Fe indicates that our forming Solar System interacted with massive stars ($\geq 30$M$\odot$) where $^{26}$Al was solely expelled by stellar winds of the Wolf-Rayet stage, and $^{60}$Fe subsequently injected during the supernova explosion associated with a dying star. Lastly, the terrestrial Ni isotope composition suggests that Earth accreted from material distinct from that of known primitive and/or differentiated meteorites.

Influence of landscape type on trace metals in small boreal catchments

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We studied temporal and spatial variations of trace metal (TM) concentrations (As, Cd, Co, Cr, Cu, Ge, La, Ni, Pb, Rb, Sc, and Y) in stream water and their correlation with catchment properties (i.e. coverage of wetland and forest), but also with Fe and Mn. During 2004 and 2005 water samples were collected from 10 streams (0.13 km$^2$ to 67 km$^2$) in the Krycklan Catchment Study, a boreal stream network in northern Sweden. Since spring snowmelt is the most important hydrological event, the monthly sampling was intensified during spring flood (April-May) when samples were collected every second day. Total and dissolved (<0.4µm) concentrations of Fe and Mn were determined by ICP-OES. Dissolved concentrations of TM were determined by ICP-MS.

Preliminary results show a seasonal variation for all TM, in particular during spring flood. In forested catchments most TM concentrations increased at spring flood, but for Rb and Sc a decrease was observed. Conversely, in wetland influenced catchments the opposite seasonal variation was observed, i.e. concentrations of all TM decreased by a factor of 2 to 3. The seasonal variation of Fe shows a similar pattern to many TM, due to the association of TM to Fe oxyhydroxides. In particular, Fe correlates significantly with Cr and Pb in a forested headwater stream ($r^2=0.77$ and $r^2=0.71$, respectively, p<0.05). In the wetland headwater stream similar correlations between Fe and TM are found, but DOC also correlates significantly with As, Cd, Ni, and Pb ($r^2=0.92$, p<0.05).

A significant negative correlation (p<0.05) was observed between coverage of wetlands and average concentrations of Cr, Cu, Ge, Ni, Sc and Y. The results indicate that wetlands act as sinks for these elements. Alternatively, there is a source limitation in wetlands and that increased concentrations during base flow are due to mineral groundwater influence. Positive correlation with wetland coverage was only observed for Pb ($r^2=0.79$, p<0.05), indicating that wetlands acts as a source for this element. Sulfate concentrations correlated negatively ($r^2=0.97$, p<0.05) with increasing coverage of wetlands, which highlights the importance of sulfate reduction within wetland areas.

This study emphasizes the importance of considering stream water chemistry from a landscape perspective.
Biogeochemical cycling of P: Isotopic insights into the P-redox cycle

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Phosphorus occurs primarily as PO₄ in the +5 oxidation state and is conventionally thought of as having no significant redox chemistry. The recent discovery of several bacteria capable of using phosphate (PO₄, +5 valence) and hypophosphite (PO₃, +1 valence) as a sole source of P via oxidation to PO₄, however, led to the hypothesis that an active "P-redox cycle" exists in natural Earth systems (Metcalf and Wolfe, 1998). Subsequent investigations reveal that ca. 1% of all microorganisms are capable of Pt oxidation. More recently, a sulfate-reducing bacterium, Desulfotignum phosphitoxidans, that uses Pt as an electron donor has been isolated from marine sediments (Schink and Friedrich, 2000). Pt and other reduced-P compounds although not abundant, are very widespread as is the ability to metabolize these compounds. It has been put forth that on an oxygen-free early Earth, reduced-P compounds were more abundant and that Pt may have been the first water-soluble, bio-available form of P. It has been recently demonstrated for organic P-org compounds that specific phosphoenzymes have specific isotope effects that are distinguishable in laboratory and natural systems, and that PO₄ derived from P-org compounds inherits O from the Porg source (Blake et al., 2005). In effort to identify and further elucidate sources and reactions of reduced-P compounds, a study of the O-isotope systematics of Pt oxidation was undertaken. The reaction mechanisms and isotopic fractionations accompanying Pt oxidation by 2 different enzymatic pathways have been investigated: (1) non-respiratory PO₃ oxidation by Pt-dehydrogenase (PtxD); and (2) Pt oxidation by D. phosphitoxidans. Results from these studies provide new insights into PO₃ oxidation mechanisms and specific isotopic signatures that may be used to elucidate processes in the P-redox cycle operating in modern systems and possibly on early earth.

Boron isotopic composition correlates with ultra-structure in the deep-sea coral Lophelia pertusa: Implications for biomineralization processes and paleo-pCO₂

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Using the CRPG-CNRS Cameca 1270 ion microprobe facility we have measured B isotopic compositions in different ultra-structural components in the deep-sea scleractinian coral Lophelia pertusa. We observe a systematic difference in the B isotopic composition of Early Mineralization Zone (EMZ) and adjacent fibrous aragonite skeleton. In EMZ, the measured δ¹¹B values are consistently low. Fibrous aragonite is characterized by systematically higher δ¹¹B values, but also display B isotopic heterogeneity associated with specific growth bands in the calyx wall. The magnitude of the observed B isotopic variations cannot be explained by changes in environmental conditions (such as seawater temperature) and are to be considered the result of biological processes involved in the biomineralization of new skeleton; i.e. ‘vital’ effects. The observed B isotopic variations are directly opposite to the predictions of existing geochemical models for vital effects, which are based on the idea that stable isotopic fractionations (including C and O) in coral skeleton are driven by changes in pH of the fluid from which the skeleton is presumed to precipitate. Our data indicate that pH variations are not responsible for the observed stable isotopic fractionations. Existing geochemical models therefore do not provide an adequate framework within which to understand coral skeletal formation. Furthermore, our observations cast in doubt efforts to reconstruct paleo-pH variations in the oceans on the basis on coral skeletal B isotopic composition.
**Impact related and late crystallisation products of Shergotty**

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Shergotty is one of the historic (fall in 1865) type meteorites, after which the SNC meteorite group is named. This group is nowadays accepted to be of Martian origin. Shergotty belongs to the basaltic subgroup of SNCs and is predominantly composed of large zoned clinopyroxene crystals intergrown with original plagioclase, which was subsequently converted into maskelynite upon shock compression. The coexistence of fayalite with silica, ilmenite, titanomagnetite and phosphates point to late crystallisation of a highly evolved residual melt fraction that crystallised at relatively high oxygen fugacity. Stöffler et al. (1986) concluded all shock features can be produced by a single shock event causing equilibrium shock pressure of $29 \pm 1$ GPa, whereas local stress and temperatures might have reached $60 - 80$ GPa and $1600 - 2000^\circ$C resulting in the formation of melt pockets. In our study we investigate fine-grained crystallisation products in order to distinguish whether they are the result of shock metamorphism or a late-stage product of magmatic crystallisation.

Thin sections of Shergotty have been analysed in detail by optical microscopy, scanning electron microscopy and transmission electron microscopy (TEM). In contact to Ti-bearing phases and phosphates, symplectites of fayalite and a SiO$_2$ polymorph or fayalite and hedenbergite occur with grain sizes ranging typically in the order of a few microns. They are similar to symplectites described first by Aramovich et al. (2002), who suggested that these symplectites are rather break-down products of former pyroxferroite and ferrosilite than crystallisation products. In interstices between clinopyroxene and maskelynite we observe several areas composed of a micrometer sized intergrowth of potassium-rich maskelynite, a SiO$_2$ polymorph, which shows a similar lamellar microstructure than those described by El Goresy et al. (2004) as post-stishovite phases, and a residual titanium-rich mafic silicate. TEM analyses indicate that these areas may have originated from shocked quartz-orthoclase symplectites reflecting a very late differentiation product of the magmatic melt.

**References**

A geochemical-mineralogical approach for the reconstruction of past flood events

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The increasing frequency of extreme flood events is a subject of debate for many years and it is speculated that this is a possible consequence of climatic change and/or recent river regulation operations. However, a well-founded discussion on the cause(s) of extreme flood events requires a more accurate record of their frequency and magnitude till a more distant past.

In looking for an adequate approach for the reconstruction of paleo-flood events we act on the assumption that the specific hydrological conditions during high water levels will entail a change in the grain size of the transported suspended matter and consequently, will also cause a change in its mineralogical and geochemical composition due to varying sources. Preliminary investigations on the suspended load of the River Rhine show that the amount of particles transported during a flood is not only much higher, but the grains are also larger in size and hold other geochemical-mineralogical features as compared to such particles transported during normal water levels. Indeed, it could be shown that the particulate matter transported during inundations is marked by a higher portion of coarse carbonate and a lower portion of fine grained fraction enriched in iron oxides.

During a flood event the suspended load is deposited on the floodplain, forming up to several centimetres thick accumulations. This material was cored on the floodplains of the Rhine close to Elchesheim-Illingen and on that of the Danube at Pfatter, by carrying out several short (up to 3 m deep) drillings which were sampled every centimetre. The relationship among the geochemical and mineralogical parameters was studied by means of factor analysis.

Results from the Rhine floodplain sediments clearly indicate a connection between individual mineral phases and specific grain size ranges. Thus the fraction < 20 µm correlates significantly with the iron oxide content, the grain size fraction 20 to 100 µm with the carbonate content, while the fraction > 100 µm is correlated with the amount of the siliciclastic components. It still has to be verified, whether the dominance of the fraction 20 to 100 µm during flood events is a local feature or if it can be extended also to larger sections of the Rhine.

These results demonstrate that a systematic and detailed study of the distribution of grain size and geochemical-mineralogical features of flood plain sediments may yield valuable insights in the occurrence of past flood events. The age of the sediments and hence the inundation can be dated e.g., by means of thermo luminescence and thus information could be obtained about the frequency and magnitude of extreme flood events far beyond historical records.

The age of the earliest continental crust and onset of plate tectonics

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We present bulk Hf and Pb isotope data obtained by solution chemistry and, respectively, MC-ICP-MS and ICP-MS for 60 new leached single Jack Hills zircons determined by SIMS spot analysis to be between 3.9 and 4.35 Ga in age. We also present bulk Pb isotope data corresponding to the MC-ICP-MS Hf isotope data of Harrison et al. (2005). Because abundant 235U was still extant during the Hadean, the 208Pb/206Pb ratio of radiogenic Pb varied extremely fast in the young Earth. Measurements with even modest precision thus provide reasonably accurate estimates of the age of old samples, provided adequate correction for common and contaminant Pb is applied. For this we used the strong correlation between 207Pb/206Pb and 208Pb/206Pb (r² = 0.985) on the assumption that Th/U of concordant zircons vary within only a narrow range (0.7±0.2). If so, the Pb isotope data show that most of the zircons have bulk ages of 4.08±0.15 Ga with a small tailing to younger ages and that no analyzed grains have bulk Pb-Pb ages older than 4.25 Ga. None of the zircons qualified by SIMS to be older than 4.3 Ga have bulk Pb isotope values consistent with such high ages, indicating these ages are overwhelmed by younger U-Th-Pb domains. Although the majority of the ICP-MS bulk Pb ages are in agreement within ~100 My with the associated SIMS spot ages, the former portray a younger and more restricted age range of Jack Hills zircons than the latter. However, this does not affect the conclusion reached by Harrison et al. (2005), based on Jack Hills zircon Hf isotope systematics and reinforced here by our new Hf isotope data (which are equally heterogeneous and exhibit both negative and positive epsilon values), that at least some continental crust began forming very early. Assuming a 176Lu/177Hf ratio of 0.015, typical of sediments and granites and low enough for our age assessments to be minimum rather than maximum estimates, and that all bulk zircon ages are ~4.1 Ga, the CHUR and DM model ages for the source (protolith) of the granites hosting the Jack Hills zircons are, respectively, 4.3-4.4 and 4.4-4.5 Ga. Because granites are the hallmark of modern plate tectonics, our Jack Hills data strongly suggest this process was active by at least 4.1 Ga. Demonstrating that it started even earlier requires independent evidence that the protolith itself was also granitic, an enticing interpretation given the heavy oxygen of a significant fraction of the Jack Hills zircons, their low crystallization temperatures (680±25°C), and the nature of their mineral inclusions.

References
Regulation of acidity generation and consumption in sediments of acidic mine lakes

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In acid mine drainage (AMD) polluted lakes, acidity generation and consumption in sediments are regulated by geochemical factors and by seepage of groundwater. We tested the hypothesis that increased inflow of groundwater can shift the sediment from an acid generating to an acid consuming state and examined the chemical factors that control iron and sulfur transformations. In columns experiments, schwertmannite bearing sediment, rich in iron, sulphur, and carbon, was percolated (0, 5 and 20 L m⁻² a⁻¹) with two solutions (1/1 mmol L⁻¹ vs. 10/15 mmol L⁻¹ sulphate/ferrous iron, pH 5). A DOC source was added after 46 days (~2.5 mmol C L⁻¹) to ease the carbon limitation of reductive processes. The sediment remained in an iron reducing and acidic state during percolation without DOC. Percolation at a high rate and addition of DOC raised pH values in schwertmannite rich layers from 2.8 to 4.5 – 5. Percolation at a high rate and addition of DOC raised pH values in schwertmannite rich layers from 2.8 to 4.5 – 5. Schwertmannite transformation to goethite partly accelerated by a factor of >2 but effectively buffered proton consumption only at the low percolation rate. With pH increase, iron reduction slowed relative to CO₂ production, sulphate was reduced, and iron sulphides were formed.

In batch experiments we examine the effects of iron sources (schwertmannite, goethite, dissolved Fe³⁺), peat humic acid, and pH (3 – 6) on iron reduction rates. At pH 3, addition of schwertmannite and goethite and dissolved ferri-c iron strongly increased, and addition of the humic acid decreased iron reduction rates. Goethite promoted iron reduction more strongly than schwertmannite. Raising pH from 3 to 4.5 – 6 strongly decreased iron reduction rates. When the pH was not fixed, addition of schwertmannite increased (6.3 mmol g⁻¹ d⁻¹) and addition of goethite decreased (1.9 mmol g⁻¹ d⁻¹) iron reduction compared to a control (3.9 mmol g⁻¹ d⁻¹). This effect can be attributed to pH values being higher and dissolved ferric iron concentrations being lower in the goethite amended samples, compared to control and schwertmannite treatment. The acidifying effect of schwertmannite was more critical for maintaining high rates of iron reduction than bulk mineral properties.

The study showed that the input of alkalinity and electron donors by percolation may shift the biogeochemical regime from acidity production to acidity consumption. However, the acidifying capacity of schwertmannite transformation is substantial and its kinetics is fast, thus stabilizing the sediments in a acidic state.

Fo 99.8 olivine in basalts:
Assimilation of meta-serpentinites or oxidation of magmatic phenocrysts?

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Rare occurrences of near endmember forsterite (> Fo 95) exist in volcanic lavas, skarns, and metamorphosed serpentinites. We identify olivines, more forsteritic than any published value, in multiple primitive basalt flows of a monogenetic vent in the Big Pine Volcanic Field, CA USA. Here, to provide a framework for understanding the effects of assimilation and alteration processes in basalts, we analyze two competing hypotheses of pure forsterite formation in lavas: incorporation of regenerated olivine from metamorphosed serpentinite or crystallization/alteration in a high fO₂ environment. Olivine compositions are bimodal, with flows either having all normal (Fo₉₇.₂–Fo₉₉.₈) or all forsteritic (Fo₉₉.₂–Fo₉₉.₃) olivine. Fo composition correlates with increased flow vesicularity but not with the systematic whole rock composition. In many grains, the nearly euhedral forsterite has a hematite and cpx rim, and internal parallel oriented planes of hematite, cpx, and opx.

During peridotite serpentinization and subsequent dehydration, Fe partitions into associated oxides and Ni remains in the serpentine. Thus, regenerated olivines commonly have both low Fe and Ni concentrations. In these lavas, there is a correlative bimodal distribution of NiO. With increasing Mg#, the normal olivines show an increase in NiO whereas it decreases in forsterites to 0.04 wt.%. We therefore can consider a scenario of dehydrated serpentinite originally from the mantle lithosphere incorporated into the ascending melt, with only the forsterite and related oxides remaining.

However, several lines of evidence are inconsistent with an assimilated serpentinite origin, and instead call for late stage oxidation of the melt in air. If metamorphosed serpentinites were selectively incorporated into certain flows, we would expect to see changes in whole rock chemistry as well as a bimodal distribution of both xenocrystic forsterites and phenocrystic normal olivines within single flows, which we do not. A closed system (other than fluids) is also likely because the reintegrated composition of the oxidized assemblage is a normal Fo₉₉ olivine. In addition, four δ¹⁸O analyses by CAMECA 1280 ion microprobe within one forsterite have typical mantle olivine values of 5.42 ± 0.3 % (1σ, 10 μm spots). Continuous oxidation of pre-existing olivine is known to generate pyroxene and oxide symplectites in an increasingly magnesian olivine that exhibit a topotaxial relationship. The BPVF olivines show these requisite reactive phases with the [100] direction of olivine parallel to the [0001] direction of the hematite, and with the symplectite planes parallel to the weak olivine cleavage planes.
Measurement and reporting of natural mercury isotopic variability

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Hg isotope analysis by MC-ICP-MS (using SnCl reduction and Hg cold-vapor generation) is an important new tool for fingerprinting Hg sources and monitoring Hg redox reactions and bioaccumulation (Smith et al., 2005; Foucher and Hintelmann, 2006; Jackson et al., 2006; Bergquist et al., 2006; Kritee et al., 2007). Unfortunately research groups have adopted different standards, definitions of delta values, and approaches to isotopic measurement. We suggest that a single standard, NIST SRM 3133, be adopted for reporting the isotopic variability of Hg isotopes. Isotope ratios should be determined by sample-standard bracketing (SSB) during analysis and reported as permil (%) deviation from NIST SRM 3133. For the highest precision and accuracy, a Tl analysis and reported as permil (%) deviation from NIST.

Isotope ratios should be approaches to isotopic measurement. We suggest that a single adopted different standards, definitions of delta values, and matrix between the samples and bracketing standard. peak zero corrections and matching of concentration and

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Magma generation and ascent beneath arc volcanoes

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Explosive eruptions of andesite arc volcanoes are driven by the generation and subsequent ascent of magma from the deep crust. Magma generation involves a combination of crystallisation of H2O-rich basalt derived from the mantle wedge and partial melting of pre-existing crustal rocks in deep crustal hot zones. Magma ascent can be divided into two regimes. The first regime involves the segregation and ascent of silicic magma through the crust. The H2O-rich magma is buoyant and inviscid and likely to ascend rapidly along dykes. The magma is, however, H2O-undersaturated and therefore will develop superheat during ascent, enabling it to partially digest residual source material and/or wall rocks. The corroded cores of many plagioclase phenocrysts may have originated in this way. Crystal retention and partial resorption by silicic melts leads to linear trends in whole-rock chemistry. We suggest that relatively few andesites represent true liquid compositions; most have an entrained cargo of ancestral crystal residues or accidental passengers acquired en route.

The second regime begins when the magma attains volatile saturation and degassing begins, preferentially removing CO2 relative to H2O. Crystallisation begins at slightly lower pressures when the volatile-saturated liquidus is encountered. The ensuing crystallisation and volatile loss due to decompression lead to a sharp increase in viscosity and density, which serve to slow magma ascent dramatically. We refer to this process as “viscous death” with the consequence that most andesite magmas are destined to form plutons. Decompression crystallisation releases latent heat and results in the paradoxical situation of magma both crystallising and getting hotter by ≤100°C. Because decompression crystallisation continues to low pressures melt SiO2 contents can be up to 80 wt% (anhyd.). Such melts are too viscous to segregate from crystals on volcanic timescales. As a consequence rather little chemical differentiation occurs at shallow levels; most of a magma’s chemistry is defined by differentiation processes in the hot zone and the entrained crystal cargo. Nonetheless, low-pressure cumulates do occur in many andesites, testifying to some crystal deposition within the sub-volcanic edifice. Exposures of sub-volcanic complexes support the idea that successive magma batches may deposit a small fraction of their cargo en route to the surface and, in a complementary way, can entrain fragments of the cargoes of antecedent magmas. An individual phenocryst in an andesite may preserve snapshots of the entire complex magmatic evolution.
Volatile fluxing and magma storage at Mount St. Helens volcano

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A major challenge of volcanology is linking the pre-eruptive movement of magma beneath a volcano to monitored signals such as seismicity and gas emissions. We have used analyses of over 210 melt inclusion (MI) and groundmass glasses from the 1980-86 eruption of Mount St. Helens to create a petrological dataset for comparison to the contemporaneous monitoring record.

H2O in MI ranges from 0 to 6.8 wt%, with the highest values from the Plinian phase of May 18th, 1980. CO2 contents indicate XH2Ovap ≈ 0.80, irrespective of H2O, suggestive of closed system degassing with high bubble fraction. Fluctuation in XH2Ovap suggests fluxing of the magma reservoir by gases exolved from below. Fluxing may play a key role in the development of oscillatory zoning in plagioclase phenocrysts.

Elevated Li in MI and plagioclase phenocrysts from the cryptodome and post-May 18th samples requires transport of Li in an exsolved H2O-rich vapour phase from deeper to shallower portions of the magma system. Maximum Li enrichment occurs at Ptot = 120-180 MPa, possibly due to condensation of a single vapour phase to H2O-rich gas and Li-rich brine. Decreasing Li contents at lower Ptot result from continued degassing during ascent. This degassing occurs on timescales slow enough to allow Li diffusion out of the melt and into the vapour, but fast enough to inhibit significant diffusive loss of Li from plagioclase.

MI evidence for gas fluxing is supported by 210Pb,226Ra disequilibrium resulting from loss and accumulation of 222Rn-bearing vapour. The magnitude of the 210Pb deficits indicate that the deeper reservoir was degassing for at least a decade prior to eruption, while 210Pb excesses in the shallow reservoir are confined to periods of elevated gas flux, as evinced by SO2 measurements.

Pre-eruptive magma storage depths, derived from MI saturation pressures, change systematically with time. The May 18 Plinian eruption discharged magma stored 5 to 11 km below sea-level (bsl). Preceding eruptions, including the lateral blast, and subsequent episodes involved shallower-stored magma. Tapping of magma from ≥2 km bsl stopped abruptly in Dec 1980, coincident with the onset of extensive shallow seismicity and a change from dominantly explosive to dominantly effusive eruption. This transition is likely a response to choking of the conduit system by highly crystallised magma. The close correspondence between petrological and monitoring records at MSH augurs well for an improved understanding of pre-cursory signals at explosive volcanoes.

Experimental Constraints on Trace Element Fluxes from Slab to Wedge

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The characteristic trace element signature of arc magmas is a consequence of the chemical flux from subducted slab to mantle wedge. The nature of this flux is determined by the different subducted lithologies, the subduction geotherm and the partitioning behaviour of trace elements between fluids, melts and slab residues. In an attempt to constrain the trace element flux that can be derived from subducted basalt we carried out H2O-saturated experiments on a trace element-doped MORB composition at 2.5 GPa, 750-900 °C and fO2=NO.

Garnet, omphacite and rutile occur at all temperatures. Amphibole, staurolite and epidote disappear above 750 °C; allanite appears above 750 °C. The tronnjemitic glass present at all temperatures was quenched from supercritical fluid. Trace element analyses of glasses demonstrate the control exerted by residual minerals on fluid chemistry: garnet controls HREE; rutile controls Ti, Nb and Ta; and allanite buffers LREE contents of fluids to low levels and preferentially holds back Th and, to a much lesser extent, U. We agree with previous experimental [1] and metamorphic [2] studies that residual allanite has a key role in selectively retaining trace elements during subduction.

Experiments and allanite-bearing rhyolites are used to derive a model for allanite solubility in melts or fluids as a function of P, T, composition and LREE (La-Sm) content. Our model reproduces LREE concentrations in allanite-saturated melts and fluids to within a factor of 1.4 from 650-1100°C, 0-4 GPa. The extreme T-dependence of allanite solubility is very similar to that of monazite [3]. Silicic fluids from basaltic (or sedimentary) protoliths will be saturated in allanite (or monazite) except at very high temperatures. For conventional subduction geotherms the low solubility of LREE (+Th) in allanite-saturated fluids raises questions about the mechanism of LREE+Th transport from slab to wedge. We suggest either that (i) locally temperatures experienced by the slab are appreciably higher than normal, e.g. by mechanical incorporation of thin slivers of sediment into the mantle wedge, or that (ii) substantial volumes of H2O-rich fluids must pass through the mantle wedge prior to melting. The solubility of accessory phases in fluids derived from subducted rocks clearly provides important geochemical constraints on subduction zone thermal structure.

References
Volatile abundances and H isotope signatures of melt inclusions and nominally anhydrous minerals in the nakhlites and chassignites

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Water and other volatiles play an important role in partial melting of mantle sources of primary magmas and their eruption and crystallization histories. The lack of pervasive alteration or shock melting in nakhlites and chassignites suggests that their nominally anhydrous minerals and melt inclusions may provide clues to the volatile abundances and H isotope compositions of their parent magmas. The abundances of H$_2$O, CO$_2$, F, S, and Cl and the H isotope signatures of nominally anhydrous minerals and the melt inclusions were measured in 7 nakhlites and 2 chassignites using standard SIMS techniques. The volatile abundances in the olivine and pyroxene in the nakhlites are lower than those of typical terrestrial basalts, mantle xenoliths, and megacrysts. The $\delta^D$ values for olivine are low and overlap with the terrestrial range (-350 to +100‰). The clinopyroxene shows a wide range of $\delta^D$, the largest in Governador Valadares (+200 to 1250‰). The olivines in chassignite have water abundances that are similar to those of mantle olivine (140 to 280 ppm) and low $\delta^D$ values (-67 to +86‰). Most inclusions in the nakhlites and chassignites have low water abundances and, by Martian meteorite standards, modest D enrichment. If the compositions of the nominally anhydrous minerals are primary, then the $\delta^D$ value of the parent magma is low. H isotopes provide clues to why the water contents of the melt inclusions are low. Degassing reduces the $\delta^D$ of the magma due to vapor-liquid equilibrium isotopic fractionation. The positive correlation between water and $\delta^D$ in melt inclusions in Governador Valadares suggests that its parent magma degassed. The negative correlation between H$_2$O and $\delta^D$ in Yamato 000593 suggests diffusive H loss. In the majority of the meteorites studied, however, there is no significant correlation between H$_2$O and $\delta^D$. Given the low water contents, any contamination may be complicating the interpretation of $\delta^D$ values. The low volatile abundances in the nakhlites and chassignites suggest that either the parent magmas degassed or volatiles were depleted in the source region of their parental melts.

Identification, interpretation and significance of fluid inclusions trapped in immiscible fluid systems

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Fluid immiscibility is an important process in the Earth’s crust and upper mantle and fluid inclusions provide the most direct evidence for the occurrence of fluid immiscibility. Fluid inclusions trapped from immiscible fluids provide information concerning the physical and chemical environment attending various geological processes. However, the identification of fluid inclusions trapped from immiscible fluids and their interpretation remain topics of discussion. Here we summarize techniques that should be used to identify and confirm that fluid inclusions were trapped from immiscible fluids, and outline techniques that should be used to obtain useful information from these inclusions.

The experienced inclusionist always envisions a phase diagram when observing fluid inclusions with the microscope, and uses this diagram to place constraints on the composition and homogenization temperature and trapping conditions of the inclusions. Thus, it is important that inclusionists be familiar with the phase relations of the more common fluid systems that serve as models for many fluids that occur in nature, including H$_2$O, H$_2$O-NaCl, H$_2$O-CO$_2$, and H$_2$O-NaCl-CO$_2$. Phase equilibria for these simple fluid systems provide the basis to understand the physical and chemical environment of inclusions trapped in immiscible fluid systems. In this presentation the PVTX properties of these systems will be reviewed using examples of the correct techniques for recognizing and interpreting fluid inclusions trapped in immiscible fluid systems.
New experimental data on Fe and Fe-S melting and the temperature at the core-mantle boundary

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Using a new method of rapid data acquisition in a double-sided laser-heating system at ESRF we measured X-ray diffraction patterns of laser heated iron to above its melting temperature in an argon pressure medium to 114 GPa, and in Al\textsubscript{2}O\textsubscript{3} to 150 GPa. Only the fcc and hcp phases were observed. Fcc iron is stable to at least 68 GPa and at higher pressures only hcp was observed making this phase again the most likely candidate for the solid-inner core. The room-temperature equation of state of these fully annealed iron samples is identical to that previously measured in a helium pressure medium (Dewaele et al., 2006). The highest P-T conditions at which melting was documented were 150 GPa and 3400 K, in excellent agreement with previous optical measurements (Boehler, 1993).

In the Fe-S system we reinvestigated the melt depression of iron using recovery experiments and electron microscopy. In contrast to our previous visual measurements there exists still a substantial melt depression of 1000 K at 50 GPa (Chudinovskikh and Boehler, 2007).

Both studies strongly suggest low core temperatures. The temperature at the core-side of the core-mantle boundary (at 135 GPa) would be substantially below 4000 K and thus, significantly decreasing the previously predicted large temperature jump across this boundary.

References

Calcium isotope budget of the Phanerozoic ocean

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We present a new Early Ordovician to Late Triassic Ca isotope record measured on brachiopods. In combination with published and new Mesozoic-Cenozoic data (Late Jurassic-Early Cretaceous belemnites and brachiopods, Late Cretaceous brachiopods, Neogene foraminifera) our $\delta^{44/40}$Ca record covers most of the Phanerozoic history. The data show significant variability on several timescales: An overall 0.5 \% increase in $\delta^{44/40}$Ca from the Ordovician to the Pleistocene is mainly due to rising values during the Mississippian followed by a drop to intermediate values in the Permian-Triassic and a second increase during the Jurassic to a Cretaceous maximum. Neogene $\delta^{44/40}$Ca values are in the same range as the Cretaceous values. Superimposed on these long-term (ca. 100 Ma) trends are several higher order oscillations (ca. 5-30 Ma) with magnitudes of up to 0.4 \%. Well documented examples of the latter occurred during the Neogene [1] and the Jurassic-Cretaceous [2].

There is currently no simple explanation for the reconstructed isotope variability of seawater calcium. Variable continental weathering fluxes and carbonate deposition in the oceans cannot explain the isotope variations. These mechanisms only influence the ocean carbon cycle, which operates on a much shorter timescale than the Ca cycle. Variable Ca isotope fractionation on the continents also is unlikely to cause significant variability in ocean $\delta^{44/40}$Ca, due to the huge size of the ocean calcium reservoir compared to terrestrial Ca sediments (e.g. in soils or travertine). The most likely mechanism to explain ocean $\delta^{44/40}$Ca variations is variable input of hydrothermal Ca and of Ca from dolomite formation. In addition, we observe a correlation of $\delta^{44/40}$Ca and seawater Mg/Ca ratios during the Paleozoic, which can be best explained by a shift from calcite dominated sedimentation during the Early Paleozoic to aragonite dominance in the Late Paleozoic and Triassic. Aragonite is stronger fractionated than calcite, so sedimentation dominated by aragonite leads to an enrichment of seawater in $^{44}$Ca. However, this correlation breaks down after the Carboniferous, possibly due to the evolutionary shift to mineralogy-independent fractionation of modern carbonate producers [3].

References
Nd isotope initials of Turku Migmatite Complex: Contemporaneous production of contrasting felsic melts

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Within the Turku Migmatite Complex (TMC) in S-Finland two types of in-situ partial melts are observed: akf-quartz-dominated melts and leucosomes comprising ‘small-scale granites’. These and the respective restites and precursors have been interpreted in a common genetic model (Johannes et al. 2003). In order to test the hypothesis of contemporaneous production of contrasting felsic melts within the same educt, Nd-isotope analyses were performed on garnet separates. U-Pb dating of zircons of the TMC indicate a 1.83 Ga partial melting event. If both types of leucocratic melt were generated at this stage, garnets of both leucosome types and of the respective restites should reveal identical initial Nd isotope compositions.

Clean garnet separates of leucosomes and restites from two different outcrops (R, L) were prepared and analyzed for their Sm-Nd isotope signatures by TIMS. Resulting present-day εNd values of garnets derived from akf-q-leucosomes are +373 and +288, from restites are +173 and +76 and from small-scale granites are -6 and +76. Recalculation of the Nd isotope composition to the zircon age of 1.832±11 reveal identical εNd (1.83Ga) of +4.2 for outcrop L and +7.0 for outcrop R for leucosomes and restites, respectively. The observed difference of 3 ε-units in the calculated initial Nd isotope compositions is probably due to local heterogeneity within the thick meta-pelite precursor. Considering the peak P-T-conditions in this area with ~800°C and 6 kbar (Johannes et al. 2003) it seems obvious that isotopic equilibration had been achieved at each outcrop during mid-crustal partial melting resulting in contemporaneous production of the contrasting types of leucosomes. The akf-q-leucosomes and the ‘small-scale granite’-leucosomes have different major and trace element composition including highly fractionated REE patterns. Akf-q-leucosomes are interpreted as cumulates formed of in-situ partial melts leaving behind an evolved liquid which crystallized to form the ‘small-scale granites’.

Reference

High-pressure behaviour of CaIrO3 perovskite and post-perovskite phases

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CaIrO3 perovskite and post-perovskite phases might be used as low pressure analogues of the correspondent MgSiO3 phases in experiments that are currently impossible at conditions of the MgSiO3 perovskite to post-perovskite transformation, provided that their high-pressure behaviour is well characterised.

Single crystals of CaIrO3 perovskite and post-perovskite phases were synthesised in a piston-cylinder apparatus at 2.5 GPa and 1525 °C and 1GPa and 1435 °C, respectively. Two single-crystals, one with the perovskite and the other with the post-perovskite structure have been loaded together in a diamond anvil cell with ruby chips as pressure calibrant and a methanol:ethanol 4:1 mixture as a pressure transmitting medium. Unit-cell lattice parameters have been measured for both crystals up to 8 GPa. The CaIrO3 post-perovskite is more compressible than the perovskite structure. The equation of state parameters determined using a second-order Birch-Murnaghan expression are $V_0=229.47(1)$ and $K_0=189.4(6)$ for the perovskite and $V_0=226.38(2)$ and $K_0=176.0(6)$ for the post-perovskite phase. The compressibility of the unit-cell axes of the perovskite structure is anisotropic with $\beta_a>\beta_c>\beta_b$. The smaller compressibility of the $b$ axis also has been reported for MgSiO3, however in the latter compound the compressibility of the $a$ and $c$ axes is practically the same. In contrast the $b$ axis is the most compressible in the post-perovskite structure, whereas the $a$ and $c$ axes have similar compressibilities and are much stiffer.

Intensity data collections at high-pressure and structural refinements are underway in order to characterise the compression mechanism of these phases.
Temperature-programmed desorption of oxalate from the goethite surface

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The TPD-FTIR technique was used to investigate the relative thermal stabilities and decomposition reactions of different oxalate complexes adsorbed on the dry goethite surface. The measurements showed that important differences in coordination have a considerable impact on the thermal stability of the surface complexes.

Three important stages of desorption were identified from both TPD (Figure 1) and FTIR data in the 300-900 K range. Stage I (300-440 K) corresponds to the desorption of weakly-bound oxalate molecules with decomposition pathways characteristic of oxalic acid. Stage II (440-520 K) corresponds to the dehydration of key surface OH2 groups responsible in stabilizing hydrogen-bonded surface complexes. These species can either decompose via typical oxalic acid decomposition pathways or convert to metal-bonded surface complexes. Finally, Stage III (520-660 K) corresponds to the thermal decomposition of all metal-bonded oxalate complexes, proceeding through a two-electron reduction pathway that converts oxalate to CO2. Experiments in the absence of oxalate were used to assess the contributions from dehydration, dehydroxylation and decarbonation reactions from the goethite bulk.

Figure 1: TPD trace of goethite in the presence of 1.7 µmol/m² adsorbed oxalate. The dry powder was prepared from an aqueous suspension of goethite equilibrated in the presence of sodium oxalate at pH 6.5 and dried at room temperature.

Trace Elements and radio nuclides in Zegrze reservoir sediments (Poland)

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The Zegrze Reservoir (Poland) is located just north of Warsaw. It is formed by a dam constructed on the lower course of the Narew and the Bug rivers, near their flow in the Vistula river. Its surface area is about 33 km².

Material and methods
64 drilling cores sampled were collected from the reservoir. The cores were divided into 178 samples. Analyses of concentrations of Ag, As, Ba, Cd, Cr, Co, Cu, Hg, Pb, Se, Sr, Sn, Ti, V, and Zn and as well U (eU), Th (eTh), 40K and 137Cs were performed for the sediment grain fraction <1mm.

Results
It results that the concentration of the most trace elements in the sediments accumulated at the bottom of the reservoir are diversified. The silt sediments characterized higher contents of trace elements than the geochemical background while sand sediments show low concentrations. In sediments maximum concentration (mg/kg) of antimony was 4.3, arsenic – 17, barium – 355, cadmium – 11.9, chromium – 95, cobalt – 8, copper – 74, mercury – 0.72, nickel – 36, lead – 48, selenium – 1.2, silver – 3.4, strontium – 342, thallium – 0.4, tin 4.8, vanadium – 45 and zinc – 538. In Zegrze reservoir radio nuclides occur in concentrations similar to characteristic values for that type of sediments.

Silts with high contents of heavy metals were accumulated in reservoir near Nieporęt, nearby mouth of Żerań channel (chromium, zinc, cadmium, copper, nickel, lead, mercury), which is connected with Vistula river in industrial part of Warsaw. And silts with distinctly high contents trace metals occur near some touristic sites localized on reservoir rim.

Conclusion
The estimated volume of silts accumulated in reservoir was 7860000 m³ and their tonnage – 13.36 mln t. It was calculated that these silt sediments contain about 2.6 t antimony, 13.4 t arsenic, 227 t chromium, 9.4 t tin, 561 t zinc, 3.2 t cadmium, 94 t copper, 107 t nickel, 134 t lead and 0.7 t mercury.
Pressure and temperature dependence of water solubility in forsterite: Implications for the activity of water in the Earth’s mantle

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The storage capacity of water in the upper mantle largely depends on water solubility in mantle olivine. Such solubility provides a fundamental information required for petrological, geophysical and geochemical models of the mantle. Previous experimental studies have shown that the water solubility in olivine increases with increasing water fugacity up to 12 GPa at 1100°C (Kohlstedt et al., 1996) and with increasing temperature at 0.3 GPa (Zhao et al., 2004). This latter contrasts with the incorporation of water in transition zone phases such as wadsleyite and ringwoodite for which water solubility decreases with increasing temperature.

The goal of this study was to determine the dependence of water maximum concentration on temperature at pressures higher than 0.3 GPa. We performed experiments at 3, 6 and 9 GPa, and temperatures ranging from 1000 to 1400°C in the MgO-SiO₂-H₂O system using a multi-anvil apparatus. The starting material consisted of forsterite and enstatite in the 1:1 molar ratio with 1 to 5 wt% H₂O. The samples were analyzed using scanning electron microscopy, electron microprobe and polarized Fourier transform infrared spectroscopy. Results show that water solubility in olivine increases with temperature only at 3 GPa. At 6 and 9 GPa, the water solubility reaches a maximum at low temperatures then decreases at high temperatures. These results agree with recent observations at 12 GPa in the MgO-SiO₂-H₂O system (Smyth et al., 2006). Such behaviour is explained by the change in water fugacity as a function of pressure and temperature due to dissolution of silicate component in the fluid. The solubilities determined in this study allow to correct for this effect and permit to establish a new model of water activity in the mantle for silicate-water fluid coexisting with olivine and enstatite.

References

Compared Mg isotope compositions of plants, rocks and waters

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Magnesium is directly involved in the biological cycle. Mg plays a major role in photosynthetic processes, as it is the central core of the chlorophyll molecule. It activates many specific enzyme systems, and helps to regulate internal transport of other major ions such as P and K. Mg in plants comes from soil minerals and atmospheric deposits. Mg absorbed from soil solution by roots is transferred to shoots where it can be stored for months to hundred of years. Plants can therefore be responsible for considerable Mg mobilization on a basin scale (mean plant Mg content is ~2000ppm). Chlorophyll can be significantly enriched in light isotopes [1]. The aim of this study is to determine Mg isotope fractionation during Mg uptake by roots and Mg translocation within the plant, and to estimate their potential impact on the isotope signature of continental waters.

We first developed a new chemical procedure to separate Mg from both geological and biological matrices. Plants, clays and granites can display significant contents in alkali, Al and some transition elements such Fe, Mn and Zn which are difficult to separate from Mg with a typical cation exchange resin. We then investigated Mg isotope fractionation induced by two plants (clover, ray grass), grown under experimental conditions, on various Mg-rich substrates (phlogopite, magnesia, nutritive solution). δ²⁵Mg and δ²⁶Mg were measured using the MC-ICP-MS.

Regular measurements of Cambridge-1 standard solution indicate long term reproducibility for δ²⁶MgDSM better than 0.15‰ (2σ). δ²⁶Mg for Cambridge-1 (-2.61‰), as well as for silicate (BE-N, -0.28‰), carbonate (CaLs, -4.59‰), seawater (BCR-403, -0.93‰) and river water (SRM1640, -1.28‰) reference materials are in agreement, within errors, with published values [2, 3]. δ²⁶Mg for plant, soil and granite reference materials are presented for the first time. The plants and organic matter analysed (rye flour BCR-382, sealetuce BCR-279 and natural wavy hairgrass) display δ²⁶Mg ranging between -0.58‰ and -1.15‰, greater than published values for chlorophyll [4]. A forest soil (TILL-1) yields a δ²⁶Mg of -0.40‰. The two granites (DR-N and GA) display δ²⁶Mg of -0.50‰ and -0.75‰ respectively.

Preliminary results for experimentally grown plants highlight different Mg isotope signatures of different organs of plants. A decrease of δ²⁶Mg from roots to shoots is observed, demonstrating isotope fractionation during Mg internal transfer. The respective roles of plant species, Mg internal recycling, and soil Mg biodisposable will be discussed.

Petrological features of lithospheric mantle beneath Santo Antao (Cape Verde Archipelago)

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Spinel peridotites in basanites from Sao Antao were studied with the aim of characterising the lithospheric mantle beneath this island, and working towards a better understanding of the nature of the mantle under the Cape Verde archipelago. Most samples examined are four-phase lherzolites with modal clinopyroxenes up to 18% and no evidence of modal metasomatism. A few are characterised by the presence of metasomatic textures such as i) glassy patches with tiny subidiomorphic crystals of secondary olivine and clinopyroxene, and ii) rare spongy pyroxenes. Texturally, clinopyroxene often occurs as clusters of small crystals (<200 microns), whereas olivine and orthopyroxene are larger (up to 1 mm), suggesting a secondary origin for this clinopyroxene. A few samples show clear evidence of host magma infiltration, allowing us to discriminate the chemical effects of this process against processes related to mantle metasomatism, i.e. magma interaction at depth. Olivine, ortho- and clinopyroxene near basalt or in contact with basaltic veins crossing the samples systematically present lower mg# and Cr2O3, and higher TiO2 and Al2O3 contents between 59.6 wt% and 66.0 wt%, whereas the orthopyroxene has a more restricted mg# range (91.2-92.2). Clinopyroxene has mg# varying from 91.7 to 93.0, with Al2O3 from 0.98 to 4.43 wt%, without any correlation between the two parameters, which rules out the idea that it results from a simple depletion event. REE clinopyroxene patterns vary from ‘humped’ to ‘spoon-shaped’ at Yb at 3-6 x Ch, with strong LREE enrichment (La 7-117 x Ch). Silicate glasses, unrelated to host basalt infillations are present just in one sample. They are rather homogeneous in composition with silica contents between 59.6 wt% and 66.0 wt%, and alkali contents up to 15 wt% with Na/K < 1. On the whole they show fractionated trace element profiles with (La/Yb)N varying from 34 to 102. These preliminary petrographic and geochemical data for Sao Antao spinel lherzolites allow a comparison with the data and model proposed for Sal, an island to the east where lherzolites contain a sub-continental mantle component, and Santiago and Fogo to the south where the lherzolite is interpreted as the result of carbonatic metasomatism and wehrlite is probably cumulate from a large magma chamber system, again involving carbonatic activity.

Polymetamorphism in the Paleoproterozoic Ubendian Belt, Tanzania

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The Paleoproterozoic (ca. 2.0-1.8 Ga) Ubendian-Usagaran orogens surrounding the SE and SW margins of the Archaean Tanzania craton contain eclogites of MORB-like chemistry which are among the oldest eclogite occurrences exposed in orogenic belts on Earth. Our study of metamorphic events by petrology and U-Pb SHRIMP dating of zircons is aimed to unravel the orogenic history of the Ubendian Belt southwest of the Tanzania Craton.

The Ubendian Belt has been subdivided into eight NW to SE elongated lithotectonic blocks the formation of which is interpreted to be of late Paleoproterozoic or Pan-African age. Lithologically the belt consists, besides minor eclogites, mainly of granitic gneisses, metapelites, some mafic granulites and amphibolites, i.e. rocks attributed to a continental environment. Melanite samples from the Wakole, the Ufipa and the Ubende terranes all revealed the same type of clockwise P-T path and thus a crustal thickening event dated with zircons (SHRIMP) at 1900±14, 1901±37, 1949±16 and 1817±26 Ma. Metamorphic mineral assemblages include biotite-muscovite-garnet-staurolite-kyanite and garnet-biotite-K-feldspar-kyanite (partly replaced by sillimanite). Peak metamorphic conditions were calculated for rocks of different parts of the belt and of different blocks. They range from 7kbar / 640°C over 9.4kbar / 670–800°C to 12.4kbar / 800°C, indicating low geothermal gradients during the crustal thickening event that was followed by a strong erosion of the crust.

Locally, metapelites of different parts of the Ubende block experienced a mylonitic overprint within the kyanite stability field. Zircon rims in these mylonites revealed a Kibaran overprint (1086±21 Ma), an age that is also found in metamorphic zircons of some non-mylonitic schists (1166±14 Ma) of that block.

Lenses of eclogites (meter to 100 meter scale) occur widespread in the Ubende and Ufipa blocks (over a distance of ca. 200 km). Some of these eclogites contain metamorphic zircons grown during a Pan-African eclogite-facies metamorphism at 520 to 590 Ma. However, at three localities the eclogite zircons contain inner metamorphic growth zones that revealed a Paleoproterozoic age (1877±20, 1886±16 Ma) in addition to the Pan-African age of the outermost rims (596±41, 548±39 Ma).

Neither the Kibaran mylonitic overprint nor the Pan-African eclogite-facies subduction metamorphism have been described so far. Their discovery demands major revision of the interpretation of the Proterozoic evolution along the southwestern margin of the Tanzania Craton.
Nano-scale interactions of fungi with mineral surface

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Classical studies of biotic weathering have mainly focussed on solution phase interactions with minerals and on the ability of plants and microorganisms to influence soil solution composition. Only recently, has the relevance of direct (contact) interactions between fungi and minerals been recognized as an important driver in weathering environments. This can be exemplified by the fungal components of lichen symbioses or the ectomycorrhizal association between plants and fungi.

For ectomycorrhiza, the distal tree roots are closely interconnected with a dense fungal mycelium network in which hyphal strands interact directly with soil organic and/or mineral surfaces. These fungal extensions are sustained by the photosynthate of the trees, and in return, they solubilize minerals and directly aid the mass transfer of a large array of elements (e.g. P, N, K, Zn, Fe, Cu etc) towards the tree roots. The exudation of protons, ligands and siderophores by hyphae tips has been suggested as the main factor controlling the weathering of minerals. However, the fungi are in close contact with the mineral surface and therefore may destabilize the lattice structure of the mineral surface, yet this dissolution process has been largely overlooked and our contribution intends to fill that gap.

In this study, we investigated the weathering of biotite induced by Sullus bovinus hyphae grown in symbiosis with Pinus sylvestris trees grown on biotite substrates within agar-perlite systems. The fungal-mineral systems were maintained under sterile conditions and fungal hyphae were allowed to colonize the biotite surface (around one cm²) for about ~ three months before removal of the mineral substrate for analysis. Half of the biotite sample was treated with a detergent to remove the fungal material and expose the weathered surface. This exposed surface was subsequently analysed by Vertical Scanning Interferometry (VSI) to quantify any changes in the biotite surface microtopography and to determine the weathered biotite volume. The other half of the biotite sample, was used for Focus Ion Beam (FIB) sections (~ 100 nm thick, 15 µm long by 5 µm wide) with sections cut across several mature filaments or across terminal hyphae segments. These sections were transferred onto TEM grids and characterized using Electron Energy Loss Spectroscopy (EELS), Energy Dispersive Spectroscopy (EDS) and Energy-filtering TEM (EFTEM). These techniques allows (i) the determination of the mass loss upon hyphae-mineral surface interaction (ii) the quantification of chemical bonds between hyphae and the biotite surface, (iii) the imaging of secondary mineral phases at the interface and (iv) quantification of uptake of elements from mineral to fungi at the molecular scale.

Dolomite nucleation on extracellular polymeric substances

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Research in natural environments, in conjunction with laboratory culture experiments, has demonstrated that microbes can induce low-temperature dolomite formation. Nevertheless, the exact mechanism and the ecological significance of the process remain unclear.

Here, we present a laboratory experiment designed to determine whether dolomite nucleation is an active microbial process at the cell wall or a passive process associated with microbially produced organic compounds. Pure strains of Desulfovibrio brasiliensis, a dolomite producing bacterium, were initially grown at 30°C under anoxic conditions in a medium whose chemical composition prevents dolomite formation. The cultures were subsequently sterilized and the chemical composition of the medium modified to permit carbonate precipitation. At this time, nucleation of Ca-dolomite occurred in the absence of living bacteria, but in the presence of fresh extracellular polymeric substances (EPS) previously produced by D. brasiliensis.

Our results suggest a key role for EPS in dolomite formation. In contrast, excretion of metabolites and nucleation on the cell wall appear less important for the process. We propose that EPS acts as a structural template at the molecular scale which, absorbing and ordering ions in a preferential way, promotes dolomite formation at 30°C. Our experiments show how microbial activity may induce biomineralization through the excretion of specific organic molecules in the environment. The occurrence of such biominerals may be unexpected if only the inorganic chemistry of the solution were considered.
Partitioning of Rb and Sr between haplogranitic melts and aqueous fluids: Information from in situ experiments using SR-XRF

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Knowledge of the partitioning of trace elements between silicate melts and coexisting aqueous fluids is essential for the understanding of mass transfer during late stage magmatic processes. Fluid-melt partitioning depends on numerous parameters such as temperature, pressure, chlorinity and pH of the fluid, and the composition of the melt. Although there are several experimental studies on trace element partitioning in various fluid-melt systems [e.g. 1, 2, 3], the effect of many compositional parameters is still insufficiently known.

We investigated the partitioning of Rb and Sr between synthetic haplogranitic melts and an aqueous NaCl fluid at 750°C and 200 MPa using cold-seal pressure vessels. The resulting partitioning coefficients (Df/m = Cf/Cm) scatter up to a factor of 5. This scatter may be caused by 1) changes in the fluid composition during quenching, 2) fluid loss during extraction from the capsules or 3) feldspar formation during the runs. Therefore, we determined the concentrations of Rb and Sr in the aqueous fluid coexisting with the melt directly at high P and T using a hydrothermal diamond-anvil cell (HDAC) and SR-XRF analyses [4]. The in-situ experiments were done at the SR-XRF microprobe at beamline L of DORIS III at HASYLAB/DESY. A glass chip doped with 2500 ppm Rb and Sr and an aqueous solution were loaded into the sample chamber of the HDAC, which was then heated to 750 °C. Equilibrium was attained in less than 20 min, as indicated by consecutive XRF spectra of the fluid. Because it was not possible to analyse the melt droplets without a contribution from the aqueous phase to the XRF signal, the Rb and Sr concentrations in the melts were measured on the quenched glass using EMP. For pure water as starting fluid, a Rb concentration of 322 ± 23 ppm was obtained in situ at 750°C and 200 MPa in the aqueous phase, which resulted in a Df/m of 0.129 ± 0.013. This is much higher than a Df/m of 0.006 at 750°C and 200 MPa reported in the literature [5] obtained from analyses of quench fluid and glass.

References

Mechanistic study of the photodissolution of lepidocrocite (γ-FeOOH) by model siderophores

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Dissolution of iron (hydr)oxides by siderophores is a process that potentially contributes to the generation of bioavailable iron in marine waters. We have recently shown that the ligand-promoted dissolution of lepidocrocite (γ-FeOOH) by model siderophores (aerobactin and desferrioxamine B) is enhanced at pH 6 under simulated sunlight [1]. Based on that study we hypothesized that the photoreactive α-hydroxycarboxylic acid moiety within aerobactin is not involved in the inner-sphere coordination at the surface of lepidocrocite. The enhanced dissolution of lepidocrocite was explained in terms of the intrinsic photoreactivity of the oxide phase itself and not by a light-induced photolysis reaction of adsorbed aerobicactin. To verify the above hypothesis, extensive batch dissolution experiments with aerobactin and the non-photoreactive desferrioxamine B were conducted between pH 3 and pH 8 in the dark as well as under irradiation. Adsorption isotherms were determined and the potential readsorption of Fe(III)-siderophore complexes was evaluated. Based on these results a kinetic rate law for the dissolution of lepidocrocite was formulated for both desferrioxamine B and aerobactin. The calculated dissolution rate constants for the two model siderophores between pH 5 and pH 8 were very similar. This is a strong indication that aerobactin forms inner-sphere surface complexes by the coordination of the terminal hydroxamic acid moieties (as is the case for desferrioxamine B) and not by the photoreactive α-hydroxycarboxylic acid moiety.

References
Pinpointing the temporal evolution of an intra-oceanic arc system: The case of the Kohistan arc complex

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The Kohistan Arc complex (KAC), in northern Pakistan, represents the exhumed section of an island arc formed within the Neo-Tethys ocean during the Mesozoic. This complex has been obducted during the Late Cretaceous-Palaeocene onto the Indian plate along the Indus Suture. Lower to mid-crustal level rocks of the Jijal and Patan-Dasu metaplutonic complexes represent the plutonic roots of the KAC section studied, accreted during the ~115-85 Ma time interval. The Jijal sequence, the deepest exhumed part of the KAC, is subdivided into a basal ultramafic section and an upper gabbroic zone of granulite facies rocks. The Patan-Dasu metaplutonic complex, more than 22km-thick, is mainly composed of gabbros and amphibolites more or less metamorphosed. Field and petrological investigations combined with detailed Sr-Nd-Pb isotopic and REE analyses performed on whole rocks, plagioclase and clinopyroxene from representative samples across the Jijal and Patan-Dasu sequences allow us to propose a three-stage geodynamical model covering the complete arc evolution through ~30 Ma. The present work is mainly focused on the temporal constraints of this model. The “in-situ” LA-ICPMS U-Pb analyses have been performed on zircons separated from the different lithologies belonging to the three identified steps of the KAC evolution and they provide temporal constraints of the main stages of this model. The model starts with the onset of the subduction at 118±7 Ma [1, 2] and is followed by the building of the volcanic arc. The 2nd stage corresponds to a major thermal event, characterized by abundant magma underplating and by granulitisation of the arc base at 95.8±1.3 Ma. The last stage, between ~95 and 88 Ma seals the end of the intra-oceanic subduction and corresponds to a limited magmatic period. A voluminous, but short, magmatic pulse occurred at ~88-80 Ma and corresponds to the Chilas complex emplacement.

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Temporal evolution of the Cabo Verde archipelago: New constraints from ⁴⁰Ar-³⁹Ar data

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The Cabo Verde archipelago, located in the Atlantic between 15 and 17°N, is composed of 10 principal volcanic islands forming two lineaments converging eastward (the Northern and Southern Islands). It occurs over the Cabo Verde Rise, an oceanic mega-swell, considered as the result of a mantle plume (Montelli et al. 2006). Those two groups of islands have been considered distinct based on the geochemical (elemental and isotopic) characteristics of the magmatic rocks (Gerlach et al., 1988; Doucelance et al., 2003). Morphological observations and historical volcanic activity argue in favour of a westward migration of the magmatism during the last 20 Ma. However, to date, the age progression of the Cabo Verde islands has not been yet clearly demonstrated by detailed geochronological studies at the scale of the whole archipelago.

We present here 15 new ⁴⁰Ar-³⁹Ar ages obtained on volcanic rocks from São Vicente, São Nicolau, Northern Islands, on one hand, and from Santiago, Southern Islands, on the other hand. Analyses were performed on whole rock samples for which chemical and isotopic characteristics have been previously studied in details. ⁴⁰Ar-³⁹Ar ages range from 6 Ma to 700 ka, from 2.6 Ma to 700 ka and from 3.8 to 1.5 Ma in São Vicente, São Nicolau and Santiago, respectively. Together with previous published ⁴⁰Ar-³⁹Ar and K-Ar studies, these new geochronological results show that the age distribution cannot only be related to the spatial distribution of the islands along the Northern and the Southern segments. We will discuss the temporal evolution of volcanic activity considering the following spatial scales: 1) single island, 2) Northern and Southern segments, 3) whole archipelago.

References
The late-stage evolution of oceanic gabbros - Combined experimental and in situ isotope study on gabbros from Southwest Indian Ridge

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Gabbroic rocks from Hole 735B at the Southwest Indian Ridge (SWIR; Legs 118 and 176), represent the longest continuous section of oceanic lower crust ever drilled by ODP (Ocean Drilling Program). About 25% of the core is strongly influenced by late-stage magmatic processes leading to Fe-rich (ferrogabbros) and Si-rich (plagiogranites) compositions as end-members. The study of natural ferrogabbros from SWIR reveal that the typical ferrogabbroic paragenesis is ilmenite ± pargasite ± magnetite ± apatite ± orthopyroxene. Phase equilibria experiments at P=200 MPa and T=900-1050°C show that Fe-Ti oxides are the liquidus phases, even at reducing conditions, leading to dramatic depletion of residual melts in FeO and TiO₂ from the beginning of crystallization. Thus, it is very unlikely that the ferrogabbroic assemblages are formed by simple differentitation of Fe-rich basaltic melts. Remarkable is that plagioclase and clinopyroxene are normally absent in natural paragenesis while these phases are stable in phase equilibria experiments. On the other hand, amphibole and orthopyroxene are typical for natural late-stage gabbros and completely absent in our experimental products. However, amphibole + orthopyroxene + An-rich plagioclase are main phases formed in partial melting experiments on gabbros [1]. These observations indicate again that the late-stage high-temperature evolution of the gabbroic suites in the lower oceanic crust can not be simply related to the differentitation of basaltic liquids but requires additional mechanisms operating in the still-hot gabbroic rocks. Potential processes responsible for the formation of mineral assemblages in ferrogabbros could be: impregnation of gabbroic protolith with accumulated phases crystallized in a late-stage melt, partial melting of gabbroic cumulates due to reaction with water-rich fluids and/or precipitation from an immiscible iron-rich silicate liquid.

In situ LA-MC-ICPMS analyses of Sr isotopes in late-stage parageneses in natural rocks were applied to discriminate between hydrous primary magmatic, and seawater-induced late-stage processes. First in situ Sr isotope analyses on An-enriched plagioclases, which are regarded to be formed during late-stage hydrous partial melting process, show seawater signatures. However, the Sr isotope analysis in such phases is a challenge due to the very low Sr contents of the plagioclases (less than 100 ppm Sr). Therefore, additional efforts are required to improve the reliability of this method.

References

Methane and organic matter as sources for excess carbon dioxide in intertidal surface sands: Biogeochemical and stable isotope evidence

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Reduced carbon is mineralized in marine sediments by microbial activity using predominantly oxygen, sulfate, and metal oxides as electron acceptors. Besides DOC compounds, methane can be oxidized to carbon dioxide. Both, CO₂ and CH₄ are strong green-house gases that may be liberated from the sediments into the bottom waters or the atmosphere. The partitioning of stable carbon isotopes is useful for the biogeochemical transformations of different C sources and is used here to identify the key reactions in the C-S cycles of intertidal surface sediments. Sediments and pore waters (top 20 cm) from intertidal sands of the back-barrier tidal areas of Spiekeroog and Sylt islands (southern and eastern North Sea) have been investigated on a seasonal base, and are analyzed for a number of geochemical parameters as, for instance, TOC, TIC, DIC, TA, methane, SRR, salinity, pH, sulfate, sulfide, and the carbon isotopic compositions of substrates and products.

Results indicate that DIC is dominated by products derived from organic compounds besides exchange via the sediment-water interface, with bioturbation having important effects. Below reduced sulfidic sediment surfaces, the isotopic composition of DIC down to -40 per mil indicates CH₄ (60 per mil) derived from the oxidation of methane as an important source. These sites promote an energy transfer from the sediments to the bottom waters.

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Weathering over a large range of erosion solid products: Insights from Amazon river depth-samplings

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Continental erosion processes produce dissolved material plus sediments. The latter are heterogeneous in terms of mineralogy, grain size, chemical composition and weathering intensity. Within large rivers, these particles are vertically sorted during their transport to the oceans, following their physical properties and stream hydrodynamics.

In order to take in account this internal variability, we sampled the Amazon along depth profiles, and carried out granulometric and chemical analysis of suspended sediments as well as bedload.

The vertical profiles of suspended sediments concentration increase exponentially downward, and can be explained by a simple sedimentary transport model, based on an equilibrium between sedimentation velocity and bedload turbulent diffusivity. This model allows depth-integrated estimates of Amazon suspended matter fluxes (total and elemental) to the oceans.

Major elements composition, along with microscopic and mineralogic analysis, shows a rather strong evolution from clay-dominated sediments near the surface towards quartz and other silicon-rich minerals downward.

The weathering indexes of Na, K and Ca (as defined by Gaillardet et al. (1999)) in the sediments of the Solimoes river, show respectively a three-fold, two-fold and two-fold increase from the bottom to the surface. In Madeira surface sediments, the apparent depletion in soluble elements is amplified by a factor of two by the granulometric sorting with respect to the integrated weathering index.

The results obtained on the Amazon system are compared with those from the Ganga-Brahmaputra system (Ga by et al., submitted) and are interpreted in terms of weathering/erosion intensities, bedrock lithology and rivers hydrodynamics.

References


Root zone of sheeted dike complex in Oman ophiolite-petrological model

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Recently, IODP (Integrated Ocean Drilling Program) has penetrated in the eastern Pacific Ocean (Hole 1256D) the root zone of the sheeted dike complex (RZSDC). In Oman ophiolites, it is a well exposed horizon ~100m thick between the main gabbro unit and above, the crustal lid (sheeted dikes and lavas). To compare with the IODP hole, a new petro-structural study was conducted in Oman. We explain this complex zone by interference between the magmatic system of the melt lens present in fast spreading ridges, and a hydrothermal system operating at very high temperatures penetrating down to the roof of this lens where it induces successive stages of hydrous anatexis. This results in a crude stratigraphy throughout the RZSDC with doleritic isotropic gabbros evolving upwards in vari-textured, pegmatitic gabbros and trondjhemite intrusions. New melt intrusions from the melt lens proceed through basaltic ‘protodikes’ which are, in the RZSDC, a relay to the overlying sheeted dikes. Injected in gabbros still at solidus temperature, protodikes develop against these gabbros a typical microgranular margin. The following phase diagram constructed for pressure 50MPa, issued from Feig et al., 2006 allows to follow the sequence of formation of the successive magmatic facies described in the RZSDC.

References

Disturbance of the monazite U-Th-Pb chronometer by fluids: A study combining stable isotopes and in situ dating

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The monazite U-Th-Pb chronometer is extensively used to date metamorphic rocks because it is usually considered to be resistant to diffusive Pb loss at temperatures as high as 800°C. However, age perturbations are sometimes documented in monazite grains showing distinct compositional and age domains. The mechanism by which Pb is lost is not well understood. Fluid-assisted recrystallization has been shown to constitute an efficient mean to reset the monazite chronometer in experimental conditions (Seydoux-Guillaume et al. 2002). Whether the same holds true in natural systems remains to be documented.

Here we present in situ U-Th-Pb ages on monazite from foliated pegmatitic veins from highly strained levels of the Central Rhodope metamorphic pile (Greece, Bulgaria), together with oxygen isotopic characterization and 40Ar-39Ar data. U-Th-Pb ages were obtained by (LA)-ICPMS on 8 monazite grains from three samples. In one sample from Bulgaria, the ages are concordant at 35 Ma, and no chemical zonation is observed. Quartz and feldspar have δ18O values consistent with equilibration at high temperatures. Microfabrics in the vein and the host rocks indicate high grade conditions of deformation. In the two other samples, from Greece, monazite grains show distinct chemical domains and yield discordant U-Th-Pb ages ranging from 52 to 36 Ma. Strong oxygen isotope disequilibrium between quartz and feldspar argues for a complex fluid history: high-δ18O fluids first invaded rocks and were followed by low-δ18O fluids at lower temperatures. Low temperature fluid circulation at around 36 Ma is consistent with 40Ar-39Ar dating of both samples at 33-34 Ma (mica plateau ages) and with microfabrics documenting a transition from high grade to greenschist facies conditions of deformation during intense shearing. These data confirm the capacity of fluids in disturbing significantly the monazite chronometer.

References

Uranium isotope ratios determined by MC-ICP-MS and the assessment of total combined uncertainty budgets

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Precise determination of uranium isotopic composition is required in nuclear environmental and geologic studies. Particular applications imply determination of extremely low 234U/238U quantities in the presence of a large excess of 235U and 236U which represent severe sources of interference in determinations of 238U.

A multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS) - Nu Plasma HR - equipped with an ion deceleration filter was applied for rapid and sensitive determination of 234U/238U, 235U/238U and 236U/238U isotope ratios in aqueous samples on a concentration level typical for digested environmental samples. Application of the ion deceleration lens system in Nu Plasma ICP-MS improved significantly the abundance sensitivity and made possible the analysis of 238U/238U isotope ratios in the 10⁻⁸ to 10⁻⁷ range. On the other hand, using the ion deceleration lens for determination of 236U/238U isotope ratios above 10⁻⁵ was found disadvantageous because it might introduce additional uncertainty. Accuracy of uranium isotope ratio measurements by MC-ICP-MS was evaluated by analysis of unknown samples obtained in the frame of a round robin exercise as well as by comparative measurements using sector-field ICP-MS with single ion detector and thermal ionization mass spectrometry (TIMS). Combined uncertainty of measured ratios ranged from 0.17% to 0.20% for 235U/238U, from 1.0% to 1.1% for 234U/238U and from 1.3% to 53% for 236U/238U. The main uncertainty contribution component to the 235U/238U ratio measured by MC-ICP-MS is the uncertainty of the applied isotopic standard. The uncertainty budget for 236U/238U strongly depends on the abundance of 238U. In particular, peak tailing and interference by 235U¹H⁺ ions increased the measurement uncertainty in the case of 236U/238U lower than 10⁻⁷. Nevertheless, accurate determination of 236U/238U isotope ratios as low as 3x10⁻⁸ was possible, which opens new possibilities for tracing this isotopes in environmental samples by using MC-ICP-MS, in particular with respect to its better time-effectiveness and lower labor expenses when compared to other highly sensitive mass spectrometric methods.
Weathering rates from top to bottom in a carbonate environment

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It is generally thought that most of the weathering reactions take place near the surface of the Earth but the contribution from deeper water circulation is less well quantified. Yet, the groundwater fluxes needs to be assessed as a recent study has inferred that up to 20\% of the weathering flux could be coming from the base flow. To address this issue, we have investigated weathering rate in a double-porosity carbonate environment by measuring U-series isotopes from the soil’s surface down to a depth of \(~70\) m to determine the rates of dissolution. The samples we analyzed include soils, drill cores, fracture and matrix fluids. The samples were all analyzed by MC-ICPMS for U and Th isotopes. The solid samples were also analyzed for trace element concentrations by ICP-MS.

The results show quite clearly preferential mobility of U throughout the profile but with a much larger effect in the first meter below the surface. The surface samples show the greatest \(230\)Th excess together with moderate depletion in \(234\)U relative to \(238\)U. Accordingly, the \(230\)Th/\(232\)Th ratios and the relative abundance of mobile trace elements are lower in the surface layers, which can be interpreted by faster dissolution of carbonates near the surface together with an enrichment in residual silicates. In this environment, the dissolution of carbonates can be easily distinguished from silicate dissolution and the dissolution rates results in a net removal of Th (and U). Redeposition of Th derived from the carbonate by adsorption or precipitation in secondary phases is not effective.

The combined \(234\)U-\(238\)U and \(230\)Th-\(238\)U systematics also allows to quantify the relative dissolution rates in the soil horizons compared with deeper horizons in the bedrock. In the surface horizons, the U-series signature can be thought of as being dissolution-dominated while in the deeper layers, it indicates slower dissolution and larger effects of recoil on \(234\)U-\(238\)U systematics. Preliminary modelling suggests that dissolution rates can vary by a factor of 10 faster near the surface (with the slowest rate obtained for a clay-rich cap rock). At depth, there is generally slower dissolution and even reprecipitation of carbonates.

An isotope and PGE perspective on the mantle xenoliths from Marsabit Volcanic field (Kenya Rift)

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PGE and Os isotopes have been determined in 14 well-characterized spinel peridotite xenoliths from the Marsabit volcanic field (Kenya Rift) pertaining to 3 different groups previously distinguished based on their textural characteristics (porphyroelastic (I) and recrystallized (II) spl-lherzolithe and porphyroelastic hazburgites (III) (Kaeser \textit{et al.}, 2006).

The overall total PGE contents of Marsabit xenoliths (Total PGE between 14 and 32 ppb) shows a rather restricted range.

Whether coarse-grained, recrystallized, deformed, virtually anhydrous or modally metasomatized, all peridotites have Pd-depleted PUM-normalized PGE patterns probably inherited from an old (archean?) partial melting event. This is confirmed by the crude correlation existing between the Ol or Cpx modal content of the rocks and their total PGE, Pd/Ir ratio or Al\textsubscript{2}O\textsubscript{3} whole rock content. However the shape of PGE patterns can greatly vary between or within different peridotite groups and probably reflects differing recent magmatic history and/or ancient metasomatism.

Calculated Re depletion ages indicate 2 possible melting events around 2 Ga (Archean – for Group III) and around 650 Ma (Panafrican? for Group II and III). Group I consistently gives future ages and its Os isotope characteristics suggest some addition of radiogenic Os (either through metasomatism or mingling between peridotite and pyroxenite).

Preliminary Sr-Nd-Pb isotopic data show that the most refertilized lherzolithes (Group II and III) display unradiogenic signatures (cpx, or wholerock) incompatible with plume-type metasomatism enrichment.

References
High biological productivity takes place on the Kerguelen Plateau in the Indian sector of the Southern Ocean known to be a HNLC region. Natural iron fertilization is suspected in that area. One goal of the KEOPS project is to understand the mechanisms controlling iron fertilization. Ra isotopes that are produced in the sediment and diffuse in the water column may be a good analogue for tracing the input of sedimentary iron and its fate on the Kerguelen Plateau. We measured all four radium isotopes during KEOPS (\(^{224}\text{Ra},\) \(^{223}\text{Ra},\) \(^{228}\text{Ra},\) and \(^{226}\text{Ra}\)) in seawater in order to provide information on the water mass pathways on the Kerguelen plateau. We also measured dissolved Ba concentrations, Ba being a chemical analogue of Ra. Here we report \(^{226}\text{Ra}\) activities and \(^{226}\text{Ra}/\text{Ba}\) ratios obtained during repeated visits of station A3 located in the middle of the bloom area on the Kerguelen Plateau. We compare these data to those obtained outside the plateau, in the HNLC area. We observe a pronounced temporal variability in the \(^{226}\text{Ra}\) activities and \(^{226}\text{Ra}/\text{Ba}\) ratios found at station A3 suggesting that the dynamic system has changed during the repeated visits or that biological activity significantly impacts \(^{226}\text{Ra}\) activities and \(^{226}\text{Ra}/\text{Ba}\) ratios.

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**Geochemistry of primary magmas of St Vincent (Lesser Antilles Arc) tracked by melt inclusions**

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The Lesser Antilles arc volcanism results from the subduction of the Atlantic plate beneath the Caribbean plate. Lavas are dominantly andesitic, but MgO-rich basalts are found in the south part of the arc (St-Vincent, Grenade islands). Major, trace elements and isotope geochemistry on whole rocks, as experimental works, suggest that magmas are generated by the melting of a N-MORB type mantle source contaminated by at least two components, involving fluids derived from subducted oceanic crust and sediments. However, the nature and the relative influence of each components and the importance of the crustal contamination are still debated (Macdonald et al., 2000). In order to discriminate the importance of these different contributions, we undertook the analysis of melt inclusions trapped in olivines of basaltic scoriae (MgO> 12.5 wt%) of St-Vincent. Major elements of more than 200 melt inclusions are measured by electron microprobe SX50, and \(\text{H}_2\text{O}, \text{Li, CI, F, } \delta^7\text{Li, } \delta^{11}\text{B, } \delta^{18}\text{O}\) of 50 melt inclusions are determined by SIMS 1270. Chemical and isotopic characterisations point out a broad variability for all the analysed elements. Major elements indicate a differentiation trend, and a second trend with lower SiO\(_2\) and higher CaO than whole rocks. B, CI and H\(_2\)O are variably enriched compared to MORB, \(\delta^7\text{Li}\) values range from -10 to +7‰, \(\delta^{11}\text{B}\) from -16 to +12‰, and \(\delta^{18}\text{O}\) from +3 to +10‰. These variations reflect addition of contaminants. Melt inclusions provide new data which confirm that primary magmas of St-Vincent are generated by melting of a N-MORB type mantle source weakly affected by the addition of fluids derived from the dehydration of AOC and the melting of sediments.

**References**

The Lu-Hf CHUR value

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Lu-Hf and Sm-Nd isotopic systems involve refractory and lithophile elements, so that the composition of Bulk Silicate Earth (BSE) should coincide with that of the Chondritic Uniform Reservoir (CHUR). BSE reference for Lu-Hf was first plotted within the terrestrial Hf-Nd isotopic array [1], and since 1997 lies just below it [2]. This raises questions of a possible hidden reservoir in the terrestrial mantle, or alternatively, a discrepancy with the CHUR parameters employed. Determination of CHUR Lu-Hf is hampered by the ~20% variation in Lu/Hf among the ordinary (OC) and carbonaceous chondrites (CC) analyzed previously [2-4], a contrast with Sm/Nd which varies by only ~3%. The Lu-Hf CHUR parameters were determined from a mean value for OC, mostly petrologic types 4 to 6, plus the two CC, Allende (CV3) and Murchison (CM2), and yielded $^{176}\text{Lu}/^{177}\text{Hf} = 0.0332 ± 2$ and $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772 ± 29$ [2].

We analyzed 20 new chondrites for Lu-Hf and Sm-Nd isotope systematics. These included: (i) thirteen H, L, and LL OC of types 3.0 to 3.8, where their low degree of metamorphism limits the growth of phosphate (main carrier of REE) compared to the equilibrated types 4 to 6 OC; and (ii) seven CC of types 1 to 3 (CI, CV, CO and CK groups). We obtained mean values ($2\sigma$ SE) of $^{176}\text{Lu}/^{177}\text{Hf} = 0.0337 ± 3$, $^{176}\text{Hf}/^{177}\text{Hf} = 0.282802 ± 23$, $^{147}\text{Sm}/^{144}\text{Nd} = 0.1961 ± 6$, and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512629 ± 16$ from the types 1 to 3 OC (n=11) and CC (n=11) from this study (n=18) and [4] (n=4). These values are our best estimates for CHUR and BSE. The CC alone give higher mean values of $^{176}\text{Lu}/^{177}\text{Hf} = 0.0341 ± 4$, $^{176}\text{Hf}/^{177}\text{Hf} = 0.282828 ± 38$, $^{147}\text{Sm}/^{144}\text{Nd} = 0.1966 ± 10$, and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512639 ± 28$. These last values are concordant with the Sm-Nd CHUR parameters that have been widely used since 1980 [5], but CC may not provide the best approximation for BSE.

The $^{176}\text{Lu}/^{177}\text{Hf}$ range obtained from all the types 1 to 3 OC and CC is now constrained to ~4%, similar to Sm/Nd. The mean values of $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ are higher than the previous estimates and reconcile the chondrite composition with the mantle array, removing any need for a hidden reservoir affecting Lu-Hf systematics. The ~20% range of Lu/Hf observed in type 4 to 6 chondrites must reflect metasomatic processes on the OC parent bodies associated with their thermal metamorphism.

References
High-precision U-Pb zircon geochronology: Progress and Potential

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One emphasis of the EARTHTIME project (www.earth-time.org) is understanding the power and limitations of high-precision U-Pb geochronology towards sequencing earth history at high precision. This involves establishing absolute chronologies both for sequences of fossil-bearing rocks and for testing models for astronomical forcing of sedimentation.

In the past decade, progress in imaging and microsampling of zircon domains prior to analysis, pre-treatment using the CA-TIMS method of Mattinson (2005), and the ability to make high-precision isotopic measurements on as little as 1-10 picograms of radiogenic Pb has revolutionized U-Pb geochronology.

With high precision and high spatial resolution has come recognition of previously underappreciated complexities that introduce both internal and systematic errors. These range from intermediate daughter product disequilibria, to distinguishing small amounts of Pb loss from protracted from intermediate daughter product disequilibria, to introduce both internal and systematic errors. These range recognition of previously underappreciated complexities that geochronology.

10 Ma. Integration of U-Pb and 40Ar/39Ar geochronology is necessary to address the above complexities. We are making differentials from simple one-stage mixing by the addition of the time dimension to the composition data. These crystals appear to have shared a considerable portion of their growth histories, with similar cores and growth patterns – up until a point when they diverged greatly, suggesting that crystals in various parts of the magma system record different but related versions of the magmatic volatile story.

References

A high resolution time-sequential record of magmatic volatiles from apatite phenocrysts

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Understanding the time-dependent variation of volatile elements in magmatic systems is essential to the study of the generation, evolution, and eruption of magmas. The mineral apatite is capable of recording volatile variations, commonly incorporating H, F, and Cl as major components, with smaller amounts of C and S usually present. Unlike melt inclusions, which are often difficult to place in a relative temporal context, apatite crystals grow from core to rim (in the absence of resorption) providing a sequential record of volatile changes in the coexisting magma.

Using Secondary Ion Mass Spectrometry (SIMS), we have analyzed H, F, and Cl in several apatite phenocrysts from the Cerro Galan ignimbrite, Argentina. For each crystal, a traverse of individual spots was performed on polished sections in the C-axis direction. A 10nA, ~20µm O primary beam was rastered ~20µm and used to sputter positive secondary ions: 1H, 12C, 19F, 28Si, 31P, 37Cl and 43Ca. Ions with initial kinetic energies of 75±20 eV, originating from the central 9µm region, were allowed into the mass spectrometer.

Traverses of 40-60 spots at 4-7µm spacing were obtained on several crystals. Most apatite phenocrysts contain homogeneous OH-rich cores (~4000ppm), mantled with oscillatory but generally lower OH concentrations. Chlorine data describe apparently related patterns, with homogeneous cores (~5000ppm) and oscillatory rims (~ up to 1500ppm), with similar patterns observed in several crystals. Fluorine variations are less well-resolved relative to analytical uncertainties, but are generally increasing towards the rim and inversely related to OH.

Relationships between OH, F, and Cl are most easily explained as parametric functions of relative time as defined by core-to-rim stratigraphy. Knowing volatiles as a function of time allows us to convert cryptic clouds of data into a history of the growth of this crystal, which give us clues as to the volatile evolution of the magma. Apatite core regions represent either growth in a stable magma chamber or residence in a stable magma chamber where any pre-existing volatile variations were homogenized. After this period of relative quiescence, these apatite crystals experienced cycles of magma mixing and or degassing – cycles which can only be differentiated from simple one-stage mixing by the addition of the time dimension to the composition data. These crystals appear to have shared a considerable portion of their growth histories, with similar cores and growth patterns – up until a point when they diverged greatly, suggesting that crystals in various parts of the magma system record different but related versions of the magmatic volatile story.
Early Lunar Differentiation and the Earth-Moon Connection

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Coupled $^{146}$Sm-$^{142}$Nd ($T_{1/2}=103$ Myr) and $^{147}$Sm-$^{143}$Nd ($T_{1/2}=103$ Gyr) systematics were analyzed on lunar samples that span the range of source compositions created in the early lunar differentiation event (ferroan anorthosites, high-Mg suite norite, KREEP, low- and high-Ti basalts). If fit with a single isochron, the data agree with previous suggestions of a ~200 Ma duration for lunar magma ocean (LMO) crystallization [1, 2], but with an initial $^{142}$Nd/$^{144}$Nd 20 ppm higher than chondritic, essentially the same as measured for terrestrial rocks [3]. Excesses in initial $^{142}$Nd ($\varepsilon^{142}$Nd = 0.27 to 0.38 relative to O-chondrites) in crustal rocks 60025 and 78236, coupled to positive initial $\varepsilon^{143}$Nd, measured in most of crustal samples, indicate that they derive from a source strongly depleted in light rare earth elements ($^{147}$Sm/$^{144}$Nd -0.23-0.24). The source reservoir for lunar crustal rocks thus would be the early depleted reservoir (EDR) formed on Earth during the first tens of Ma of Solar System history ($^{147}$Sm/$^{144}$Nd = 0.209) [3]. This geochemical signature cannot be reconciled with the current lunar magma ocean (LMO) models that suggest that the crust formed after approximately 70% crystallization of an LMO that initially had chondritic relative REE abundances. Two alternatives exist: 1) The lunar crust formed by post-magma ocean remelting and diairism of LREE-depleted cumulates from the lunar interior [see also 4]. A two-point isochron for the crustal rocks provides an age of 64 (+97, -58) Ma after the beginning of Solar System formation or 4.50 Ga. If the thick crust is a secondary product, there is no reason to invoke its insulating qualities for explaining a delay of the LMO crystallization. Fitting the Sm-Nd data for the different groups of lunar samples (crustal rocks, low-Ti and high-Ti basalts) independently allows rapid (~60-120 Ma) evolution of the LMO at the limit of lifetime of $^{182}$Hf [5, 6]. 2) If all the lunar igneous rock groups are considered together and related to crystallization of a single LMO, then the Sm-Nd data suggest a prolonged (~200 Ma) LMO crystallization interval and a bulk LMO with LREE-depleted character in common with the EDR of the Earth. This strengthens the Earth-Moon connection by requiring formation of the Moon from an already differentiated Earth.

References
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Release of C-14 from a closed final repository for low-level radioactive waste to the biosphere

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Introduction
The contribution of C-14 to radiation exposure in the biosphere from a repository for low-level radioactive waste can be significant. The pathways and processes of C-14 relevant to its release from a closed final repository for low-level radioactive waste are under investigation. Because a conservative approach may lead to undue overestimation of the potential radiation exposure, a more realistic approach is outlined.

Results
A more realistic approach includes:
- a reference scenario including technical measures
- the inventory of C-14 with specification
- geochemical reactions in all compartments
- gas generation
- gas pathways
- isotope exchange reactions
- sorption, precipitation
- exposure scenario

Figure 1: Distribution of C-14

Summary
At the present level of refinement, a more realistic assessment of the release of C-14 after closure of a final repository for low-level radioactive waste in a mine shows a significantly lower release of C-14 than previously used conservative approaches. This assessment predicts a significantly lower potential radiation exposure, thus increasing the safety margins to federal limits.

With this approach it is possible to demonstrate that a repository in a mine complies with the ALARA (as low as reasonably achievable) principle, thus facilitating licence approval. Conservative approaches are unable to demonstrate compliance other than with the limits for radiation exposure.
Os-He isotope systematics of Iceland picrites: Evidence for a deep origin of the Iceland plume

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Recent work on the origin of the Iceland hotspot suggests that it may result from upwelling upper mantle material rather than a deep plume. To constrain the depths of origins of Iceland mantle sources, Os and He isotope systematics were obtained on a suite picrites that span the compositional range observed within the neovolcanic zones.

The Iceland picrites display a range in $^{187}$Os/$^{188}$Os from 0.1297 to 0.1381 (gOs = 0.0 to 6.5) and uniform $^{186}$Os/$^{188}$Os of 0.1198375±32 (2s). The value for $^{186}$Os/$^{188}$Os is within uncertainty of the present-day value for the primitive upper mantle of 0.1198398±16. These Os isotope systematics are best explained by ancient recycled crust or melt enrichment in the mantle source region. If so, then the coupled enrichments displayed in $^{186}$Os/$^{188}$Os and $^{3}$He/$^{4}$He from lavas of other plume systems must result from an independent process, the most viable candidate at present remains core-mantle interaction. While some plumes with high $^{3}$He/$^{4}$He, such as Hawaii, appear to have been subjected to detectable addition of Os (and possibly He) from the outer core, others such as Iceland, appear to have not.

A positive correlation between $^{187}$Os/$^{188}$Os from 0.1297 to 0.1381 and $^{3}$He/$^{4}$He from 9.6 to 19 Ra in Iceland picrites is best modeled as a two stage process. In stage 1, 500 Ma or older ancient recycled crust is mixed with a primitive-like mantle for Os and He systematics, creating a hybrid source region. In stage 2, the hybrid source mixes with the convecting MORB mantle during ascent and melting. This multistage mechanism to explain these isotope systematics is consistent with ancient recycled crust juxtaposed with more primitive, relatively He-rich mantle, in convective isolation explaining the $^{3}$He/$^{4}$He signature in Iceland lavas.

The lack of a resolvable seismic signature of conduit-like plume flow under Iceland at some depths may result from sporadic flow of material from depths near the core-mantle boundary, consistent with recent dynamical models (Farnetani and Samuel, 2005, GRL 32, L07311).

Modelling of phase diagrams for migmatitic paragneisses of the Epupa Complex, NW Namibia

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Mesoproterozoic (1.37-1.32 Ga) migmatitic metapelites and metagreywackes (Orue Unit) of the Epupa Complex, NW Namibia, record several melt-producing reactions. Partial melting of the paragneisses and the evolution of their mineral assemblages can be adequately interpreted by calculated phase diagrams in the Na2O-CaO-K2O-FeO-MgO-Al2O3-SiO2-H2O (NCKFMASH) system. The development of the different observed mineral assemblages reflects variations of the bulk-rock composition but also indicates regional differences in the metamorphic grade between the various structural parts of the Orue Unit. The evolution of the mineral assemblages is interpreted in terms of simple heating-cooling P-T paths at different crustal levels: early mineral assemblages of Bt-Sil-Qz in the paragneisses and of Bt-Qz in the metagreywackes, preserved as mineral inclusions in peak-metamorphic porphyroblasts, break down via melt-producing reactions to higher-temperature garnet-bearing and/or cordierite-bearing assemblages under upper-amphibolite facies conditions. According to the calculations, melting occurs at uniform temperatures of 650-700°C, close to the thermal peak of metamorphism. The relatively Fe-rich (XMg: 0.36-0.28) cordierite-bearing paragneisses with or without garnet which are restricted to the northern part of the study area equilibrated at peak-temperatures of 700-750°C and low pressures of 3-4 kbar as constrained from geothermobarometry and calculated mineral isopleths. The slightly more magnesian Grt-Bt-Sil greisses (XMg: 0.43-0.32) which are exposed in the southern part of the study area record similar peak-temperatures (670-750°C) but higher pressures of 5.5-6.5 kbar. Retrograde back-reactions between restite and in situ crystallising melts are recorded by the replacement of garnet by Bt-Sil (Al-rich samples) and/or Bt-Ms intergrowths (Al-poor samples).

The P-T axes are interpreted to result from a regional scaled thermal perturbation of the normal geotherm in mid-to-upper crustal levels induced by magmatic accretion of mantle-derived melts. This process is presumably related to the emplacement of the c. 1.38 Ga anorthositic Kunene Intrusive Complex. A contact metamorphic overprint is restricted to a narrow reaction zone along the margin of the Kunene Intrusive Complex and is recorded by highly aluminous metapelitic Grt-Crd-Sil hornfelses which equilibrated at peak-conditions of 700°C and 5-6 kbar.
Bedrock to soil: Earth’s weathering engine

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Seawater chemistry responds to changes in terrestrial weathering over time in response to the forcing functions of tectonism, climate, and anthropogenic activity. Many researchers have attempted to read the effects of weathering solute fluxes in sediments in the rock record. For example, the Sr isotope record in marine limestones has been interpreted with respect to continental weathering fluxes due to changes in Earth’s weathering engine. Our ability to predict such fluxes forward in time is limited because of difficulties in calculating weathering fluxes and the rates of formation of soils on weathering or eroding bedrock.

Weathering solute fluxes are recorded in many areas as chemical and textural profiles imprinted on regolith. These profiles, when observed on noneroding regolith in the absence of significant deposition, propagate downward as the regolith pile thickens with time. Such a profile can be described as a quasi-stationary state. If the rate of erosion of such regolith is increased larger than the weathering advance rate, the regolith thickness must decrease with time. For such a condition, the regolith eventually disappears unless some process accelerates the weathering advance rate. During weathering, as regolith thins, the rate of weathering advance can increase because porefluid chemistry at the bedrock interface becomes more corrosive. Thus, the rates of erosion and weathering advance can be coupled through porefluid chemistry, maintaining regolith thickness at steady state values. Solute fluxes and regolith profiles can be predicted for simplified lithologies under these assumptions.

The weathering advance rate is not, however, observed to be the same when calculated at the watershed, soil profile, and hand specimen scales. Several phenomena contribute to this observation. Approaches will be described to understand the prediction and modeling of weathering advance rates across scales as well as the controls on weathering solute fluxes.

The role of impurity doping during oriented α-alumina-on-mullite growth

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This work presents a recent case study on the benefits of impurity doping for producing unique ceramic microstructures which are difficult to process by other means.

Topotactic orientation relationships between thin α-alumina (00•1) platelets and Czochralski grown 2/1 mullite substrates are discussed in the light of annealing experiments of 2/1 mullite (001), (010) and (001) single crystals sections in the two-phase regime <mullite plus α-alumina> (1200-1650°C) in different atmospheres (dry vs. wet air) at normal air pressure.

Thermal decomposition of 2/1 mullite gives rise to the simultaneous formation of α-alumina platelets and an initially siliceous glassy phase completely wetting the platelets. Its chemical composition is shifted to a Na-Mg-Ca bearing aluminosilicate composition via uptake of network modifying cations from external impurity sources (kiln furnace material, alumina reaction tube) during the annealing experiments. It is this glassy phase modified via impurity doping which filled the mullite dissolution paths driven forward by the platelets and provided a build-in flux for platelet growth.

In wet annealing experiments employing higher gas velocities and temperatures the glassy phase is lost due to substantial silica and alumina volatilization. With no more sink for impurity doping provided, the unique corundum-on-mullite microstructure gives way to complex etching patterns of the mullite surfaces due to selective corrosion by the water vapor-rich atmosphere.
Bacterial interactions with solid substrates: Applications for microbial fuel cells, carbonate surfaces and metal oxide reduction

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*Shewanella oneidensis* MR-1 is a flexible microorganism that can use a broad range of electron acceptors, including several solid substrates. MR-1 reduces Mn(IV), Fe(III) oxides, impacts the surface morphology of carbonates, and produces power in microbial fuel cells. A microbial fuel cell (MFC) utilizes the catalytic action of bacteria to convert the chemical energy of organic or inorganic compounds into electrical energy. MR-1 catalyzed power generation and metal oxide reduction appears to be strongly dependent on how these bacteria are grown, and their ability to produce and employ specialized cytochromes for extra-cellular electrons transfer. These cytochromes are hypothesized to directly pass electrons to substrates via the cell membrane and extra-cellular appendages i.e. nanowires. MR-1’s ability to change the chemistry of its local environment may also play a role in changing the surface characteristics of carbonate and other substrates during attachment. We study interactions between MR-1 and substrates with a multifaceted combination of experimental and theoretical methods. Different MR-1 deletion mutants were generated to explore the role of cytochromes in power production and metal-oxide reduction. The results show that a few key cytochromes play a role in all of the processes explored, but that their degree of participation in each process is very different.

Characterisation of Mo and V interactions with ferrihydrite as an analogue for deep-sea hydrothermal plumes processes

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In deep-ocean hydrothermal plumes molybdenum and vanadium are known to be readily scavenged by freshly formed iron oxihydroxides nanoparticles (i.e., ferrihydrite, FH) forming during the oxidation of hydrothermal vent fluids via mixing with seawater. These scavenging processes have important implications for the cycling and budget of Mo and V in the ocean, yet, no quantitative information about the mechanisms that govern the interaction between FH and Mo or V are available.

In order to study the mechanisms involved, poorly ordered ferrihydrite nanoparticles were characterised for their particle size, crystallinity and surface charge (point of zero charge = 7.96). Furthermore, the influences of sorbed inorganic carbon species, of co-precipitated Mo or V, and of ionic strength (0 - 1 M) on the ferrihydrite surface charge were studied.

The comparison between adsorption and co-precipitation for ferrihydrite and Mo or V will be discusses based on differences in the maximum uptake capacities from kinetic and thermodynamic approaches. For the first time, maximum sorption capacities of 1.32mmol Mo/g FH and 1.79 mmol V/g FH were derived, indicating that both metals have a high binding affinity for the FH surface. Interestingly, Mo-edge X-ray absorption spectroscopic measurements of the bonding environment of Mo sorbed on-or co-precipitated with FH showed no difference in Mo speciation between the adsorbed or the co-precipitated system (tetra coordinated Mo with Mo-O first shell bond distances of 1.76 Å in both cases). These results provide evidence that in deep-sea hydrothermal plumes the chemistry of molybdate and vanadate is strongly controlled by the presence of and interactions with neoformed FH nanoparticles.

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Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is an analytical tool for surface analysis. Applying ToF-SIMS the impact of primary ions leads, among others, to the desorption of secondary ions that are characteristic for the composition of the sample’s surface. These secondary ions are mass separated and detected by a Time-of-Flight analyzer.

ToF-SIMS offers brilliant imaging options as it is possible to focus the primary ion beam and to raster it over the surface of the sample: The intensity of each detected secondary ion in each rastered pixel can be displayed according to a colorscale. Thus, information on the distribution of elemental as well as organic chemical components can be gained.

Whereas most inorganic components can already be analyzed routinely by this technique ToF-SIMS has developed into a mature technique for the characterization of biomaterials. Nevertheless, imaging applications in this area have been sparse due to the fact that the achievable lateral resolution is not only a function of the primary beam diameter but also of the achievable secondary ion yields (i.e. the number of generated secondary ions per impacting primary ion) of the respective materials. Up to a few years ago typical values for the lateral resolution routinely obtained were in the order of some micrometers using monoatomic primary ion sources. This value can be improved tremendously using recently developed polyatomic primary ions: Just as well as their monoatomic counterparts these projectiles can be focussed down to 50 nm but – more importantly – show a remarkable enhancement of secondary ion yield for molecular secondary ions. Therefore, organic imaging well in the sub-μm range now becomes possible as it could already be shown for a number of samples, e.g. in the field of biochemistry and pharmacetics.

This paper will show the state-of-the-art on ToF-SIMS imaging of biomaterials. Starting with an overview on the general principle of the technique it will focus on the possibilities and limitations regarding the analysis of substances and samples of interest for biogeochemistry.

Petrogenesis and geochronology of jadeitites from the Cycladic blueschist belt, Greece

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Jadeite is a relatively rare rock type which is usually found in association with high-pressure/low temperature rocks and serpentinites in subduction zone settings. The formation of this rock type is yet not fully understood but precipitation from aqueous fluids or fluid-assisted metasomatic alteration of a pre-existing rock represent the most plausible petrogenetic concepts (Harlow & Sorensen, 2005). In the Cycladic blueschist belt jadeitites have been recognized as minor constituents of eclogite- to epidote blueschist-facies mélangé sequences on the islands of Syros, Tinos and Andros. These jadeitites commonly are zircon-bearing and thus are suitable targets for U-Pb geochronological studies. Correct interpretation of zircon ages requires in-depth understanding of the jadeitite-forming process. In order to unravel the origin of these occurrences, we have initiated a study that combines field observations with petrological, geochronological and geochemical aspects, including trace element compositions of zircon.

Preliminary mass balance calculations indicate substantial metasomatic addition of Na to meta-igneous and meta-sedimentary mélangé blocks on Syros. These observations are consistent with experimental results which show that Na concentrations can be considerable in subduction zone fluids (Topper and Manning, 2004). It is possible that these Na-rich fluids were also important for jadeitite formation.

New ionprobe ⁹²⁹⁰⁶Pb/²³⁸⁰⁶U results for two samples from Syros yielded weighted mean averages of 80.6 ± 1.7 Ma and 82.0 ± 2.1 Ma, respectively. Two samples from Tinos provided ⁹²⁹⁰⁶Pb/²³⁸⁰⁶U ages of 82.3 ± 1.7 Ma and 78.4 ± 1.8 Ma. These results further corroborate the geological significance of a previously reported Cretaceous age group for mélangé blocks. Work in progress aims to document unambiguously the jadeitite- and zircon-forming process and to link U-Pb ages to a specific stage in the evolution of this rock type.

References
Molecular fossils and early life

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Life in the Precambrian was dominated by bacteria and archaea, organisms that rarely leave diagnostic cellular remains in the fossil record. However, hydrocarbon biomarkers, the molecular fossils of natural products such as lipids and pigments, can yield a wealth of information about Precambrian ecosystems. Biomarkers often retain the diagnostic carbon skeleton of their biological precursors and may survive in sedimentary rocks for hundreds of millions of years. Many biomarkers are diagnostic for specific microbial groups such as methanogens, methanotrophs or phototrophic bacteria and, thus, may give information about ancient biodiversity. For instance, biomarkers discovered in mudstones that were deposited in a seaway in northern Australia 1,640 Ma ago describe a marine habitat that was Earth history. In this ancient sulfidic marine basin, eukaryotic life responded to massive glaciations in the Neoproterozoic. However, there is a major obstacle that hampers the potential biomarkers produced by microorganisms, even if those 99% of microorganisms that can not yet be cultured may survive in sedimentary rocks for hundreds of millions of years. Many biomarkers are diagnostic for specific microbial groups such as methanogens, methanotrophs or phototrophic bacteria and, thus, may give information about ancient biodiversity. For instance, biomarkers discovered in mudstones that were deposited in a seaway in northern Australia 1,640 Ma ago describe a marine habitat that was fundamentally different from ecosystems observed later in Earth history. This ancient sulfidic marine basin, eukaryotic algae were either insignificant or absent, and primary production was dominated by phototrophic green and purple sulfur bacteria. Generally, biomarkers could answer outstanding questions about Precambrian ecology and evolution, such as how ecosystems responded to the oxygenation of the atmosphere ~2.4 billion years ago or how life responded to massive glaciations in the Neoproterozoic.

However, there is a major obstacle that hampers the application of biomarkers as palaeoenvironmental proxies: the incomplete knowledge of the lipid biosynthetic capacity of living organisms. According to some estimates, less than 1% of microorganisms can be isolated from the environment and grown in pure culture, and the biomarker content of these uncultivated microbes remains almost always unknown. Detecting and describing the lipids and pigments produced by those 99% of microorganisms that can not yet be cultured would boost the value of biomarkers extracted from ancient rocks.

This great challenge might be solved in the coming decade by combining lipid research with environmental genomics and microbial community proteomics. Of particular interest will be studies of communities where it is possible to reconstruct nearly complete genomes, proteomes and lipid profiles of dominant microorganisms taken directly from modern environments without cultivation. These genomes will be screened for genes involved in lipid and pigment biosynthesis and matched with corresponding enzymes and lipids detected in the same sample. In addition to defining the diversity of as yet unknown branches of the tree of life, this will contribute to new understanding of the phylogenetic distribution of potential biomarkers produced by microorganisms, even if they evade isolation. The intricate knowledge of the lipid biosynthetic machinery of present ecosystems will then serve to elucidate new biomarkers and biomarker patterns in ancient sedimentary rocks.

Synthesis, crystal structure and application of compounds with Copiapite- and Voltaite structure

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Voltaite is a three-dimensional polymerization of complex octahedral-tetrahedral chains with K in located in the interstices [1] with the following composition [2]:

\[ M^{2+}_{2}(OH)(H_2O)_4(SO_4)_3 \cdot 12H_2O \]

M^{2+}: K, Rb, NH₄, Ti, Li
M^{3+}: Mg, Mn, Fe, Co, Zn, Cd
M^{3+}: Fe
M^{2+}: Al, Fe

In the copiapite-group minerals, corner-sharing [M₂(TO₄)₂Ø₂] clusters link through additional tetrahedra to form [M₄(TO₄)₃Ø₂] chains along [101], which are linked together by hydrogen bonds involving unconnected \{Fe²⁺(H₂O)₀\}octahedra and interstitial water groups [1]. The general chemical formula of the copiapite group minerals is [3]:

\[ M^{2+}_{2}(OH)(H_2O)_3(SO_4)_3 \cdot (M^{2+}(H_2O)₀\cdot(H_2O)_6 \]

M^{2+}: Na⁺, K⁺, Cu²⁺, Mn, Mg, Zn, Al, Fe⁴⁺, Fe³⁺, Al³⁺

Synthesis and Results

Voltaite minerals can be synthesized by reaction of metalsulfates and sulphuric acid in an aqueous solution. The crystallisation process takes place at a temperature of 80°C.

Copiapite can be synthesized by the method developed by MAJZLAN [4] and SCHARIZER [5].

The phase identification and characterisation is done by X-ray diffraction, thermogravimetry, scanning electron microscopy and IR-spectroscopy.

Conclusions

The improvement of the synthesis and the investigation of the capacity of reaction under changing conditions of solubility and stability is the intent of the investigation.

The high ability of the exchange of cations indicates a possible use in agriculture, as a water binder or as a short time storage mineral, which will be investigated.

References

Comparisons between fluoride and hydroxide incorporation in nominally anhydrous and fluorine-free mantle minerals.

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The importance of water to the behaviour of the mantle is now widely recognised. A substantial body of data on the solubility of water in nominally anhydrous minerals has been obtained, and a range of constraints on the distribution of water in the mantle have been proposed. In contrast, the solubility of fluoride in nominally fluorine-free minerals (NFFMs) and the consequences for the global fluoride budget, the effects of fluoride on mantle properties and volatile recycling in subduction zones are all completely unexplored. Very few measurements of the F concentration in NFFMs have been reported (Hervig and Bell, 2005).

In this study, the solubility of fluoride in NFFMs was determined under shallow mantle conditions, by equilibrating forsterite and enstatite with fluorides, fluoro-clinohumite or fluorspar rich silicate melts. Experiments were performed in piston-cylinder apparatus at pressures of 1-2 GPa and 1350-1600°C, and the phases present in the quenched samples were determined using SEM and EPMA. The concentration of F in olivine was measured using EPMA with a beam current of 100-200nA and an accelerating voltage of 15-20 kV.

Extraordinarily high solubilities up to 0.45 wt% F have been observed in olivine in the system Mg₃SiO₄-MgF₂. There is no apparent correlation between F and Mg concentrations in the olivine, implying that the high F concentrations are not simply due to inclusions or lamellae of MgF₂ or clinohumite. The fluoride solubilities observed in the Mg₃SiO₄-CaF₂ and Mg₃SiO₄-NaF systems are lower, for reasons which will be discussed. 19F NMR and TEM studies are underway in order to definitively establish whether the high apparent solubility of F in forsterite is influenced by the incorporation of clinohumite lamellae in the structure, or is entirely associated with point defects such as oxygen vacancies.

The implications of a high solubility of F in NFFMs in the mantle could be wide ranging. For example the low recycling efficiency for F in subduction zones (Straub and Layne, 2003), could be explained by retention of F in NFFMs rather than by incorporation in hydroxyl-bearing minerals such as amphibole and serpentine. The differing partitioning and diffusion behaviour of OH and F imply that measurements of both F and OH concentrations in mantle-derived rocks could help constrain the mantle water cycle.

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Water in the mantle: The effect of olivine and orthopyroxene composition and fO₂

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Hydroxyl defects dissolved in olivine and orthopyroxene dramatically affect the physical, chemical and mechanical properties of the Earth’s upper mantle. Understanding the processes governing the incorporation of these species is also essential before the total hydrogen contents of the Earth can be constrained. Here, we investigate hydroxyl speciation and solubility in both natural and experimentally re-equilibrated single crystals using polarised IR spectroscopy.

Our IR spectra demonstrate that the particular hydroxyl defects dissolved in olivine and orthopyroxene are strongly influenced by sample chemistry and experimental fO₂. As a result, extreme caution must be exercised when developing models for solubility in both these phases in the upper mantle, particularly if models are based on data extrapolated from samples synthesised in chemically simple systems and/or experiments conducted under thermodynamic regimes not relevant to mantle conditions.

Experiments on olivine and orthopyroxene crystals from subduction-related, amphibole-bearing Ichnionemagata xenoliths show that hydroxyl solubility in both phases increase with pressure and temperature. However, if all other variables remain constant (P, T, and aSiO₂), the effect of fO₂ on hydroxyl solubility in olivine contrasts sharply with orthopyroxene. Water contents in olivine crystals re-equilibrated at QFM and QFM -4 decrease from 65 to 50 ppm respectively, whilst the concentration in coexisting orthopyroxene increases from 550 to 640 ppm. Partitioning of hydrogen between these two phases will, therefore, vary as a function of oxidation state in the upper mantle.

Comparing spectra for a whole range of experimentally re-equilibrated samples with those in natural phases from Ichnionemagata demonstrates that hydroxyl defect species and concentrations dissolved in natural crystals of olivine and orthopyroxene were inherited at near water-saturated conditions, similar to those of major element re-equilibration in the upper mantle (1.5 GPa, 950°C, QFM, enstatite buffered aSiO₂). Both the hydroxyl stretching modes and dissolved water contents are reproduced in the experimental samples. Water solubilities are lower than current solubility models would suggest, but do not appear to be the result of low pressure equilibration with the host magma during ascent.
Biologically-mediated weathering of minerals from nanometre scale to environmental systems

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The Weathering Science Consortium is a multi-disciplinary project that aims to create a step change in understanding how biota control mineral weathering and soil formation (http://www.wun.ac.uk/wsc). Our hypothesis is that rates of biotic weathering are driven by the energy supply to the organisms, controlling their biomass, surface area of contact with minerals and their capacity to interact chemically with minerals. Symbiotic fungal mycorrhiza of 90% of plant species are empowered with an available carbohydrate supply from plants that is unparalleled amongst soil microbes. They develop extensive mycelial networks that intimately contact minerals, which they weather aggressively. We hypothesise that mycorrhiza play a critical role through their focussing of photosynthate energy from plants into sub-surface weathering environments.

Our work identifies how these fungal cells, and their secretions, interact with mineral surfaces and affect the rates of nutrient transfer from minerals to the organism. Investigating these living systems allows us to create new concepts and mathematical models that can describe biological weathering and be used in computer simulations of soil weathering dynamics. We are studying these biochemical interactions at 3 levels of observation:

1. At the molecular scale to understand interactions between living cells and minerals and to quantify the chemistry that breaks down the mineral structure
2. At the soil grain scale to quantify the activity and spatial distribution of the fungi, roots and other organisms (e.g. bacteria) and their effects on the rates at which minerals are dissolved to release nutrients
3. At soil profile scale to test models for the spatial distribution of active fungi and carbon energy and their seasonal variability and impact on mineral dissolution rates.

A geochemist’s view of environmental science at the molecular level

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Molecular Environmental and Interface Science (MEIS) has evolved over the past two decades in response to the need to understand the speciation and properties of environmental contaminants at the molecular level and the chemical and biological processes at environmental interfaces that control speciation and properties. This highly interdisciplinary field has grown rapidly and is making increasing use of a sophisticated array of instrumentation and major user facilities. Synchrotron radiation sources and the micro-structural, micro-compositional, surface-sensitive, and spectromicroscopy techniques they have enabled are having an increasing impact on our ability to determine the speciation, spatial distribution, and phase association of important heavy metal, metalloid, and xenobiotic organic contaminants in complex environmental samples. In addition, studies of model systems under controlled laboratory conditions are providing fundamental insights about the factors controlling chemical reactivity at environmental interfaces, where much of chemistry of the natural environment occurs. In this talk I will review some of these factors, including defect density, cooperative effects among adsorbate molecules, surface structure, solid variables such as the isoelectric point, solution variables such as pH, and coatings of organic matter and microbial biofilms on mineral surfaces. I will also discuss recent synchrotron-based studies by members of my research group and members of the Stanford Environmental Molecular Science Institute of the structure of bulk water, uranium speciation in the vadose and groundwater zones at Hanford, WA, and the reactivity of nanoparticles of biogenic UO₂(s) and hematite with respect to aqueous Zn(II). Finally, I will offer some thoughts on the future of MEIS following the introduction of hard x-ray free electron lasers.
Speciation of mercury in mining environments

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Hg, in its methylated form, is one of the most toxic contaminants in the environment and is also one of the most highly biomagnified contaminants in aquatic ecosystems. Hg in various chemical forms enters the environment from a number of activities, including Hg mining, historic gold mining, and gaseous emissions from coal-fired power plants and crude oil refineries. For example, 90-100 lbs/d of Hg was released into the local environment from individual kilns used for roasting cinnabar ore during operations of the New Almaden and New Idria Hg mines in N. California over a sustained time period, and about 3,000 lbs/y of Hg is released through gaseous emissions into the San Francisco Bay area from five crude oil refineries in the north Bay. Key questions concerning Hg are what are its most common chemical forms, what is the potential bioavailability of Hg in its various forms, and in what chemical forms is it transported from mining environments, where it is typically present as cinnabar (HgS(hex)) or metacinnabar (HgS[cubic]). Over the past few years, we have conducted a number of field- and laboratory-based studies to address these questions. Using a combination of column experiments, XAFS spectroscopy, and TEM, we have found that nanoparticles of cinnabar and metacinnabar are likely forms transported from Hg mines in the California Coast Range. Such nanoparticles are also found in the placer gold deposits in the Sierra Nevada foothills of N. California. We have also found that certain Hg minerals result in higher evaporation of gaseous Hg than others, and that oxidized and reduced forms of S and Fe affect the reactivity of Hg and cause its desorption from goethite. In addition, we have found that a bacterial consortium in the New Idria acid mine drainage can enhance the solubility of HgS by ≈10³⁹. The impact of these processes on the cycling of Hg in mining environments will be discussed.

NEO-sample return mission

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Small bodies, as primitive left-over building blocks of the solar system formation process, offer clues to the chemical mixture from which the planets formed some 4.6 billion years ago. Near Earth Objects (NEOs) representative of the population of asteroids and dead comets are thought to be similar in many ways to the ancient planetesimal that accreted to form the planets. NEOs are interesting and highly accessible targets for scientific research. The chemical investigation of NEOs having primitive characters is thus essential in the understanding the planetary formation. They carry records of the solar system’s birth and early phases and the geological evolution of small bodies in the interplanetary regions. Moreover, collisions of NEOs with Earth pose a possible hazard to present life and, additionally, they could have been one of the major deliverers of water and organic molecules on the primitive Earth playing an active role in the origin of life on Earth. For all these reasons the exploration of these objects is particularly interesting. A sample return mission to a NEO and its scientific objectives will be here presented.
Evidence of ancient water on Mars by the APXS onboard the Mars Exploration Rover Opportunity

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In January of 2004, one of the two Mars Exploration Rovers (MER) landed in Meridiani Planum [mission details in Squyres et al., 2006], a site primarily selected for its hematite signature as observed from orbit by TES [Christensen et al., 2000]. As in most terrestrial cases, hematite is formed by aqueous activities and under oxidizing conditions, which makes hematite a tracer for (ancient) water episodes. Lag deposits of iron- and hematite-rich spherules were observed along the rover’s traverse by the Alpha Particle X-ray Spectrometer (APXS) [Brückner et al., 2006] and the Mössbauer Spectrometer (MB) [Morris et al., 2006].

The APXS data are used to determine the chemical composition of soil and rock samples; water (hydrogen) cannot be detected due to the applied method but indirect evidences can be derived. Almost all rocks encountered at Meridiani are sulfur-rich sediments [Rieder et al., 2004] making S with up to 12 wt. % a major element. The formation of these sediments are explained by a two-component mixing model of siliciclastic and sulfur-rich end members. Careful inspection of all data obtained during the last three years of APXS operation revealed unique relationships of major and minor element concentrations with S contents. For Si and Al concentrations, a dilution with increasing S contents is observed indicating that these two elements occur only in the siliciclastic end member. Calcium and Fe show no dilution effects with increasing S; constant concentrations are pointing to an occurrence as sulfates and as rock-forming silicates. Besides other phases, ferric sulfates could be detected by the MB [Morris et al., 2006]. Similar concentration relationships were also found for minor elements, such as Na, P, and K. Magnesium shows two different effects: a positive correlation with S for samples from the first 220 sols, pointing directly to Mg sulfates, and a rather constant concentration afterwards (no dilution by S). Since all the data are observed over a 10-km distance, the sediments formed in an environment that assisted in mixing and distributing the different compounds on large scales. Liquid water was the most probable carrier of such processes, at least for short episodes.

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Miocene incorporation of peridotites into the lower crust during opening of the Algerian basin: Insight from U-Pb LA-ICP-MS analyses

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Sizeable pieces of deep mantle material croup-out worldwide within orogenic belts involving major continental collisions or within regions with rift-thinned continental margins. From their original mantle position these peridotites have been transferred into the crust by tectonic processes involving subduction, collision or extension and, although minor components of most metamorphic belts, the understanding of how and when they were emplaced within the continental crust and their subsequent exhumation is paramount. A U-Pb age of 17.84±0.12 Ma (2σ) was obtained from monazites separated from a diatexite migmatite collected in close proximity to a small peridotite massif incorporated into the lower crustal sequence of the Edough massif (eastern Algeria), a southern segment of the peri-Mediterranean Alpine Belt. Monazites, extracted from a neighbouring deformed leucogranite, yield a similar age of 17.4±1.3 Ma (2σ) whereas coexisting zircon with magmatic characteristics yield an age of 308±7 Ma (2σ) interpreted as dating the magmatic crystallisation of the leucogranite during the hercynian orogeny. These results emphasize the polycyclic evolution of basement rocks preserved in the crystalline units of the western Mediterranean and indicate that part of their metamorphic features was inherited from older events. Taken together with published Ar-Ar datings, the late Burdigalian age of monazites, indicates a fast cooling rate of \textit{c.} 300°C/Ma and is regarded as closely approximating the emplacement of the peridotites into the hercynian basement. This age is significantly younger than those recorded for orogenic peridotites from the Betic-Rif orocline and for lithospheric extension forming the Alboran sea. It is also younger than rifting and back-arc extension opening the Liguro-Provençal basin. The late Burdigalian age is interpreted as dating the incipient rifting event that opened the Algerian basin. At the scale of the western Mediterranean, opening of the Algerian basin provides a link between the late Oligocene-early Miocene extension in the western part (Alboran basin, Valencia trough and Liguro-Provençal basin) and the upper Miocene extension in the eastern part (Thyrrenian basin) of the western Mediterranean.
Patterns in major and trace element dynamics during long-term decomposition of boreal forest litters

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Background

The dynamics of a large number of major and trace elements were examined during a series of long-term litter decomposition experiments in Swedish boreal and nemoboreal forests during the 1980s and -90s. Litterbags with leaf litters from Norway spruce (Picea abies), Scots Pine (Pinus sylvestris), Bilberry (Vaccinium myrtillus) and European beech (Fagus sylvatica) were incubated for between 4 and 8 years at sites with a wide geographic distribution in Sweden. In 2004 these samples were reutilized for multielement analysis (ICP-MS).

Multielement dynamics

Principal component analysis and manual scatter plots revealed groups of elements behaving in a similar manner during the decomposition process, although there were some differences between the needle and leaf litters. One group consisted mainly of nutrients, and had a general trend with decreasing amounts during decomposition. Another group contained mostly unessential elements, whose total amounts generally increased during the decay process. An exception from this trend was found for a few elements e.g. Cd and Hg, for which the amounts increased initially followed by a net leaching from the litter. An interesting anomaly in the behaviour of Thallium was discovered, as the total Tl amounts in all needle litters decreased during decomposition, whereas the opposite was seen in the leaf litters. This indicates a difference in the plants uptake or translocation mechanisms, where the deciduous plants are able to protect themselves from the highly toxic Tl.

Conclusions

The results indicate two distinct general trends in element behaviour during litter decomposition. There are however several subgroups or exceptions from these general patterns, e.g. slight differences between the species groups.

The fact that the samples were collected at a time of higher atmospheric metal deposition than at present, provides additional information and usefulness of the results.

Statistical evaluation of anomalous compositions in fluid geochemistry

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Outliers have been defined by Barnett and Lewis (1994) as observations characterised by their extremeness and their discordancy, being unreasonable statistically in terms of some basic model. Thus outliers have be considered in relative terms with respect to a univariate or multivariate random variable assumed as model for the population from which data have been drawn. The problem of detecting outliers in a multivariate matrix is thus equivalent to the problem of determining if all the observations can be considered as representatives of the population under study, characterised by an appropriate distribution function, or if some of them have to be considered atypical or discordant. Identification of anomalous compositions in a database results to be an important item to point out extreme compositions called end-members. Their reconnaissance allows us to evaluate the contributions of the different sources to each of the observation vectors (geochemical samples) of the data set and to understand processes affecting mixtures of fixed source compositions systems. Since geochemical data concerning composition of fumarolic gases are expressed in µmol/mol, to capture the pattern of variability of these datasets it is necessary to use adequate probability distributions (Aitchison, 1986). In this work a discussion about the use of different probability models will be presented by considering samples of fumarolic gas periodically collected at Vulcano Island (Sicily, southern Italy) in the last six years. The implications of the presence of anomalous samples will be discussed on the light of both end-member identification problems to be related to different sources and surveillance problems (monitoring programs of compositional changes). Since many systematic and random processes control the chemistry of gas discharges from active and quiescent volcanic areas, our results indicate that stochastic modelling represents one of the possible way to quantify uncertainty and to assume responsible interpretation of natural phenomena.

References


Serpentinites of the Tethys lithosphere and their role in the exhumation of the HPLT Zermatt-Saas ophiolites

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Large volumes of serpentinine are intimately associated with the Zermatt-Saas ophiolite of the Central Alps. The ophiolite represents Tethys ocean floor that formed in the Mesozoic and was destroyed by subduction in the late Cretaceous to early Tertiary. The ophiolite consist of high-P metagabbro, blueschist, eclogite and metasediments.

Antigorite schist is the dominant rock of the serpentinite. The isotopic composition of antigorite is typical of serpentinization by seawater or by “metamorphic water” with δD ranging from -65 to -55 ‰ and δ18O from 2 to 7 ‰.

Assemblages in mafic rocks of the ophiolite suggest that the subduction PT path has reached 27 kbar and 600°C. At this depth (~ 80 km), conditions for serpentinite dehydration are reached. Continued subduction has the consequence that the subduction PT path has reached 27 kbar and 600°C. Once the slab has passed the isograd, rocks may not be returned to the surface by buoyant backflow and high-density peridotite and eclogite will disappear into the deeper mantle.

Dehydration of serpentinite at 90 km depth in the Zermatt-Saas subduction zone released a large amount of water (~100 kg/m³) which has several significant effects. (i) It creates a water excess zone at return point depth. In this area, portions of the overlying mantle wedge was serpentinized so that serpentines formed structurally above mafic rocks of the ophiolite. Thus, many of the Zermatt-Saas serpentinite slices may represent a depleted sub-continental harzburgite protolith rather than ophiolitic mantle. Serpentinite formed in this manner can by scraped off the wedge. Together with serpentinite from the oceanic mantle they enclose lenses of eclogite and other high-P mafic rocks and return them to the surface due to buoyant flow aided by lubrication of dehydration water. (ii) In the water excess zone at return point depth, the mantle part of the oceanic lithosphere is completely serpentinized. Normally, oceanic mantle is serpentinized to variable extent (~20–30%). The ultramafic rocks of the Zermatt-Saas complex have been serpentinized 100%, and most of this serpentinization occurred in the water excess zone at return point in the subduction zone.

Upheaval Dome – Impact approved

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Upheaval Dome (Utah, USA) has earlier been interpreted, amongst others, as a pinched-off salt diapir [1] or as an impact structure [2]. In previous petrographical studies, no non-ambiguous evidence for shock metamorphism was identified [2]. Nevertheless, most arguments, such as seismic reflection studies, structural features [3], and microstructures in quartz grains [4] agree with an impact origin of Upheaval Dome.

We recently found some single quartz grains in sandstones of Upheaval Dome target rocks suspect to be shocked quartz with multiple sets of planar deformation features. Planar elements in quartz grains of sandstones of the Upper Jurassic Kayenta Formation turned out to be impact-diagnostic planar deformation features provided by both microscopic studies and our TEM investigation.

Shock wave attenuation to magnitudes below the Hugoniot elastic limit of quartz can be deduced for most zones of the target rocks presently exposed at Upheaval Dome [3]. In sandstones of the Kayenta Formation, inhomogeneities in the stress wave induced maximum pressure peaks of ~10 GPa, necessary to generate planar deformation features in quartz grains. Microstructures in quartz grains investigated by the authors have to be explained as distinct features of shock metamorphism and, thus, we interpret this as ultimate evidence for shock metamorphism in the target rocks and for the impact origin of Upheaval Dome.

References
The thermal state of the Earth: Geochemical solutions to geophysical problems?

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Recent geophysical arguments for radioactive elements in the core are motivated by inconsistencies in thermal models for the evolution of the core. Predictions based on typical estimates of heat flow from the core (e.g. 5 to 10 TW) yield a young inner-core age and an implausibly hot temperature at earlier times. Such high heat flows are difficult to avoid because current estimates of the present-day core temperature yield a large temperature drop across D”, and this normally implies a large core heat flow. High heat flow may also be required to supply the power needed to drive the geodynamo, particularly at early times when the inner core was small or absent. However, high heat flow from the core is not easily sustained over the age of the Earth without additional energy sources. Radioactive elements in the core offer one possible explanation if the concentration of elements is sufficiently high.

Other solutions are possible, but none are without their own problems. Arguments for low power consumption by the geodynamo can lower the necessary heat flow and circumvent the problem of high temperatures at early times. However, a low heat flow still needs to be reconciled with estimates of the present-day core temperature. Low heat flow is also permitted by reducing the thermal conductivity of the core, but the same problem applies. Both of these explanations are contingent on some means of lowering heat flow when the core temperature is high. Sequestering radioactive elements in D” is one option, but this imposes another set of demands on the distribution of radioactive elements.

Progress in resolving these questions is likely to rely on many different disciplines. For example, isotopic evidence for an enriched primitive layer at the base of the mantle bolsters arguments for heat sources in D”. Seismic evidence for a phase transition (or transitions) near the base of the mantle would help to constrain the temperature, although the complex dynamics of the region may frustrate any attempt to extrapolate this temperature to the top of the core. It is also possible that the thermal models are incomplete. An important (but neglected) source of gravitational energy is possible if the solubilities of mantle components in liquid iron change as the core cools and the inner core grows. Difficult experiments are needed to quantify core-mantle geochemistry, but the effort may ultimately resolve an important geophysical problem.

A natural analog of "boron-mullite" in granulite-facies metapelites from Mount Stafford, central Australia

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Werner Schreyer and his colleagues gave the name “boron-mullite” to ternary mullite-like phases synthesized in the B₂O₃-Al₂O₃-SiO₂(-H₂O) system. These phases have been synthesized at 1200 °C from mullite + B₂O₃, 1520-1600 °C from BAS melts and at 500-1050 °C, 1 atm-8 kbar from gels (e.g., Figure). A possible natural analog resembles sillimanite; optical properties are in the range for mullite: α = 1.627(1), β = 1.634(1), γ = 1.649(1), 2Vγ = 56(1)°. It is heterogeneous on a very fine scale; compositions range from close to sillimanite to nearly half way to Al borate (B determined by EMPA); FeO and MgO contents rarely exceed 1 wt%. “Boron-mullite” is found in silica-undersaturated, boron-rich metapelites dominated by sekaninaite (Fe-cordierite), hercynite and K-feldspar. “Boron-mullite” typically forms overgrowths mostly <0.1 mm long on the Fe-dominant analog of werdingite, commonly in the vicinity of andalusite or sillimanite, but in one section, it also occurs as prisms up to 0.4 mm long in fringes overgrowing sillimanite bundles. Ominelite (Fe-grandidierite) and biotite are present in most sections; tourmaline is present locally. Granulite-facies conditions reached at least 775-785 °C, at 3.3-4 kbar. “Boron-mullite” appears to be prograde and might have formed from incongruent melting of werdingite in the presence of granite melt, a possibility suggested by the melting of werdingite at 1200 °C, 1 bar under nearly anhydrous conditions in MgO-BAS (Werding & Schreyer 1992), but occurring at lower temperatures and under higher pressures in the more complex natural system.

References
Earliest evidence of life on Earth

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A key problem for geochemistry, paleobiology and astrobiology is how to recognize the first traces of life on Earth. Because particularly ancient rocks are scarce and poorly preserved, and because traces of primordial life might differ from the remains of modern organisms, the topic has proved especially contentious. Here I present a personal view of the subject, emphasizing the diversity of approaches that can be used to address it. Nobody else will agree with my conclusions.

Microfossils represent the preserved bodily remains of primordial life, but in the absence of evidence of behaviour, it is often difficult to prove that an organic sphere or filament was once alive. The most ancient such objects clearly showing signs of behaviour are from the ~2.6 Ga Transvaal Supergroup of South Africa. Stromatolites and other macroscopic trace fossils of microbial activities have a considerable Archean history. Molecular fossils of microbial activities have a considerable Archean history. Molecular fossils of microbial activities have a considerable Archean history. Molecular fossils of microbial activities have a considerable Archean history. Molecular fossils of microbial activities have a considerable Archean history. Molecular fossils of microbial activities have a considerable Archean history.

Stromatolites and other macroscopic trace fossils of microbial activities have a considerable Archean history. Molecular fossils of microbial activities have a considerable Archean history.

History of the Rumuruti chondrite asteroid by $^{40}$Ar-$^{39}$Ar dating

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Previous $^{40}$Ar-$^{39}$Ar dating on Rumurutiites yielded complex age spectra, precluding firm conclusions on the early thermal history of Rumuruti and its parent body [1,2]. In an ongoing initiative to constrain the history of meteorite parent bodies [3-6], we applied thermochronological modeling [7,8] to $^{40}$Ar-$^{39}$Ar age spectra of different Rumuruti lithologies (a light type 5/6 clast, a clastic matrix type 3.8 sample, and a type 3 clast). The age spectra show diffusive $^{39}$Ar loss (low temperature extractions), partial plateau segments and age drops at high degassing temperatures due to $^{39}$Ar recoil. The disturbing features correlate with grain size of the main K carrier phase plagioclase (glass). The coarse grained type 5/6 lithology has the best defined age plateau with 4.53±0.01 Ga. Taking into account that K-Ar ages are about 30 Ma too young due to bias in the K decay constants [3,9], a corrected age of 4.56 Ga implies a very short metamorphic history of the asteroid by $^{40}$Ar-$^{39}$Ar dating.

References

Unravelling the origin of zircon from sheared and altered ultramafic rocks of the Cycladic blueschist belt: A record of fluid infiltration?

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The eclogite- to epidote bluechist-facies sequences of the Cycladic blueschist belt in the Aegean Sea include mélanges with meta-igneous blocks and tectonic slabs (< 1 meter to several hundred meters) that are enclosed in an ultramafic or metasedimentary matrix. Due to its lithological variability, high block abundance and eye-catching metasomatic reaction zones at contacts between blocks and an ultramafic matrix, the HP mélangé on the island of Syros has attracted much attention, but less spectacular and less studied block-matrix associations are widespread on a regional scale (e.g. Tinos, Andros, Evvia, Samos). Ultramafic rocks have not been reported from all occurrences and the importance of serpentinite as matrix-forming rock is highly variable, both within and between individual outcrops. Many blocks are only surrounded by a rather thin envelope of serpentinitic material or talc, -chlorite- and actinolite-rich schists which formed by shearing of ultrabasic rocks that locally still are preserved as massive, largely undeformed rock bodies. The focus of our study is on these matrix rocks, which often contain considerable modal amounts of zircon, whereas non- or only weakly deformed ultramafic blocks are zircon free. The presence of zircon in the sheared and altered zones might indicate the incorporation of debris derived from mechanical disintegration of zircon-bearing rocks during deformation. Alternatively, this zircon might represent a newly grown phase that documents Zr release during HP metamorphic mineral reactions or precipitation from syn- or post-HP metamorphic aqueous fluids. In order to test these alternatives, we are studying block-matrix associations on Syros and Tinos. Microtextural criteria and zircon characteristics (morphology, internal structure, trace element patterns, ionprobe U-Pb ages) will be used to constrain the origin and geological significance of zircon occurring in ultramafic high-strain zones.

Methane oxidation, BIF carbonates and glaciation during the earliest Paleoproterozoic

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Diminishing methane levels have been thought to be responsible for the disappearance of mass independent fractionation in S isotopes (S-MIF) and multiple glacial events during the time period between 2.43 and 2.32 Ga (Zhanle et al., 2006). The earliest of the three glacial events is preceded by deposition of largest banded iron formations (BIFs) at a very rapid rate (> 30 m/Ma) (Barley et al., 1997) and a mafic magmatic event as is evident from the Hamersley Group and the Transvaal Supergroup. In other sequences where such large BIF litho-units were absent, the earliest glacial deposits seem to overlie the unconformity represented by quartz pebble conglomerates and paleosols as in the Huronian Supergroup. Thus it appears that the BIF deposition at a very rapid rate has a causal effect on the initiation of the first of global scale multiple glaciation events and also the disappearance of S-MIF. Here we propose that the 13C depleted carbon isotope compositions associated with various BIF lithofacies in both the Hamersley and Transvaal basins have been resulted due to oxidation of methane. The δ13C compositions of carbonate and organic carbon of the various lithofacies of BIFs in both Hamersley and Transvaal basins is given in the following table and also of the source carbon assuming normal organic carbon burial:

<table>
<thead>
<tr>
<th>Lithofacies</th>
<th>δ13C_carb</th>
<th>δ13C_org</th>
<th>δ13C_in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide facies</td>
<td>-12</td>
<td>-18.6</td>
<td>-13.3</td>
</tr>
<tr>
<td>Siderite facies</td>
<td>-7.4</td>
<td>-37.8</td>
<td>-13.5</td>
</tr>
<tr>
<td>Carbonate facies</td>
<td>-1.3</td>
<td>-43</td>
<td>-9.6</td>
</tr>
<tr>
<td>Clastic facies</td>
<td>-3.5</td>
<td>-36.6</td>
<td>-10.1</td>
</tr>
</tbody>
</table>

Considering that highly depleted δ13C values are resulted under normal burial conditions of organic carbon, i.e., 20% total input carbon being stored in organic form, the δ13C of the input carbon during the BIF depositions would range from -13 to -8 ‰. Our calculations suggest that the ambient seawater inorganic carbon pool exchanged with CO2 formed due to oxidation of atmospheric methane (δ13C of -47 ‰) in proportions of ~ 15 to 30 %. This would amount to ~ 1017 moles of atmospheric methane drawdown.

Reference
Voltammetry as a tool for detecting metal sulfide particles and nanoparticles in natural waters

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This paper deals with voltammetric characterization of metal sulfide nanoparticles (PbS, HgS, FeS, CdS, AgS and CuS) at the Hg and the glassy carbon electrodes in 0.55 M NaCl + 0.03 M NaHCO3 electrolyte, pH = 8.5. The aim was to investigate a possibility of using voltammetry in the detection of metal-sulfide nanoparticles in natural waters. The proposed electrochemical approach was applied in the detection of metal sulfide nanoparticles in two stratified lakes: saline Rogoznica Lake on the eastern Adriatic coast and Lake Pavin, a crater lake in the Central Massif, France.

The results of this work demonstrate that Pb, Hg, Fe, Cd, Ag and Cu sulfides, either as suspended powders or as precipitated nanoparticles, yield cathodic peaks between −0.9 and −1.7 V. Different experimental conditions (i.e. ageing of the particles, deposition potential and accumulation time) can affect shapes and positions of these reduction peaks. In anoxic natural samples, reduction peaks similar to those observed in model solutions were detected suggesting that voltammetry is a promising method for determination of metal sulfide nanoparticles. However, reduction peaks in the same potential range have been observed by other authors, who assigned them to the reduction of multimeric FeS(aq) complexes or clusters. The key findings of this work that other analytes: Cu2S, CuS, PbS, HgS, CdS, Ag2S nanoparticles, metal sulfide powders and sulfur powder produce similar reduction peaks. Therefore, here, we propose an experimental procedure to clarify the origin of voltammetric peak around -1.1 V in anoxic natural waters.

Thermodynamic properties and stability of the high-pressure silicate ellenbergerite in natural systems

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Ellenbergerite, [(Ti,Zr)2Mg2]Mg18Al18Si24O84(OH)30, was first described by Chopin et al. (1986) as inclusions in pyrope megacrysts from the Dora-Maira UHP-quartzites of Parigi, western Alps, Italy. Three major endmembers are known: two silicate endmembers (titanian and zirconian ellenbergerite) and an isostructural Mg-phosphate endmember (phosphoellenbergerite), along with the isostructural iron-arsenite ekatite. The upper thermal and the lower-pressure stability limits of Ti-ellenbergerite were determined by Chopin et al. (1992) and the limiting lower pressure / lower temperature reaction by Burchard et al. (2001). The upper thermal and lower-pressure stability limits of Zr-ellenbergerite were determined by Burchard & Schreyer (1996). Comodi & Zanazzi (1993 a & b) published compressibility and thermal expansion data.

All these data were used to retrieve the entropy and the enthalpy of formation of Zr- and Ti-ellenbergerite at standard conditions (H° f,298,Ell and S° 298,Ell). The Gibbs free energy of formation of Zr- and Ti-ellenbergerites, calculated according to Berman & Brown (1988) and Holland & Powell (1998), is highly sensitive to water activity and bulk iron content of the rock, which may justify the rarity of ellenbergerite in nature.

References

ERDA of hydrogen content in hydrous and nominally anhydrous mantle phases

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Nuclear methods, more especially ERDA (Elastic Recoil Detection Analysis) are used since a long time to determine the bulk hydrogen content of any kind of matrix material. The advantage of this method is that (1) the analysis is absolute with respect to H with an uncertainty of less than 10% relative, (2) all the H is characterized, not only H bonded with oxygen, (3) the samples are investigated on a micrometric scale. Whereas the method is extremely reliable to quantify hydrous geologic samples (e.g. Bureau et al, 2003), the few attempts made to characterize anhydrous phases were not so successfull because of too high backgrounds usually observed on the ERDA spectra, due to surface’s H (e.g. Sweeney et al., 1997). During the past four years, we have tried to improve the ERDA method in the nuclear microscope of the Pierre Süe laboratory. The setup has been modified, we perform scannings on large sample areas (200x800µm² at maximum) in order to reduce the H loss due to the 3 MeV incident 4He beam (4x16µm² during the ERDA analysis). The maps are processed using a specific software (RISMIN, Daudin et al. 2003). Therefore different areas of a same sample can be selected in order to measure their respective H contents. The detection limit has been measured on dehydrated San Carlos olivine to be 130 ppm wt H₂O (15 ppm wt H). Another advantage is that RBS (Rutherford Back Scattering) and PIXE (Proton Induced X-Rays Emission) are performed simultaneously providing a chemical characterization of the sample with respect to major and some trace elements. In this presentation we will review a few recent results: we have measured the hydrogen content of various kind of geological samples: volcanic glasses and glassy inclusions; synthetic and natural nominally anhydrous minerals (see also Carraro and co-workers, this issue).

References

Tracking groundwater contribution to rivers by combining hydrogen isotopes and cation concentrations

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While the hydrological response of a basin to various water inputs may be described by models based on hydrographs only, isotopic and chemical analyses are often necessary to understand the mechanism of groundwater flows as well as the interactions between water, soils and rocks. We worked on the upper basin of the Moselle river (France). Samples were collected every 10 days during 18 months and comprised various water compartments such as i) precipitations, ii) groundwater sources, iii) main tributaries and iv) the river itself at 3 different sites. Meteorological and physical parameters were used along with hydrogen isotopes, major and trace elements analyses.

Major groundwater sources in the area yielded homogeneous δD values over the year and very similar to the composition of the weighted average of annual precipitations. This suggests a long residence time of water in the underground reservoirs. Furthermore, the δD values measured for river water during low flow periods are also very comparable to that of groundwater sources, suggesting a major contribution of groundwater to rivers during these periods. During flood periods, the shift in δD values measured in river water implies that only 30-40% of the total water flow may be attributed to precipitation (or snow melt), leaving 60-70% of the water discharge due to an increased contribution from groundwater (piston effect).

Positive relationships are found between dissolved cation (Ca, Mg, K) fluxes and water discharge at a given locality and over the 18 months of sampling. This implies that the increasing water discharge after precipitation events do not lead to a simple dilution of the dissolved species. Rather, an increase of the groundwater input is needed to increase dissolved cation flux. At one site, the relationship is very similar for the three cations, suggesting a simple larger contribution of the groundwater present during the low discharge periods. At other sites, different relationships are found for Ca, Mg or K, suggesting that more than one groundwater mass contributed.
Further constraints on Helium partitioning in mantle minerals

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The He isotopic composition of the Earth's mantle varies by at least factor ≈5, with mid-ocean ridges characterized by more radiogenic He than ocean islands. There has clearly been significant, ancient He - U fractionation in the mantle but does less radiogenic He represent less or more processed mantle processed?

Heber et al [1] measured DHe\textsuperscript{mantle-melt} by growing olivine and pyroxene from a He-saturated melt whereas Parman et al [2] 'doped' existing olivine grains with a He atmosphere (without melting the olivine). The presence of inclusions in artificially grown minerals could bias the grown olivine results of [1] (which nevertheless provide a maximum estimate of DHe = 1.7 x10\textsuperscript{-4}) whereas the Parman approach - using gem-quality olivine as a starting material - should not be affected by inclusions therefore should result in DHe ≤ that of grown olivines. Surprisingly, equilibration with a He atmosphere resulted in DHe = 2.5 – 6 x10\textsuperscript{-3} or > 15 times higher that of the grown olivines.

We equilibrated 100µm thick forsterite wafers with 100% \textsuperscript{4}He at 1600°C; the wafers were then irradiated with 220 MeV protons following [3]. Proton irradiation produces \textsuperscript{3}He homogeneously in the olivine matrix [3].

Helium was extracted from doped-irradiated olivines by stepped-heating and measured by mass spectrometry at CIT. \textsuperscript{4}He/\textsuperscript{3}He is highly variable (10 - 1000) in these samples, in contrast to a constant \textsuperscript{4}He/\textsuperscript{3}He which would be the only solution consistent with homogeneous \textsuperscript{4}He dissolution in the olivine matrix. While difficult to interpret, these data imply that a) He is not simply in a single solubility site in the olivine matrix; b) the concentration of He in doped olivines probably overestimate He solubility, and therefore DHe; c) Heber et al's estimate (3 x10\textsuperscript{-5}) remains the best DHe\textsuperscript{ol/melt} upper limit.

References

Schwertmannite reduction and iron(II)-monosulfide formation in acidified coastal lowlands: Iron-sulfur geochemistry and implications for water quality

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Drainage of formerly waterlogged-sulfidic soils in coastal lowlands has resulted in widespread pyrite oxidation in many areas. This oxidation process liberates acidity, Fe and S; which, in turn, leads to the accumulation of schwertmannite (Fe\textsubscript{8}O\textsubscript{6}(OH)\textsubscript{6}SO\textsubscript{4}). Here we present the results of in-situ studies and laboratory-based experiments examining Fe-S geochemistry and the effects on water quality when schwertmannite accumulations are subjected to reducing conditions. This occurs (1) during diagenesis in the benthic sediments of acidified estuarine waterways; and (2) during prolonged waterlogging of acid sulfate soils as a result of wetland re-establishment.

In acidic (pH 3 – 4) and organic-rich (10% – 25% organic C) soils/sediments, bacterial reduction of schwertmannite-derived Fe(III) occurs readily under anoxic conditions. This produces abundant Fe\textsuperscript{2+}, SO\textsubscript{4} and HCO\textsubscript{3} which thereby drives pH increases to pH 6 – 7 and sequesters some Fe\textsuperscript{2+} via precipitation of siderite (FeCO\textsubscript{3}). As the pH increases above pH 5, adsorption of Fe\textsuperscript{2+} to schwertmannite catalyses the very rapid transformation of schwertmannite to goethite. The combination of near-neutral pH and the effective replacement of schwertmannite by goethite is accompanied by the formation of elemental S and acid-volatile sulfide. Examination by X-ray diffraction, electron microscopy and electron diffraction show that the acid-volatile sulfide mainly comprises nanoparticulate mackinawite (tetragonal FeS). The formation of elemental S and mackinawite reflect significant levels of SO\textsubscript{4}-reduction, even though the soils/sediments contain very large amounts of oxalate-extractable Fe(III). This is curious, as traditional theory (based on overall free energy yields) indicates that SO\textsubscript{4}-reduction should not occur significantly until near-complete reduction of Fe(III). The apparently anomalous co-occurence of Fe(III)- and SO\textsubscript{4}-reduction (as observed in both the field and laboratory) can be explained by an alternative partial equilibrium model of the thermodynamic favourability of Fe(III)- versus SO\textsubscript{4}-reduction. Central to this alternative model is the Fe\textsuperscript{2+}-catalysed transformation of schwertmannite to goethite – a process that facilitates co-occurence of Fe(III)- and SO\textsubscript{4}-reduction, and that promotes the accumulation of nanoparticulate mackinawite. The formation and fate of mackinawite has important water quality implications with regard to acidity fluxes and trace element behaviour.
Stable and radiogenic isotope variations accompanying continental weathering

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Many natural isotope systems (both stable and radiogenic) are sensitive to variations in weathering process. The difficulty lies in distinguishing variations that result from weathering process from those caused by differences in rock type. One approach that circumvents this problem is the study of monolithologic catchments, where variations such as catchment age, runoff, physical and chemical weathering, vegetative cover and soil development can be related to riverine chemistry.

This study presents an overview of our recent work on radiogenic and stable isotope in rivers, soils and estuaries from catchments in Greenland, Iceland and Europe. Each case study illustrates the effects of weathering process on the riverine isotope signal, and the estuarine data indicates how this signal is transferred to the oceans. Aside from variations in rock type, the principal controls on isotope variations accompanying weathering are; (i) for many radiogenic isotope systems, preferential (incongruent) weathering of specific primary mineral phases, where those phases possess a markedly different parent/daughter and hence radiogenic isotope composition; (ii) for many stable isotope systems, preferential removal of an isotope into secondary phases formed during weathering, leaving residual waters depleted in that isotope. Recent studies have also shown the importance of biological removal and accompanying fractionation for certain isotope systems.

Taken together, these results clearly demonstrate that weathering processes can exert a significant effect on the isotope composition of natural waters, and for some of those isotopes marine sedimentary archives preserve a record of the changes in such processes with time. For marine records the challenge remains in unravelling the effects of weathering from those caused by variations in rock type, or a simple change in flux or geographical source.

The CO2 sealing efficiency of caprocks

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Shale lithotypes of various compositions occur abundantly in sedimentary basins and act as natural seals for petroleum and natural gas reservoirs over extended geologic periods. Based on their mechanical, petrophysical and chemical/mineralogical properties, shales are becoming increasingly important in the context of geological long-term storage of anthropogenic carbon dioxide in saline aquifers, depleted oil and gas reservoirs and coals.

Due to its chemical reactivity and physico-chemical properties, CO2 is expected to differ substantially from other natural gas components in terms of transport behaviour and interaction with the mineral/water system. An experimental procedure has been developed to measure molecular diffusion of CO2 in water-saturated shales. This non-steady state method provides information on the effective diffusion coefficients and the CO2 storage capacity of the shales. Storage capacities were found to vary significantly but can be as high as 0.14 mmol CO2/g sample. Manometric sorption experiments with CO2 at pressures up to 20 MPa have been performed on dry and moist shale samples to verify the findings noted above. The results of these experiments revealed unexpectedly high storage potentials of the same order of magnitude as those from the diffusion measurements. The CO2 storage capacities do not correlate with organic carbon content. A separate set of experiments with pure clay minerals (Kaolinite, Illite, Montmorillonite....) revealed that some of these materials had high sorptive CO2 storage potential. Comparison of pre- and post-experiment X-ray diffraction patterns showed indications of changes in mineralogy.

These findings provide a new view on the issue of caprock integrity. In addition to their sealing properties, natural shale sequences could represent a significant sink or buffer for carbon dioxide deposited in the subsurface by fixing and immobilising it and hence reduce the risk of leakage to the surface.
Catalytic action of aqueous Fe(II) and S(II) on the transformation of schwertmannite to goethite

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The mineralisation of ferric oxides is of fundamental relevance to the geochemistry of marine and freshwater benthic sediments. In acidic landscapes affected by the oxidation of sulfides, schwertmannite (Fe8O8(OH)6(SO4)2) is a common ferric oxide. Due to its high surface area and intrinsic reactivity, schwertmannite is an important sink for metal contaminants and nutrients. The accumulation of schwertmannite occurs often at the oxic/anoxic boundary of benthic sediments. Under acidic oxygenated conditions the schwertmannite transforms slowly (i.e. 1-2 yrs) to more crystalline iron oxides such as goethite. Near-neutral anoxic conditions are known to enhance the rate that schwertmannite transforms to goethite (i.e. 2-3 months). Here we present the results of controlled laboratory batch experiments that examine the catalytic influence on schwertmannite of two strong and often abundant reductants that occur in the porewaters of benthic sediments, aqueous Fe(II) and S(II).

In the presence of Fe(II) and at a pH > 5.0, the schwertmannite transformed rapidly (i.e. within 15 min) to goethite and lepidocrocite. At pH < 5, Fe(II) had no effect. The increasing tendency for Fe(II) sorption at pH > 5.0 is responsible for the catalysed transformation of schwertmannite to more crystalline phases. Increasing pH and increasing Fe(II) concentration further enhanced this mineralisation reaction. The presence of S(II) caused a similarly rapid transformation of schwertmannite to more crystalline iron oxides. S(II) reacted within minutes with structural Fe(III) in the schwertmannite, producing elemental sulfur and Fe(II), with excess S(II) reacting with Fe(II) to form nano-particleulate mackinawite (FeS).

The catalytic effect of Fe(II) and S(II) can be attributed to electron exchange between the sorbed reductant and structural Fe(III) at the mineral surface, leading to destabilisation of the schwertmannite, its dissolution and transformation to more crystalline iron oxide phases. The catalytic influence of Fe(II) and S(II) on the transformation of schwertmannite to more crystalline iron oxides, and in the case of S(II), formation of elemental sulfur and mackinawite, have important implications for understanding the dynamics of Fe and S cycling, metal contaminant behaviour and water quality in acidic landscapes.

Evidence for nitrogen enrichment during oceanic crust alteration

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Because N is present at only low concentration level in the Earth’s mantle, subducting altered oceanic crust may have a significant contribution to the long-term evolution of the N content and isotopic composition of the mantle. To date, whether N is enriched or released during hydrothermal alteration of oceanic crust remains uncertain. Hall [1] measured N content of spilitized basalts from Cornubian massif and suggested that N was enriched during alteration. However, spilitization might not be representative of seawater-oceanic crust interactions. Nitrogen contents of oceanic basalts from several DSDP/ODP Sites support the interpretation of N enrichment but show smaller magnitude than basalts from Cornubian massif [2,3]. The analysis of altered basalts from the ODP Hole 504B contrasts with these results, and indicates a loss of N from rock to fluid [4]. These authors extracted N using a pyrolysis technique, heating samples in molybdenum crucibles. However, N was recently shown to be strongly reactive with molybdenum at high temperature [5]. The low N concentrations measured in altered basalts from Hole 504B may thus result from the incomplete recovery of N rather than a specific type of alteration. To test this hypothesis, we analyzed samples from the Hole 504B using a sealed tube combustion technique, with samples embedded in platinum foils. The results show significant N enrichment (up to 12 ppm) relative to fresh degassed MORB (~1 ppm). This confirms that oceanic crust alteration acts as a sink for N from surface reservoirs and must be considered in subduction zone budget to evaluate the efficiency of N recycling to the mantle.

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Mineral weathering rates coupled to bedrock fracturing and saprolite formation

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Spheroidal weathering is a common mechanism by which bedrock corestones disaggregate to form saprolite. In the Rio Icacos watershed in the Puerto Rican rainforest, quartz diorite bedrock weathers spheroidally, producing a 0.2-2 m thick zone of concentric, partially weathered rock layers (~2.5 cm each) called rindlets. Spheroidal fracturing has been modeled to occur when a weathering reaction with a positive $\Delta V$ of reaction builds up elastic strain energy (Fletcher et al., 2006). The rates of spheroidal fracturing and saprolite formation are therefore controlled by the rate of the weathering reaction.

Based on petrographic evidence and thermodynamic calculations, we have identified biotite oxidation as the most likely fracture-inducing reaction. Oxidation of Fe(II) within the biotite lattice occurs with a concomitant loss of interlayer K+ to maintain charge balance. Adsorption of water to the interlayer could produce a positive $\Delta V$ of reaction sufficient to initiate fracturing if it occurs before other weathering reactions increase porosity enough to relieve the stress generated. Thus, detection of incipient weathering reactions is crucial for identifying the rate-controlling reaction.

Evidence for progressive biotite oxidation across the rindlet zone was inferred from the decreasing K content of the biotites and by decreasing Fe(II) content in bulk samples of the rindlets. Using a 1-D linear model (White, 2002) of the gradient in Fe(II), we calculated a biotite oxidation reaction rate of 7.2x10^{-14} mol m^{-2}s^{-1}. Evidence for incipient biotite oxidation was documented within the bedrock corestone by hard X-ray microprobe mapping and XANES, both performed at Beamline 2-3 at the Stanford Synchrotron Radiation Laboratory. Maps of Fe(II) and Fe(III) at 2 µm resolution revealed oxidized zones within individual biotite crystals. This ability to map oxidation states within individual crystals holds promise for identifying incipient weathering reactions within “pristine” bedrock, which in turn will allow quantification of rate limiting reactions in coupled processes such as spheroidal weathering.

References

Paradox of the plankton: Why is Proterozoic export production dominated by cyanobacteria?

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Eukaryotic organisms are well documented in the fossil record from at least the Mesoproterozoic, but the distribution of 2-methylhopanoid biomarker molecules suggests that cyanobacteria continued to dominate marine productivity until the Phanerozoic (Summons, R. E., et al. 1999. Nature 400:554–557). Although poorly resolved, the switchover to modern-style, eukaryote dominated export production can be broadly linked to the early Cambrian (Tommotian) “explosion” of animals, trace fossils and small ornamented acritarchs, the latter reasonably interpreted as the cysts of eukaryotic phytoplankton. The coincidence of these various signatures points to a fundamental shift in marine ecology.

The subdued expression of pre-Cambrian algae has been attributed to nitrogen limitation associated with a sulphidic deep ocean, but this is not supported by recent experimental results (Zerkle et al. 2006. Geobiology 4:285–297). Nor can the switch be simply attributed to appearance of eumetazoans, which precede the Cambrian explosion by some hundred million years and appear to have been exclusively benthic. The first real opportunity for eukaryotic phytoplankton came as metazoans moved into the water column to graze directly on primary productivity. In the absence of predation, unicellular phytoplankton are expected to evolve to minute size, without morphological elaboration, playing strongly to the strengths of cyanobacteria. The key to eukaryotic success, however, lies in their capacity for morphological differentiation, in this case the diverse ornamentation of early Cambrian acritarchs serving to frustrate grazing mesozooplankton. By selectively removing the long-standing cyanobacterial incumbents – and providing the trophic link between unicellular phytoplankton and macrozoaons – mesozooplankton can be held responsible for uniquely eukaryotic expression of the Phanerozoic biosphere.

References
Evidence for cross formation hot brine flow from integrated $^{87}$Sr/$^{86}$Sr and REE data in Central Tarim

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In Central Tarim, commercially oil and gas has been produced from fluorite reservoirs in the Ordovician carbonates. The fluorite occurs as replacement of carbonate wallrock and fracture fillings. Associated minerals with the fluorite include barite, anhydrite, calcite, quartz and pyrite. Calcite veins show wide ranges of fluid inclusion homogenization temperatures (HTs) and $^{87}$Sr/$^{86}$Sr ratios (0.70797 to 0.70977) and have $\delta^{13}$C values close to the ambient limestone. Anhydrite and fluorite veins have lower HTs and show much higher $^{87}$Sr/$^{86}$Sr ratios (0.70912 to 0.71036) than barite (~0.7090) and bulk limestone (0.7064 to 0.7094), but closer to the present brines (0.71026 to 0.71109), suggesting mixing of relatively hot Ba-rich and $^{87}$Sr-depleted fluid with relatively cool $^{87}$Sr-rich fluid. The cooler $^{87}$Sr-rich fluid has been proposed to have been derived from the west to the Central Tarim (Cai et al., 2001a). The hotter fluid was most likely derived from pre-Cambrian clastic rocks or/and from the basement. This proposal is supported by REE data. REE data of calcite, anhydrite and fluorite veins are characterized by a similar pattern with a positive Eu anomaly and LREE enrichment relative to HREE. The positive Eu anomaly indicates a reducing, hot fluid (>200 °C) during migration. The positive correlative relationships of Eu to Ba, Sr and Zn suggest that the hotter fluid was enriched in Eu$^{2+}$, Ba$^{2+}$, Sr$^{2+}$ and Zn$^{2+}$. When the hotter fluid mixed with the cooler fluid, barite and calcite precipitated at ~145 °C. Moreover, there was still diffraction peak corresponded to Ca-minerals including calcite, anhydrite and fluorite, resulting in the Ca-minerals having more radiogenic Sr than structure water of clay. This work is financially supported by China’s 973 projects (2006CB202304 and 2003CB214605) and NSFC 40573034.

References

Significance of the variation characteristics of interlayer water in smectite of source rocks

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The characteristics of interlayer water bonded to organic matter in interlayer of smectite were determined by thermo-XRD, DTA, TG and PY-GC for organo-clay complexes extracted from source rocks, and it plays an important role in explaining formation and migration of hydrocarbon in source rocks. As revealed by XRD curves, the $\delta^{34}$S reflected peak decreases under temperature of 250°C-500°C and not reaches 1.00‰ until 550°C, which is obviously different from smectite that keeps on 1.00‰ from 250°C to 500°C. Similarly, DTA curves show some exothermic peaks in the same temperature range. These observations clearly indicate that there is organic matter in smectite interlayers. PY-GC results show that the number of expelled organic matter is large under temperature of 250°C -500°C and in turn the temperature range is the just expulsive temperature span for interlayer organic matter. These pyrolysis products have a bimodal distribution dominated by short-chained C5 and long-chained C25 hydrocarbon, suggesting the interlayer organic matter correlate to oil components.

There are two vales, interlayer water and textural water endotherm vales, near 100°C and 600°C respectively, in DTA curves, which are similar to smectite completely, while a new endotherm vales appears at 500°C, which is characteristic of organo-clay complexes. PY-GC results also provide evidences supporting the existence of endotherm vale at 500°C. Moreover, there was still diffraction peak corresponded to smectite at 500°C XRD curve, implying smectite structure kept intact and the expelled water is interlayer water rather than structure water of clay.

Taken together, we find interlayer organic matter expelled at 500°C, followed by expulsion of interlayer water, suggesting the water may be water bridge between organic matter and smectite, which has a great influence on the hydrogenation on hydrocarbon generation. Curve fitting of the DTA and TG show that the expelled water at 500°C accounts for 4-6%, which may provide dynamic force and be a good medium for petroleum migration.

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In situ natural radionuclides transport and retardation in coastal groundwater of the southern China

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238U and 232Th decay-series disequilibria in groundwater naturally occur as a result of water-rock interactions. The studies connected with them provide site-specific, natural analog information which improve the understanding of migratory behavior of radionuclides in groundwater. In these studies, a mass balance model was used to relate the distributions of decay-series radionuclides among solution, sorbed and solid pools in an coastal aquifer system to processes of water transport, sorption-desorption, radioactive ingrowth-decay and α-recoil. Isotopes of Ra (226Ra, 228Ra, 224Ra) and Rn (222Rn) were measured in coastal groundwater from Xiamen, China, where both seawater intrusion and submarine groundwater discharge are found which make the rock-water interaction probably more remarkable there.

The results show that α-recoil supply rates of 222Rn (Pr,Ra) and 224Ra (Pr,Ra224) decrease seaward from 206 to 5.4 atoms L⁻¹ min⁻¹ and from 295 to 7.8 atoms L⁻¹ min⁻¹, respectively, which give good explanations for their spatial distributions. Pr,Ra224 is larger than Pr,Ra in each station, suggesting solids in studied aquifer may contain more thorium than uranium. Pr,Ra224/Pr,Ra increases seaward from 0.3 to 0.9 along the path with an average value of 0.6, suggesting the primary source of groundwater 222Rn is α-recoil of 226Ra decay in solid pool, and it is also seen that the ratio increases along the path. 226Ra decay in the sorbed pool (Rs,Ra226/Ar,a226) attributes about 40% of total source of coastal groundwater. 222Rn. Pr,Ra224/Ar,a224 ranges from 14.0 to 333.0, with an average value of 177.8, almost two orders higher than that of Pr,Ra/Ar,a, while α-recoil supply rate (Pr) from the aquifer rocks of both nuclides are within the same order. This shows that retardation of different nuclides by groundwater are differ greatly: α-recoil supply rate of 224Ra by aquifers rock is much faster than other radionuclides in Xiamen coastal groundwater, revealing aquifers rock have strong retardation on radium isotopes, while the immigration scale of 222Rn is longer than radium isotopes in groundwater.

The retardation factor of radium isotopes (Rf,Ra) in groundwater decrease seaward from 2.19×10⁷ to 0.94×10⁷, with average value 0.8×10⁷, while its liveliness extent increase gradually, which result in the decreasing of 222Rn of groundwater in a certain degree.

Calculation by the mass balance model also suggest that observed 224Ra/226Ra)a.r. of groundwater are mainly controlled together by α-recoil in aquifer solid pool and retardation by rocks. Both of effects decline gradually from land to sea, and make 224Ra/226Ra)a.r. increase gradually seaward the cooperatively.

Phanerozoic ocean chemistry and anthropogenic ocean acidification

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Phanerozoic ocean carbonate chemistry

Phanerozoic ocean carbonate chemistry can be estimated using estimates of surface ocean carbonate mineral saturation states, calcium concentrations, temperature, and atmospheric carbon dioxide content. Any Phanerozoic carbonate chemistry reconstruction must be interpreted at best as indicating likely trends and magnitudes of past variation and not as a quantitatively accurate record.

Figure 1: Ocean pH computed assuming constant surface-ocean carbonate mineral saturation

Phanerozoic carbonate mineral saturation

There is no direct record of surface ocean carbonate mineral saturation states, but some idea can be gained by looking at the latitudinal extent of carbonate reefs, taking into consideration factors such as paleo-temperature and the dominant lithology of reef builders at any given time. It is likely that organisms have become more efficient at building carbonate skeletons due to the selective advantage bestowed upon organisms able to calcify in less saturated waters.

Variations in saturation states also follow geologic CO2 degassing rates. High CO2 degassing means high atmospheric pCO2 means high silicate weathering means high cation flux to the oceans. Ocean carbonate-ion concentrations must increase in response until the carbonate mineral saturation increases enough to induce carbonate burial that balances riverine inputs. Thus, on multi-million year time scales surface ocean carbonate saturation state tend to parallel atmospheric CO2 concentration.

Future carbonate mineral saturation

This situation contrasts markedly with what may occur over the next decades and centuries. Because of the rapidity of our CO2 emissions, over the next decades and centuries carbonate mineral saturation states will be approximately inversely proportional to atmospheric CO2 concentrations. Unabated anthropogenic CO2 emissions could produce surface ocean saturation conditions that are lower than any since the Cretaceous-Tertiary boundary extinction event.
Evidence of mantle metasomatism beneath São Tomé Island (Cameroon Volcanic Line)

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The occurrence of CO\(_2\) rich and carbonatitic metasomatic fluids as fertilizing agents of sub-continental mantle sources of the Cameroon Volcanic Line has been frequently referred. This report provides evidence for metasomatic processes in the mantle beneath São Tomé Island (oceanic sector of the CVL) based on mineralogical and geochemical data from primitive lavas and ultramafic xenoliths.

São Tomé primitive basalts (Mg\# > 57; Ni > 170 ppm) geochemistry reveals a non-p rimordial, heterogeneous, oxidized, amphibole bearing source, characteristic of metasomatic activity in the magma sources. Incompatible trace element patterns show an overall enrichment (e.g., Ce/La = 0.55 ± 0.02) implying a non-primordial character of their mantle sources. Observed variations on trace element contents and ratios (e.g. \(\Delta\log(\text{Ce/La})\)) suggest mantle heterogeneities sampled by low, but variable, partial melting degrees (< 17%), whereas K negative anomalies and D\(_{\text{K}_2}\text{O}\) > D\(_{\text{Rb}}\) and D\(_{\text{Sr}}\) > D\(_{\text{Ba}}\) indicate amphibole as the predominant K-rich residual phase. High \(\Delta\log(\text{Ni})\) values estimated for São Tomé primitive magmas reflect the oxidized nature of their asthenospheric magma sources. These features, together with sub-chondritic Ti/Eu ratios (5669 ± 706), uncorrelated with Mg\# and negatively correlated with Zr/Hf, La/Sm, and Th contents, suggest that mantle metasomatism was induced by interaction with carbonatitic melts.

Lack of correlation between silicate mineral Mg\# values and modal compositions in spinel peridotite xenoliths enclosed by São Tomé basaltic lavas indicate that these xenoliths are not simple residues, suggesting the occurrence of metasomatic activity within the regional lithospheric mantle. Abundant carbonate and CO\(_2\) rich fluid inclusions (Tm = -56.6°C), development of low-Al\(_2\)O\(_3\) secondary clinopyroxene, and high \(f_O_2\) [\(\Delta\log(\text{Ni})\) ~ 1] in peridotitic xenoliths are consistent with the inferences on geochemical processes operating at their host magma sources, providing further support for carbonate (fluid/melt) related metasomatism in the mantle beneath São Tomé Island.

Nickel stable isotopes as biogeochemical tracers

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Nickel (Ni), a bioessential trace metal, is functionally important to predominantly prokaryotic microorganisms (Archaea & Bacteria) in which, for example, Ni-containing enzymes act as catalysts in very specific metabolisms such as methanogenesis. Only one known enzyme, urease, in higher-order organisms (e.g. fungi & plants) requires Ni. Thus, from a biological point of view, it seems that the importance of Ni is relegated to more primitive and probably, ancient metabolisms that existed before the appearance of oxygen (Frausto da Silva and Williams, 2001).

We undertook an exploratory study of the Ni stable isotope system in an effort to determine natural variability for geochemical and particularly, biological applications. With the exception of extraterrestrial materials, Ni isotope studies have not previously been carried out. Additionally, as an astrobiological tool, Ni stable isotopes may potentially be utilized as biosignatures in characterizing and understanding microbial metabolisms and trace metal acquisition. A proven Ni isotope biomarker could be a useful tracer for microbial processes in which the geologic record of Ni isotopic composition might be employed in evaluating the evolutionary history of certain metabolisms, such as methanogenesis. Similarly, Ni isotopic compositions may be useful for assessing the metabolic characteristics of modern microbial ecosystems.

Method development and isotopic measurements were carried out at the University of Bristol. Initial experiments were of a biological nature and results will be presented.

References

Reconciling potentiometric titration and Second Harmonic Generation measured diffuse layer potential of an aqueous silica suspension

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The mineral surface potential plays a significant role in the quantitative understanding of mineral dissolution, contaminant transport and mineral colloid stability yet generally is not directly accessible experimentally. In particular, for most mineral surfaces of interest there are thought to be (at least) two relevant surface potentials: that of the mineral surface ($\phi_{\beta}$ and/or $\phi_0$) and, some distance into the aqueous phase, a diffuse layer potential ($\phi_d$). Surface potential is generally determined using electrokinetic techniques. However, these methods require hydrodynamic perturbation of the system and necessitate employing a model with difficult to constrain parameters to calculate $\phi_0/\phi_{\beta}/\phi_d$.

Second Harmonic Generation (SHG) is a second order nonlinear optical process, driven by an intense laser source, which is sensitive to interfacial electrical fields. For this reason the variation in the intensity of measured SHG ($I_{SHG}$) with changes in pH (for systems where H$^+$ is the sole potential determining ion) and salt concentration has previously been used to describe the surface potential of a variety of noncrystalline organic materials in water, as well as to determine the $pH_{bic}$ of several mineral/water systems. Here we measure the $I_{SHG}$ for the colloid silica/water system as a function of salt concentration at a variety of pH and use the results, in tandem with potentiometric titration, to quantify the mineral surface potential as a function of solution chemistry.

Origin and application of GOI data of oil inclusions in structurally complex Junggar Basin (NW China)

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GOI (grains containing/with oil inclusions) data are commonly used to identify paleo-oil columns and to map original oil-water contacts in hydrocarbon reservoirs. However, in superimposed China’s basins, oil-water contacts mostly have changed for variable times due to complex tectonic evolution. Thus, those threshold lines suggested in previous literatures, such as 1% for water zone and 5% for oil zone, can still be used effectively?

The Junggar Basin is one of the typical tectonically complex but most prolific oil provinces in China. In this study, five typical wells with different oil and gas shows were selected for GOI analyses in the Mosuowan area, central Junggar Basin. Discussion on analytical results from 48 reservoir samples indicates that the GOI data were mostly decided by intensity of reservoir hydrocarbon charging. However, due to the complex petroleum charge histories in superimposed basins, it is suggested that we should not simply use the GOI data to define petroleum migration according to previous threshold lines (e.g., 1%, 5%). It is more probable that based on geologic background, firstly to discuss the origin of GOI composition and then to have an application in reservoir characterization.

The case study in the Mosuowan area of the central Junggar Basin infers three specific points. Firstly, a GOI value of less than 1% was not always indicative of water zone or only migration of oil, but possible of gas reservoir or dysmigration of hydrocarbons. Secondly, the GOI values below 5% were still likely to indicate expose to high oil saturation when considering the difficulty in capture of oil inclusions in places. Thirdly and lastly, the threshold line of 6% GOI was likely the criterion for migration of industrial hydrocarbon reserves in the study area.

In a word, GOI method is still effective in quantitative evaluation of petroleum migration in structurally complex basins, but should be used comprehensively in combination with geologic background.

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Treatment of high metal concentration AMD using Dispersed Alkaline Substrate (DAS), a novel passive treatment system

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In spite of the existence of many Passive Treatment Systems used for remediation of Acid Mine Drainage (AMD), with moderate metal concentrations and acidity, all of these systems shown severe problems when exposed to high metal concentrations such as those present in AMD from sulfide mining districts. To overcome this problem we have developed a novel Dispersed Alkaline Substrate (DAS), consisting in a mixture of a fine-grained alkaline reactive (limestone sand in T1 and T2 and MgO dust in T3; Fig. 1) and a coarse inert matrix (wood chips). AMD at Monte Romero (Iberian Pyrite Belt, SW Spain) has a pH of 3-3.5, net acidity of 1400-1650 mg/L as CaCO₃, 320 mg/L Fe (95% Fe²⁺), 310 mg/L Zn, 75 mg/L Al, 0.1-1 mg/L Cu, As, Pb, Co, Ni and Cd. The pilot-scaled field experiment (Fig. 1) presents encouraging results. T1+D1+D2 remove 100% of Al, As, Pb and Cu, 50% of Fe, 15% of Cd and 5% of Zn from the inflow water. T2+D3+D4 remove almost 100% of Fe and T3 is designed to remove the remaining Zn and Cd, although results for T3 are not available yet.

Figure 1: Localization and schematic representation of the DAS pilot treatment plant developed at Monte Romero Field Site (SW Spain).

(Mg,Fe,Al)(Si,Al)O₃ post-perovskite and the D” layer

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We perform first-principles calculations based on density-functional theory to investigate the effects of Fe-Mg and MgSi-AlAl substitutions on the properties of MgSiO₃ perovskite (pv) and post-perovskite (ppv).

Our results show that Fe²⁺ partitions preferentially in ppv and significantly reduces the pv-ppv transition pressure. Fe²⁺ is in high-spin state; it decreases the seismic wave velocities and slightly decreases the seismic anisotropy of MgSiO₃. Al partitions preferentially in pv and increases the pv-ppv transition pressure. It decreases the seismic wave velocities and considerably increases the seismic anisotropy of post-perovskite. Consequently the D” layer can be explained by the pv to ppv transition in pyrolite, suggesting that D” is not only a repository of sunken slabs:

The variation of the physical properties of pv and ppv with chemistry also suggest that the regions where the D” layer is thicker should be rich in iron. They should have lower seismic wave velocities than the Fe-poor regions and comparable shear wave splitting. The ultra-low velocity zones, situated at the base of the D” layer may thus be even iron richer. The regions where the D” layer is thinner should be poor in iron and richer in alumina. These regions will have lower seismic wave velocities and will show larger shear wave splitting. In a hot mantle regime the transition is narrower as the variation of the element partitioning is reduced compared to a cold mantle regime where the transition is broadened.

We can also correlate seismic anisotropy with the crystal orientation and the chemical composition of pv and ppv.
Isotope tracing of atmospheric metals (Pb, Zn, Cd, Hg)
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Among other heavy metals, Cu, Zn, Cd and Pb concentrations are often well correlated in aerosols, precipitation or lichen samples, suggesting common sources of atmospheric emissions. However, quantifying the relative proportions of anthropogenic and natural metals and identifying different pollution sources is not straightforward unless sampling is done in the area of a known specific emitter (smelters, waste incinerators, ...). On the other hand, the isotopic composition of atmospheric Pb was revealed to be a powerful tool to discriminate anthropogenic from natural sources and between pollution sources having different isotopic compositions.

Relationships between Pb isotopes and metal concentrations (Pb, Zn, Cd, ...) may be looked at in order to document any coherence between sources and metal compositions in both space and time. Concentration relationships sometimes suggest that metal sources are decoupled and/or that metals have different reactivity during transport, leading to different atmospheric residence time. Zn concentrations in aerosols and precipitation samples are often found in excess relative the other metal concentrations, suggesting a significant source for Zn in atmospheric fallout that is not well constrain, either natural or anthropogenic. For example, a systematic difference in chemical and isotopic compositions (Pb-Zn) is observed between wet and wet+dry atmospheric depositions in NE North America. The data suggests that dissolved and particulate matter are not in isotopic equilibrium and that the different phases do not originate from the same sources. As an other example, Hg concentrations are also often decoupled from those of other heavy metals. In some coastal areas, Hg concentration is rather related to that of halogen elements, suggesting either a source relationship or atmospheric chemical reactions. Isotope fractionation of the $^{202/198}$Hg may be expected between gaseous metal Hg and an oxidised form such as HgCl$_2$ or HgBr$_2$ so that Hg oxidation by halogen elements should be isotopically traceable. In addition, volatile metals like Cd and Hg might be isotopically fractionated by industrial processes (volatilisation and condensation) and be traced in the environment. Combined to Pb isotopes, new isotopic systems such as Zn, Cd, Hg should provide further useful information about surface cycles of heavy metals.

Delta zero reference materials for stable isotope analysis and applications to in situ measurements
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For the last 3 to 5 years, measurement of the isotopic composition of various elements, which were classified as "non-traditional", exploded with the development of multi-collector ICP-MS. The data production was faster than consensual agreements on the expression and the notation of all these isotopic systems. In the mean time, simple conventions, such as primary and secondary reference materials (RM) and isotopes of normalisation, were adopted by many laboratories worldwide. Most primary "delta zero" RM were selected out of existing materials, namely from NIST or IRMM. According to the available certificate of analysis, some RM would not be sufficiently homogeneous in isotopic composition to fit the high measurement precision and accuracy now achieved in various laboratories. Except for the NIST SRM 981 Mg, which was effectively inhomogeneous at ±1% for the $^{25/24}$Mg ratio, Ca, Li, and Fe selected primary RM (respectively NIST SRM 915a, CAL-S, IRMM-14) revealed isotopic composition that was much more homogeneous than the reported uncertainties. This made the materials suitable for being delta zero RM. However, these are delivered as a powder or a liquid form, not suitable for in situ analysis techniques such as LA-MC-ICP-MS and SIMS.

Moreover, as bulk material is introduced in the mass spectrometer for in situ measurements, the instrumental mass bias is very dependent on the sample matrix analysed and a similar matrix is needed for reference materials. Thus, SIMS laboratories usually develop their own internal reference materials (IRM). These IRM are tested for their chemical and isotopic homogeneity at the microscale and are analysed by bulk methods relative to the appropriate delta zero RM. For each isotope system and sample matrix, two IRM are needed, one for normalisation and the other for checking on the signal linearity and accuracy. In order to distinguish true isotopic variations from "cryptic" matrix effects, we measured $^{44/40}$Ca in synthetic samples having different Mg/(Mg+Ca) ratios.

The measurement of O isotopes in garnet required 3 garnet IRM being Ca, Fe and Mg rich respectively. An integrated correction of mass bias using these IRM was used for samples of known chemical compositions (Vielzeuf et al., 2005).

References
Chondrite Barium, Neodymium and Samarium isotopic heterogeneity and early Earth differentiation

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Understanding the early earth differentiation requires using a cosmochemical reference that represents the bulk composition of the planet. The difference of ~20 ppm measured between chondritic and terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$ have been interpreted to reflect an early silicate differentiation of the Earth [1], $^{142}\text{Nd}$ being formed through time by the radiogenic decay of $^{146}\text{Sm}$ (half-life = 103 Myr). A critical requirement in this application is demonstration that the small isotopic variations do not simply reflect isotopic heterogeneity in the Solar nebula caused by imperfect mixing of the various stellar contributions [2].

New determinations of Ba, Nd, and Sm isotopic composition in 12 chondrites from different groups show that carbonaceous chondrites contain well-resolved $s$- and $p$-process deficiencies in these elements relative to ordinary and enstatite chondrites. Using $^{146}\text{Nd}/^{144}\text{Nd}$ to correct for the observed $s$-process deficiency produces a chondrite $^{146}\text{Sm}$-$^{144}\text{Nd}$ isochron that is consistent with previous estimates of the initial Solar System abundance of $^{146}\text{Sm}$ and a $^{142}\text{Nd}/^{144}\text{Nd}$ at average chondrite Sm/Nd ratio that is 21 ± 3 ppm lower than measured in terrestrial rocks [2, 3]. This result strengthens the conclusion that the deficiency in $^{142}\text{Nd}$ in chondrites compared to terrestrial rocks reflects $^{146}\text{Sm}$ decay.

Despite showing large variation in Lu/Hf, both refractory and lithophile elements like the REE, chondrites from different groups show little variation in their Sm/Nd ratios. No chondrites measured so far have $^{147}\text{Sm}/^{144}\text{Nd}$ high enough to explain the terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$. The $p$-process deficits in $^{146}\text{Sm}$ measured in carbonaceous chondrites suggest that ordinary and enstatite chondrites are better analogs for the bulk composition of the earth. Only superchondritic $^{142}\text{Nd}/^{144}\text{Nd}$ have been measured in terrestrial rocks. These results suggest that a major volume of Earth’s mantle was depleted in incompatible elements as a result of magma ocean crystallization. We are pursuing evidence for the presence of the complementary enriched reservoir, which should be preserved in the deep mantle despite 4.5 Gyr of mantle convection.

References

Ensuring accuracy in high-precision isotope ratio measurements

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Recent improvements in isotope ratio measurement precision are most clearly associated with physical improvements in the instruments used to make these measurements. Factors such as faraday cup efficiency, detector linearity and dynamic range, and consistent ion focussing clearly were critical in pushing precisions below the 10 ppm level. A number of other factors enter into the precision, and particularly the accuracy of isotope ratio measurements at this level. Common to both TIMS and ICP-MS are the question of the correct form of the instrumental mass fractionation correction, and the difficulty of detecting, and correcting for, isobaric interferences that may be a million times smaller than the signal analysed. ICP sources and the desire to measure stable isotope fractionation add another suite of issues that include: a richer and more complex atomic and molecular interference spectrum; the need to correct for sample mass fractionation that may occur during sample volatilization (in laser ablation), chemical separation, introduction into the plasma (particularly when using desolvating nebulizers), evaporation and ionization in the plasma, ion-electron separation, and ion extraction and focussing. Simple mass-only dependency of fractionation in the ICP was revealed as a myth as precisions moved from the hundreds to tens of ppm range. Many of these issues add to our dependency on high quality standards to ensure interlaboratory comparison. For TIMS Nd, for example, all available standards have more Ce and Sm than rock samples separated using modern procedures. For ICP-MS, standard comparison often cannot be done with relatively easily prepared single-element solutions, but requires standards with matrices similar to the samples being analysed to show that chemical separation and sample introduction effect standard and sample in similar ways. With care, these issues can be dealt with well enough to obtain isotope ratio precisions within a factor of 2 to 4 of counting statistics. Therefore, future precision improvements are likely to come from instruments that produce nanoamp beams from micrograms of sample instead of picoamps from nanograms, and have faraday detectors that can maintain perfect collection efficiency at this increased level of abuse. Improving precision of small sample analysis likely will depend primarily on improved sample utilization (delivery, ionization and transport) efficiency and on the development of electron multipliers that provide better linearity, dynamic range and longevity.
Saturation state of seawater with respect to the otavite-calcite solid solution

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In the oceans, the vertical distribution of dissolved cadmium (Cd) generally exhibits a nutrient-type profile. For this reason, it has been admitted that its depletion in the surface waters is regulated by biogeochemical processes. On the other hand, experiments on the sorption of Cd$^{2+}$ to calcite and/or aragonite surfaces have shown the effectiveness of these minerals – especially aragonite – in removing Cd from freshwater solutions (e.g. Prieto et al., 2003).

Our aim in this study has been to thermodynamically evaluate the possible occurrence of an inorganic removal of Cd from seawater, by sorption/coprecipitation onto/calcite, to form otavite-calcite solid solutions. This research has resorted to chemical modelling, previous to experimental observations.

Using the geochemical computer code PHREEQC (Parkhurst and Appelo, 2003), and JGOFs data collected from the equatorial Pacific (lat=0º, long=−140º) at depths from 20 to 175 meters, we have calculated the saturation state of this seawater with respect to the pure endmembers of the (Cd,Ca)CO$_3$ solid solution. We observe that seawater is supersaturated with respect to pure calcite and subsaturated for pure otavite. Furthermore, by computing the “stoichiometric supersaturation function” (Prieto et al., 1993) for the whole solid solution compositional range, we observe that the maximum supersaturation of seawater deviates slightly from the pure calcite composition, i.e. the solid phase most likely to precipitate from the aqueous solution is a Cd-bearing solid. Also, an increase in the dissolved Cd in the aqueous solution leads to a higher equilibrium distribution coefficient, which in turn results in a higher mole fraction of Cd in the precipitating solid phase.

These findings may suggest that an uptake of Cd from seawater on an inorganic basis might have some influence in the Cd depletion of the surface oceans. This inorganic removal would, however, depend on the availability of inorganic calcitic and/or aragonitic particles in the surface waters, among other factors.

References

Earthworms and mineral weathering

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The role of organisms in mineral weathering has been investigated by several authors. Studies have shown that bacteria, fungi, lichen and plants all have a role in mineral weathering. The role of annelid worms in mineral weathering has been little studied. Mineral weathering has been demonstrated in marine annelids (McIlroy et al. 2003) and there is some indication that earthworms may also play a role in mineral weathering (Suzuki et al. 2003). Earthworms interact intimately with the mineral soil and have a major influence on the physical structure and chemistry of soils. They increase the porosity and the water holding capacity of soils. Their casts have more available plant nutrients than the bulk soil. They transport material from the lower horizons to the soil surface and they are responsible for the incorporation of organic matter into the lower horizons. A series of experiments were run to investigate the effect of an epigeic earthworm (*Dendrobaena attemsi*) on soil minerals weathering. The minerals anorthite, biotite, olivine, kaolinite and smectite were mixed with a sterilized manure substrate. Four treatments were used to investigate the effect of the earthworms on the minerals; earthworms and minerals, and no earthworms and minerals. The earthworms were left to process the substrates for 1, 2, 4 and 6 months. Four sacrificial replicates were used. Changes in mineralogy were investigated by several authors. The role of organisms in mineral weathering has been little studied. Mineral weathering has been demonstrated in marine annelids (McIlroy et al. 2003) and there is some indication that earthworms may also play a role in mineral weathering (Suzuki et al. 2003). Earthworms interact intimately with the mineral soil and have a major influence on the physical structure and chemistry of soils. They increase the porosity and the water holding capacity of soils. Their casts have more available plant nutrients than the bulk soil. They transport material from the lower horizons to the soil surface and they are responsible for the incorporation of organic matter into the lower horizons. A series of experiments were run to investigate the effect of an epigeic earthworm (*Dendrobaena attemsi*) on soil minerals weathering. The minerals anorthite, biotite, olivine, kaolinite and smectite were mixed with a sterilized manure substrate. Four treatments were used to investigate the effect of the earthworms on the minerals; earthworms and minerals, earthworms and no minerals, no earthworms and minerals, and no earthworms and no minerals. The earthworms were left to process the substrates for 1, 2, 4 and 6 months. Four sacrificial replicates were used. Changes in mineralogy were investigated by several authors. The role of organisms in mineral weathering has been little studied. Mineral weathering has been demonstrated in marine annelids (McIlroy et al. 2003) and there is some indication that earthworms may also play a role in mineral weathering (Suzuki et al. 2003). Earthworms interact intimately with the mineral soil and have a major influence on the physical structure and chemistry of soils. They increase the porosity and the water holding capacity of soils. Their casts have more available plant nutrients than the bulk soil. They transport material from the lower horizons to the soil surface and they are responsible for the incorporation of organic matter into the lower horizons. A series of experiments were run to investigate the effect of an epigeic earthworm (*Dendrobaena attemsi*) on soil minerals weathering. The minerals anorthite, biotite, olivine, kaolinite and smectite were mixed with a sterilized manure substrate. Four treatments were used to investigate the effect of the earthworms on the minerals; earthworms and minerals, earthworms and no minerals, no earthworms and minerals, and no earthworms and no minerals. The earthworms were left to process the substrates for 1, 2, 4 and 6 months. Four sacrificial replicates were used. Changes in mineralogy were investigated by several authors.

References
Hydrogen concentration in mantle xenoliths from the Veneto Volcanic Province (NE Italy)

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Hydrogen contents were quantified in olivine (ol) and clinopyroxene (cpx) grains using the nuclear microprobe. The analysed minerals form spinel peridotite xenoliths with protogranular to porphyroclastic texture, hosted in alkaline basalts from two localities of the Eastern Veneto Volcanic Province (NE Italy). Mineral compositions indicated good re-equilibration at T-P upper mantle conditions (T = 850-950°C and P = 1.7±0.04 GPa). A combination of ERDA (Elastic recoil Detection Analysis) and RBS (Rutherford Back Scattering) methods were used for H measurements (Laboratoire Pierre Süe, France). The following analytical conditions were applied: 4He+ energy = 3.0 MeV, beam spot size = 4x4 µm2, 4x16 µm2 for ERDA, scanned on large sample areas, scattering angle = 170°, recoil angle = 30° (see also Bureau and co-workers, this issue). 22 samples were prepared following a specific protocol in order to decrease the effect of H absorbed at the surface of the polished samples. The same grains were analysed with electron microprobe, in order to check possible chemical heterogeneities in the areas investigated by ERDA. Chemically homogeneous ERDA maps were selected using Daudin et al. (2003): results reported below are referred to H depleted zones:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt ppm H</th>
<th>H2O ppm wt oxyde</th>
<th>Tot rel uncert</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ol-vpol2</td>
<td>24</td>
<td>213</td>
<td>15</td>
</tr>
<tr>
<td>Ol-vsol4</td>
<td>17</td>
<td>145</td>
<td>15</td>
</tr>
<tr>
<td>Cpx-vppx2</td>
<td>50</td>
<td>444</td>
<td>14</td>
</tr>
<tr>
<td>Cpx-vspx3</td>
<td>45</td>
<td>398</td>
<td>13</td>
</tr>
</tbody>
</table>

All cpx grains show H contents in the ranges reported from the literature for mantle analogue phases, obtained by commonly used IR spectroscopy, whereas ol grains have H concentrations close to or higher than maximum values reported for mantle ol (Ingrin & Skogby, 2000). Cpx samples systematically show H contents higher than those found for olivine: this is confirmed by recent IR data (Demouchy et al., 2006) and probably due to the fact that H diffusion at mantle temperatures is faster in olivine than in pyroxene.

References

In situ cosmogenic nuclides in river bedload. Implications for catchment-scale erosion rate and surface exposure dating

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Terrestrial Cosmogenic nuclides (TCN) have been widely used to date the exposure of alluvial surfaces and to estimate catchment scale erosion rates. However, dispersion in TCN concentrations in distinct samples of the same locality remains to be explained.

We develop a numerical model to calculate the TCN concentration at a clast center on hillslope and along a main river path. The hillslope model is an analogue to freeze-thaw and rock fall. In river, transport velocity of clasts depends: 1- on a probability to be buried in a mixing sediment layer, which depends on clasts size, or within adjacent terrace, 2- on clast size, which decreases downstream by abrasion. Below a specified size, clasts go in the washload. We run the path of numerous clasts of variable size and we analyse statistically their TCN concentration at river outlet.

Clast abrasion tends to increase the mean and variance of concentrations of the small clasts fraction because this class incorporates initially big clasts which traveled a long distance and initially small clasts launched near outlet. However, the final size-concentration relationship depends on the initial size distribution. This suggests that minimizing inheritance in surface exposure dating requires the analysis of clast size distribution and lithology. Moreover, this size-concentration relationships suggests that the largest hillslope inheritance is not necessarily in fine sand but may be in coarser fractions. The distribution of concentrations does not evolve any more from a certain river length corresponding to a no-deposition critical travel length. This suggests that bedload might integrate only material from the bottom of large catchments, which might bias TCN-derived catchment-scale erosion rates. The proposed theory can be tested from measurements in bedload sediments of differing sizes. In addition, we provide approximate analytical solutions which could permit to constrain the mean transport velocity law for a clast.
Benthic foraminifera as a novel substrate for deep-water Nd isotopes

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The neodymium (Nd) isotopic composition of Fe-Mn crusts, fish teeth and leachates of Fe-Mn oxides from bulk sediment have all been used to reconstruct deep ocean circulation. However, each has its limitations, including low temporal resolution or terrigenous contamination. Here we present species specific Nd isotope records, coupled with multiple element/calcium ratios, from a highly available substrate, benthic foraminifera. Comparisons are made with a seawater Nd isotope profile to assess their ability to accurately represent modern ocean composition.

Holocene depth profiles from two sites, and core-top scrapings from 4 sites, all in the NE Atlantic, were hand picked for monospecific samples of Cibicidoides wuellerstorfi, Planulina ariminensis, Melonis barleaneum, and Uvigerina peregrina. Nd concentrations are found to be three times higher in epifaunal species than in infaunal (1.5ppm compared to 0.5ppm). The epifaunal εNd profile reveals a constant down-core (0-10cm) value of -12, whilst the infaunal profiles are identical for all but the upper 2cm. Nd concentrations in benthic foraminifera are also found to co-vary with Cd/Ca ratios, a widely used palaeoceanographic water mass proxy, providing confidence in the use of Nd isotopes from benthic foraminifera.

The foraminifera Nd isotope data are compared with both a new nearby seawater profile and with Fe-Mn oxide leachate data. Though the εNd of bottom water, foraminifera and leachates all agree, elevated Nd concentrations in bottom water samples suggest an addition of Nd to bottom water from sediment and/or pore water. Benthic foraminifera are therefore thought to reliably record bottom water Nd isotopic composition. Bottom water at this ocean margin site is influenced by interaction with sediments as recently proposed for many ocean margin settings [1].

References

Mantle-derived carbonados: Insights from Dachine diamonds (French Guiana)

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Carbonados are black/greyish almost graphitic in appearance non gemmy polycrystalline diamonds, up to 3100 carats in size, made of sintered irregular diamond grains in the nano- to micrometer range. Carbonado sensu-stricto seem geographically restricted to Brazil and Central Africa. Understanding the formation of carbonado is one of the most enigmatic problems in diamond geology. It has been suggested that carbonado may either be formed during impact metamorphism, by irradiation of carbonaceous-rich material or even formed in exploding super-novae. A mantle-derived origin is generally rejected based on the observation that carbonados do not occur within either lamproite and kimberlite which bring deep mantle-related diamonds to the surface and because carbonados have a series of features clearly distinct from any other type of diamond: among them their carbon isotope signatures centered at ~-28‰ (e.g. [1]) and their poorly advanced nitrogen aggregation state [2] which require that the sample spent virtually no time in the Earth’s mantle.

We studied 160 diamonds from the Dachine area (French Guiana). These diamonds are the only samples recovered so far from a volcaniclastic komatiite [3]. The samples are monocrystalline (i.e. non polycrystalline) macrodiamonds (>500 microns) mostly (>95%) irregular in shape with resorbed octahedron and cubes being occasionally recognised. No syngenetic inclusion has been identified yet. Most (>90%) samples are nitrogen free (Type II) and the few samples containing nitrogen (Type I) are characterised by low aggregation states. Their carbon isotope compositions range from -31.9 to +0.15‰ with an average of -24.4‰.

The observed general 13C-depletion among diamonds from Dachine including both octahedron and cuboids (and their respective resorbed forms), among both Type II and Type I diamonds demonstrates that an entire diamond population with 13C-depletion can originate from the mantle. Thus the long-standing statement that carbonados could not derive from the mantle based on distinct carbon isotope composition and N-speciation is now contradicted by our new data and the possibility of carbonados being formed in the mante deserves closer examination. A mantle-related formation of carbonados would succeed in explaining first order observations in particular their large size.

References
Compositional gradient of Cpx produced by fluid assisted eclogitization

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The Precambrian granulite facies assemblages (P ≤ 10 kbar, 800°C) of the anorthositic rocks of the Bergen Arcs, Western Norway was overprinted by eclogite facies assemblages (P=15-20 kbar, 650-700°C) along shear zones and fluid pathways associated with the Caledonian orogenic cycle (Jamtveit et al. 1990).

The aim of this study is to investigate the mechanism of fluid-mineral interaction that take place as the granulite facies clinopyroxene is altered to omphacite using microscopy and micro-analytical techniques (SEM, EMP and TEM).

The investigated sample comes from the margin of a shear zone and contains relicts of garnet and clinopyroxene while the former plagioclase domains are reacted to kyanite, omphacite, amphibole, clinozoisite and white micas (paragonite and phengite). Relict clinopyroxene in contact with plagioclase domains is replaced by the following sequence of reaction zones: 1) a core of Al-rich diopside (granulite facies), locally with domains of intergrown garnet and diopside. 2) An inner zone consisting of coarsely intergrown pyroxene (Jd 24) and amphibole (symplectite A). 3) An intermediate zone of porous pyroxene (Jd 43) with inclusions of dolomite. 4) An outer zone consisting of grains of omphacite (Jd 59) surrounded by symplectites of amphibole and plagioclase (symplectite B).

The reaction zones that developed around the granulite facies pyroxene core have a total width of ca 500 µm and formed during reaction between the infiltrating fluid and the original pyroxene.

References
A 23,000 year molecular isotopic record of variability in SE African vegetation and hydrology from Lake Malawi

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Vegetation change is controlled primarily by the influences of temperature, hydrology, and atmospheric [CO₂]. In tropical Africa, hydrological variations appear to be more important than either temperature or [CO₂]. Furthermore, hydrological variability in tropical Africa has a much more profound impact on human welfare than temperature or [CO₂]. Thus, reconstructing the timing of past wet and arid phases in this region is critical to understand the role and response of the tropics to global climate change. Here, we present a molecular isotopic record of vegetation and climate change from a well-dated sediment core from Lake Malawi spanning the period from the Last Glacial Maximum (LGM) to the present.

Our data show that the region surrounding Lake Malawi was cooler and drier during the LGM and the Younger Dryas (YD) than through the Holocene. This change of hydrology directly influenced the vegetation in the surrounding watershed, with a greater proportion of C4 plants such as grasses (which compete well in dry conditions) during these times. Conversely, the wetter and warmer Holocene is characterized by an increase in the proportion of C3 plants (such as trees) that require greater amounts of moisture to be successful. Finally, we note that at 11 cal ka there is a shift in the coherence between the Lake Malawi aridity record and high latitude ice core methane records (records of global tropical wetness); these records are in phase prior to 11 cal ka, and antiphased after this time. We attribute this to a shift in the dominant mechanisms controlling aridity associated with a shift in the mean latitudinal position of the Intertropical Convergence Zone.

The origin of high ³He/⁴He values in oceanic lavas: Arguments against a heterogeneous upper mantle source

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One of the contentious issues fueling the debate on the origin of intraplate magmatism is the source of high ³He/⁴He ratios in oceanic lavas. The contemporary hotspot hypothesis posits that the high ³He/⁴He signature is coming from a distinct source reservoir that lies relatively deep in the mantle whereas others argue that there is no such a reservoir. For example, the SUMA (Statistical Upper Mantle Assemblage - Meibom & Anderson, EPSL 17, 2003) hypothesis argues that the compositional variability of oceanic lavas results from sampling upon melting of the heterogeneous upper mantle. It claims that extreme isotopic signals, such as high ³He/⁴He ratios, of some oceanic lavas are due to small degrees of partial melting that preferentially sample dispersed, anomalous mantle components. In contrast, large degrees of partial melting sample a larger volume, and hence many components of the heterogeneous mantle; these also promote more effective mixing of the resulting melts, producing a relatively homogeneous composition typified by that of N-type MORB.

To constrain the source of high ³He/⁴He lavas, we analyzed a dozen representative samples from the axis and near-ridge seamounts in the 11°45’N to 15°00’N segment of the EPR. Axial lavas are N- to T-type MORB that came from a heterogeneous mantle source (Castillo et al., G3 1, 2000). Seamount lavas extend the compositional variability of axial lavas to both higher and lower Sr, Nd and Pb isotope values, suggesting that seamount lavas indeed result from smaller degrees of partial melting of the heterogeneous mantle beneath the region. Our preliminary results, however, also show that the majority of both axial and near-ridge seamount lavas have indistinguishable, MORB-like ³He/⁴He values, at 8 +/- 1 RA, over a range of He concentrations. The remainder have ³He/⁴He < 8 RA. Thus we conclude that the heterogeneous Pacific upper mantle cannot provide the high ³He/⁴He signature in oceanic lavas.
Metamorphic history of the pre-3750 Ma Nuvvuagittuq Supracrustal Belt, Québec (Canada)

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The ca. 3750 Ma Nuvvuagittuq Supracrustal Belt (NSB) in northwestern Québec is among the oldest volcano-sedimentary sequences thus far discovered; it overlaps in age with the Eoarchean Isua Supracrustal Belt and the Akilia association supracrustal enclaves in West Greenland [1]. Mapped NSB sequences are dominated by amphibolites (± Gt), ultramafic rocks, granitoid gneisses and leucogranite intrusions, but also comprise both chemical and detrital metasediments such as finely laminated banded iron-formations and quartzite. Like other pre-3600 Ma terranes, the NSB has been thermally metamorphosed and multiply deformed. Our preliminary garnet-biotite and plagioclase-amphibole geothermometry coupled with U-Pb zircon geochronology suggests that the belt last reached the mid- to upper amphibolite facies (550-600°C) consistent with growth in a metamorphic fluid. The core age yields an age 2736±25 Ma with very low Th/U (0.009) consistent with growth in a metamorphic fluid. The core age of 3743±26 Ma was reached at a depth of 4.6 km thick overgrowth on the R.H. axis. Shaded regions have implausible O₂ fluxes. After the advent of oxygenic photosynthesis, photochemically-stable anoxic oroxic atmospheres can exist (Fig. 1). A ~3% increase in the ratio of O₂:CH₄ fluxes to the atmosphere causes a transition to the anoxic state. In an anoxic environment, O₂ and CH₄ flux to the atmosphere in a 2:1 redox neutral ratio, according to CO₂ + 2H₂O = 2O₂ + CH₄, the net reaction of photosynthesis + methanogenesis. This ratio increases if sufficient sulfate allows microbial anerobic oxidation to change the reduced partner of O₂ to CH₄. Alternatively, with increasing sulphate, the reduced partner of O₂ may change from CH₄ to biogenic sulphur gases. These gases, unlike CH₄, are kinetically more stable than O₂ and may have left a signal in S-MIF. References


Archean methane, oxygen and sulfur

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Mass-independent fractionation (S-MIF) of S isotopes marks the 2.4 Ga division of Earth’s anoxic and oxic atmospheres. We emphasize that S-MIF also indicates abundant Archean atmospheric CH₄. In addition, the magnitude of S-MIF reflects the size of S gas fluxes to the atmosphere. Thus, high amplitude S-MIF in the late Archean may indicate the advent of significant biogenic S gases. Relatively inert CH₄ leaves little geochemical trace. For many years, the only evidence that Archean CH₄ was abundant came from a global distribution of 2.5-2.8 Ga ²³C-enriched kerogens attributed to methanogenic CH₄ incorporated into methanotrophs. S-MIF now provides independent evidence. S-MIF occurs when S exits the atmosphere in soluble sulfate and insoluble polymerized sulfur (S₈) [1]. Our models [2] show that O₂ <1 ppmv and a high abundance of CH₄ are required for significant rainout of S₈. Sufficient CH₄ enables the reduction of S-bearing gases to sulfur (S₈). Plentiful H₂ is an alternative but is implausible because H₂ is biologically converted to CH₄.

Fig. 1: Fluxes in a 100 ppmv CH₄ atmosphere. Plus symbols (+) indicate the ratio of O₂ (φO₂) to CH₄ (φCH₄) bio-fluxes, on the R.H. axis. Shaded regions have implausible O₂ fluxes. After the advent of oxygenic photosynthesis, photochemically-stable anoxic oroxic atmospheres can exist (Fig. 1). A ~3% increase in the ratio of O₂:CH₄ fluxes to the atmosphere causes a transition to the anoxic state. In an anoxic environment, O₂ and CH₄ flux to the atmosphere in a 2:1 redox neutral ratio, according to CO₂ + 2H₂O = 2O₂ + CH₄, the net reaction of photosynthesis + methanogenesis. This ratio increases if sufficient sulfate allows microbial anerobic oxidation to change the reduced partner of O₂ from gaseous CH₄ to solid sulphide. Alternatively, with increasing sulphate, the reduced partner of O₂ may change from CH₄ to biogenic sulphur gases. These gases, unlike CH₄, are kinetically more unstable than O₂ and may have left a signal in S-MIF. References

Source depletion versus extent of melting in the Tongan Sub-arc mantle

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The currently active Tonga arc produces some of the most depleted compositions found in oceanic arcs. This signature is observed most strongly in their depletion in High Field Strength Elements (HFSE) relative to Depleted MORB Mantle (DMM) and Light Rare Earth Elements (LREE) compared to Heavy Rare Earth Elements (HREE). Previous work on low HFSE concentrations (DMM) and Light Rare Earth Elements (LREE) compared to Heavy Rare Earth Elements (HREE) observed most strongly in their depletion in High Field Strength Elements (HFSE) relative to Depleted MORB Mantle (DMM) and Light Rare Earth Elements (LREE).

Here we present new Nb-Ta data for Tongan volcanics in order to try to differentiate between arc magma production (i) prior melt extraction in the back-arc that depletes the source of arc magmas in the most incompatible elements [1]; or (ii) higher degrees of partial melting during melting in the Tongan Sub-arc mantle has produced two fundamentally different models; (i) prior melt extraction in the back-arc that depletes the source of arc magmas in the most incompatible elements [1]; or (ii) higher degrees of partial melting during arc magma production [2]. Here we present new Nb-Ta data for Tongan volcanics in order to try to differentiate between these models by developing a model for melt generation in the mantle underlying the Tonga arc/Lau Basin back-arc system.

Nb/Ta ranges from 18-3.5, with Nb between 0.2-0.4ppm. Data were acquired by LA-ICPMS of non-fluxed sample glasses produced using a molybdenum strip fusion technique. Significantly, the lowest Nb/Ta values are found in the north of the arc where both subduction and attendant back-arc spreading rates are greatest. These findings are in agreement with a model whereby greater degrees of mantle melt extraction in the back-arc produces more depleted source compositions beneath the arc [3].

Large degree batch melts (up to 35%) of DMM fail to reproduce the sub-chondritic Nb/Ta values (<17) of the arc. Alternatively, melting of source compositions having undergone 0.1-7% prior melt extraction produce melting curves that bracket the dominant arc trend.

Nb normalised plots of fluid immobile elements (e.g. Yb vs. Sm) produce a linear array that plot parallel to mixing lines for 20-35% remelting of 0.1 and 7% depleted DMM sources. Simple calculations show that the average sub-arc Tongan source melts at between 1-1.25% depletion. In the case of the Lau Basin spreading centre, this corresponds to the incorporation of the lower 4-5km of the melt column in to the sub-arc melting regime. This is in excellent agreement with current models for melting regimes at active spreading centres whereby only the lower most portion of the melt column has flow paths within the convecting asthenospheric mantle [4].

References

In situ determination of arsenic speciation in natural fluid inclusion from Au-rich quartz veins

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Elemental speciation (i.e., oxidation state, nature of aqueous complex) in hydrothermal fluids is crucial for modelling fluid-fluid and fluid-rock interactions. Elemental speciation in hydrothermal fluids preserved as fluid inclusions can be studied by heating the host mineral while performing X-ray absorption spectroscopy. This technique was applied to fluid inclusions from gold mineralisations at the arsenic K-edge. As and Au are closely associated in many Au deposits, but the cause of this association remains controversial. We aim to better understand As transport in Au-bearing fluids by comparing speciation in natural fluids with recent experimental results on synthetic systems.

XRF mapping of single fluid inclusions showed heterogeneous elemental distributions at room temperature (Fig. 1), thus stressing the need of performing spectroscopic analyses at homogenisation temperature.

Figure 1: left: optical view of a CO2 rich fluid inclusion. Middle: As distribution in the same inclusion. Right: XANES spectrum at the As-K edge at room temperature in an inclusion of the same generation.

XANES experiments were performed using a Linkam THMSG-600 heating-stage on the new microfocus end-station installed on the ESRF FAME beamline. XANES spectra (Fig. 1) were measured from 25 to 350°C to record evolution in arsenic speciation in those fluid inclusions.

This work details arsenic speciation changes upon heating and stresses the high interest of fluid inclusion studies based on experiments performed in situ.
Geological storage as a carbon mitigation option

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The most promising approach to solve the carbon problem involves widespread implementation of zero-emission power plants. These are likely to be fossil fuel-based plants with carbon capture and storage (CCS) technology. Low-emission electricity has the secondary advantage of allowing for electrification of the transportation sector, and as such can lead to very large reductions in CO\textsubscript{2} emissions if implemented at the global scale. While a variety of storage options are being studied, geological storage appears to be most viable. Injection of captured CO\textsubscript{2} into deep geological formations leads to a fairly complex flow system involving multiple fluid phases, a range of potential geochemical reactions, and mass transfer across phase interfaces. General models of this system are computationally demanding, with the problem made more difficult by the large range of spatial scales involved, and the importance of local features for both fluid flow and geochemical reactions. An especially important local feature involves leakage pathways, with one example being abandoned wells associated with the century-long legacy of oil and gas exploration and production. Such pathways also have large uncertainties associated with their properties. Therefore, inclusion of leakage in the storage analysis requires resolution of multiple scales, and incorporation of large uncertainties. Taken together, these render standard numerical simulators ineffective due to their excessive computational demands. In this lecture, I will present a series of simplifications to the governing equations that can ultimately render the system solvable by analytical or semi-analytical methods. These solutions, while restrictive in their assumptions, allow for large-scale analysis of leakage in a probabilistic framework.

Palaeohydrology of the Mulhouse Basin: Are fluid inclusions in halite tracers of past seawater composition?

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Brine reactions processes were the most important factors controlling the major-ion evolution in the Oligocene, Mulhouse Basin (France) evaporite basin. The combined analysis of fluid inclusions in primary textures in halite by Cryo-SEM-EDS with sulfate-δ\textsuperscript{34}S, δ\textsuperscript{18}O and \textsuperscript{87}Sr/\textsuperscript{86}Sr isotope ratios reveals hydrothermal inputs and recycling of Permian evaporites, particularly during advanced stages of evaporation in the Salt IV member which ended with sylvite formation. The lower part of the Salt IV evolved from an originally marine input. Sulfate-δ\textsuperscript{34}S shows Oligocene marine-like signatures at the base of the member (Fig.1). However, enriched sulfate-δ\textsuperscript{18}O reveals the importance of re-oxidation processes. As evaporation progressed other non-marine or marine-modified inputs from neighbouring basins became more important. This is demonstrated by an increase in K concentrations in brine inclusions, Br in halite and variations in sulfate isotopes trends and \textsuperscript{87}Sr/\textsuperscript{86}Sr ratios. The recycling of previously precipitated evaporites was increasingly important with evaporation. Therefore, regardless of the apparent marine sequence (gypsum, halite, potassic salts), the existence of diverse inputs and the consequent chemical changes to the brine preclude the use of trapped brine inclusions in direct reconstruction of Oligocene seawater chemistry.

**Figure 1:** SO\textsubscript{4}-δ\textsuperscript{34}S, δ\textsuperscript{18}O and \textsuperscript{87}Sr/\textsuperscript{86}Sr isotope trends.
Origin of calcium isotope fractionation in river waters: Evidence from the Strengbach catchment, France

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Understanding calcium isotope systematics in river and surface waters plays a key role in unravelling the calcium oceanic cycle as well as characterizing chemical weathering processes in continental systems. However, only few studies have focussed on deciphering the factors controlling calcium isotope fractionation in continental river waters. In order to shed light on the origin of calcium fractionation in river waters, we investigated the different reservoirs for calcium isotopes and their interactions in a forested first order scale catchment (Strengbach, France).

Variations of $\delta^{44/40}$Ca within springs, brooks and river waters are small (0.17-0.87‰) and display typical values for continental rivers, reflecting the control of lithology on calcium isotopic composition of water on a global scale. Compared to these values, soil solutions are significantly depleted in light calcium ($\delta^{44/40}$Ca: 1.00 to 1.47‰) whereas vegetation is enriched in light calcium ($\delta^{44/40}$Ca: -0.98 to +0.19‰). At the small watershed scale, our results suggest that vegetation controls the calcium isotopic composition of waters: (i) the origin of depletion in light calcium in soil solutions is directly linked to calcium recycling and fractionation within plants, (ii) the calcium isotopic composition of the water at the outlet of the watershed shows a yearly cycling directly related to the activity of vegetation.

In summary, surface waters are influenced by vegetation whereas deep waters preserve the calcium isotopic signature inherited from the parent rock. Therefore, calcium isotope analysis clearly helps to evaluate the role of vegetation and to unravel the hydrologic cycle at the watershed scale.

Durability and degradation of oil well cement exposed to a source of H$_2$S and CO$_2$ gases

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Introduction

Usually, the oil industry gives relevance to failures in metallic structures produced by the corrosion caused by H$_2$S and CO$_2$ and its implication in the well life. The search of new reservoirs in deep environment conditions, in which concentrations of H$_2$S and CO$_2$ are noteworthy, requires the study of the sour gas effect on nonmetallic structures, such as oil well cement.

Methods

Recent studies have demonstrated the effect of degradation in the chemical and mechanical properties of oil well cement exposed, in the short term, to aggressive atmospheres, thus, endangering the well life (Centeno et al., 2005). This study shows the influence of H$_2$S and CO$_2$ gases and their mixtures, in different H$_2$S/CO$_2$ ratios (0.1; 0.2 and 0.4), on the chemical and mechanical properties of cement samples (class G and H) exposed to high pressure and temperature in well bore real conditions, using a exposure time of 20, 40 and 80 days. Test tubes were exposed to the action of a mixture of CO$_2$/H$_2$S, dissolved in water, in a Parr reactor for HPHT. The test solution was analyzed by Inductive Coupled Plasma -ICP- (elements) and Ionic Chromatography (anions). Solid phase mineralogy was determinate by SEM and X-ray analysis.

Results and Conclusions

The H$_2$S and CO$_2$ mixtures have an effect on cementing material causing a mass profit corresponding to CaCO$_3$ formation, that is maximum when the H$_2$S/CO$_2$ relation approaches to 0.2. This CaCO$_3$ mass profit was detected with test tube weight comparison, before and after acid attack, and mineralogy analysis. For H$_2$S/CO$_2$ ratios > 0.2 a mass loss was observed, which causes degradation of cementing material verified by compressive strength decrease.

The results allow to model the effect of oil well cement dissolution with time, for H$_2$S/CO$_2$ ratios < 0.2 using second degree polynomials, in which the dependent variable is a chemical species such as: Ca$^{2+}$, Na$^+$, K$^+$ or SO$_4^{2-}$, or a physical measure such as the compressive strength.

References

Dissolution of oil well cement in presence of CO$_2$/H$_2$S under HTTHP. Geochimica et Cosmochimica Acta 69, supplement 1, pp. 1-915
Stability of nanoparticles in the presence of biological material and their toxicity

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Cerium is the most abundant lanthanide and generally the only one to undergo redox reactions at the Earth’s surface. Because their unique electron transferring properties, Ce-minerals have been proposed as optimal material for nanotechnological applications. Yet, to date, little mechanistic information is available on the stability of Ce-bearing nanoparticles in the presence of biological material and their toxicity.

Here, we study molecular interactions between small-sized CeO2 and biomolecules (e.g., DNA, RNA, proteins) using carbon and cerium spectroscopy. As determined by aggregation kinetics by Dynamic Light Scattering (DSL) and UV, the aggregation behavior of nanoCeO2 is susceptible to pH variations imposed by the presence of biological moieties. The aggregation kinetics of aggregation is of zero-order with respect to solid concentration. Results show progressive transformation of biological material (as % carbon) with decreasing CeO2 particle diameter (13 < d < 84 Å), which substantiates an intimate relation between CeO2 unit cell expansion and reactivity towards organics susceptible to undergo redox transformations. As evidenced by C and Ce spectroscopy, organic polymers that form because of oxidation are distributed next to the mineral surface and its occurrence is coupled to Ce reduction-oxidation. Analyses by nephelometry of acidophiles and fungi cultures incubated with nanoCeO2 at pH 2 show variations in the population density and growth rate values, which reveal bonding site specificity and in agreement with non-enzymatic results.

Experimental determination of equilibrium solubility quotients of the natural colemanite in NaCl solutions up to 2.0 m

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Colemanite (CaB3O4(OH)3:H2O) is an important evaporite borate mineral. Experimental studies on the solubility constants of colemanite in a wide range of ionic stengths are few. In this study, we experimentally determined the equilibrium solubility quotients of the natural colemanite from the Kestelek, Turkey, in NaCl solutions ranging from 0.1 m to 2.0 m at 20 °C. The solubility constant of the natural colemanite at infinite dilution at 20 °C from this study regarding the following reaction,

$$\text{CaB}_3\text{O}_4(\text{OH})_3\cdot\text{H}_2\text{O} + 4\text{H}_2\text{O} = \text{Ca}^{2+} + 3\text{B(OH)}_4^- + \text{H}^+$$

is $-17.5\pm0.1$ (2σ) based on the Specific Interaction Theory (SIT) model for extrapolation to infinite dilution according to the weighted linear regression. The derived ∆ε is 0.027. By using $\varepsilon(\text{Ca}^{2+}, \text{Cl}^-)$ and $\varepsilon(\text{H}^+, \text{Cl}^-)$ from Xiong (2006), the $\varepsilon(\text{Na}^+, \text{B(OH})_4^-)$ derived from this study is $-0.09\pm0.02$. This value is in excellent agreement with the literature value of $-0.07\pm0.05$ evaluated by Ciavatta (1980).

The above solubility constant is significantly different from the one calculated regarding the above reaction from the Gibbs free energy of formation of colemanite predicted by Li et al. (2000) in combination with the auxiliary data from Wagman et al. (1983), which is $-13.41$ in logarithmic unit at 25 °C, or $-13.57$ at 20 °C according to the enthalpy of the reaction to extrapolate to that temperature. This means that colemanite is more stable than previously predicted.

References

Geochemical and geophysical insights into a large magmatic system in Central Java, Indonesia

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Ascent and stalling of primary arc magmas in the crust promotes modification by numerous processes including crystallisation, magma mixing and crustal interaction. We have studied a suite of recent lavas, crystals, enclaves, plutonic inclusions, and crustal xenoliths to evaluate the role of these processes in magmatic evolution at Merapi volcano and the nature of the magmatic system feeding volcanism.

Crystalline components in recent Merapi lavas and hosted inclusions provide us with two complimentary sets of data:

1. Petrochemical and geobarometric analysis of igneous inclusions combined with geophysical techniques yields information on the structure of the Merapi plumbing system. Our results indicate that Merapi overlies a network of numerous magma bodies reaching down to the upper mantle. This is a far more extensive supply system than previously considered, with recycling of igneous material and the potential for increased interaction with the crust beneath Merapi.

2. Skarn-type meta-sedimentary xenoliths highlight the influence of the carbonate country rock on Merapi magma. Crystals from Merapi lavas show clear signs of interaction with this crust and their correlation with crystals in meta-sedimentary xenoliths may indicate integration of xenocrystic material. This interaction is not preserved in whole rock isotope analyses. Whole rock compositions may be buffered given the scale of the system feeding Merapi and potential recycling of igneous material.

Combined petrochemical and geophysical data indicate the development of a large and complex magmatic system in the crust of Central Java. These findings require a re-evaluation of how Merapi and potentially other similar systems are considered.

Murmanite lujavrites: A neglected member of the peralkaline intrusive sequence at Lovozero (Kola, Russia)

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Although murmanite lujavrites (ML) were distinguished at Lovozero (Kola, NW Russia) some 40 years ago, they are completely neglected in the recently published literature. These rocks occur as a discrete intrusive suite in the Lovozero composite pluton; they are emplaced into the earlier-formed Differentiated and Eudialyte-Lujavrite Units as small plugs and dike(let)s lacking chilled margins. The name ML alludes to a characteristic trachytoid texture of these rocks and the presence in them of abundant oikocrysts of exotic minerals (e.g., murmanite, lamprophyllite and lorenzenite). Clinopyroxene (Cpx), amphiboles (Amp) and eudialyte occur both as euhedral groundmass crystals and as oikocrysts. The groundmass also comprises alkali feldspars, nepheline (Ne), sodalite and accessory REE, Sr, Ti-Nb, U and Th minerals.

Cpx has the compositional range $\text{Ae}_{69-94}\text{Di}_{7-17}\text{Hd}_{0-20}$; Amp is zoned from (fluor-)magnesio-arfvedsonite to (potassic-)arfvedsonite; Ne typically has higher Ks and lower SiO$_2$ contents (mol.%) in the rim (overall range Ne $69-82$Ks$15-22$Qtz$1-14$). The ML are peralkaline rocks ($K_{\text{peralk}} \geq 1.4$) enriched in silica, Na, K, Rb, Mn, Sr, REE, Zr, Hf, U, Ta and W, but depleted in Mg, Ca, Fe$^{2+}$, Sc, V, Ti and P relative to the bulk Lovozero composition. This petrographic suite is characterized by its consistently superchondritic Zr/Hf (40-55) and subchondritic Nb/Ta signature (7-15). The ML are isotopically indistinguishable from the major intrusive units: ($^{87}\text{Sr}/^{86}\text{Sr}$)$_i = 0.7037-0.7043$; $\varepsilon$Nd) = 3.4-3.8. We interpret the ML suite to have crystallized from a highly evolved phonolitic melt similar to the one that produced the Eudialyte-Lujavrite unit (EL melt), but containing higher normative Na$_2$SiO$_3$ and lower CaMgSi$_2$O$_6$. The ML parental magma could be derived from the EL melt by fractionation of Cpx, eudialyte, loparite and apatite.
Geospeedometry as a tool for identifying different lithotectonic packages in Higher Himalayan Crystallines, Sikkim, India

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The Higher Himalayan Crystallines (HHC) in Sikkim, India is made up of an interlayered sequence of pelitic migmatites (Qtz-Kfs-Pl-Silik-Bt-Grt-Ilm-Rut-Crd-Spl, with Kfs > Pl), quartzofeldspathic gneisses (Qtz-Pl-Kfs-Grt-Ilm-Bt) and minor metabasites and calc-silicates. Unlike in the adjacent sections in Eastern Nepal (e.g. Goscombe et al., 2006), there is no obvious lithological contrast within the section of HHC studied by us in Sikkim. Thermobarometry indicates metamorphic pressures and temperatures of ~ 8 Kbar, 700 - 850 °C. Textural relations indicate an early decompressional path (documented by breakdown of garnet to cordierite, plagioclase or plagioclase + spinel), followed by cooling. This is similar to the path deduced by Ganguly et al. (2000) for other rocks from nearby regions. There is evidence of melts produced during the decompression (e.g. Harris et al., 2004), which presumably reacted with garnet during cooling to produce various symplectitic textures. While all of these features are found spread across the entire HHC sequence between the Main Central Thrust (MCT) and the South Tibetan Detachment System (STDS), compositional zoning in garnets are clearly different in different parts. We have modeled these compositional gradients using a code that allows multistage thermal histories with different boundary conditions to be handled. In the northernmost part of the HHC, just south of the STDS, compositional zoning indicates very rapid cooling (e.g. from 800 - 600 °C within 100000 years). In contrast, in the southern part of the HHC just north of the MCT, there appear to be two groups of rocks: (i) initial rapid cooling for about 50000 years followed by slower decompositional cooling over the next 2 myrs., and (ii) single stage, relatively slow cooling between 800 - 600 °C over 0.5 myrs. These results show that it is possible to use geospeedometry to distinguish lithotectonic packages evolving with different P-T-t histories, even when petrographic criteria fail to reveal obvious distinctions. This may prove to be an easily applicable but useful tool for mapping in high grade terrains.

References

Cenozoic topographic evolution of the Western North America Cordillera

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Stable isotopic studies of intermontane basins in the Rocky Mountains, Basin and Range and Sierra Nevada record the isotopic fingerprint of an evolving landscape during the Cenozoic. During the early Eocene the western edge of this orogen consisted of high proto-Sierra Nevada and to the east lay a broad plateau of the Sevier hinterland bordered on its east by intraforeland basins with local basement uplifts. Mean elevation was spatially and temporally transient with increased peak elevations and elevated relief migrating from north to south. This occurred at 50-47 Ma in SW Montana, at 40-35 Ma in N. Nevada, and by ~22 Ma in S. Nevada, as evidenced by large negative shifts in O isotopes that are diachronous in the Basin and Range. During this time the drainage basins in the Sevier foreland were reorganized which resulted in river capture events that caused rapid (<200 ka) and large O isotope shifts in these lakes. Sr isotopic studies of lacustrine rocks in the intraforeland basins and paleosols in the hinterland suggest that the drainage networks of these basins evolved from local networks draining adjacent basement uplifts to large catchments that extended deep into the Sevier hinterland. This drainage reorganization is diachronous first occurring in the north and sweeping south with time, as evidenced by the temporal variation in O isotope profiles in the intraforeland basins. North to south migration of a high rugged landscape is contemporaneous with the timing of core complex formation and volcanism. As such, our work is consistent with tectonic models calling for north to south removal of the Farallon slab or delamination of the mantle lithosphere, both of which would have caused a rise in surface elevations and triggered dissection of a pre-Cenozoic continental plateau.
Steady state chemical weathering in an eroding landscape

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We developed a steady-state chemical weathering model that describes the advection of fresh rock into the weathering zone and the dissolution of minerals during weathering (Waldbauer and Chamberlain, 2005, Ecol. Studies 177). This model has been modified to account for the growth of secondary minerals during weathering (Chamberlain et al., 2005, EPSL) and to examine the competing affects of reaction kinetics and rock advection (Hilley et al., in review, GCA). To first-order the model predicts chemical weathering rates at spatial scales from global to orogens to individual catchments (Hren et al., in press, AJS). Two overarching results come from this analysis. 1) The supply of fresh rock to the weathering zone is the dominant control on weathering rates except under extremes in uplift rates, temperature and precipitation. 2) Landscapes can be quantified as reaction- and supply-limited with much of the Earth’s surface between these two extremes. The results of this body of work have implications to CO₂ uptake in both ancient and modern environments. The ability of forest ecosystems to uptake carbon dioxide depends, in part, on the supply of rock-derived nutrients. Of these, phosphorus is particularly important, and we have combined models with field data to predict the P supply to landscapes in different tectonic settings (Porder et al., 2007, Ecosystems). Unlike forests on stable cratons, those on tectonically active areas are less likely to be P limited and may have a greater ability to increase productivity as a result of increases in CO₂. On longer timescales, we show that areas of high uplift will have the highest silicate weathering rates contributing to the long-term drawdown of CO₂.

Formation of biomineralized stalks by a marine iron-oxidizing bacterium

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Aerobic, neutrophilic iron-oxidizing bacteria (FeOB) are abundant at Fe(II)-dominated hydrothermal vent systems. They grow by O₂-dependent oxidation of ferrous iron to highly insoluble ferric iron. A distinctive feature of many FeOB is the formation of extracellular structures covered in iron oxyhydroxides. Beyond their distinctive appearance, little is known about the composition or function of these structures. One hypothesis is that these polymers control the precipitation of iron and move it away from the cell, thereby preventing mineral encrustation of the cells. 

Mariprofundus ferrooxydans PV-1 is a marine FeOB isolated from iron microbial mats at hydrothermal vents at the Loihi Seamount, Hawaii. M. ferrooxydans produces mineralized ribbon-like stalks that are prominent constituents of these microbial mats. Because this morphology is often used as a signature of FeOB activity in both modern and ancient (i.e. fossilized) environments, we need to determine what role it plays in the metabolic process, in order to be able to interpret the meaning of this potential signature and positively link it to the FeOB metabolism.

To this end, we have analyzed the ultrastructure, chemistry, and formation process of the Mariprofundus ferrooxydans PV-1 stalk. We developed a microslide culture method for PV-1 and coupled this with in situ light microscopy and time lapse imaging, allowing us to observe cell growth and determine rates of stalk formation. Stalk ultrastructure, mineralogy and cell-stalk-mineral spatial relationships were observed using transmission electron microscopy (TEM). This work showed that the stalks consist of a discrete number of fibrils (25-200 nm wide) mineralized initially by poorly crystalline FeOOH, and later coated with lepidocrocite. The juxtaposition of the poorly crystalline FeOOH within the stalk fibrils, and more crystalline lepidocrocite on the surface implies that organics in the fibrils retard mineral growth. Synchrotron-based scanning transmission x-ray microscopy (STXSM) was used to map the spatial distribution of iron, carbon, and nitrogen, and characterize the organic functional group chemistry of the stalk. The element maps show that iron is localized on the stalk, whereas the cell is relatively free of iron. Together these approaches show that the stalks do indeed play an important role by binding ferric iron and transporting it away from the cell in a manner that prevents entombment of the cell in iron oxyhydroxides.
Geochemistry and tectonic significance of peridotites from the Kiogar ophiolite, SW Tibet

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The Kiogar ophiolite in southwest Tibet forms part of the Indus-Yarlung Zangbo suture zone that marks the collision between the Indian continent and the Lhasa Block of Eurasia (Ganseer 1964; Aitchison et al. 2003). The ophiolite is dominated by a mantle sequence of clinopyroxene-bearing harzburgite, dunite, olivine orthopyroxenite and chromitite with trace amount of gabbro-norite. The dunite pods and dykes cut the cpx-bearing harzburgite and are characterized by U-shaped REE patterns, low incompatible element abundances and high Cr # (0.74-0.80). This is in contrast to the cpx-bearing harzburgites that display upward spoon-shaped REE patterns with low incompatible element abundances and low Cr # (0.37-0.55). Trace element modelling shows that the cpx-bearing harzburgites represent the residues of 15-20% partial melting. The compositions of cpx compare well with those of abyssal peridotites. Using field, textural and geochemical evidence, we suggest the Kiogar ophiolite formed in a two-stage process. The cpx-bearing harzburgites originated from melting of a MORB-source at a ridge, which were subsequently modified to dunites by interaction with boninitic melts in a supra-subduction environment. The modified lithosphere was emplaced onto the deformed Mesozoic continental margin sequence of the north Indian plate prior to the closure of Neo-Tethys in the Paleocene.

References


Geochemical analyses using a benchtop polarized beam XRF spectrometer

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Principle of polarized-beam XRF spectrometry

X-rays scattered through an angle of close to 90° are strongly plane polarized. Most of the background in XRF spectrometry results from the scatter of the “continuous spectrum” (Bremsstrahlung) produced in the X-ray tube. The fluorescent X-rays used for analysis, of course, originate in the sample. Polarization of the primary X-rays in a plane at a right-angle to the sample largely eliminates the background. The analytical precision and detection limits are thereby enhanced.

Measurement of X-ray photon intensities

Si(Li) detectors have been used in polarized beam spectrometers since the first commercial instruments were developed. Silicon drift detectors (SDD) are a modification of the Si(Li) that show some dramatic improvements in performance. The SDD require only moderate cooling (~–30ºC) that can be achieved electrically. They can measure much higher intensities, up to 10⁶ cps, and there are significantly fewer detector artefacts, particularly in the newer versions. Their disadvantage is that they are very thin and therefore relatively inefficient for elements such as Sn, Ba and the REE in the K spectrum.

An SDD polarized beam XRF spectrometer

The XEPOS instrument incorporates a recently developed SDD in a benchtop XRF spectrometer. A 50 W X-ray tube produces radiation from a very small area (1 mm x 1 mm). For the lightest elements a divergent beam of Pd Lα radiation from that “point source” can be focussed onto a sample using curved graphite that diffracts the beam at close to 90º, so that the beam incident on the sample is strongly plane polarized. We will report data obtained with this instrument; some Na and Rb contents for reference materials are listed here, measured on fused glasses and powder pellets, respectively.

| % Na₂O cert. meas. ppm Rb cert. meas. |
|------------------|------------------|
| DTS-2 0.027 0.030 AN-G 1.0 1.1 |
| SCO-1 0.90 0.94 UB-N 4.0 3.5 |
| BIR-1 1.82 1.94 MRG-1 8.5 8.2 |
| PM-S 2.08 2.07 BE-N 47.0 46.3 |
| GSP-2 2.78 2.77 AC-E 152 148 |
| GS-N 3.77 3.75 GH 390 382 |
| AGV-2 4.19 4.09 FK-N 860 871 |
| AC-E 6.54 6.47 Mica-Mg 1300 1301 |
| AL-I 10.59 10.64 MA-N 3600 3614 |
Infracrustal and supracrustal granites – The Nanjing separation

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In 1974 we proposed that granites are derived from two contrasting sources, igneous and sedimentary, giving the I- and S-type granites. At the 1982 Nanjing Symposium on Granites and their Metallogenic Relations we suggested that the terms “infracrustal” and “supracrustal” describe the two types in a more fundamental way. This Nanjing separation has not been widely taken into account by later workers and, for example, it is hard to reconcile with suggestions that I- and S types are transitional, parts of a spectrum of granites.

Since our initial studies of eastern Australian granites in the 1960’s, we have realized that the I-type granites were derived from rather homogeneous sources, which cannot have been supracrustal or volcanic rocks. This understanding predated our recognition of the S-type granites. Such a conclusion is required by the extremely strong correlations between elements, typical of the low-temperature I-type granite suites.

Inter-element correlations are relatively poor among granites of S-type suites and isotopic compositions can be quite variable. For example, ten initial Sr isotopic values for the Jillamatong Granodiorite, exposed over an area of 101 km² and formed from a single batch of S-type magma, range from 0.7111 to 0.7153. Also, the more mafic S-type granites contain supracrustal enclaves carried from depth, whereas mafic enclaves that were derived from igneous rocks are rare.

We provide examples of these contrasting patterns of geochemical behaviour. The origin of the source rocks of the supracrustal granites is clear, with debate about the proportions of introduced mantle components.

The infracrustal granites, generally developed by partial melting of crust, must have had a major and often dominant ultimately mantle-derived source combined in some way with a crustal component, shown by isotopic compositions (Sr_i = 0.704-0.710; εNd = +4 to -9; δ¹⁸O = +6 to +11 in the Lachlan Fold Belt for granite suites in which the more mafic rocks contain hornblende). Chemical and isotopic relationships show that such variations cannot have been a result of large-scale magma mixing/mingling, or of assimilation during evolution of the magmas. The evidence strongly indicates that the observed isotopic compositions and specific chemical features of granite suites were also characteristics of rather homogeneous source rocks before partial melting. The precise way in which those features were acquired remains a problem. The possibility that many I-type granite source rocks resulted from prior mixing between mantle-derived melts and melted crust should be considered.

Surface analytical studies of feldspar surface reaction with U(VI)

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Feldspar minerals are thermodynamically unstable in the near-surface environment and their surfaces are well known to react readily with aqueous solutions, leading to incongruent dissolution at low pH values, but congruent dissolution at neutral and high pH values. Interactions with mineral surfaces are an important control on the environmental transport of trace elements and detrital feldspars are abundant in soils and sediments.

The interaction of U(VI) ions with the feldspar surface has been studied. Sorption experiments with uranyl ion (UO₂⁺) at pH 2, 6 and 10 were carried out and measurable uptake, generally through surface complex formation, was only found at pH 6 and 10. Reacted surfaces were analysed by X-ray photoelectron spectroscopy and secondary ion mass spectrometry. At pH 6 and at an initial U(VI) concentration above 21.0 µM, precipitation of a surface phase was observed by atomic force and scanning electron microscopies, and this was identified as becquerelite (Ca[UO₂(OH)₂]·2.8H₂O) by grazing incidence X-ray diffraction. Secondary ion mass spectrometry showed diffusion of uranium into the altered surface layer.
A new approach to precise Pb dating of CAI’s by thermal extraction and thermal ionization in silica melt

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Calcium-aluminum-rich inclusions (CAIs) from carbonaceous chondrites are known to contain primary Pb that is highly radiogenic but at very low concentrations (0.3 – 0.01 ppm). The challenge to precise dating of these refractory phases by 207Pb/206Pb chronometry is an efficient removal of terrestrial contaminant Pb. Presently, this is done through leaching, dissolution and chromatographic separation in clean-lab environments (Amelin et al. 2002). A novel method is described here that embeds whole CAIs in silica glass on a Re filament for thermal Pb-isotope extraction and efficient ionization in a mass spectrometer (TE-TIMS). CAI fragments were obtained from Allende (Royal Ontario Museum, specimen #M29173 and Dr. O. Bogdanovski) by freeze-thaw disaggregation. After washing in clean H2O and acetone, whole-chips were mixed directly with clean concentrated silicic acid + H3PO4 on rhenium filaments. The mix was slowly fused to a glass under vacuum, taking care to fully embed the CAI fragments inside the glass. Pb/Pb-ratios were measured on a VG354 thermal ionization mass spectrometer (TIMS) in ion-counting mode using a Daly detector.

Initial results on two ca. 0.1 mg samples yielded mostly thorogenic Pb (208Pb/204Pb = 160 and 260). 208Pb emission began to increase at 1580C and attained between 16 – 30 kcps over about about 40 min. Thus, the presence of a whole CAI in the melt does not appear to have significantly reduced the ionization efficiency of the Pb and precise ratios can be measured if sufficient sample can be embedded on the filament. The low concentration of uranogenic Pb combined with significant common-Pb (206Pb/204Pb = 16) precludes precise dating of these samples. BSE imaging and EDS analysis of the embedded sample after melting showed extremely high concentration of Re in the CAI. Dissolved Re from the filament may have been efficiently partitioned into a molten Fe phase. No detectable Re could be found in the glass or unheated CAIs.

Aside from initial washing of the specimen, no clean chemical separation is required. In addition, thermal pre-treatment may prove useful for differential evaporation of contaminant Pb from meteoritic materials, as shown with zircon (Kober 1987 and Davis, this volume).

References

Early saturation of ilmenite and plagioclase buoyancy in Fe-Ti deposits associated with Proterozoic anorthosites

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The igneous origin of Fe-Ti deposits associated with Proterozoic massif-type anorthosite anorthosites is unanimously accepted but magmatic processes responsible for these oxides concentrations are still debated. New data on the trace element content of ilmenite from various Fe-Ti ores are modelled by a fractional crystallization process of a Fe-Ti-rich ferrodioritic melt. The sequence of crystallization has ilmenite as an early liquidus phase after plagioclase and before ferromagnesian silicates. Cotectic proportions of ilmenite calculated from linear trends in log-log diagrams are in the range 15-20 wt.%, which is commonly lower than the modal proportions of ilmenite observed in Fe-Ti deposits. The mechanism responsible for the ilmenite enrichment is removal of plagioclase through segregation by flotation. Indeed, the plagioclase has a lower density (2.61-2.65 g.cm-3 for An60-40) than ferrodioritic melts from which it crystallizes (ca. 2.75 g.cm-3). Direct evidences for plagioclase buoyancy are found in the Tellnes (SW Norway) and Lac Tio (Quebec) deposits where anorthositic rocks outcrop close to Fe-Ti deposits and commonly at a higher stratigraphic level. These grey anorthosites significantly differ from their host pink massif-type anorthosite and represent the complementary liquidus phases to the non-cotectic cumulates of the ore bodies. Flotation of plagioclase is also described in the Grader layered intrusion (Quebec) where the saturation of apatite is reached after that of plagioclase and ilmenite. Ilmenite-apatite rocks (nelsonites) thus occur in plagioclase-free layers. This thus implies that nelsonites actually represent cumulates rather than Fe-Ti-P-rich immiscible melts. The cumulate origin is thus largely documented for different types of Fe-Ti ores in anorthosites and related rocks. It is accompanied by plagioclase floatation which is responsible for the relative enrichment of Fe-Ti oxides and may be a major controlling factor in the genesis of Fe-Ti deposits.
Diverse sources for Oruanui rhyolite (NZ): Evidence from feldspar and zircon
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In many arcs, the erupted products reflect the integrated effects of differentiation mechanisms, which modify primary magma(s) as they ascend from their source region(s). Radiogenic isotope systematics can aid discrimination among various differentiation processes if the different end-members have contrasting isotopic signatures. Use of crystal isotope microstratigraphy, which employs microanalysis for Sr isotopes, shows that intra-crystalline isotopic and compositional heterogeneities exist within many volcanic rocks.

The 26.5 ka Oruanui eruption (530 km³, magma) from Taupo volcano in New Zealand is the world’s youngest supereruption. Oruanui rhyolite is mildly zoned (mostly 73-76% SiO₂) but was tapped non-systematically. Within some pumices, 1-5% of the plagioclase feldspars have grey cores mantled by clear rims. High resolution EMP traverses and Normarski imaging show a growth history punctuated by magmatic events that are seen as unconformities and inclusion rich zones within the crystals.

The grey cores have 87Sr/86Sr of 0.70540, and the clear rims are 0.70562, the latter being compatible with Oruanui rhyolite whole-pumice values. Intermediate zones sometimes have large excursions to very radiogenic 87Sr/86Sr values (max. ~0.7076). Accompanying these variations are changes from ~An₃₀ at the rim (in equilibrium with the host pumice) to ~An₆₅ in the core. Associated timescales of these variations in the grey-cored crystals are obtained from SIMS 238U-230Th model ages of zircons included within some of the growth zones. These ages can be compared with the age spectrum of zircons present as free crystals in the host pumice to show that incorporation of both xenocrystic and antecrystic material occurred during assembly of the Oruanui magma body.

Bacterial surfaces inhibit the oxidation of Fe(II)
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Bacteria are known to affect the fate of metals through sorption reactions. Secondary minerals, such as iron-oxides, are another important phase scavenging metals in the environment. It has often been suggested that bacterial surfaces favor the precipitation of iron-oxide phases. In this study, we demonstrate that this is not the case. We have mimicked the processes occurring at an oxic interface, which lead to the formation of iron oxides, by introducing progressively a fixed total amount of Fe²⁺ ions at a fixed pH of 6.5 in an aerobic reactor in the absence and in the presence of increasing concentrations of Bacillus subtilis bacterial cells. Alternatively, increasing amounts of Fe²⁺ ions were added to a fixed concentration of Anoxybacillus flavithermus bacterial cells. The kinetics of the reaction were monitored by measuring the rate of addition of the base needed to maintain the pH constant. In another set of experiments, we added Fe²⁺ ions at once in anaerobic conditions and oxygenated the suspension afterwards. The rate of oxidation of the Fe(II) was then measured directly using the ferrozine colorimetric method. In both types of experiments, it was clearly observed that the kinetics of oxidation of the Fe(II) are dramatically reduced by the presence of the bacterial cells. This is an important result, as the oxidation state and the speciation of the sorbed Fe impact the immobilization by the bacterial-iron composite suspensions of other metals. For instance, we have observed that a given amount of Fe reduces the Cd sorption ability of the cells, and it does this more effectively when it occurs as a sorbed Fe(II) species as when it is precipitated as adhering iron oxide nanoparticles.
Elemental distributions in zircons from diamondiferous UHPM rocks from the Greek Rhodope: A TOF-SIMS study

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The Rhodope Massif in N. Greece is a newly established ultrahigh-pressure metamorphic (UHPM) province in the world (Mposkos & Kostopoulos, 2001). Microscopic observations on zircons separated from a garnet gneiss revealed a simple zoned structure consisting of a somewhat rounded detrital core and a metamorphic overgrowth rim. This is ascribed to zircon growth in the presence of garnet under UHP conditions. By contrast, Li shows the reverse distribution pattern being negligible in the rim domain. This suggests a significant input of Li at subduction depths well in excess of 100 km. It is well established that phengite can host significant amounts of Li and that it is an important phase stable during subduction of crustal material to pressures up to 10 GPa. Since the peak PT conditions of the Rhodope UHP rocks have been estimated at 7 GPa / 1000°C, we favour the interpretation of phengite breakdown along its dehydration solidus during diamond formation. Sulphur, Cl and H distribution maps display high concentrations of these elements in the vicinity of diamonds strongly implying diamond precipitation from supercritical C-O-H-S-Cl fluids.

References

Recycled oceanic crust and sediments control the Hf-Nd mantle array

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Hafnium and neodymium isotopes measured on ocean island basalts and mid-ocean ridges define a linear array, the “Mantle array” that passes above the Bulk Silicate Earth value (BSE). No convincing explanation of the origin of the discrepancy has yet been suggested. Patchett et al (EPSL, 2004) argue that with a slightly more radiogenic Hf isotopic composition for a similar Nd isotopic composition, the BSE value would lie in the OIB array. Alternatively, the mantle array could lie above BSE, suggesting that plume sources are different from primitive mantle: either lower mantle is not primitive or plumes do not sample lower mantle. In both cases, a reservoir with a low Hf isotopic ratio is required to balance the OIB-MORB mantle source. Continental crust, as compiled by Vervoort et al (EPSL, 1999), is not a good candidate for this low Hf reservoir. As an alternative, kimberlites or a deep-mantle reservoir have been suggested, with important implications for mantle structure and dynamics. Here, we propose that the reservoir could be created by sedimentary processes.

We determined the average Hf isotopic composition of a representative section of old, altered Pacific oceanic crust and overlying oceanic sediments sampled during ODP Leg 185. The average basaltic crust composition is similar to that of present-day MORB while the average sediment composition falls in the field of Fe-Mn crusts and nodules with an elevated $\varepsilon_{Nd}$ relative to $\varepsilon_{Hf}$. We use these $\varepsilon_{Hf}$ values combined with the average composition given by Su (2002) for average MORB, and Plank & Langmuir (Chem. Geol. 1998) for global subducted sediment (GLOSS) to evaluate the effect of recycling in the past of similar materials into the convecting mantle and its influence on the composition of the mantle. Over Earth history, such recycling had a marked effect on the mantle and would have shifted its composition towards higher Hf isotopic ratios. This process could explain the position of the mantle array above BSE. Using a Monte Carlo simulation of reasonable mixtures of sediment and basalt with surrounding mantle, we can reproduce the compositions of OIB and MORB and their position above BSE.

The high $\varepsilon_{Hf}$ relative to $\varepsilon_{Nd}$ typical of deep-sea sediments could have its complement in another sedimentary reservoir. We suggest it might be sand rich in heavy minerals which are present in large quantities along continental margins. Given that the “crustal array” of Vervoort is mainly based on fine grained sediments it might not be representative of the continental crust as a whole. The continental crust could contain a higher proportion of the coarser grained sediments with low $\varepsilon_{Hf}$ than previously thought. The “crustal array” could therefore lie below the “mantle array” in $\varepsilon_{Hf}$ versus $\varepsilon_{Nd}$, and a deep-seated mantle reservoir would not be necessary.
Fate of CO2 leaked from seabed
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Models and Case Runs
We estimated the fate of CO2 droplets leaked from seabed and the physiochemical impacts produced on seawater column by means of numerical simulations. The model (Chen et al., 2003) used in this study is a full two-phase small-scale turbulent ocean model, of which the submodels had been calibrated by both lab. experiments and field observations. Predicted distances drops could move to from variant leakage depths (deeper than 800m) and initial drop sizes (Do mm) is shown in Fig.1. The water column impacts indicated by pH change are given in Fig.2 for cases of variant leakage rate (M, kg/s), Do, and current speed (Uc m/s) at leakage time of one hour. The background ocean is Okinawa.

Discussion of Results
The drop rising distances are almost linearly proportion to Do with a rate of 38m/mm and independent to the leakage depth if Do<15 and a rate increased from 10.3 to 24.7 as deeper leaked for large deformed drops. The maximum pH change can be reduced from 1.6 of Case B(M=0.6, Uc=2.5, Do=8) to 1.2 by reducing M=0.1 (Case A) and 1.1 by a larger Uc=25, (Case C). Smaller Do=5 produces a larger pH change, of which is balanced by a smaller M=0.3 (Case D).

Conclusions and Suggestions
At leakage depth larger than 800, no pure CO2 is found to be able to reach to the ocean surface even at size as large as 40mm. Physiochemical impacts of leaked CO2 on seawater can be reasonably estimated by using models developed with monitoring data of droplet plume height, from which the Do can be determined, and local leakage rate. For monitoring CO2 drops leaked, acoustic sonar technology is a suggested method. For CO2 leaked from shallow seabed, more lab. data are expected for calibrating the models, such as bubble drag and shrinking rate.

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Zircon Lu-Hf isotope and its significance to ultra-high pressure metamorphic rocks from Dabie Terrain, Eastern China
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Zircon intragrain Lu-Hf and U-Pb isotope analyses were carried out for ultra-high pressure eclogite, jadeite quartzite and granitic gneiss from Shuanghe, Huangzhen and Xindian, Southern Dabie Terrane, Eastern Central China by using LA-MC-ICP-MS and SIMS (CAMECA) technique, respectively. The results show that zircon Hf isotope distributions are mainly controlled by the formation age of metamorphic precursor. Metamorphic zircon succeeded basically Hf isotopes of their protolith. The results also show systematic change among 206Pb/238U age, initial Hf isotopic compositions, Th/U and Lu/Hf ratios in zircons from different genetic domains. Metamorphic growth domains are characterized by low Th/U(<0.1), low Lu/Hf(<0.0005) and low 206Pb/238U ages, but high 176Hf/177Hf ratio relative to igneous core and mantle with partial recrystallization of pre-metamorphic ages. The low Lu/Hf and Th/U ratios of metamorphic growth zircon were caused by the decreasing of Lu and Th, and increasing of Hf, the high 176Hf/177Hf ratio relative to igneous core and mantle with partial recrystallization of pre-metamorphic ages. The low Lu/Hf and Th/U ratios of metamorphic growth zircon may represent the Hf isotope composition of the whole rock at the same time. In some cases Hf isotope compositions of metamorphic and inherited zircons are undistinguishable within same range.

The trace of initial Hf isotope composition of Hf and the Hf model age of depleted mantle TDM and U-Pb age for inherited zircon core indicates that their age and origin are different for metamorphic precursor. Eclogite from Shuanghe show the source mixture of depleted mantle of 2.5Ga with at least 2.7Ga late Archean crust. The material for eclogite precursor from Huangzhen and Xindian was formed mainly by melting of juvenile crust, with few old crust contamination. The material of gneiss precursor from both localities show same formation age and were derived from mixing of weak depleted mantle and crust. Whereas gneiss from Huangzhen shares the common source with eclogite. The zircon Lu-Hf isotope of UHP metamorphic rocks from Dabie orogen reflects new crust growth during 0.7-0.8 Ga and 1.8-1.9 Ga, which was consistent with wide magmatism and tectonic setting of north margin of Yantze Craton.

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Tectonic implication of detrital muscovite from Carboniferous sedimentary rocks in the Northern Dabie Mountains, China: Evidence from single grain Rb-Sr dating

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The Dabie ultrahigh-pressure orogenic belt represents the eastern part of the Qinling-Dabie orogenic belt in China, which was formed by collision of the North and South China Blocks during Early Mesozoic. Time of this collision has been constrained at ca. 230-220 Ma by numerous radiometric studies [1-2]. The Dabie belt is geologically made up of four tectonically juxtaposed zones, from south to north, the Susong HP zone, South Dabie UHP zone, North Dabie gneiss zone, and Beihuayang low-grade zone. UHP metamorphic mineral inclusions are found in garnet and zircon, indicating subduction of continental crust during the collision.

Low-grade metamorphic Paleozoic sedimentary rocks are exposed along northern margin of the Qiling-Dabie orogenic belt. Provenance and tectonic setting of these low-grade rocks are constrained at ca. 230-220 Ma by numerous radiometric studies [1-2]. The Dabie belt is geologically made up of four tectonically juxtaposed zones, from south to north, the Susong HP zone, South Dabie UHP zone, North Dabie gneiss zone, and Beihuayang low-grade zone. UHP metamorphic mineral inclusions are found in garnet and zircon, indicating subduction of continental crust during the collision.

This study presents results of detrital biotite and muscovite minerals of Carboniferous sedimentary rocks exposed in the northern margin of the Dabie Mountains. About 15% of detrital muscovite grains are phengitic in composition indicated in high Si/Al ratios of >3.3. Single grain Rb-Sr isotopic analyses show that either phengite or muscovite give about 400 Ma isochron age, while detrital biotite grains are scattered in two groups of Rb-Sr isotopic composition, likely suggesting different sedimentary sources of old crustal and juvenile material probably of magmatic rocks related to Paleozoic convergence along southern margin of the North China block. Whole-rock Nd isotopic composition of the sedimentary rocks also demonstrates a mixture of sedimentary sources of different ages, similar to the conclusions proposed previously [3]. Paleozoic detrital phengite can be originated from the North Qinling terrain where Paleozoic subduction and subsequent collision have been proposed [4].

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References

Zn isotope measurements in freshwater and its use as a probe of anthropogenic contamination in the Seine River

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The recent development of MC-ICP-MS allows a precise and accurate determination of Zn isotopic compositions (1,2), and a total variation of about 2‰ for δ66Zn has been determined among terrestrial materials. Despite its potential pollution impact on aquatic environments, only few studies exist on Zn isotopic ratios in natural waters and none for rivers. In this context, it is worth studying its behaviour and isotopic composition in the Seine river basin, a basin with significant anthropogenic input (250 persons/km²). The human impact has been demonstrated by the continuous increase in Zn concentration from headwater to estuary both in the dissolved phase (17 times) and in the particulate phase (4 times).

We have developed a new two-column protocol for the direct ion-exchange separation of Zn from freshwater samples with very small dissolved Zn concentrations. This avoids the evaporation of large quantities of sample (~200 ml). The protocol is proven to be reproducible by tests on standard-doped distilled water and column-purified Seine river water, with an average yield of 100% and no isotopic fractionation (mean δ66Zn for all purification tests is 0.005‰).

For Zn isotope measurements, the instrumental mass discriminations are corrected statically for each measurement session using a method of internal reference element doped sample-standard bracketing (Zn for Cu; Cu for Zn isotopic measurement) (3). Repeated measurements of Zn and Cu AAS standards during 15 months yielded a precision of 0.04‰ (2σ) for δ66Zn in water samples of the Seine river basin, and a total variation of about 2‰ for δ66Zn in water samples of the Seine river basin, and a total variation of about 2‰ for δ66Zn in water samples of the Seine river basin, and a total variation of about 2‰ for δ66Zn in water samples of the Seine river basin.

Isotopic characterization of Zn in various phases (dissolved, suspended, colloidal) provide clues about both the source of metal pollution and the geochemical and biochemical processes in river water system.

References
~2.5Ga Sanukitoids from Guyang greenstone belt, North China

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The late Archean Guyang greenstone belt, the largest greenstone belt in the Western block of North China Craton (NCC), locates in the central Inner Mongolia, North China. It consists of three tectonically contacted low-grade volcanic-sedimentary assemblages, and the main emplacement age is around 2.5 Ga (Li et al., 1987; Wang, 1993).

The sanukitoid suite occurs in middle part of the lower assemblage. The suite is predominately andesitic (SiO2 = 58-65%) and is characterized by high Mg number (0.52-0.57), as well as high K2O contents (2.5-4.4%), high K2O/Na2O ratios (0.7-2.1) and low FeO/MgO ratios (1.6-2). The high K2O/Na2O and low FeO/MgO ratios are consistent with calc-alkaline serie trend. The high Ba (349-1062 ppm) and Sr (0.7-2.1) and low FeO T/MgO ratios (1.6-2) of the suite are significantly higher than comparable to modern adakites. However, Cr (114-350 ppm) and Ni (60-118 ppm) of the suite are significantly higher than adakites, indicating a high-extent hybridization with mantle peridotites (Smithies and Champion, 2000). The sanukitoids also have high Zr/Y ratios ranging from 8.6 to 30.7. In the primitive mantle normalized spider diagram, depletion of Nb and Ti relative to neighboring REE is significant (Nb*=0.07-0.47, Ti*=0.33-0.67), while Zr and Hf anomalies are less evident, comparable to average compositions of sanukitoids in Martin et al. (2005).

In Guyang greenstone belt, the sanukitoids occur in association with Nb-enriched basalts (NEB) (Chen, in preparation, 2007). The association has widely been proved to be the magmatic products of interaction between slab derived melts and overlying mantle wedge, hence is indicative of a modern-style subduction setting developed around 2.5Ga in the western block of NCC.

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Are peridotite xenoliths in Mesozoic plutons inherited from Paleozoic kimberlites?

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Mantle xenoliths-fragments of the Earth’s mantle, are transported to the surface via volcanic/subvolcanic exclusively [1]. As direct mantle samples, these peridotite-dominated xenoliths provide principal approach to investigate the nature of the Earth’s mantle. Recently, peridotite xenoliths are exceptionally found in some Mesozoic diorite-gabbro plutons of North China Craton (NCC), and their genesis is still controversial [2-5]. Here we use zircons from a composite dunitie-phlogopite orthopyroxenite xenolith from Tietonggou pluton in Laiwu, one of Mesozoic plutons in the NCC, to trace the nature of these xenoliths. This sample is composed mainly of phlogopite-rich orthopyroxenite and subordinate pebble-like dunites [6]. Two stages (130 Ma and 450 Ma) of zoned zircons are found in this sample, the ages of which are concordant with those of the host pluton and of the Paleozoic kimberlites of the NCC, respectively. The similarities of Hf isotopes and rare earth element patterns, as well as the clear correlations between T(Ti) and Th/U ratio and T(Ti) v.s. Hf content for both the zoned Cretaceous zircons and the diorite zircons, demonstrate that these zircons were crystallised in the same magma chamber. In contrast, similarities in the compositional signature of phlogopite and the Nd-Hf isotopic compositions suggest that this composite xenolith was originally Paleozoic kimberlite with dunitie xenoliths before incorporation by the host pluton. We therefore suggest that peridotite xenoliths found in the Mesozoic plutons are inherited from the destroyed Paleozoic kimberlites.

References
Mineral H isotopes and water contents in UHP eclogite-gneiss contact from CCSD core samples

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By taking advantage of having depth profiles between contrasting lithologies from core samples of the Chinese Continental Scientific Drilling (CCSD) project, a combined study was accomplished by means of TC/EA-MS and FTIR methods to examine changes in mineral H isotope, total water and hydroxyl contents in garnet and omphacite across the contacts between ultra-high-pressure (UHP) eclogite and gneiss in the Sulu orogen, east-central China. The results are used to decipher both origin and availability of metamorphic fluid during exhumation of deeply subducted continental crust. The samples of interest were from two continuous core segments from the CCSD main hole at depths of 734.21 to 737.16 m and 929.67 to 932.86 m, respectively. The results show δD values of −116 to −64‰ for garnet and −104 to −82‰ for omphacite, consistent with incorporation of meteoric water into protoliths of UHP metamorphic rocks by high-T alteration. Both equilibrium and disequilibrium H isotope fractionations were observed between garnet and omphacite, suggesting fluid-assisted H isotope exchange at local scales during amphibolite-facies retrogression.

While bulk water analysis gave total H2O concentrations of 522 to 1584 ppm for garnet and 1170 to 20745 ppm for omphacite, structural hydroxyl analysis yielded H2O contents of 80 to 413 ppm for garnet and 228 to 412 ppm for omphacite. It appears that significant amounts of molecular H2O are present in the minerals, pointing to enhanced capacity of water storage in the UHP eclogite minerals. Hydrogen isotope variations in the transition between eclogite and gneiss show correlations with variations in their water content. Petrographically, the degree of retrograde metamorphism generally increases with decreasing distance from the eclogite-gneiss boundary. Thus, retrograde metamorphism results in mineral reactions and H isotope variation. Because hydroxyl solubility in nominally anhydrous minerals decreases with dropping pressure, significant amounts of water are expected to be released from the minerals during decompression exhumation. Decompression exsolution of structural hydroxyl from 1 m3 volume of eclogite composed of only garnet and omphacite results in release of a quantitative estimate of 3.07 to 3.44 kg water that can form 140 to 156 kg amphibole during exhumation. Therefore, it is concluded that fluid for retrogression of the eclogites away from the eclogite-gneiss boundary was derived from the decompression exsolution of structural hydroxyl and molecular H2O in nominally anhydrous minerals. For the eclogites adjacent to gneiss, in contrast, the retrograde metamorphism was principally caused by aqueous fluid from the gneiss which is relatively rich in water.

New achievements in the study of the excess argon in HP-UHP metamorphic minerals

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Based on the study of the genesis, diffuse and transference of excess argon in the High and Ultrahigh-pressure metamorphic minerals using classical Ar-Ar and laser microprobe Ar-Ar dating method, the following conclusions can be drawn:

1. In the eclogites of different time (from the Caledonian to Indo-Sinian epoch) and different area in China, not only the phengites contain large amounts of excess argon, but the other trace potassium minerals, such as olivine, garnet and pyroxene, also contain excess argon and even the biotites in some eclogites also contain excess argon.

2. Four phengites for Ar-Ar dating are concentrated from the eclogites range from the margin to the center of the eclogite body on the top of the Qinglong Mountain in eastern China. The excess argon content of the four samples from the outer to the inner part of the rock body within 60 cm is 73%, 74%, 76% and 78% respectively, which indicates that the excess argon in the phengites of the eclogites is distributed unevenly and show a little positive gradient. Therefore, the excess argon is basically believed to be inherited from its parent rock and not from its outside.

3. The phengites in the eclogite of Yuka area in the northern margin of the Qaidam Basin in western China, whose country rock is marble, do not contain excess argon, which indicates that the lithology of the country rock is a key factor to control the occurrence of the excess argon in eclogite.

4. The content of the excess argon in the phengites is found to be positively correlated with the ratio of its Na/(Na+K) and the correlation formula is:

\[ y = -112.14 + 10710x - 251844x^2 + 3 \times 10^6x^3 - 1 \times 10^7x^4 \]  
\( (R^2=0.997) \)

In which y is the content of the excess argon (%) and the x is the ratio of Na/(Na+K).

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C- and S-isotope study on depositional environment of late Cryogenian Mn carbonate, Datangpo Fm., South China  

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The Datangpo manganese carbonate deposit overlies diamictite of Tiesi’ao Formation (equivalent to Sturtian) and occurs at base of Datangpo Formation which underlies diamictite of Nantuo Formation (equivalent to Marinoan). Considerable $^{13}$C-depleted Mn carbonate and highly $^{34}$S-enriched pyrite from the base of the Datangpo Formation document unique oceanic chemical environment before the final oxygenation of the Earth’s surface.  

The observation of most $\delta^{18}$O~10 and no linear correlation between $\delta^{13}$C and $\delta^{18}$O suggests that C-isotope compositions of the Mn-carbonate are unaltered by late diagenesis. The $\delta^{13}$C values (meanly -7.2‰) below the mantle or crust values (-5~6‰) are consistent with the early diagenetic model for stratiform Mn carbonate deposit, which argues participation of carbon derived from bacterial remineralization of organic matter during Mn-carbonate precipitation. However, the relatively small standard deviation (0.81‰) of $\delta^{13}$C values indicates carbonate precipitation occurs near the water-sediment interface rather than in the oxic pore water, thus the $\delta^{13}$C values were inherited from the bottom water. The best-fitting line ($r^2=0.69$) of $\delta^{13}$C vs. fractionation ($\Delta$) between carbonate and organic carbon yields a slope=0.78 and an intercept of -26.94, which cannot be readily explained by steady-state model of carbon cycle. Therefore, we suggest that negative $\delta^{13}$C excursion was resulted from oxidation of part of a large dissolved (including suspended) organic carbon reservoir. In addition, large $\Delta$ values (meanly 25.3‰) imply high CO$_2$ concentration in the atmosphere.  

High $\delta^{34}$S values of pyrites within the Mn-carbonate indicate extremely $^{34}$S-enriched sulphate in a restricted basin. The pyrites probably precipitate in the relatively oxic pore water beneath sea water with low sulfate concentration, which is consistent with the observation of large and scattered pyrite framboids that are symbolic of diagenetic formation beneath dysoxic bottom waters.  

In conclusion, the Mn-carbonate deposit at the base of Datangpo Formation records abundant paleoenvironmental information, such as high CO$_2$ concentration in the atmosphere and low sulphate concentration in the ocean after the Sturtian ice age, considerable O$_2$ concentration in the atmosphere which caused the ocean chemocline moving to the water-sediment interface in the outer shelf, large dissolved organic carbon reservoir which was partly oxidized by Mn oxides and SO$_4^{2-}$ enzymatically near and below the chemocline. (This study is supported by NSFC grant 40572017.)

Authigenic carbonates in the Chinese loess-paleosol sequence: Morphologic and isotopic study  

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Carbonate is a common component in the eolian loess-paleosol sequences, north China. Usually carbonate content is about 10 wt% in loess while lower (e.g. 0.3 wt %) in paleosol due to pedogenic leaching (Liu, 1985). Carbonate is easily leached out and accumulated in the loess profile. In this study we found at least six types of authigenic calcium carbonate accumulation in the Luochuan loess-paleosol sequence: coatings, rhizoconcretions, fossil snail shells, pseudomyseliums, nodules and nano-scale rods. Various carbonates have different morphologic features and isotopic compositions (Table 1), showing different forming conditions. Among them, carbonate nodules were precipitated under multi–alternations of heavy rainfall and intense evaporation without biological processes. Other authigenic carbonates may form from biological-controlled or biological-induced interactions. Detailed study on these authigenic carbonate can provide a reasonable way to trace the biogeochemical process in the loess sequence.  

### Table 1 Stable isotopic composition of some types of authigenic carbonates in the Luochuan loess-paleosol sequence, China  

<table>
<thead>
<tr>
<th>Authigenic Carbonates</th>
<th>$\delta^{18}$O (‰ PDB)</th>
<th>$\delta^{13}$C (‰ PDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhizoconcretion (L1)</td>
<td>-9.0 ~ -8.0</td>
<td>-5.9 ~ -4.4</td>
</tr>
<tr>
<td>Fossil Snail Shell (L1)</td>
<td>-9.4 ~ -6.3</td>
<td>-9.7 ~ -6.9</td>
</tr>
<tr>
<td>Coatings (L1)</td>
<td>-9.5 ~ -8.0</td>
<td>-9.0 ~ -8.0</td>
</tr>
<tr>
<td>Nodules (S1)$^{a1}$</td>
<td>-9.0 ~ -9.8</td>
<td>-5.6 ~ -4.2</td>
</tr>
<tr>
<td>&lt;2µm samples (L1)</td>
<td>-7.7 ~ -6.9</td>
<td>-6.1 ~ -5.2</td>
</tr>
<tr>
<td>&lt;2µm samples (S1)</td>
<td>-6.7 ~ -6.4</td>
<td>-10.1 ~ -8.9</td>
</tr>
</tbody>
</table>

$^{a1}$Han et al, 1995  

Acknowledgment  
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References  
Can rutile thermometry link to rutile U-Pb age?
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T-t information of metamorphic rocks is basic and critical content in petrogenesis study. Rutile U-Pb dating are often used to constrain cooling age of metamorphism. Zr-in-rutile thermometry is a newly developed single mineral thermometry. According to the experimental data, diffusion parameter of Pb and Zr are similar in rutile. So can we link rutile thermometer to its’ U-Pb dating?

Jinheqiao 99JHQ-1 eclogite is the only one which has got precise rutile U-Pb age in China up to now11. It is tectonically located in the South Dabie UHPM zone. Peak conditions estimated in Jinheqiao area were 680–940°C and 3.2–4.3Gpa. Here we present Zr content of rutiles analyzed by electron probe in 99JHQ-1 eclogite and discuss the link between rutile temperature and its’ U-Pb dating.

Fourty-two rutiles were analyzed and gave Zr content between 37–118ppm, average in 67ppm. Rutiles as garnet inclusion have a little higher Zr (75ppm) than rutiles in matrix (64ppm), but they share the similar variation range. Temperatures calculated by Watson2 and Zack3 were 519–563°C and 507–600°C respectively. Zr-in-rutile thermometry are often used to calculate peak temperature of high grade metamorphic rocks. However, rutile Zr temperature in 99JHQ-1 eclogite is obviously lower than the peak temperature calculated by garnet-quartz O isotope thermometry of 695°C, but is significantly higher than Tc of about 460°C for U-Pb system in rutile and rutile-quartz O isotope thermometry of 460±15°C estimated in this eclogite.

Petrographical observation show that 99JHQ-1 eclogite had experienced strong retrograde metamorphism. Omphacite were almost transformed into simplectite, garnets were always surrounded by a wide rim of hornblende, and many rutiles were partly transformed into ilmenite or titanite. These phenomena show that the retrograde fluid were intensive during the exhumation of this eclogite. Rutiles were re-crystallized or retrogress to various extent. Large variation of Zr content in rutile indicate that Zr in rutile had also been reset to various extent, i.e. Zr in rutile were not equilibrate with retrograde zircon and quartz.

In summary, Zr-in-rutile thermometry may bear any geologic meaning in highly retrograde eclogite. Despite the experimentally similar diffusion parameter of Zr and Pb, O in rutile, Tc of Zr may be higher than those of Pb and O in actual geological condition, and one should be careful in linking the rutile thermometry to its’ U-Pb dating.

Reference

Rates of eclogitic metamorphism of subducted continental slab
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Knowledge of the duration of concurrent processes affecting the rocks such as heating, recrystallization and deformation is fundamental to an understanding of metamorphism. Various approaches such as thermal modeling, radioisotopic dating, chemical and textural analysis can be utilized to envisage these durations. Combined textural analysis (CSDs), chemical analysis with Lu-Hf and Sm-Nd geochronology study on the Dabie HP/UHP eclogites can thus provide a comprehensive understanding regarding garnet growth histories so as to the subduction and exhumation processes of its host rocks. Garnet compositional profiles show well-preserved growth zoning with a decrease in Mn, Ca and heavy rare earth elements (HREEs) and an increase in Mg towards rims. Textural quantification analysis for the garnets reveal apparent pseudo-lognormal CSDs, which alone can be interpreted by several plausible nucleation growth mechanisms; however, the mineralogy of inclusions in garnets and the compositional zoning patterns reveal a three-episodic nucleation and growth process. The Rayleigh-type HREE zoning and near-constant MREE zoning in the garnets indicate that the obtained ~5 Ma time span, defined by the decoupling between 224.2±1.9 Ma Lu-Hf and 217.8±4.2 Ma Sm-Nd ages, represents timing of the last garnet growth episode deviating from the nucleation process. Based on the absence of significant diffusional reequilibration as indicated by the compositional zoning, the textural analysis and the mineralogy of inclusions in garnets, we interpret the initiation of garnet growth during prograde metamorphism must have predated the 224.2±1.9 Ma Lu-Hf age and the 217.8±4.2 Ma Sm-Nd age is an estimation for the closure of garnet growth corresponding to the amphibol-facies overprint along exhumation path; therefore, the time elapsed at eclogitic condition should be extremely short.

Reference
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High-precision MC-ICP-MS lead isotope analysis using Tl-normalization: Calibration and applications to lead isotope study of ore deposits

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The demands for radical improvement (compared to conventional TIMS method) of lead isotope ratios measurements precision exist in isotope geochemistry for last 30 years. It becomes practicable owing to multicollector-ICP-mass-spectrometry which makes possible to correct lead isotopes mass-discrimination with $^{205}$Tl/$^{203}$Tl ratio. This method was elaborated and adapted to different MC-ICP-MS instruments in wide number of works (for example, [1-5]).

Developing this method [5] we use 9-collector-ICP-MS NEPTUNE. The $^{205}$Tl/$^{203}$Tl value in TlNO$_3$ reference sample instruments in wide number of works (for example, [1-5]).

The $^{205}$Tl/$^{203}$Tl ratio in two mixtures Tl+-Pb (SRM 982) and Tl+-Pb (SRM 981) in 10 parallel analyses for each one respectively are: 2.3898±12 and 2.3888±20. Analyses of both mixtures yield $^{205}$Tl/$^{203}$Tl ratio in excellent agreement between them, when a total mean value 2.3889±1 coincides in error limits with recent data 2.3887±7 [3] and 2.3889 [4].

Isobar interference of $^{204}$Hg$^+$ contribution to total peak 204 m/e intensity was controlled and corrected by $^{202}$Hg$. Its contribution didn’t exceed 4×10$^{-17}$A or <0.001% in terms of $^{204}$Pb$^+$ peak. Background signals in analyses were less than 1.5×10$^{-15}$A, whereas $^{204}$Pb$^+$ peak intensity during analyses ranges from 2.5×10$^{-11}$ to 8×10$^{-11}$A.

Precision of the method involved has been evaluated from long-term (1.5 years) reproducibility of 90 parallel analyses of common lead standard SRM 982 and galena samples (±2SD): $^{206}$Pb/$^{204}$Pb = ±0.016%; $^{207}$Pb/$^{204}$Pb = ±0.016%; $^{208}$Pb/$^{204}$Pb = ±0.018%; $^{207}$Pb/$^{206}$Pb = ±0.005%; $^{208}$Pb/$^{206}$Pb = ±0.009%.

The method described was applied to detailed lead isotope study of same well known ore deposits. Systematic study of 12 massive sulphide and base metal deposits of Ural, Russia was performed. Another object was Banska Stiavnica Au-Ag deposit (West Carpathian, Slovakia), which demonstrated perfect homogeneity of lead isotope composition.

References

Stable nitrogen isotopic composition of amino acids: Implications for aquatic food web studies

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Compound-specific stable nitrogen isotope analysis of amino acids is a potential tool for elucidating trophic position of organisms in the food web (McClelland and Montoya, 2002). Large $^{15}$N-enrichment (~7‰) in glutamic acid along the trophic level provides a greater scope for defining trophic position than the small change (~3‰) in bulk material, and little change in $^{15}$N of phenylalanine along the trophic level provides information of nitrogen sources at the base of the food web. However, it is still uncertain whether or not the $^{15}$N relationship observed in McClelland and Montoya (2002) is generally applicable to other sets of ecosystems.

We investigated the nitrogen isotopic composition of individual amino acids from macroalgae and gastropods in a natural marine coastal environment, to further evaluate them as a tool for ecological studies and to understand the factor(s) controlling the isotopic compositions in terms of biosynthetic and metabolic processes (Chikaraishi et al., 2007). The isotopic compositions of 12 amino acids range from -3.3 to +12.9‰ for marine algae, and from -0.6 to +16.6‰ for gastropods (Fig. 1). The isotopic distribution between algae and gastropods are consistent with those in the previous report, suggesting them to be quite useful for studying the food web structure. The nitrogen isotopic variation between amino acids would strongly reflects their biosynthetic and metabolic processes. We suggest that the metabolic fate is an important factor to produce the distinct trophic relationship in the nitrogen isotopic compositions between amino acids.

Figure 1: Nitrogen isotopic composition of individual amino acids in marine macroalgae and gastropods.

References
Removal of Hg(II) by natural zeolite

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Natural zeolite will be more widely considered for roles in environmental clean-up processes—especially those involving radioisotopes and heavy metals (Dyer, 1995). The limited data are also available for mercury ion exchange with the clinoptilolite in terms of equilibrium isotherms and kinetics using radiochemical analysis with 203Hg and 22Na as a radiotracer. (Misaelides et al., 1994).

Modified natural zeolite with sodium produced a cation exchangeable material which has been tested for the ability to remove Hg(II) from aqueous solution with nitric acid using a flow injection mercury system (FIMS 400). The amounts of adsorption depend mostly on contact time, acid concentration of aqueous solution and initial mercury concentration, mixed cation of mercury and its subgroup elements. The study of the kinetics of mercury uptake revealed that all sorbents exhibit a fast rate of sorption. The highest sorption capacities were observed for the sodium forms (TSA-Na, TEC-Na, TUS-Na) and were up to 5 times higher than for the natural zeolite (TSA, TEC, TUS).

The maximum sorption capacity toward mercury is determined as 0.09286 µg/g at an initial concentration of 10µg/L for TSA-Na. The sorption of Hg (II) has an ion-exchange nature and consists of three stages, i.e., the adsorption on the surface of microcrystals, the inversion stage, and the ion exchange in the interior of the microcrystal. Sorption capacity decreases with the increase of mercury concentration. The presence of other metal ions such as Cd(II), Cu(II), Ni(II) and Zn(II) increases Hg(II) uptake capacity. Finally, sorption for Hg(II) was investigated in batch systems and were up to 5 times higher than for the natural zeolite (TSA, TEC, TUS).

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The experimental observations suggest a mechanism based on the protonation of FeS surface (Chirita and Descostes, 2006) followed by oxidation of FeS by dissolved oxygen to produce Fe²⁺, S²⁻ and SO₄²⁻. Fe²⁺ is unstable in oxidative conditions (Descostes et al., 2002) and transforms into Fe(OH)₃ and goethite after approximately 30 h of reaction.

Pyrrhotite oxidation in weakly acidic solutions

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The kinetics and mechanism of pyrrhotite (for simplicity noted FeS) oxidation by dissolved oxygen was investigated in weakly acidic solutions as a function of pH (2.75 to 3.45) and temperature (25 to 45°C). The changes in Eh, pH and total dissolved iron were monitored to quantify the reaction progress. Additionally, Fourier transform infrared spectroscopy (FTIR) was used to characterize the oxidation products of FeS.

The experimental results demonstrate the importance of temperature and initial pH for the FeS oxidative dissolution. The amounts of dissolved iron (nFe) and removed H⁺ (nH) increase with temperature and initial [H⁺]. The activation energy of FeS oxidative dissolution is 41.6±10.7 kJ mol⁻¹ at initial pH=3.00 suggesting that the kinetic regime is controlled by a mix of diffusion and surface reaction (De Guidici et al., 2005). It was found that the reaction order of oxidative dissolution of FeS is 1.03±0.02 (25°C) with respect to initial [H⁺].

FTIR spectroscopy indicated the presence of several sulfur species (S⁰, S²⁻, S₄O₆²⁻, SO₃²⁻ and SO₄²⁻) and ferric hydroxides or oxyhydroxide (Fe(OH)₃ and goethite) on residual FeS surface.

It is important to note that the experimental ratios of nH over nFe (nH/nFe) observed at 25°C decrease over a first period of time (0-4 h) of FeS oxidative dissolution from 7.97 down to 2.01. Afterwards, the nH/nFe ratio becomes lower than 2 and remains roughly constant (4-72 h). At higher temperatures (35 and 45°C) and pH 3.00, nH/nFe<2 and is quasi-invariant over the reaction time.

The experimental observations suggest a mechanism based on the protonation of FeS surface (Chirita and Descostes, 2006) followed by oxidation of FeS by dissolved oxygen to produce Fe²⁺, S²⁻ and SO₄²⁻. Fe²⁺ is unstable in oxidative conditions (Descostes et al., 2002) and transforms into Fe(OH)₃ and goethite after approximately 30 h of reaction.

References


References
Here we present results from the development of a novel in-situ approach to measure accurate and precise $^{30}$Si/$^{28}$Si and $^{29}$Si/$^{28}$Si ratios in minerals and glasses. We have developed an in situ-method for precise and rapid measurements of $^{30}$Si/$^{28}$Si and $^{29}$Si/$^{28}$Si ratios in silicates at a spatial resolution of 50 micrometers using our in-house built 196nm UV-femtosecond laser ablation system coupled to high-resolution MC-ICPMS. The use of medium resolution mode (m/Δm= 8000) permits to resolve spectral interferences on $^{30}$Si, $^{29}$Si and $^{28}$Si as verified using a three isotope plot that shows an equilibrium mass dependent fractionation law which can be represented as $\delta^{30}$Si=1.93*$\delta^{28}$Si. Sample-standard bracketing is used to correct for the mass discrimination and the possible drift occurring between two measurements and thus $\delta^{29}$Si and $\delta^{30}$Si are calculated using NIST NBS28 (synthetic quartz sand) as bracketing standard. Different types of matrices have been analysed by laser ablation. Thus $\delta^{28}$Si and $\delta^{29}$Si have been determined for the silicon isotope standard IRMM-017 ($\delta^{30}$Si= -1.26 %o $\pm$0.24 %o ; 2 s.d. n=89) and BigBatch ($\delta^{30}$Si= -10.55±0.42‰ ; 2 s.d., n=15), as well as San Carlos Olivine ($\delta^{30}$Si= -0.81±0.19‰ ; 2 s.d. n=14), Caltech Rose Quartz ($\delta^{30}$Si= 0.10±0.13‰ ; 2 s.d., n=14) and JER-diopsode glass ($\delta^{30}$Si=0±0.09‰ ; 2 s.d., n=14) samples. Silicon isotope standard IRMM-018 has also been measured and confirmed to be homogeneous.

Samples where Si is inially present in solution can also be measured. This approach has been verified by dissolving JER-diopsode glass, separating the Si [Georg et al., 2006; Brzezinski et al., 2003] and measuring $\delta^{28}$Si and $\delta^{29}$Si by laser ablation from a film of precipitated Si-gel.

First results will be presented that show that sponge needles from a given specie and environment are homogeneous within and between individual needles. In contrast, hydrothermal quartz shows substantial internal isotope zonation.

**References**
Green rust sodium/potassium sulfate

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Green rust (GR) is the generic name, which refers to a family of compounds consisting of brucite-like layers of Fe(II),Fe(III)-hydroxide. GR is a layered double hydroxide (LDH), also known as hydrotalcite-like materials (HLM). They have been identified in nature in soil taken from the redox boundary where groundwater is oxidised and they are important first solids during corrosion of iron in remediation barriers. The presence of Fe(II) in the brucite-like layer, makes GR very reactive towards redox sensitive elements, such as Cr, Se, Np and chlorinated solvents and pesticides. Understanding the GR system is thus interesting with regards to remediation techniques. It will also aid to better understand the redox processes taking place in the groundwater zone and to improve prediction of contaminant transport.

Previous studies have reported structurally bound water and anions in the interlayers, the thickness of which is assumed to be defined by the anion. Compounds with spherical or planar anions, such as Cl- or CO3 2-, produce similar X-ray diffraction (XRD) patterns and are known as Group 1 GR. Group 2 compounds incorporate three dimensional anions, such as tetrahedral SO4 2-, and produce larger basal-plane spacings.

If we want to predict redox reactions and contaminant transport, it is important to know the structural parameters of the various GR types. GR$_{SO_4}$, which is used in many studies, has not been characterised correctly in the past. We used several high resolution techniques including XRD, Mössbauer spectroscopy, ICP-AES and atomic force microscopy to investigate the GR$_{SO_4}$ compounds. We observed a difference in X-ray diffraction patterns depending on which monovalent cation was dominant during formation.

Within the last decade, two observations of naturally occurring sodium and sulphate-containing hydrotalcites have been described: nikischerite, NaFe$_{2+1}$Al$_3$(SO$_4$)$_9$(OH)$_{12}$•12H$_2$O and shigaite NaAl$_3$Mn$_2^+$$_2$(SO$_4$)$_9$(OH)$_{12}$•12H$_2$O. We refined the structure for green rust sodium sulfate and potassium sulfate using the nikischerite structure as a basis. The calculations, as well as careful chemical analyses, clearly indicated presence of Na or K in the structure. Thus we present new chemical formulae and new crystal structures for GR$_{Na,SO_4}$ and GR$_{K,SO_4}$: NaFe$_{2+1}$Al$_3$(SO$_4$)$_9$(OH)$_{12}$•12H$_2$O, P-3, a-axis = 9.520 Å, c-axis = 10.932 Å and KFe$_{2+1}$Fe$_{3+}$$_3$(SO$_4$)$_9$(OH)$_{36}$•XH$_2$O, P-3, a-axis = 9.530 Å, c-axis = 11.183 Å.
Zircon and whole-rock Hf isotope constraints on the petrogenesis of Transhimalayan plutonic rocks

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Hf isotopes of whole-rock (WR) samples and their zircon separates can be used in much the same way as Nd isotopes. Moreover, in situ zircon Hf isotopes, combining U-Pb ages, often record “hidden” information that allows more detailed studies of the petrogenetic processes. This study reports Hf isotope data from principal Transhimalayan intrusions, which include Jurassic, Cretaceous and Paleogene I-type Gangdese batholiths, resulting from Neotethyan subduction prior to the India-Asia collision. Major conclusions are reached: (1) There are significant variations in Hf isotopes of magmatic zircons, up to ~15 ε-units in some samples, suggesting magma mixing and/or magma-source isotopic heterogeneity to be common features; (2) A “hidden” DM (depleted mantle) component, with εHf(T~80Ma) values to +19.8, is identified in the Gangdese magmatic zircons. This DM-type component has never been revealed by any WR isotope analysis (WR-εHf(T): -0.1 to +13.5); (3) According to the linear correlation between the Gangdese WR Hf and Nd isotope ratios, this DM endmember has an equivalent εNd(T~80Ma) value of ca. +8 and thus shows an affinity to the India rather than Pacific DM source involved in the petrogenesis.

Figure 1. Hf isotopes of zircons and host rocks from the Gangdese batholiths, southern Tibet.

Particularities of Mn\(^{2+}\) uptake by living and dead *Shewanella putrefaciens*

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Sorption to microbial cell walls influences the fate and cycling of metals in the environment. Sorption of Mn\(^{2+}\) by living and dead *Shewanella putrefaciens* (widely spread in the environment gram-negative reducing bacterium) was studied in batch conditions: pH effect, kinetics of adsorption, equilibrium isotherms, the effect of the bacteria doses on adsorption, and speciation of dissolved forms in the experimental solutions.

Although FR-IR spectra of live and autoclaved cells of the facultative anaerobic bacterium *S. putrefaciens* do not reveal differences in cell wall functional groups, sorption of Mn\(^{2+}\) by suspensions of living and dead cells deviate significantly from one another. Sorption to dead cells is characterized by rapid equilibration and the data can be described by an isotherm. In contrast, sorption to live bacteria exhibits complex time-dependent kinetics, which cannot be captured by a single isotherm. Although the live bacteria release proteins and carbohydrates to solution, electrochemical analyses do not indicate strong aqueous complexation by organic ligands. FT-IR spectra of the (initially) live bacterial suspensions show evidence for the presence of MnO\(_2\) after 24 days, implying the occurrence of manganese oxidation. Mn\(^{2+}\) oxidation by living *S. putrefaciens* is a temperature dependent process.
Field relations and petrography in the Wadi Haymiliyah, Oman ophiolite: Evidence for a very heterogeneous plutonic lower crust

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According to the "ophiolite model", the lower oceanic crust formed at fast-spreading ridges is regarded to consist of a relatively simple "pan cake" sequence: from bottom to top, Moho-transition zone (MTZ), layered gabbros developing to isotropic gabbros, and sheeted dikes. Actually, this model is mainly based on Oman ophiolite studies. However, the "real" lower oceanic crust of the Oman may show a much higher complexity which is expressed by numerous intrusions of late plutonics of different rock type. We studied a special section of lower crust of the Oman ophiolite in the Wadi Haymiliyah (Halyn block), which is well-known for its complexity (Juteau et al., 1988). Here, we started small-scale mapping projects for a detailed structural, petrographic and geochemical characterization of selected outcrops within the lower parts of the plutonic crust.

The data presented here result from field work in a 250 m long river section in the Wadi Haymiliyah, which is geographically situated at N 23°33.975 and E 57°11.963. The mapping project uncovers typical layered gabbros probably emplaced during the on-axis accretion stage of a fast-spreading oceanic spreading center forming the basic matrix of the crust. Subsequently, the layered gabbro sequence was intruded by magmas or crystal mushes of different lithologies resulting in a variegated suite of late-stage plutonic rocks: poikilitic wehrlites, olivine gabbros, clinopyroxene gabbros, "hydrous" gabbros, as well as oceanic plagiogranoites. The contacts of the intrusions exhibit no chilled margin or any major textural discontinuity. Furthermore, plastic deformations are practically absent, implying that the layered gabbros were still very hot or even in a state of dense mush during the intrusion of the later magmas. Thus, it is indicated that the late intrusives also belong to the on-axis accretion stage. The gabbro in direct contact with the wehrlites shows those typical microstructures characterized by zones of An-enriched plagioclase on grain boundaries (Koepke et al., 2005), implying that water-rich fluids derived from the wehrlites triggered hydrous partial melting reactions in the gabbro.

References

Origin and Re-Os systematics of bitumen hosted in Lower Cretaceous volcanic rocks, northern Chile

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Bitumen-bearing strata-bound copper deposits hosted in volcanic-volcanoclastic sequences of Lower Cretaceous age are common in northern and central Chile. Solid bitumen and pyrobitumens (residual petroleum) are intimately associated with Cu-(Ag) sulfides. These deposits have several similar characteristics, such as the same type and age of the host rocks, the same number and type of hydrothermal stages (an early Fe-rich stage followed by a late Cu-rich stage); and the same ore paragenesis. In all locations, the textural relationships between bitumen and sulfides indicate that bitumen was present prior to the precipitation of the Cu-sulfides.

The origin of these Cu-(Ag)-bitumen deposits is associated to the evolution of the Lower Cretaceous back-arc basin. The source of the hydrocarbons is attributed to the thermal maturation of marine organic-rich facies accumulated in the back-arc basin during Jurassic and Early Cretaceous time. The necessary heat for distillation of hydrocarbons from source rocks has a probable origin in the burial temperature, coupled with the high thermal gradient associated with the extension and thinning of the crust under the ensialic floor of the back-arc basin and/or the hydrothermal fluid circulation associated with active magmatism during the Early and Late Cretaceous. Fe-rich hydrothermal fluids first removed the hydrocarbons from their source rocks and then precipitated them in the upper levels of the Lower Cretaceous sequence. Later, Cu-rich hydrothermal fluids precipitated the Cu-sulfides and contributed to the thermal maturation and cracking of the migrated oil to form pyrobitumens. The temperature of about 130ºC obtained from bitumen reflectance indicates the temperature of the first Fe-rich hydrothermal event and indirectly the regional maturation level, whereas temperatures between 170 and 380ºC, obtained from the reflectance of pyrobitumens, indicate the temperatures of the second Cu-rich hydrothermal event, which physically and chemically altered the original bitumen.

Preliminary Re-Os analyses of bitumen from the Copiapo area show high Re and Os concentrations (~670 ppb and ~2 ppb, respectively). The 187Re/188Os ratios are very high with values between ~11500 and 12800, and the Os isotopic composition is very radiogenic, with 185Os/185Os ratios over 50. These preliminary results indicate a very radiogenic source for the Os contained in the bitumen. Further Re-Os work on other bitumen samples and Cu-sulfides is in progress to determine time constraints for the formation of bitumen and sulfides in these deposits.
Vegetation regulates dissolved B in forested watershed

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The mechanisms by which the vegetation influences geochemical fluxes at the catchment scale remain difficult to describe because of a lack of knowledge on their links and feedbacks. In particular, it is still a question to know at what level the nature of the vegetal cover can regulate the river water chemistry or influence the reactivity of soil horizons.

To address these points, we have conducted a comprehensive study of B isotopes in a small-forested watershed (Strengbach, NE France). Water was sampled along the hydrological pathways from rainwaters down to springs via throughfalls and soil solutions in two distinct parcels covered by spruces and beeches.

It comes out that the amount of B yearly cycled by vegetation is about twice the amount of B exported out of the basin. This demonstrates that the biological activity is the key factor that regulates the B geochemical cycle in forested area. Moreover, the B isotopic signature of the vegetation is enriched in $^{11}$B far from any other reservoirs. These two features make B a highly reliable and easy-to-follow element for investigating the mechanisms of geochemical transport that involve the vegetation cycle.

In soil solutions, there is an exponential-like decrease of the $[^{11}B]$ indicating that B mostly originates from throughfalls. Associated with the isotopic analyses, the behavior of B primarily reflects the reactivity of soil horizons in terms of ion exchange intensity. At depth greater than 60 cm, soils developed under spruces and beeches show distinct isotopic composition, each fingerprinting the corresponding spring water. It then strongly suggests that the nature of the vegetal cover directly influences the reactivity of the soil from which it growths and then drives the B isotopic composition of the sub-surface waters.

Overall, this study demonstrates that the geochemical cycle of B isotopes in forested catchment is controlled by vegetation cycling and that B can be used for closer investigation of the relative impact of the biosphere on the mass transfer at regional scale.

Sulfate, methane, and the rise in atmospheric oxygen

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Using two distinct numerical models, we have developed a conceptual picture that implicates sulfate as a key player in ushering in the late Archean global ice age and ultimately leading to complex-life sustaining levels of atmospheric oxygen. We attempt to provide a theoretical framework for understanding the Archean records of increasing mass-dependent sulfur isotope fractionation ($\delta^{34}S$) concurrent with a decrease in the mass-independent signal $\Delta^{33}S$ (MIF-S). Increasing $\delta^{34}S$ is commonly linked to increasing oceanic sulfate availability. First, we describe results from a global redox box model which investigates how slight increases in oceanic sulfate concentration could affect anaerobic methanotrophy in the Archean/Proterozoic biosphere. We show that this metabolism enhances a positive feedback on the atmospheric destruction of methane by oxygen, by acting as a throttle for methane fluxes from the seafloor. We next describe results from a 1-D photochemical model which is used to explore the transition between weakly reduced and weakly oxidizing atmospheres. We show that the disappearance of MIF-S is better explained by a decline in atmospheric methane levels, rather than by a rise in oxygen levels. Increasing oceanic sulfate thus hastens a collapse in atmospheric methane to below 10 ppm, which halts the MIF-S signal. These conditions can lead to a global ice age, and are favorable for increasing amounts of free oxygen in the atmosphere. Oxygen levels and climate stabilize in the early Proterozoic once sufficient ozone forms to allow methane to re-rise to levels of approximately 100 ppm.

References
Comparative geochemistry at Gusev Crater and Meridiani Planum, with implications for aqueous activity

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Correspondences and Similarities
Soils, sediments and even certain rock compositions at the Mars Exploration Rover landing sites have geochemical correspondences in spite of their far-separated locations (nearly diametrically opposite sides of the planet). Yet, as we shall show here, there are diagnostic discriminators and significant differences in their history of aqueous alteration.

Soils at Meridiani are typically quite similar to soils measured at other sites, including Gusev, but are often somewhat enriched in Fe, presumably from fragments of hematite-rich spherules that form an abundant lag. However, they record little if any of the signature of obviously-weathered sulphate-rich outcrop that pervades the Opportunity site.

The Meridiani outcrop materials themselves evidence a rich mineralogy. Certain samples derived from the whitish materials at Tyrone area in Gusev have almost identical levels of Si, S, Fe, Mg, Al, Na and P.

Geochemical Discriminators
Minor elements Cl, K, Ti, Mn and Zn are lower at Gusev, while Cr, Ca, and Ni are higher. Inferred mineralogies and explanation of the sources of the Meridiani outcrop are quite different from the Gusev Tyrone-derived samples.

Tyrone samples can be explained as salt-silica-soil mixtures, whereas outcrop geochemistry can be explained as derivation from “source basalt(s)” and a very acidic brine. Although the hypothetical source basalt is not in evidence at Meridiani or in the martian meteorite collection, a very good match for all elements (with the sole exception of trace element Ni) is provided by rock class Irvine discovered at the Gusev site. Whereas Paso Robles class ferric sulphate-rich salts from the Tyrone area must have formed by a strong enrichment process, such as extensive aqueous processing, the Meridiani outcrop material also is very high in sulphate, but with a significantly different outcome.

Geochemical Variability
The range of chemical variability in the Columbia Hills at Gusev crater is startling, with virtually every element present in at least one or more rocks at anomalously high or low concentrations. Some of these extremes can be traced to igneous differentiation processes, but others clearly must be due to aqueous alteration in sedimentary or metasomatic processes. In contrast, except for some meteoritic materials, Meridiani outcrop lies within a well-defined geochemical range – variations in Mg, S and other elements can be readily explained as salt migration in an evaporitic sandstone formation.

Re-establishing recycled sediment in mantle plumes – Evidence from Gough Island

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Sediment is an integral part of recycling slabs and has long been held responsible for enriched signatures found in many ocean island basalts associated with mantle plumes. However, to date the evidence for deep recycled sediment is generally weak and our knowledge on the modification of recycled sediment in the subduction factory is limited, which resulted in a recent surge of alternative models of mantle metasomatic enrichment processes and lower crustal recycling. An important characteristic of pelagic clays, calcareous oozes and chert is their negative Ce anomaly inherited from seawater, resulting frequently in negative Ce anomalies of present day subducting sediment. The presence of negative Ce anomalies in arc volcanic rocks is a strong indication for the preservation of Ce anomalies to the depth of arc magma formation. Thus, Ce anomalies present themselves as a useful tracer for deep sediment subduction.

A sediment contribution to the Gough mantle source has previously been suggested based on high La/Nb, Ba/Nb and 207Pb/204Pb ratios compared to other OIB, though the lack of raised oxygen isotope ratios limits bulk sediment to <1.5%. High precision trace element data (acquired by ICPMS) on mafic volcanic rocks from Gough Island reveal negative Ce anomalies, with Ce/Ce* values in Gough lavas extending down to values as low as ~0.92. Weathering processes, identified as the cause for Ce anomalies in some OIB, can be excluded here based on element-element systematics, indicating magmatic trends rather than weathering-induced element mobility. Shallow-level contamination by local sediments can be excluded on Ce/Pb systematics. We suggest that Ce anomalies in Gough lavas demonstrate the presence of recycled, subduction-modified sediment in the mantle source of the Gough Island magmas. With the exception of fluid mobile elements, the trace element systematics of Gough lavas can be reproduced by adding up to ~10% subducting sediment with negative Ce anomaly (using estimates of present-day subducting sediment columns as a proxy to ancient oceanic sediment) to the mantle source of Gough magmas. These calculations suggest loss of fluid-mobile elements in the subduction zone. Low degree melting of the sediment at some stage can explain the lack of a sediment oxygen isotope signature. We explore scenarios of sediment modification in the subduction factory in order to match the enriched trace element systematics in the Gough mantle source.
Genesis of K-enriched felsic magmas:
A collection of contrasting crustal connexions

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High-K calcalkaline granitic (s.l.) magmas are formed in late orogenic, post-orogenic and anorogenic settings. Proposed origins include; assimilation of crustal rocks by basaltic magmas, partial melting of the enriched mantle with fractionation, reactive assimilation of wall rocks by normal-K magmas, magma mixing, and melting of composite sources with interlayered pelites and amphibolites. Metabasaltic rocks are not suitable sources; nor are any experimentally studied metagreywackes, metatonalites or metadacites. High-K are andesites and certain metaluminous Bt-Pl-Qtz gneisses could be suitable protoliths, so neither the protoliths nor the conditions in high-K magma genesis need to be special or complicated. Nevertheless, sometimes the main protoliths are not crustal, and the processes involved are very complex.

K-rich adakites occur over wide areas and lack either temporal or spatial association with subduction. They have all the geochemical attributes of typical subduction-related adakites except that K₂O/Na₂O > 0.95, over a broad range of SiO₂ (≈ 58 to 74 wt%), so low-degree partial melting or fractionation are not viable origins. Isotopes indicate strong crustal involvement. Near-liquidus experiments were carried out on a typical K-adakite, at 2, 4 and 6 wt% H₂O, with the constraint that the assemblage should contain Grt but not Pl. This work showed that K-adakites were high-T (> 1075 °C), very hydrous magmas (~ 6 wt% H₂O) formed by fluid-absent partial melting of metatonalites, meta-andesites, and possibly potassic metabasalts at P > 2 GPa.

Felsic sanukitoids are Late Archean, post-tectonic, K-rich, high-Mg rocks that have geochemical characteristics similar to both mantle- and crust-derived magmas. High-T (1200 °C?) melting of Phl peridotite could explain their peculiar chemistry. Near-liquidus experiments on a monzodiorite from Panozero produced Phl near the liquidus, confirming residual mica in the protolith. However, neither Ol nor Grt is present. Thus, the source may have been phlogopite clinopyroxenite, rather than peridotite, formed in a global enrichment event.

In conclusion, K-enriched, metaluminous, felsic magmas have a wide variety of origins. The K sometimes originates directly from a crustal protolith but is commonly from the enriched mantle, subduction-zone fluids being the ultimate source. Given the difficulty of forming the more mafic granitoids by crustal melting, we should take a fresh look at the mantle for the origin of many granitic series, not through direct derivation but through fractionation of enriched mafic magmas.

Identification of aromatic organic matter from comet 81P/Wild 2

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Comets provide a unique perspective on the formation of the Solar System and provide a missing link to the progenitor dense molecular cloud from which it arose. Due both to their small size, and site of accretion in the outer reaches of the Solar System, comets have escaped large-scale differentiation and thermal alteration and so may retain much of their original presolar volatile inventory. The study of cometary material can therefore help to reconstruct the early history of our Solar System.

We have used the technique of ultrafast two-step laser mass spectrometry (µlatra-L²MS) to investigate the nature and distribution of aromatic organic matter from comet P/Halley and returned by the STARDUST sample return mission. [1] We have identified complex aromatic hydrocarbons in cometary particles entrained along several aerogel tracks. Although terrestrial contamination issues from the aerogel remain a concern, a substantial fraction of the observed organics appears indigenous. [2] The aromatic fraction of the total organic matter present appears to be lower than that typical of carbonaceous and ordinary chondrites, but shows a greater spectral complexity. Simple fused ring polycyclic aromatic hydrocarbons (PAHs) such as benzene (C₆H₆), naphthalene (C₁₀H₈), acenaphthalene (C₁₂H₁₀), phenanthrene (C₁₃H₁₀) and pyrene (C₁₆H₁₀) are present along with their homologous alkylation series, Ar-(CH₂)n-H, extending up to n ~ 6. In addition, prominent odd-mass peaks are interspersed within these familiar PAH series and are consistent with several interleaved alkylation series of N-containing PAHs (NPAs).

We have used the technique of ultrafast two-step laser mass spectrometry (µlatra-L²MS) to investigate the nature and distribution of aromatic organic matter from comet 81P/Wild 2 dust particles collected in aerogel and returned by the STARDUST sample return mission. [1] We have identified complex aromatic hydrocarbons in cometary particles entrained along several aerogel tracks. Although terrestrial contamination issues from the aerogel remain a concern, a substantial fraction of the observed organics appears indigenous. [2] The aromatic fraction of the total organic matter present appears to be lower than that typical of carbonaceous and ordinary chondrites, but shows a greater spectral complexity. Simple fused ring polycyclic aromatic hydrocarbons (PAHs) such as benzene (C₆H₆), naphthalene (C₁₀H₈), acenaphthalene (C₁₂H₁₀), phenanthrene (C₁₃H₁₀) and pyrene (C₁₆H₁₀) are present along with their homologous alkylation series, Ar-(CH₂)n-H, extending up to n ~ 6. In addition, prominent odd-mass peaks are interspersed within these familiar PAH series and are consistent with several interleaved alkylation series of N-containing PAHs (NPAs).

The N is unlikely to be present in the form of N-heterocycles given the experimental conditions of the µlatra-L²MS analysis, rather the most probable form of the N functionality is as nitrile (Ar-CN). This may be related to the 2.3 & 4.6 μm absorption features observed in the spectra of many young stellar objects and some comets, and which has been attributed to a solid material known as “XCN” believed to be synthesized by ultraviolet and/or ion bombardment of presolar icy grains in circumstellar environments. [3] Comparison of the STARDUST spectra with a range of other astromaterials analyzed by µlatra-L²MS under comparable experimental conditions show a striking similarity with several cluster IDPs.

U-Pb dating of stable isotope records in Alpine speleothems from the late Pliocene/early Pleistocene

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Speleothems from the Wilder Mann and Wildmahd caves in the Allgäu Alps, western Austria have well-preserved, probably annual, microscopic laminae and high resolution stable isotope records suggesting no post-depositional alteration. These samples encapsulated a detailed history of environmental variations at the time of speleothem growth. These speleothems are characterised by high uranium concentrations, typically around 10 ppm, and coupled with some initial lead concentrations as low as 2 ppb this leads to highly radiogenic lead compositions at the present day.

Two flowstones and two stalagmites have been dated using the U-Pb isotopic system. All four samples yielded sufficient spread in isotopic composition to define chords on the Tera-Wasserburg diagram from which concordia ages were calculated using an iterative procedure to account for the effects of isotopic disequilibrium. Ages are in the order of 2 Ma and for samples of this age ‘normal’ levels of initial $^{234}$U excess are no longer detectable. The Wildmahd sample All 1 is the youngest at 1.73 Ma with a probable uncertainty of 0.03 Ma allowing for unknown initial $^{238}$U excess within a range of ± 40‰. The Wilder Mann samples range from 2.30±0.07 to 1.99±0.05 Ma on the same basis. One of the stalagmite samples shows significant variation along its length from 2.11±0.04 to 2.03±0.03; further analyses on the oldest parts are in progress.

The results demonstrate that these speleothems date from the late Pliocene/early Pleistocene interval and thus provide (a) a minimum age for these high-altitude caves (2450m asl), and (b) a continental record of environmental change at an early stage in the late Cenozoic glaciations.

Tectonic subduction erosion, arc magmatism and the maintenance of the continental crust

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Estimates of modern continental crustal recycling in subduction zones can be made from plate convergence velocities, the thicknesses of trench sediments, volumes and ages of accretionary complexes together with rates of trench retreat. Plate convergence rates appear to be the primary control on crustal subduction, with convergence >7.5 cm/yr associated with tectonic erosion. Collision of aseismic ridges with trenches drives around two thirds of forearc tectonic erosion over periods >10 m.y.. Globally material subduction at least as deep as the magmatic roots of arc systems is around 3.0 Armstrong Units (1 AU = 1 km$^3$/yr), of which 1.65 AU comprises subducted sediments, with 1.33 AU of eroded forearc crust. Recycling rates along a single margin may show strong temporal variation over 1 m.y. periods. Isotopic variations in Costa Rican tephra suggest that sediment accretion is the most common mode of tectonism, but this is separated by short periods of dramatic erosion that cause net crustal loss. Even where erosion is continuous this can operate in a fast steady-state mode or a slower temporary style. On the Central Andean margin tectonic erosion since 20 Ma has caused trench retreat, but slow subsidence under the coastal zone implies steepening of the forearc taper rather than large scale retreat. The Neogene mass loss rate of 13 km$^3$/m.y./km is 5-10 times lower than the long-term average. Since 2 Ma this rate has slowed further due to underplating under the coastal zone. A climatic role in driving continental erosion and moving the margin into a more accretionary state has been suggested but is hard to demonstrate. Average global mass loss requires that Cenozoic arc productivity lies close to 75 km$^3$/m.y./km if the volume of the continental crust is to be maintained. Efficient accretion of oceanic arc crust is essential in maintaining the total crustal volume. In the classic Taiwan-Luzon example local crustal mass balancing implies that ~90% of the igneous arc crust is accreted.
Pb elemental concentrations and isotopic compositions in environmental survey: Is lichen transplantation efficient?

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Lichens are known to be sensitive to various pollutants and are considered a good biological indicator of the air quality. Lichens are epiphytic, which means that their influx is exclusively atmospheric (precipitation, fog, mist, particles, gas...), so they integrate the atmospheric fallout signal and generally contain much higher concentrations of trace metals than, e.g., rain. Another advantage of lichens is their ubiquity and the ease of sampling. However, lichens are not found everywhere. To compensate for the absence of lichens in certain areas, transplantation techniques have been developed and are now commonly used. These techniques consist in an importation of lichens from one area to another one, in which they are originally absent.

In this work, lichens (Hypogymnia physodes) have been transplanted from one reference site to 5 different sites including the reference site itself and 2 peri-urban sites. The other 2 sites have been chosen for their proximity to a highway and the proximity to an industrial site. The impact of two different system set-ups (one covered and one non-covered) has been tested. The main difference between the two set-ups is protection from the rain for the covered set-up. Samples have been collected 14, 34 and 68 days after transplantation. Pb concentrations and Pb isotopic compositions already accumulated in thallus have been measured by ICP – mass spectrometry.

A systematic difference between the two set-ups (covered and non-covered) is found for Pb concentrations. Lichens coming from the non-covered set-ups provide higher Pb concentrations. Lead concentrations in covered set-ups have been found lower than or equal to the original concentration, whereas the Pb concentration in lichens from the non-covered set-ups is higher for all the sites after 68 days. Pb isotopic compositions also show a systematic difference between the two set-ups, with the Pb isotopic composition of lichens from the non-covered set-up being more radiogenic. Pb isotopic compositions of lichens coming from the covered set-ups remain in the same range, whereas substantial changes in the Pb isotopic composition are recorded for lichens coming from the non-covered set-up, even after only 34 days of transplantation in some cases. Nevertheless, interpretation of the Pb isotopic composition variation is not straightforward.

Nano-spinel synthesis using Fe(III)-reducing bacteria

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Geobacter sulfurreducens is a bacterium capable of reducing amorphous iron(III) oxide through electron transfer coupled to organic matter oxidation, converting the iron to nano-sized magnetic particles of magnetite (Fe₃O₄), with a size of approx. 20 nm [1] (Fig. 1).

Nano-spinels of the general chemical formula MₓFe₃₋ₓO₄, where M is a transition metal cation other than Fe, such as Co, Ni or Mn, have been produced using the capability of G. sulfurreducens to form nanomagnets[2]. These materials have different electrical, magnetic, and structural properties, from coarse grained materials making them ideal for use in technical devices. Characterization of these nanoparticles has been carried out using the synchrotron radiation spectroscopies XMCD (x-ray magnetic circular dichroism) and EXAFS in addition to SQUID magnetometry and TEM.

Figure 1. SuperSTEM images of (A) Co-biospinel, (B) Ni-biospinel.

The extraordinary capability of bacteria to produce nanomagnets has not yet been exploited by industry and such processes have enormous commercial potential. In addition, the ability of the bacteria to precipitate magnetite from Fe(III) oxides could be used as a bioremediation strategy to clean up environments contaminated by Fe(III)-oxides, such as acid mine drainage (AMD) sites, inexpensively and effectively.

References
Uptake of U(VI) by hydrated and degraded cement

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The use of cement in engineered barrier systems of radioactive waste repositories emphasize the proper understanding of uranium interaction with hardened cement paste. This study presents experimental and modelling results on uptake of U(VI) in batch experiments by hydrated and degraded cement in contact with MilliQ and aged cement pore water respectively.

Kinetic experiments show that equilibrium between cement and U(VI) is reached in less than two days. Equilibrium uranium concentration denotes a high uranium uptake by cement phases (up to 99% in some cases). Rd values for hydrated cement (with S/L ranging between 0.05 and 10 g/L) vary between 7 and 65 m³/kg (for initial uranium concentrations of 1·10⁻⁶M) and between 5 and 30 m³/kg (for initial uranium concentrations 1·10⁻⁸M). Regarding degraded cement, Rd values (with S/L ranging between 0.1 and 20 g/L) are in the range 10-25 m³/kg for [U]₀= 1·10⁻⁶M. At [U]₀=1·10⁻⁸M, the aqueous concentration of U(VI) at the equilibrium falls below the detection limit of the used analytical technique.

A surface complexation model has been used to explain the experimental results on uranium interaction with hardened cement paste. This model takes into account both, aqueous U(VI) speciation and speciation of silanol sites in the typical C-S-H phases of cement. The possible precipitation of solid uranium phases has been also assessed in this work.

Hydrogen solubility in synthetic rutile

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Hydroxyl solubility in rutile was determined as a function of pressure, temperature, and fO₂ (buffered with nickel-nickel oxide NNO, or magnetite-hematite, MH). Pure, synthetic rutile and H₂O were sealed in a Pt or Pd/Ag inner capsule and placed within a Au outer capsule containing an fO₂-buffering assemblage. Experiments employed a piston-cylinder apparatus and NaCl-graphite furnaces. OH concentrations were determined using FTIR spectroscopy and the calibration of Maldener et al. 2001. The [OH] in rutile increases from 108 to 956 ppm H₂O at 1 GPa over the range 500-900ºC at the NNO buffer; a fit to the data produces the relationship [OH] (ppm H₂O wt.) = 4.73 e0.006T, R²= 0.96. The higher fO₂ of the MH-buffered experiments produced a similar T dependence, but lower overall [OH]; at 1 GPa, [OH] increases from 84 to 267 ppm H₂O from 600-900ºC ([OH] (ppm H₂O wt.) = 7.28e0.0039T, R²= 0.97). The effect of pressure on the [OH] in rutile is less pronounced than the temperature effect. At the MH buffer and 800ºC, [OH] (ppm H₂O wt.) = 79±13 x P(GPa) + 88±15 from 0.5-2 GPa. For the experiments conducted at NNO and 800ºC, [OH] (ppm H₂O wt.) = 169±31 x P(GPa) + 409±33 from 0.5 to 2 GPa. Over the 25 seconds it takes to quench the experiments, loss of OH from rutile along the c crystallographic axis is significant — a 33% decrease in [OH] over a distance of 0.35 mm for an unbuffered experiment at 1000ºC and 1 GPa was observed. Measurements of OH concentration should be obtained in the center of rutile grains at least 0.5 mm in diameter along the c-axis to obtain equilibrium values.

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Melt inclusion records of degassing from persistently active volcanoes: Etna, 2006

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Introduction

Mt Etna, Sicily, is Europe’s laboratory volcano. Etna is persistently active, and responsible for 5-10% of global annual volcanic emissions of CO2, SO2 and volatile trace metals (Pyle & Mather, 2003). Activity on Etna has changed dramatically over the past 5 years. In 2001 – 2003, the eruptions were vigorous and volatile-rich, in contrast, eruptions in 2004 and July 2006 started with the slow effusion of gas-poor magma. We collected a suite of olivine hosted melt inclusions and matrix glasses in newly erupted products from Mt Etna, Sicily, spanning the major eruptions of the previous 5 years. These glasses have been measured for the concentrations of volatile (H, C, Cl, F) and selected trace elements (Li, Zr) by ion microprobe at the University of Edinburgh and for major and trace elements with a particular focus on the volatile trace metals by electron microprobe and laser ablation ICP-MS at the University of Cambridge.

Discussion

Preliminary results will provide data to constrain the nature of the relationship between the earlier (2001-2003) volatile-rich magmas and the later (2004, 2006) volatile-poor magmas. As expected, many of the 2006 melt inclusions show evidence for shallow storages and degassing: dissolved water contents are low; dissolved Li contents are variable, and don’t correlate with involatile incompatible tracers; and melt inclusions extend to more evolved compositions than those erupted rapidly during the 2001-2003 eruptions. When combined with new data on dissolved C contents of melt inclusions, we will be able to determine the coupled effects of fractional crystallization, gas loss and gas accumulation on the compositions of Mt Etna magmas.

Conclusion

This thorough investigation into the degassing processes of Mt Etna will not only provide new information into the importance of volatiles for determining the eruptive character and processes of Mt Etna volcano but will also have implications for the environmental and economic effects of the behaviour of metals in such systems.

References

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**Impact of vehicle-emitted platinum group elements on the human respiratory and digestive tracts**

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**Introduction**

The use of platinum group elements (PGEs) in vehicle exhaust catalyst (VECs) represents a source of highly dispersed environmental contamination and these metals have been identified in a variety of airborne samples, dusts, soils and waters. The VEC-emitted PGEs can interact with several ligands in the environment and be transformed into soluble species that can enter the food chain with potential environmental and health risks. In order to evaluate the potential pathways of PGEs from VECs into humans, physiologically based tests were used to study the uptake of PGEs by the human respiratory and digestive tracts.

**Method**

The tests were used to provide quantitative data on the bioavailability of PGEs from road dust, powdered exhaust catalyst and metal hydroxide samples. The digestive assay was implemented in two phases, simulating the passage of ingested dust from the acidic environment of the stomach to the near neutral conditions of the small intestine. The respiratory tests employed various simulated lung fluids. All the extracted samples were analyzed for PGE content by inductively coupled plasma mass spectrometry.

**Discussion and conclusions**

The results show that PGEs in road dust samples provide the greatest fractions of bioavailable PGEs (up to 87%), probably due to transformation into soluble and mobile species through complexation by ligands common in the roadside environment. The highest PGE releases were observed in lung solutions analogous to the fluid with which inhaled particles would come into contact after phagocytosis by cells.

A high % of PGEs from VEC-emissions (i.e. road dust) is dissolved in the respiratory and digestive tracts. From the toxicological perspective, it is important to consider the possible formation of PGE-chloride complexes due to the presence of Cl ions in the stomach and lung environments, perhaps with increased health risks because of their known toxic and allergenic effects on animals and human beings.

**References**


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**Geodynamical transition in the mantle at the end of the Hadean**

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The rock record begins around 3.9–Ga ago. Before, very little observations exist for what is called the Hadean eon. Our knowledge of mantle dynamics in the early Earth comes from small zircons found at Jack Hills (Australia) and Acasta (Canada) which can be as old as 4.2-4.4Ga, and from the composition of mantle derived rocks in isotopes coming from extinct radioactivities. It has been suggested, from geochemical studies on the Hadean zircons, that the Earth is already close to modern by 4.4Ga, having large continents (Harrison et al., 2005), liquid oceans (Valley et al., 2002) and potentially plate tectonics (Harrison et al., 2005). The present work confronts this hypothesis to modeling of Xe isotopes produced by extinct radioactivities. We show that the transition from the Hadean to the Archean corresponds to a change in the thermal and mechanical regime of the Earth’s mantle: the transition from magmatic to modern solid state mantle convection.
Nature of metasomatizing agents in suprasubduction and intraplate settings as deduced by glass and amphibole geochemistry

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Glasses and amphiboles in spinel peridotite mantle xenoliths hosted in calc-alkaline s.l. magmas from the subduction-related Western margin of Pacific Plate (Kamchatka, Japan, Philippine) are compared with glasses and amphiboles in spinel peridotite entrained in alkaline basalts from several intra-plate localities (Cape Verde, Antarctica, Gran Comore, Lessini). At comparable SiO2, subduction-related glasses, especially those from Kamchatka, are characterized by lower alkalies contents than glasses from intra-plate settings. As a consequence the former tend to be more SiO2-saturated, as also evidenced by the widespread presence of secondary orthopyroxene in xenoliths from suprasubduction setting. Subduction-related glasses have Na2O content similar to carbonatite-metasomatised intra-plate glasses, but the latter presents consistently higher CaO and Nb abundances. Subduction-related glasses have also lower Rb, Ba, Zr, Ti and HREE contents than alkali-silicate intra-plate glasses, bearing analogies with slab-derived melt. Irrespective of textural positions, amphiboles in mantle xenoliths from intra-plate settings present much higher Nb and, to a lesser extent, Zr and Ti contents than amphiboles found in xenoliths from suprasubduction setting. Similar indications, although less robust for crystallographic and statistical reasons, can be found for clinopyroxene and orthopyroxene. These data strongly suggest that metasomatizing agents in the mantle wedge above a subduction zone are richer in SiO2 and depleted in Nb, Zr and Ti with respect to fluids migrating in intra-plate setting. The presence of accessory phases such as rutile and zircon in the downgoing slab, retaining HFSE during dehydration and/or melting and producing HFSE-depleted fluids seems to account for the observed geochemical features. The commonly observed occurrence of “plume-related” alkaline magmatism in the back-arc setting which follows in a time span of few to ten millions of years a subduction process will be also addressed in the light of the above reported data.

New SHRIMP ages from the Permo-Triassic boundary at Meishan

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Determination of the age of the Permo-Triassic boundary has been a test case for zircon geochronology in the presence of pervasive Pb loss and inheritance. SHRIMP ages are presented for zircons for five volcanic ashes from the global stratotype at Meishan, China, and compared with previous zircon ages for these beds. Subtle inheritance and Pb loss have been detected and screened in most Meishan zircons. No significant age differences are detected here between Bed 17 through Bed 36, so the Permo-Triassic boundary at Meishan is estimated as their mean age at 251.6 ± 0.2 Ma. This agrees with Bowring et al. (1998) but it is ca. 0.5% younger than Mundil et al. (2004). Rather than hidden Pb loss, the difference may be due to interlaboratory bias, which remains to be assessed by comparison of standards analyses.

References

Mantle heterogeneity evidence from South Patagonia, Argentine indicated by noble gas analysis on mantle xenoliths.

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Studying the subcontinental lithospheric mantle evolution and heterogeneity can be very complex for many reasons: in addition to the complex history of its own origin, after being formed, the subcontinental lithospheric mantle can be exposed to different processes related or not to the crust formation as: re-melting, delamination from the crust, re-fertilization with fluids from different origins as lithospheric, sub-asthenospheric, subduing slabs and so on. Spinel- and/or garnet-bearing ultrabasic mantle xenoliths brought to the earth’s surface by intraplate alkaline basalts provide direct information on the nature and processes involved in the modifications of the subcontinental mantle lithosphere as mantle metasomatism.

The western South American plate is a natural laboratory for petrological investigations of the subcontinental lithosphere due to the complex tectonic arrangement of the Andes. We performed noble gas analysis (He, Ne, Ar, Kr and Xe) in thirty samples of mantle xenoliths hosted by Eocene to recent alkaline basalts to determine the origin of the xenoliths and to constrain the processes that modified the mantle. Noble gases were extracted by crushing and stepwise heating method. Except for high ³He/⁴He ratios observed for few samples at low temperatures of stepwise heating indicating some cosmogenic ³He, the majority of the samples show ³He/⁴He ratio around of 7.22±0.93RA. The lower ³He/⁴He ratio than the MORB value (8±1RA) indicates higher (U+Th)/³He ratio than the MORB source mantle. ⁴⁰Ar/³⁶Ar ratios obtained with crushing method vary from 326 to 1476. The rough correlation ³He/³⁶Ar ratio of the lithospheric mantle beneath South Patagonia could argue for metasomatism by slab-derived component for some samples. However, the large variation of ²⁰Ne/²²Ne from 9.27 to 12.0 and the narrow variation of ²¹Ne/²²Ne from 0.0279 to 0.049, in addition to the good correlation between ²⁰Ne/²²Ne vs. ²³Ne/²²Ne could suggest some OIB like characteristic for the metasomatic fluid.

Geochemical characteristics of the LB-07A and LB-08A cores from the Bosumtwi Impact Structure, Ghana

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Cores extracted from the central uplift (LB-08A) and deep crater moat (LB-07A) of the 1.07 Ma Bosumtwi impact structure, Ghana, consist of alternating suevite, polymict lithic breccia, and monomict breccia (in LB-07A only) that overlie fractured country rocks comprising metabreccia and metapelitic sediments.

In both cores, the impact breccias have compositions intermediate to the identified target rocks [1] and are well-homogenized with respect to the silicate component. Interestingly, the different lithologies in LB-07A show less variation than those from LB-08A; however, a number of major and trace elements show more variation in the metabreccia and metapelitic sediments for both cores. Impactite trace element concentrations are significantly different from other lithologies, and appear to be controlled by greywacke-phylite and shale proportions. Hydrothermal alteration, which has been noted petrographically, has affected both the CaO and MgO contents of the rocks [2 and 3, for more detail], which correlate with LOI. In general, the chemical signatures of fallout suevites from the northern crater rim and fallback suevites from the cores are similar, but different MgO, CaO, and Na₂O contents were noted. Additionally, the Ivory Coast tektites have narrower ranges of MgO and CaO content than the fallback suevites. This may be due to varying degrees of alteration, but it must be noted that the fallback and fallout suevites differ significantly in clast population [particularly with regards to calcite and granite content], as well as a higher proportion of melt fragments in the fallout suevites. Rare earth element concentrations of fallout suevites from the northern crater rim and fallback suevites from the cores are similar, but different MgO, CaO, and Na₂O contents were noted.

Siderophile element abundances in the suevites in the cores are not obviously higher than those seen in the country rocks and outer suevite occurrences; thus no evidence for a meteoritic component has been detected.

References
Refining step-leaching Pb-Pb dating methods for meteorites and their components

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Whereas Pb-Pb dating potentially offers the most precise ages for old meteorites and their components, this method has been commonly compromised by terrestrial contamination, uncertainty in the initial Pb isotopic composition and analytical uncertainties related to poorly-constrained instrumental mass fractionation using a thermal ionization mass spectrometer (TIMS). With the latter issue addressed by the use of a 202Pb/205Pb double spike, we have experimented with step-leaching procedures of differentiated meteorites and chondrules in an attempt to first effectively remove terrestrial contamination and then to generate Pb fractions of sufficient size and spread in Pb-Pb space to adequately define meaningful isochrons. Samples are abraded, rinsed in an ultrasonicator, lightly crushed in the clean laboratory and then repeatedly pre-cleaned using distilled ethanol, water and acetone. Subsequent steps of weak HCl and HBr acids combined with ultrasonic agitation and modest heating effectively removes terrestrial contamination in most samples we analyzed. Subsequent exposure to warm 4M HNO3 typically isolates the least-radiogenic component of the leaching series. Leaching with HCl of increasing molarity with longer and higher temperature heating steps returns more radiogenic Pb fractions. The most radiogenic Pb fraction typically corresponds to the first warm 1M HF step with subsequent steps in stronger HF yielding progressively less radiogenic signatures. Importantly, the Pb extracted in the dissolution of the final residues with 28M HF + 14M HNO3 typically plots slightly below the isochron defined by previous leach steps, corresponding to a slightly younger $^{206}\text{Pb}/^{238}\text{U}$ model age than the inferred actual age. The wide range of total Pb contents (20 - >2000 pg) in leach fractions returned by this method requires analyses by TIMS using a high-efficiency Pb emitter and diligent monitoring of laboratory Pb blank, including running parallel Pb blank analyses for every leach fraction. ICP-MS analyses of major elements in aliquots of each leachate indicates that different combinations of minerals are breaking down throughout the sequence. As expected, U and Pb are highly and variably fractionated during the leaching step such that no U/Pb age information is recovered. Using this procedure we have revisited the ages of chondrules from CB chondrite Gujba and CV chondrite Allende and several differentiated meteorites including SAH-99555.

A view of the upper-crustal component of oceanic hydrothermal systems at fast-spreading ridges

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Hydrothermal circulation through the upper oceanic crust at mid-ocean ridge axes leads to major chemical fluxes largely between the sheeted dike complex and seawater. Metamorphic mineral assemblages, fluid inclusions and geothermometry in the sheeted dike complex requires temperatures of fluid-rock reaction of ~250°C to ≥500°C throughout the sheeted dike complex. However, models of recharge to the hydrothermal system suggest large fluxes of cold water into the crust, most likely in the near axis region. If correct, this recharge flux should cool the sheeted dike complex rapidly raising the question of when the hydrothermal metamorphism of the sheeted dike complex occurs.

To better understand the thermal evolution in the sheeted dike complex Coogan et al. (2005) developed a geospeedometer applicable to this region. The partitioning of lithium between plagioclase and clinopyroxene is strongly temperature dependent and lithium diffusion in both phases is very rapid. During subsolidus cooling of a dike lithium diffuses out of plagioclase into adjacent clinopyroxene and the closure temperature for this exchange is dependent on the cooling rate of the dike. Thus, the measured distribution of lithium between these phases can be used to determine the cooling rate (Coogan et al., 2005).

Applying this approach to ODP Hole 504B reveals very rapid cooling rates in at least the upper half of the sheeted dike complex. This is consistent with the sheeted dike complex being cooled efficiently by down-welling fluid. This suggests that the hydrothermal metamorphism of the sheeted dike complex may occur either: (i) during the cooling of an individual dike; (ii) during thermal rebound after hydrothermal recharge ceases in the off-axis; or (iii) during upflow of hydrothermal fluids. The first model appears to be inconsistent with the consistency of vent fluid compositions and experimentally determined reaction rates. The second model appears to be inconsistent with: (a) the inhomogeneity of alteration, (b) the requirement for fluid flow during alteration based on isotope tracers, and (c) thermal modelling of this process.

Current data seem to require that the hydrothermal metamorphism of the sheeted dike complex occurs largely during hydrothermal upflow. As fluids heated by an underlying magma chamber migrate upwards they reheat the surrounding rocks and react with them producing the typical greenschist facies assemblage observed within the crust. Temporal changes in the location of upflow can lead to the prograde metamorphism of the entire sheeted dike complex.

Reference

A tale of two peaks: Effects of continental insulation and the partitioning of heat producing elements on the Earth’s heat loss

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Continental lithosphere plays two roles in the Earth’s heat loss: (1) it locally insulates the mantle beneath it and (2) it sequesters radioactive elements from the convecting mantle. These two roles have potentially opposing contributions to Earth’s heat loss, as the former effect increases the average mantle temperature whereas the latter decreases the internal mantle temperature. Understanding this duality becomes important since the internal mantle temperature influences mantle rheology, melt production, convective vigor and other geological processes that impact the dynamics and chemistry of the Earth’s interior. To determine the net consequence of the competing influences on the Earth’s heat loss, we conducted simulations that couple the convection of a mixed internally- and bottom-heated mantle to the conduction through a radioactively enriched continental crust. While holding the total heat production within the system constant, we varied the enrichment and the surface area of the continental crust. In addition, we also varied the bottom-heated Rayleigh number. We found that increasing continental surface area enhances global heat loss for a range of heat production distributions and Rayleigh numbers explored. The effect of the enriched continents and varied heat production distributions was evident in value of the Rayleigh number that maximizes global heat loss. For mid-range ratios of continental to mantle heat production, the dependence of global heat loss on continental surface area showed two peaks. This double peak effect could reflect trade off between mantle heat production depletion and the increased continental insulation. Finally, the insulating effect of continents was shown to alter the temperature signature associated with bottom- vs. internally-heated convection. In addition, that the presence of continental lithosphere could increase average mantle temperature despite the mantle being depleted suggests that continents can significantly influence mantle potential temperature.

Alpha thermochronology of calcite

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High-U minerals such as zircon, apatite and others have proven to be valuable tools in assessing the thermal history of rocks as they pass through the upper crust. However, there are many locations in which high-U minerals are absent; we are investigating the prospect of using the low-U mineral calcite as an alpha thermochronometer.

Step-heating experiments on 17 calcites from 11 different samples and 6 dolomites from 5 samples suggest a closure temperature ($T_c$) of He in carbonates ~70±10 °C for a cooling rate of 10°C/m.y. The bulk $T_c$ in some samples may tend to be slightly higher due to the presence of diffusion domains larger than the sites in which the majority of He resides. The diffusivity of He in calcite is independent of the genesis of the mineral (igneous, metamorphic or sedimentary) or the source of the He (radiogenic, common, or laboratory induced). Compilation of available diffusion data for He in calcite, dolomite and apatite shows a strong similarity with average values of $E = 32.5±3.8$ kcal/mole and log $D_0/a^2$ = 5.3±2.3 log (sec$^{-1}$) for carbonates and of $E = 32.3±3.6$ kcal/mole and log $D_0/a^2$ = 5.4±1.6 log (sec$^{-1}$) for apatite.

Although calcite is a low-U mineral, this shortcoming can be overcome by analyzing large samples. A sample 3.8 mm in diameter with concentrations of U, Th, and Sm of 0.1, 0.01, and 1 ppm, respectively will produce enough $^4$He to allow for an analysis that is 1% blank in ~1 m.y. However, this assumes no common He; our experience shows that this is usually not correct and therefore the problem is not having enough He to overwhelm the common He. Using the criteria of geologic reasonableness, we find very few samples with [U]<100 ppm to be suitable and most samples with [U]>250 ppm to give good results.

Calcite columns have shown to be potentially valuable thermochronometers; preliminary data for the shells of *Inoceramus sp.* suggests a $T_c$ similar to other calcite.

Analysis of secondary calcite from subsurface samples of the Ordovician Ellenberger Group suggest that this unit experienced karstification in the Permian in west Texas but that diagenesis in the Llano uplift area is Tertiary in age.

Early work has concentrated on coarse-grained calcite but it is clear that the diffusion domain size is less than the grain size in all material analyzed so far. We are investigating fine-grained travertine deposits in the Miocene Barstow Fm of southern California, which have [U]>100 ppm in order to determine how fine-grained calcite can be and still give geochronologically reasonable results.
Use of multiple tracers for studying the inter-relationships between climate and recharge conditions of groundwater in a region of France: The past half-millennium

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Temporal variations in the noble gas temperature (NGT), the excess air component (ΔNe) and the deuterium excess (δ) in groundwater from the Fontainebleau Sands Aquifer (France) reveal changes in European climate during the past half millennium. The reconstructions of the NGTs back to 1500 suggest cooler recharge conditions throughout the 16th-19th centuries than present. Moreover, the NGTs recorded periods of weak warming in the 17th-18th and cooling in the 19th that are in conformity with other temperature records for France and Europe. High ΔNe values seem to record periods of high intermittency of recharge events. Slightly lower amounts of ΔNe are observed in groundwater recharged in the 19th despite a slighty higher precipitation rate. In the 17th-18th centuries, with slightly lower precipitation rates, more intermittent rainfall events probably induced larger variability of the water table and consequently larger amounts of air were trapped during recharge. The ΔNe in groundwater from this aquifer seems to be more linked to the oscillations of the water table produced by the temporal variability of the rain events than to the total amount of precipitation.

δ varies in parallel with NGT, and indicate a maximum in the period between 1700-1750. Inter-annual variations in the seasonality of precipitation and its intensity, combined with changes of the soil coverage in the recharge area, seems to be responsible for the variation observed in the δ in groundwater.

Our reconstructed parameters (NGT, ΔNe and δ) show noticeable relationships with available climate records. Such comprehensive studies of the link between climate and recharge conditions enhance our understanding of the effects of climate change and climate variability on groundwater resources sustainability.

Timescales of melt extraction from a heterogeneous mantle beneath the Central Indian Ridge at 19.2°S

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We propose to document the timescale of the magmatic processes occurring beneath the slow-spreading Central Indian Ridge (CIR, 19.2°S) through the study of the chemical variations recorded by the lavas erupted on-axis. The samples were collected along a 40 km-long profile made transverse to the ridge and running from the axial trough up to the Branshi-Matuyama isochrone (~800 Ky, GIMNAUT cruise). The lavas are greatly homogeneous in term of Mg# (67 ± 2) but range from N-MORBs to E-MORBs in terms of trace element concentrations (0.6<La/SmN< 3.4). Their Sr-Nd isotope ratios start from the center of the isotopic field of the CIR lavas and overlap its enriched end. Trace element ratios plotted along the profile describe saw-tooth patterns characterized by enriched spikes regularly and symmetrically distributed on both sides of the ridge axis. Consequently, the lava compositions are an indicator of magmatic processes that have fluctuated periodically through time. Based on the position of the enriched lavas along the profile, the timescale of such magmatic processes has been estimated to 230 Ky. Fractional crystallization can be ruled out to explain the observed chemical variations. Thus, they reflect the variations through time of the primary melt composition, partly governed by mantle source heterogeneity according to the Sr-Nd isotopes. To reproduce the observed periodicity, we propose an interconnection between the source heterogeneity and the variation of the melting rates: The most enriched lavas are the products of very low melting of a fertile enriched mantle component. This component may have been specifically introduced in the melting column each ~230 Ky or the melt extraction modalities may have changed with the same timescale. Apart from these enriched events, mixing between enriched and depleted primary melts occurs normally due to magma genesis/aggregation and the enriched signatures are diluted into a N-MORB-type composition.
New metal-silicate partition coefficients and constraints on core composition and oxygen fugacity during Earth accretion

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High-pressure metal-silicate partitioning experiments demonstrate that the mantle contents of some moderately siderophile elements (Ni, Co, P, W, Mo, V) are consistent with core-mantle equilibration at high pressures and high temperatures (e.g. [1-4]). This conclusion is one of the bases for the magma ocean theory, in which molten core materials segregate through a largely molten silicate mantle. To constrain further such theory, one should ask whether these conditions of core formation are consistent with the mantle contents of other elements.

We present the results of new partitioning experiments between molten metal and silicate melt for a series of elements regarded as refractory lithophile and moderately siderophile and volatile. These include Si, Ti, Ni, Cr, Mn, Ga, Nb, Ta, Cu and Zn. Our new data obtained at 3.6 and 7.7 GPa and between 1850 and 2200 ºC are combined with literature data to parameterize the individual effects of oxygen fugacity, temperature, pressure and composition on partitioning.

From the derived parameterization, we predict that the silicate Earth abundances of the elements mentioned above and V, Co, P and W are best explained if core formation took place under increasing conditions of oxygen fugacity, with final conditions near IW-2. From our estimate of the most likely oxygen fugacity path during accretion, we predict that the core contains about 10 times more Cu than the Silicate Earth as well as a smaller but significant portion of the Earth’s Zn, Ga, Nb, Ta, Mn and Cr. Furthermore, our predictions show that the core should contain some Si and at least a small amount of Ti. Finally, our results suggest that in addition to volatilization, core formation would contribute to the depletion of Ga, Cr, Mn and Zn in the silicate Earth. At present, the uncertainties of our parameterization are too large to predict whether the Nb/Ta ratio of the core is superchondritic. Additional experiments are underway to constrain further our predictions.

References

Biogenic mineral dissolution and transformation of arsenopyrite

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Arsenopyrite (AsSFe) is one of the most important natural sources of Arsenic on Earth. In oxic environments, such as highly weathered soils or surficial seawater, microorganisms and higher plants produce biogenic ligands such as siderophores to mobilize Fe that otherwise would be unavailable. We conducted batch-dissolution experiments for arsenopyrite in the presence of desferrioxamine (DFO-B), a common siderophile ligand, at pH 5. Arsenopyrite specimens (0.149-0.1mm) from mines from Panasqueira, Portugal, were used for this study. Detected concentrations of Fe, As, and Pb were 0.3, 0.26, and 0.13 µM (CV < 5%), or ca. 0.06, 0.13, and 0.01 µM (CV < 2%), in the presence of DFO-B or water only, respectively (t < 100 h). The effectiveness of DFO-B for releasing Pb was found to be almost three times higher than that for releasing Fe. These results cannot be accounted for by size-to-charge considerations prevailing in metal complexation by DFO-B only. Elemental sample enrichment as evidenced by EDX analysis support the idea the Fe-S subunit bond energy is limiting for Fe release, while likely, the mechanism(s) of dissolution for Pb is independent and occurs concurrently to than that for Fe and As. Coupling between redox-induced elemental transformations and the formation of small-particle size secondary minerals will be discussed.
Sb(V) retention mechanisms in alkaline environments

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The increased application of antimony has allowed it to find its way to a number of environments such as soils and groundwaters but also to wastes and residues of industrial processes like smelting or waste incineration. The latter materials have a much higher pore water pH (>10) than average soils and sediments, often a high salinity and thus a quite distinct geochemistry which has been thoroughly studied because these residues contain relatively high amounts of toxic heavy metals. Sb has, however, received little attention due to its relatively low total content but its high mobility calls for a better understanding of the geochemistry in alkaline matrices. In most instances the most important oxidation state is Sb(V), occurring as the oxianion antimonate (Sb(OH)₆⁻) in aqueous media. It has been established that in soils of intermediate porewater pH, Sb(OH)₆⁻ is closely associated with iron (hydr)oxides. At high pH, however, the retention mechanisms are at present unknown.

To develop efficient geochemical models to predict Sb(V) leaching in alkaline environments, the precipitation equilibria of Sb(OH)₆⁻ with the most abundant multivalent cation, Ca²⁺, was studied as well as the interaction of Sb(OH)₆⁻ with commonly occurring minerals. Simultaneously, alkaline residues such as municipal solid waste incinerator bottom ash and a Sb⁵⁺-spiked cement sample were characterised with respect to leaching. It was found that regardless of pH, no other calcium antimonates other than Ca(Sb(OH)₆)₂ precipitate but modelling with the geochemical speciation code PHREEQC showed that in alkaline environments, saturation of Ca(Sb(OH)₆)₂ is seldom attained. However, Sb(OH)₆⁻ was found to associate with portlandite (Ca(OH)₂), ettringite (Ca₆Al₂(OH)₁₂(SO₄)₃·26H₂O), mono-sulphate (Ca₄Al₂(OH)₁₀·2SO₄·13H₂O) and hydrogarnet (Ca₃Al₂(H₂O)₆). It was suspected that in alkaline environments, Sb(OH)₆⁻ forms solid solutions replacing sulphate in the structure of ettringite and monosulphate. To demonstrate this, Sb⁵⁺-analogues of ettringite and monosulphate were synthesized and characterised using XRD, SEM-EDX and TGA. Solubility experiments and calculations in PHREEQC allowed the determination of the solubility product (Kₚₒ) of these analogues. It was shown that assuming ideal solid solution as an additional mechanism next to precipitation of Ca(Sb(OH)₆)₂, greatly improved modelling of Sb leaching behaviour in alkaline environments. However, the leaching potential of Sb(OH)₆⁻ was now underestimated which calls for quantification of non-ideality to allow more precise modelling.

Geochronology, geochemistry and isotopes of orthogneisses from the Greek Rhodope

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The Hellenides formed from Cretaceous to Mid-Tertiary times as a result of plate convergence and collision of Africa and Europe. The easternmost part of the Hellenides is represented by the Rhodope Massif which occupies the major part of NE Greece and S Bulgaria. Two groups of orthogneiss protolith-ages have been established in the central Rhodope Massif: A Permo-Carboniferous group (275-290 Ma), corresponding to the structurally upper part of the massif, the Thracia Terrane and a Late Jurassic-Early Cretaceous group (134-164 Ma), corresponding to the structurally upper part, the Rhodope Terrane (Turpaud & Reischmann 2003, Turpaud 2006). In this study, felsic orthogneisses from the northeastern part of the Greek Rhodope were geochemically and geochronologically investigated, to find out, if the two terrane-model is applicable here. Zircons from 15 orthogneisses from the Eastern Rhodope were dated by LA-SF-ICPMS (U-Pb) and U-Th-Pb SHRIMP, respectively. Most of the analysed samples are around 300 Ma in age and contain many inherited cores whereas zircons from one bt-gneiss gave an age of 145 ± 5 Ma. The chemistry of all samples is very similar to orthogneisses from the Thracia Terrane in the central part of the Rhodope. The protolith of the orthogneisses can be chemically classified as subalkaline granite of a volcanic-arc tectonic setting. The isotopic ratios of ⁸⁷Sr/⁸⁶Sr range between 0.7031 and 0.7167; εNd values are negative and vary mostly between –3.8 to –7.9. REE patterns show enrichment in LREE and negative Eu anomalies. We conclude that the Thracia Terrane can also be identified in the northeastern part of the Greek Rhodope whereas the identification of the Rhodope Terrane is still under question.
Residence times of silicic magmas associated with calderas

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In the last two decades there has been a large wealth of geochronological information produced at caldera related volcanic systems. This contribution explores what systematics can be extracted from it and how the magma residence times may be related to other parameters such as cooling times of igneous bodies, or process durations determined from chemical zoning in crystals and diffusion models. Magma residence times are obtained from the difference between the eruption age and the age obtained by radioactive clocks and phases that may be a closed system at high magmatic temperatures (e.g., U-Pb system in zircon).

Large ranges of residence times between different systems are found. The shortest are those of Oruanui and Rototoi magmas (Taupo Volcanic Zone) with 4 ky and 9 ky of residence, respectively, followed by the Dry Creek (7 ky) and Lava Creek (19 ky) Yellowstone magmas. There is not a good correlation between magma volume and residence time, although most eruptions < 10 km³ have residence times < 100 ky, and those > 100 km³ have residence times of up to ca. 400 ky (Fish Canyon Tuff). The residence times of some small (< 10 km³) pre-and post-caldera magmas reflect that they are batches extracted from the same caldera-forming reservoir because they fall on the same time evolution line (e.g., Long Valley, Taupo). In contrast, the residence times of other small volume magmas may be the result of crystals being recycled from previous cycles of caldera-forming magmas (Yellowstone), or from plutonic rocks of the same caldera cycle with or without erupted equivalent on the surface (Crater Lake, Taupo, Long Valley) or even from not completely solidified caldera-forming magma reservoir (Taupo). These interpretations are in agreement with cooling rates and solidification times obtained from simple thermal models of magma reservoirs. Magma production rates were calculated from the ratio of erupted volume and residence time, and they vary between < 0.001 km³y⁻¹ for small deposits (< 10 km³) to ca. 0.1 km³y⁻¹ for the Oruanui eruption (530 km³). Estimates for most eruptions > 500 km³ are within 2 ± 2 * 10⁻³ km³y⁻¹, values that are comparable to global eruptive fluxes from basalts (e.g., Hawaii). Most residence times are of several thousand years or more, which is much longer than the durations of processes obtained from the reequilibration of chemical gradients in minerals, which are more on the order a few hundred years. This difference may be explained by considering that the residence times could record the entire history of the system whereas some of the diffusion data only the last event that leads to the eruption.

Petrology and phase equilibria of Ti-andradite and titanite in alkaline ultramafic rocks of the Tamazeght complex, Morocco

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The elliptical (5 × 15 km) Tamazeght (syn. Tamazert) alkaline igneous complex (High Atlas Mountains, Morocco) was emplaced during the middle Eocene and intrudes Jurassic to Cretaceous limestone. It comprises numerous intrusive phases that document a progression from ultramafic to felsic magmatism. A wide range of lithologies are present, including ultramafic rocks, shonkinites, gabbroic to monzonitic phases, and feldspathoidal syenites, which predominate. Moreover, carbonatites and lamprophyres occur as diatremes and dykes.

This study focuses on the petrology, paragenesis and phase equilibria of the ultramafic lithologies (pyroxenite and glimmerite). Pyroxenite is dominated by cumulus clinopyroxene (aluminous diopside) and garnet, with the latter locally rimmed by mica (phlogopite) and/or titanite. Olivine, nepheline, apatite and interstitial calcite are minor phases. In glimmerite, large poikilitic mica predominates (≤ 65 %), along with minor cumulus pyroxene-I (Al-rich), garnet, perovskite (rimmed by titanite), Fe-sulphides and apatite. Occellular textures, consisting of clinopyroxene-II (Al-poor), calcite and mica, occur throughout. Garnet occurring in the ultramafic rocks have TiO₂ contents of between 5 and 11 wt. %. It is therefore Ti-andradite. Where present in some of the more evolved units (e.g., syenites) garnet occurs only as an accessory phase and TiO₂ concentrations are uniformly lower (around 4 wt. %).

Here we present petrological, electron probe and LA-ICP-MS data, and will focus on the paragenesis, phase equilibria and stability relations between the phases present in order to track the evolution of intrinsic parameters (such as T, a(Al₂SiO₅), f(O₂)) during the formation of these rocks.
Femtosecond laser ablation ICP-MS of fluid inclusions: Validation and prospects

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Experimental Protocol

LA-ICP-MS is now a commonly used analytical technique in the study of fluid inclusions. Unlike typical nanosecond UV laser ablation systems (Ar:F or Nd:YAG), the new femtosecond ablation systems can provide athermic ablation. One advantage of this is a lower risk of fluid loss due to thermal shock during opening of the inclusion. In our experiments, we used a femtosecond Ti:Sapphire 800 nm laser ablation system, following the analytical protocol outlined by Heinrich et al. (2003).

The fluid inclusions studied are hosted in quartz from the Trimouns talc-chlorite deposit (Ariège, France). Before ablating the inclusions, we performed petrographic and microthermometric studies, and calculated Na concentrations ablating the inclusions. Femtosecond laser enabled both precise and reproducible ablation of fluid inclusions and NIST glasses, following the analytical protocol outlined by Heinrich et al. (2003).

Results and discussion

We could measure the concentration of a wide range of elements within the fluid, including major cations and anions (e.g., Na, Ca, K, Cl), minor elements such as Li, Mg, and REE (La, Nd). Reproducibility of NIST 610 data were 5% for every element studied, except for K (20%) and Cl (50%). We were able to measure a very large range of concentrations within a single analysis: from 200,000 ppm for major elements like Ca to about 5 ppm for the Rare-Earth Elements (La).

This study validates the use of a femtosecond laser ablation system used for LA-ICP-MS analysis of fluid inclusions. Femtosecond laser enabled both precise and reproducible ablation of fluid inclusions and NIST glasses. However, using a NIST glass as an external standard leads to important errors on some major elements in the fluid (about 50% on Cl), which are probably due to 1) very low concentration of some of the elements in NIST 610 compared to the sample, and 2) interferences or low output of the ICP-MS.

References


Titan’s current and future exploration

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Anhydrite as a tracer of sub-seafloor hydrothermal circulation and vent deposit formation

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The mineral assemblage and geochemistry of seafloor hydrothermal vent deposits are dictated by temperature, pH and redox conditions, and by concentrations of aqueous species in circulating fluids, during deposition. These variables are, in turn, influenced by near-seafloor fluid circulation and mixing of fluids of distinct origin (e.g., high-temperature seawater-derived hydrothermal fluid, locally entrained seawater, magmatically-derived volatile-rich fluid). Anhydrite (CaSO₄) is a useful tracer of these processes and conditions, being precipitated during mixing of high-temperature hydrothermal fluid with seawater.

Abundant anhydrite has been recovered from the PACMANUS hydrothermal system, eastern Manus Basin, both at the seafloor [Tivey et al. 2006] and from depth subsurface (ODP Leg 193 [Binns et al., 2007]). This affords the first opportunity to directly explore subsurface processes associated with hydrothermal activity in a back-arc basin.

In situ microbeam techniques (laser ablation-ICP-MS) are used to explore fine-scale variability in isotopic (Sr, S) and elemental (Mg, Sr, Ba, REE, Y, etc.) signatures of anhydrite, from various depths and locations at PACMANUS. First analyses indicate significant differences in Sr-isotope ($^{87}$Sr/$^{86}$Sr > 1000 ppm), S-isotope ($^{34}$S > 5 %) and REE content of anhydrite are observed between and within sites at PACMANUS over scales ranging from m’s to mm’s. Variable and light $^{34}$S (+16.6 to 19.0 %) in anhydrite from depths ~ 300 mbsf indicate possible contribution from an isotopically-light magmatic source in the high-temperature fluid. Large grain-scale variability in $^{87}$Sr/$^{86}$Sr (0.7043 to 7.089) indicates significant variation in the extent of mixing between the hydrothermal fluid and seawater. REE patterns range from light-REE enriched to light-REE depleted, both with positive and negative Eu-anomalies, to flat, non-fractionated REE. While the majority of data is still to be collected, the patterns recorded thus far suggest fractionation of REE during anhydrite precipitation or differences in fluid compositions. Isotopic data indicate three end-member mixing, including a possibly magmatic component. Comprehensive coupled elemental and isotopic microanalyses will enable us infer the effects of fluid source versus fractionation process during anhydrite precipitation.

References


Geochemical and isotopic variation of Mt. Etna volcanic rocks: The role of a heterogeneously metasomatized source region of magmas

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New clues for investigating on some features not yet clarified at Mt. Etna (Italy), such as the genesis of magmas and the intrinsic characteristics of the source region, come from an extensive sampling of historic (pre-1971) and recent (1971-2007) volcanic rocks, carried out prevalently on the southern flank of the volcano. In spite of the relatively similar major element compositions, recent volcanic rocks are clearly distinct in terms of incompatible trace elements and Sr – Nd – Pb isotope ratios from the historic ones. Post-1971 volcanics, and especially those later than 2001 eruption, show enrichment trends for K, Rb and $^{87}$Sr/$^{86}$Sr and a progressive decrease especially for Th contents and Pb isotope ratios. The role of crustal contamination at shallow levels in generating such a variation has been ruled out on the basis of trace elements and of the restricted $\delta^{18}$O variability within the entire examined sequence. In alternative, we suggest a geochemical and isotopic evolution of the source region of magmas highly consistent with the presence of an increasingly amount of hydrous phases, prevalently phlogopite, involved in the partial melting process. A reason for the short-term evolution of magmas may then be found by considering a partial melting process which occurs in mantle domains affected by variable and increased degree of metasomatism with time, revealing the heterogeneous nature of the source at the melting scale.

Trace element geochemistry provides also evidence that the generation of recent magmas would derive from a higher degree of partial melting in respect to the previously emitted products. This feature may be connected with the higher amounts of metasomatic influxes that have stabilized fluids into the mantle, enhancing in turn the extent of partial melting. In such an articulated context, a limited mantle upwelling, related to the intrinsic convective processes (plume-like) and/or to the lithospheric stretching due to extensional deep faults, could rather easily trigger partial melting processes of these metasomatized peridotites, generating melts different in composition depending on heterogeneities. Furthermore, since the increased extent of partial melting will result in an increased melt production at the source, such a geochemical evolution of the mantle with time is consistent with the development of volcanic phenomena at the surface. The occurrence of such a heterogeneously metasomatized mantle would therefore explain the increased frequency of events and emission rates of volatile-rich magmas observed just following the 1971 and especially during the 2001-2007 eruptive period.
**Pb isotopes and glacial/interglacial weathering intensity**

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To gauge the impact of weathering on Quaternary CO₂ cycles, we need better constraints on the flux of cations from the continents. For the substantial portion of the continents that have been glaciated in the Quaternary, early stage weathering of U+Th rich accessory phases freshly exposed during glacial periods should preferentially release radiogenic Pb. Thus the seawater Pb isotopic composition might act as a regional proxy for the riverine alkalinity flux to the oceans. Here we discuss the development of this proxy at high resolution and its application to sediments from Feni Drift (ODP Site 980) spanning the last 45 ka.

Pb isotope data from ferromanganese crusts (1) have been used to postulate greater weathering intensity during interglacial than glacial periods, but low temporal resolution precluded investigation of the detailed structure of the record at glacial inception and termination. To obtain higher resolution, we applied a tested method of Pb extraction from authigenic Fe oxide phases in marine sediments (2). The results contrast with existing crust data in that the Pb isotope variation is much larger (²⁰⁸Pb/²⁰⁶Pb ranges from 18.90 to 21.09 cf with 18.96 to 19.22 in crusts) with the most radiogenic Pb occurring at the Last Glacial Maximum. The Pb signal shows strong correlation to other proxy records from the same and nearby sites. A pronounced ~1.2 to 2 ka periodicity, particularly during MIS 3, most likely reflects the same and nearby sites. A pronounced ~1.2 to 2 ka signal shows strong correlation to other proxy records from North Atlantic land masses. This preliminary investigation raises several issues pertaining to the direct interpretation of leached Fe oxides as archives of seawater Pb isotopic composition. Although the radiogenic signal is consistent with early stage weathering, the extreme variation in Pb isotope ratios may reflect a predominance of Fe oxide formation in terrestrial rather than marine environments, thus highlighting the importance of understanding continent-ocean Pb transport pathways and their implications for environments of Fe oxide formation prior to marine deposition.

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**Mechanisms of Fe isotope fractionation during dissimilatory Fe(III) reduction by *S. putrefaciens* and *G. sulfurreducens***

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Microbial dissimilatory iron reduction (DIR) is widespread in anaerobic sediments and is a key producer of aqueous Fe(II) in suboxic sediments that contain reactive ferric oxides. Here we compare Fe isotope fractionations produced by similar cultures of *G. sulfurreducens* and *S. putrefaciens* during reduction of hematite and goethite. Both species produce aqueous Fe(II) that is depleted in the heavy Fe isotopes, as expressed by a decrease in ⁵⁶Fe/⁵⁴Fe ratios or δ⁵⁶Fe values. The low δ⁵⁶Fe values for aqueous Fe(II) produced by DIR reflect isotopic exchange among three Fe inventories: aqueous Fe(II) (Fe(II)aq), sorbed Fe(II) (Fe(II)sorb), and a reactive Fe(III) component on the ferric oxide surface (Fe(III)rec). The fractionation in ⁵⁶Fe/⁵⁴Fe ratios between Fe(II)aq and Fe(III)rec was 2.95 ‰, and this remained constant over the timescales of the experiments (280 d). The Fe(II)aq-Fe(III)rec fractionation was independent of the ferric Fe substrate (hematite or goethite) and bacterial species, indicating a common mechanism for Fe isotope fractionation during DIR. Moreover, the Fe(II)aq-Fe(III)rec fractionation in ⁵⁶Fe/⁵⁴Fe ratios during DIR is identical within error of the equilibrium Fe(II)aq-ferric oxide fractionation in abiologic systems at room temperatures. This suggests that the role of bacteria in producing Fe isotope fractionations during DIR lies in catalyzing coupled atom and electron exchange between Fe(II)aq and Fe(III)rec so that equilibrium Fe isotope partitioning occurs.

Although Fe isotope fractionation between Fe(II)aq and Fe(III)rec remained constant, the absolute δ⁵⁶Fe values for Fe(II)aq varied as a function of the relative proportions of Fe(II)aq, Fe(II)sorb, and Fe(III)rec during reduction. In the case of hematite reduction, the effect of Fe(II)aq on the δ⁵⁶Fe values for Fe(II)aq was insignificant, <0.05 ‰. Sorption of Fe(II) produced small, but significant effects during reduction of goethite, reflecting the higher proportion of Fe(II)sorb and larger measured Fe(II)aq-Fe(II)sorb fractionation. The isotopic effects of sorption on the δ⁵⁶Fe values for Fe(II)aq were largest during the initial stages of reduction when Fe(II)sorb was the major ferrous Fe species during goethite reduction, on the order of 0.3 to 0.4 ‰, but decreased to <0.2 ‰ with continued reduction; our results show that the effect of sorption is much less than has been proposed in other studies. These experiments provide a breakthrough in our understanding of the mechanisms that produce Fe isotope fractionation during DIR, and form the basis for interpretation of Fe isotope variations in modern and ancient natural systems where DIR may have driven Fe cycling.
Fe- and Mg-cordierite: A calorimetric and thermodynamic study

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Cordierite is a key phase in many metamorphic rocks and it also has important technical applications in industry. Thus, knowledge of its thermodynamic properties is necessary for a variety of investigations. In order to enable more quantitative calculations, heat capacity measurements between 5 and 300 K were carried out on milligram-sized synthetic samples of anhydrous low Fe-cordierite (Fe-Cd), as well as on anhydrous and hydrous low Mg-cordierite (Mg-Cd), using heat-pulse calorimetry (HPC).

From our HPC results, the standard entropy values at 298.15 K for anhydrous Fe-Cd, anhydrous Mg-Cd and hydrous Mg-Cd were calculated as 460.5 ± 0.5, 406.1 ± 0.4 and 450.9 ± 0.5 J/(mol·K), respectively. Heat capacity (Cp) polynomials for anhydrous Fe- and Mg-cordierite at T > 250 K are:

$$C_{P,Fe-Cd} = 911.1 \pm 9.7 \cdot T - 5829.2 \pm 363 \cdot T^{0.5} - 13.9424 \cdot 10^6 \cdot T^{-2} + 1470.4 \pm 454.84 \cdot 10^6 \cdot T^{-3},$$

$$C_{P,Mg-Cd} = 882.0 \pm 4.9 \cdot T - 5155.8 \pm 167 \cdot T^{0.5} - 20.7584 \cdot 10^6 \cdot T^{-2} + 2736.0 \pm 112.73 \cdot 10^6 \cdot T^{-3},$$
as derived from the HPC data and published DSC data.

Lattice and non-lattice contributions to the Cp values were modeled for Fe-Cd. The values $S_{vib}^{0} = 447.7$ J/(mol·K) and $S_{el}^{0} = 13.6$ J/(mol·K) were obtained for the vibrational and electronic contributions to the standard third law entropy.

Using phase equilibrium data for the reaction $3Fe-Cd\cdot H_2O = 2almandine + 4sillimanite + 5quartz + 3H_2O$ (Mukhopadhyay & Holdaway 1994), $\Delta H^{\circ} = -8448.26$ kJ/mol was obtained for anhydrous Fe-Cd and the values $\Delta H^{\circ} = -8750.23$ kJ/mol and $S^{0} = 520.6$ J/(mol·K) were derived for hydrous Fe-Cd.

Phase relations in the FeO-Al₂O₃-SiO₂(+/-H₂O) system and isohydrons for H₂O in Fe-Cd were calculated and respective phase diagrams constructed.

References


Gas-particle partitioning, atmospheric deposition and long range transport of persistent organic pollutants over the oceans

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Gas-particle partitioning of persistent organic pollutants plays an important role on the atmospheric deposition and long range transport potential of persistent organic pollutants. Aerosol organic and elemental carbon composition has been recognized as important bulk composition parameters controlling the distribution of POPs between gas and aerosol phases. However, sea salt aerosols and desert dust could play a role over some oceanic regions. Furthermore, atmospheric deposition of POPs will also be affected depending on this partitioning processes. On the other hand, trophic status of the ocean does also play a role as controlling factor of gaseous exchange and to lesser extent of dry deposition. In this work, gas-particle partitioning, deposition and long range transport are assessed in terms of aerosol and surface receiving geochemical processes. Results are shown for the tropical Atlantic, the Mediterranean sea and polar (Antarctic) waters.
Mo isotope variations in meromictic Lake Cadagno

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Mo isotope systematics can be used to infer the extent of ocean oxygenation in the past. Isotope fractionation during adsorption to Mn-oxides exerts an important influence on the isotopic composition of the oceanic Mo reservoir. Measurements indicate that this process was less important between 1.7 - 1.4 Ga compared to today (Arnold et al. 2004) consistent with other lines of evidence (Canfield 1998). However, quantitative interpretation of Mo isotope variations in ancient sediments requires an understanding of how Mo isotopes fractionate in sulfidic environments in which Mo removal from the water column is not quantitative.

The alpine Lake Cadagno in Switzerland offers an opportunity to examine Mo isotope fractionation in a sulfidic water column. Mo exists as the soluble molybdate anion in the oxic surface zone. Mo concentration decreases by 30-50\% below the chemocline, where Mo speciation presumably is dominated by particle-reactive oxythiomolybdates. Isotopically, in the oxic part of the lake we find $\delta^{97/95}$Mo = 0.5-0.6‰, matching the riverine inflow. In contrast, the sulfidic deeper waters are heavier: $\delta^{97/95}$Mo = 1.1-1.2‰.

The mechanism by which this isotope shift occurs is at present uncertain. It is possible that heavy Mo enters the deep waters from dolomitic subaquatic springs. Alternatively, isotope fractionation may occur at or below the chemocline. The data could be explained by preferential adsorption of light Mo onto ferromanganese particles below the chemocline. In cases of incomplete Mo removal in euxinic waters the isotope effect is unknown and needs to be studied.

References

Nd isotopes in Bering Strait and Chukchi Sea water

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The Nd isotopic composition, $\varepsilon_{Nd(0)}$, was determined for the first time in filtered (0.22 μm) water samples collected from the Bering Strait and the Chukchi Sea in the Arctic Ocean. Vertical profiles and surface waters were collected in the east and west passages of Bering Strait, the Chukchi Sea, and the Chukchi Abyssal Plain.

In Bering Strait $\varepsilon_{Nd(0)}$ vary between -4.02 and -5.94, with slightly more radiogenic values at the surface. Temperature and salinity profiles show a well mixed water column with a surface layer of 5-10 m depth, which is warmer and less saline. The isotopic composition is primarily influenced by inflow from the north Pacific Ocean with values of -4 to -5. The slightly lower surface values can be explained by input from local sources to the Bering Sea, e.g. Yukon River water.

Two surface water samples collected in the Chukchi Sea have more negative $\varepsilon_{Nd(0)}$ compared to Bering Strait water, indicating a different source than Pacific Ocean water, possible river water from Russian rivers.

In the Chukchi Abyssal Plain $\varepsilon_{Nd(0)}$ decreases with depth from -6.52 at the surface to -11.47 close to the bottom. Salinity and temperature profiles show a well-defined stratification, and the variation with depth is clearly related to the origin of these different water masses. The surface value of -6.52 demonstrate the significance of Chukchi Sea shelf waters, while less radiogenic values at depth are related to warm Atlantic derived water and Canada Basin bottom water.

Nd concentrations (C$_{Nd}$) determined with isotope dilution vary between 24.6 and 39.5 pM in the Chukchi Abyssal plain and Bering Strait respectively. In this filtered fraction no significant variation in C$_{Nd}$ can be observed with depth in Bering Strait or the Chukchi Abyssal Plain.

$\varepsilon_{Nd(0)}$ values in samples from Bering Strait and the Chukchi shelf are more negative than reported values from the North Pacific surface water. This indicates that the isotopic signal changes in water flowing from the Pacific Ocean into the Arctic. This shift may be caused by interaction with suspended particulate matter on the shallow shelf surrounding Bering Strait and in the Chukchi Sea. Support for this theory can be observed in measured C$_{Nd}$ in this study, which show higher concentrations on the shelf area compared to North Pacific surface water.

These new data are setting important constraints for inflow and mixing of Pacific Ocean water with the general circulation of Arctic Ocean water.
Soft x-ray scanning transmission spectromicroscopy of cementitious materials

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Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of hazardous and radioactive wastes in underground repositories. Cement is used to condition the waste materials and to construct the engineered barrier systems. Therefore, a mechanistic understanding of the processes governing the binding of heavy metals in cement systems is essential for long-term predictions of the environmental impact of cement-stabilized waste forms. From a chemical standpoint, cement is a very heterogenous material with discrete particles in the nano to micrometer size range, which makes it an ideal system to be investigated with scanning transmission x-ray microscopy (STXM).

In this study the soft x-ray STXM end station at the Advanced Light Source-Molecular Environmental Science (ALS-MES) Beamline 11.0.2 has been utilized to investigate metal precipitates formed in Ni- and Co-doped cement pastes. The ALS-MES STXM collects both images and near-edge x-ray absorption fine structure (NEXAFS) spectra with a spatial resolution of 30 nm. NEXAFS spectra of the Ni and Co 2p edge were utilized to collect spectroscopic information on the Ni- and Co-precipitates formed in the cement matrix. This study complements previous micro-spectroscopic investigations on the speciation of Ni(II) and Co(II) in cement pastes (Vespa et al., 2006, 2007). For Ni(II)-doped cement pastes, the formation of a Ni(II)-Al layered double hydroxide phase was observed by Vespa et al. (2006). In Co(II)-doped cement pastes, however, partial oxidation of the initially added phase was observed by Vespa et al. (2006). In Co(II)-Al doped cement pastes, the formation of a Ni(II)-Al layered double hydroxide phase was observed by Vespa et al. (2006). In Co(II)-doped cement pastes, however, partial oxidation of the initially added phase was observed by Vespa et al. (2006).

References

Xingcheng abiogenic alkane gas field in Songliao Basin, China

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Xingcheng gas field is located in the Daqing and Anda city of Heilongjiang province and geologically in the volcanic uplift zone in the centre of Xujiaweizi rift, Songliao basin. Six exploration wells have been drilled in this gas field. The proved geologic reserve of natural gas in Lower Cretaceous volcanic and conglomerate rocks is 459.84×10⁶m³ within an area of 41.70 km². Xuxi, Xuxi and Xuzhong faults developed in a long period in Xujiaweizi rift. Xuxi and Xuzhong faults extend 58 and 96 kilometers, respectively, and the faults throw is up to 1800m. Faults cut off the basement rock, reach the mantle magma chamber, lead to violate volcanic movements during multiple stages. The main stage of volcanic eruption is Yingsheng Formation of Lower Cretaceous.

The natural gas geochemistry characteristics show that: CH₄ accounts for more than 93%, and the hydrocarbon gases above C₂ account for ~3%. The δ¹³C values which range from -25.9‰ to -28.9‰ are the heaviest among the alkane gases, and the trend of δ¹³C values gets lighter with increasing carbon numbers (δ¹³C₁>δ¹³C₂>δ¹³C₃>δ¹³C₄). So the gases of Xingcheng gas field is abiogenic (Dai et al., 2005). The δ¹³C values of volcanic-magmatic and mantle genetic carbon dioxide are -6±2‰ (Dai et al., 2005). The δ¹³C values of Xingcheng gas field are within the range of -4.8‰~8.2‰, so the CO₂ is of magma-mantle genetic characteristic; The values of ³He/⁴He in the upper mantle are between 1.1×10⁻⁵ and 1.4×10⁻⁵, and the values of ⁴He/³He in radiogenic strata are from 10⁻⁵ to 10⁻⁴ (Wang, 1989). The value of ³He/⁴He in the gas field is 10⁻⁶, which may be the results of ³He from the mantle. It also proves that some of the alkane gases originate from the mantle; Many experiments show that catarinite can catalyze the reaction between CO₂ and H₂ to form CH₄ in hydrothermal fluid (Horita J et al., 1999), and chromites can catalyze the reaction to form CH₄, C₂H₆ and C₃H₈ (Foustoukos D I et al., 2004). In Xingcheng gas field, CO₂ exists widely and H₂ is discovered in some wells. The active stage of volcano and hydrothermal fluid movements are multiple. At present, the average temperature gradient in Songliao basin is 3.7°C/100m and the maximum reaches 6.1°C/100m. All the conditions are favorable for the reaction of Fischer-Tropsch synthesis to form abiogenic alkane gas.

References
Hf, Sr, Nd and Pb isotopes in primitive Tongan lavas: Constraining mobility in slab fluids

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This study presents new Hf, Sr, Nd and Pb isotope data for a suite of glassy submarine basalts and basaltic andesites dredged from the Fonualei Rift zone and the Tongan arc north of Tongatapu.

The Tongan arc is a prime example of an intra-oceanic arc with a geochemical signature dominated by prior depletion of the mantle wedge and a slab-fluid input. Depletion of the mantle wedge is thought to increase northwards along-arc, and probably results from melt extraction during the opening of the Lau backarc basin. In addition, trace element and isotopic compositions indicate that the northern extremity of the arc contains a contribution from volcanioclastic material derived from the subducted Louisville Ridge Seamount Chain, and possibly an input from ‘Samoan-type’ mantle.

Southern submarine volcanoes (south of Fonualei) have trace element characteristics (e.g. extremely high Ba/Th ratios) indicative of slab fluid being the major subduction flux along this part of the arc. Lower 143Nd/144Nd, higher 206Pb/204Pb and elevated Ta/Nd in samples north of Fonualei are consistent with proposals by previous authors that these melts have a signature. The volcaniclastic input (or plume influence) of high field strength elements (HFSE) in subduction zone fluids.

Is Lichades the northern end of the Hellenic Volcanic Arc? Clues from helium isotopic composition in gases

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The Hellenic Volcanic Arc (HVA) straddles across the Southern Aegean Sea. Its activity started in the late Pliocene and it comprises many volcanic systems most of which are considered active at present. The westernmost active volcanic system is considered to be Methana, a peninsula in the Saronikos Gulf and remnants of Plio-Pleistocene volcanic activity are found at Sousaki, some tens of km further north, close to the isthmus of Corinth.

About 100 km further north, in the northern Evoikos Gulf, sparse trachy-andesitic volcanic rocks of Quaternary age crop out. The most important of these form the islet of Lichades. Although this volcanic system is generally considered to be due to back-arc extension, recently Papoulia et al. (2006), on the basis of seismological studies, consider it to be the most northern end of the HVA.

The area is also affected by distensive tectonic that formed a graben between the island of Evia and mainland Greece, limited on both sides by a series of important direct fault systems. Along these tectonic structures many thermal springs (water temperatures 40 - 90 °C) are found. Most of these are characterised by the presence of a CO2-rich gas phase whose helium isotopic composition ranges from 0.06 to 1 R/Ra. The highest mantle contribution (4-12 %) is attributed to the progressive contamination of the mantle source with crustal material (Parello et al., 2001). The similar trend, observed in the volcanic systems of southern and central Italy (from 7.3 to 0.5 R/Ra in the north direction), is attributed to the progressive contamination of the mantle source with crustal material (Parello et al., 2000). The similar geologic history and the geographic closeness of the Greek region could suggest a similar process governing the trend of helium isotopic composition in the HVA. If this would be confirmed by further studies, the mantle contribution to the gases collected close to Lichades would be even greater.

References
Possible paleo-climatic record from fossil hydrothermal systems in the Ross Sea area, Antarctica

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During Cenozoic time, diffuse alkaline magmatism related to the rifting in the Ross Sea Embayment intruded the northeastern region of the Wilson Terrane, Antarctica. Plutons with syenitic-monzonitic to gabbroic compositions provided the necessary heat source for local hydrothermal systems to occur in fractured rocks.

Oxygen and hydrogen isotope investigation of altered granitoids along the Ross Sea coastline were undertaken to constrain the characteristics of Eocene fossil hydrothermal systems. These were combined with Ar-Ar ages of the intrusions to provide a temporal framework for interpreting isotopic data. δ18O values, as low as 4 ‰ in K-feldspar of country rocks, and δD values of biotite/amphibole in the range of -100 ‰ to -200 ‰, indicate that these minerals interacted with meteoric-dominated hydrothermal waters.

Altitude, latitude, local climate conditions and tectono-thermal histories were considered similar for all the outcrops; thus the hydrogen isotope composition of hydrothermal minerals was used as a proxy for paleo-climatic reconstructions, provided the water-vapor hydrogen fractionation in the atmosphere is temperature-dependent.

By combining δD values of the hydrothermal waters with Ar-Ar ages, the isotopic compositions for meteoric recharge waters could be calculated for a fairly continuous time interval between 52 and 26 Ma. This low resolution palaeo-climate curve shows several similarities to the high-resolution curve between 52 and 26 Ma. This low resolution palaeo-climate curve may provide a proxy based on continental records for palaeo-environmental reconstruction in the southern sector of Antarctica.

References

Zircon growth and resorption in an incrementally filled granite pluton: Insights from in situ U-Pb, trace element and Hf isotopic analyses

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High uranium contents and lack of radiation damage due to its young age, permit high precision U-Pb zircon dating of the Monte Capanne monzogranite (Elba, Italy), one of the youngest granitic plutons exposed on Earth. The results are consistent with field relationships and indicate that the last zircon growth increment ranges from 7.85 ± 0.11 Ma in a mafic microgranular enclave (MME) to 7.27 ± 0.15 Ma in a mafic (Orano) dyke of similar monzogranitic to granodioritic composition. The spatial distribution of ages is consistent with incremental intrusion of the three petrographically-defined facies of the pluton (Dini et al. 2002). The San Marino porphyry (7.84 ± 0.14 Ma) was immediately succeeded by the San Francesco facies (7.76 ± 0.17 Ma) while the San Piero (7.53 ± 0.07 Ma) and Sant’Andrea facies crystallized later (7.57 ± 0.46 Ma) before the Orano dykes (7.27 ± 0.15 Ma). Importantly each component of the pluton displays a range of magmatic zircon ages spanning up to two million years, tentatively interpreted as dating the duration of magmatism. Much older inherited zircons occur, particularly in the San Francesco facies. These range in age from Archaean to Mesozoic and are interpreted as being derived from the source or wall rocks. Petrographically and in their trace element and Hf isotopic signatures, the zircons record repeated episodes of growth, partial resorption and regrowth, interpreted as evidence of iterative magma mixing and recharge (Gagnevin et al., 2007) consistent with previous models for the evolution of the Monte Capanne pluton derived from chemical and isotopic zoning in K-feldspar megacrysts (Gagnevin et al., 2005a, b) as well as whole-rock geochemical studies(Gagnevin et al., 2004).

References
Gagnevin et al. (2007) This volume.

References
**In situ** high P-T melting and phase equilibria experiments on the Allende meteorite

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Because chondritic materials are thought to be the building blocks of terrestrial planets and planetesimals, crystallization of chondritic and peridotic material can be used to simulate accretion and differentiation of a bulk planet. The objective of this study is to measure the liquidus phases and temperatures in situ for a number of planetary mantle analog materials at P > 20 GPa.

Experiments were conducted in the Large Volume Press at the Advanced Photon Source, Argonne National Laboratory. Phases were identified using energy-dispersive X-ray diffraction (EDXRD) with a fixed diffraction angle (2θ) of ~6° and data collection times of 60 sec. Heating runs up to 2200 °C were performed at 400, 600, and 700 tons, sampling a pressure range from 18-32 GPa.

A 3mm TEL beamline modified Fei-type assembly was used in experiments. MgO was used as the pressure standard. Temperature at the hotspot, the region of interest for analyses, was calculated using the thermal modeling program developed by [1].

Radiography image of compressed sample though the Re slits and alumina windows. Maximum pressure achieved was 19.1 GPa. The pressure standard was located immediately above the sample. The dark area in the upper left is an area where the slit in the Re foil ends.

The solidus is comparable to previous results, but the majorite liquidus temperature occurs near 2250 °C, compared to previous results of 2000 °C [2,3]. The majorite-Mg-perovskite coticet occurs before 22 GPa, as opposed to around 25 GPa [2,3]. Although Mg-perovskite was identified as the liquidus phase above 22 GPa, the ferropericlase-out line is very steep, and may become the liquidus phase above 23 GPa. The higher liquidus temperature with the large field of melting would tend to support a shallow magma ocean model with a large zone of crystal mush.

Reference
Mineralogical characterization of Mn ores of shallow marine origin in northeast Vietnam

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Geological and mineralogical properties

Important Mn deposits occur in the Halang basin, located in the Cao Bang Province in the northeastern part of Vietnam. The Mn ore in this region is of neritic origin, representing a chemical sediment, and was described as consisting of primarily pyrolusite and “psilomelane” (Le, 1988). The Mn ore seams are hosted by grey recrystallized limestone of Devonian age. The Mn deposits are distributed mainly at the margin of Devonian synclines or at their juncture. The productive Mn-bearing seam varies in thickness from 0.2 to 2 m, and is overlain by black siliceous rocks. The average chemical composition of the deposits is as follows: Mn = 30 wt%; Fe = 6.38 wt%; SiO₂ = 22.79 wt%; P = 0.224 wt%. The reserves have been estimated at more than one million tons.

The banded Mn deposits were strongly affected by various geological processes, which postdate ore formation. Folding and faulting led to a complicated distribution pattern of the ore seams. Weathering in the humid subtropical climate has resulted in supergene enrichment in Mn as well in the formation of various secondary minerals, thus producing a mineralogically complex ore. Layers of secondary calcite and quartz are intercalated with the Mn-rich seams.

X-ray diffractometry, EMPA analysis and mineral formula calculations based on the procedure of Saini-Eidukat (1993) revealed that the following minerals are present as major Mn hosts [average composition in brackets]: pyrolusite [MnO₂]; hausmannite [Mn₂⁺₀.₀₁Mn³⁺₁.₀₁O₁]; manganite [Mn³⁺₀.₉₄O(OH)₃]; jacobsite[(Mn³⁺,Fe³⁺)₀.₀₇(Mn³⁺,Fe²⁺)₁.₇₅O₄]; hollandite [(Ca₀.₁K₀.₄₄Ba₀.₀₂Fe₂⁺₀.₃₄,Mn²⁺₀.₄₃,Mn⁴⁺₀.₄₃)O₁₆H₂O] and possibly birnessite. In addition, the ores contain hematite, Mn-rich hematite [(Fe³⁺₁.₂₆,Mn²⁺₀.₆₈)O₁], bixbyite [Mn²⁺₁.₁₇,Fe³⁺₀.₈₃]O₃], goethite, ferrihydrite, quartz, and apatite. The Mn minerals are often intimately intergrown, on a µm-scale, with other minerals.

Discussion of results

The results indicate that not all the Mn minerals are of sedimentary origin but rather, that some of the Mn phases were formed during subsequent alteration. Based on these results we can establish an effective processing technology to improve the ore grade.

References


The application of chrome-spinel in the tectonic discrimination of mafic-ultramafic rocks: New developments from the analysis of gallium

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Chrome-spinel, [(Mg,Fe)(Al,Cr)₂O₄], is well-established as a useful, alteration-resistant petrogenetic and tectonic setting indicator for mafic-ultramafic rocks (e.g. Dick and Bullen, 1984; Barnes and Roeder, 2001). Among its many applications, chrome-spinel geochemistry provides a means of interpreting ophiolites and serpentinites emplaced along continental suture zones, and of interpreting mafic-ultramafic intrusions in the deep crust.

The most effective fingerprints are based on occupancy of the Y (Cr,Al) site of the chrome-spinel with covariations between Cr# [Cr/(Cr + Al)], Fe³⁺# [Fe³⁺ / (Fe³⁺ + Cr + Al)], V and Ti providing sensitive indicators of degree of melting, oxygen fugacity and melt-rock interaction. This work extends this suite of elements by including gallium, analysed by LA-ICP-MS using a 213nm UV laser and well-characterised chrome-spinel standards. Ga values for a suite of peridotite samples from modern-day tectonic settings range from 70 ppm to just above the L.O.D. of 5 ppm.

Of particular significance is the covariation of Ga and Fe³⁺. These elements have similar ionic radii but only Fe³⁺ is redox-dependent. Thus, melting and fractionation trends retain a near-constant Fe³⁺#/Ga ratio, but spinels from supra-subduction zone dunites have higher Fe³⁺#/Ga ratios than those from non-subduction dunites. This Fe³⁺#/Ga fingerprint has been tested on crustal and mantle dunites from the northernmost blocks of the Oman ophiolite, where it confirms lava and dyke evidence for an evolution from a mid-ocean ridge to a supra-subduction zone setting.

References

Rapid melting of small planetesimals

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The presence of highly non-radiogenic 182W in Fe meteorites has been used to estimate that rapid formation of Fe meteorites took place in < 1.5 Ma of formation of solar system [1]. The timing of formation of solar system is determined from 206Pb/208Pb ages of constituents of primitive meteorites the Cal-Al-rich Inclusions (CAIs) [e.g., 2]. The CAIs have some of the highest observed abundance of short lived radionuclide Al26 (half-life ~ 0.7 Ma) which decays to Mg26, with 26Al/27Al ~ 5×10^{-5} [3]. The early melting and differentiation of planetary bodies is attributed to the decay of heat generating 26Al [4, 5]. The ability of 26Al to melt an object will be determined by its abundance and the size of the planetary body [6]. Bodies with radii < 20km will not undergo complete melting; however a part of the inner core temperatures may exceed the solidus (~1200°C) when radius > 5km [6]. The radii of parent bodies of Fe-meteorites range from 3-165km [7]. Melting of a small planetary body with ~ 3 km radius and chondritic composition cannot be easily explained. Furthermore, based on 26Al abundance a hiatus of ~ 2 Ma is estimated between formation of CAIs and chondrules [e.g., 8]. If CAIs formed at a rapid rate they would have experienced gas drag resulting in their spiralling in to the early Sun [9]. The two possible mechanisms suggested to preserve CAIs is turbulent flow or rapid accretion of CAIs into small bodies. We report preliminary results of thermal evolution of small planetary bodies with CAI abundance greater than chondritic bodies resulting in higher than normal Al abundance. This will increase the 26Al content per unit mass of the body, resulting in higher energy generation due its radioactive decay. In our calculations we observe that if the CAI content is varied between ~25% and 50% in a 3 km (radius) body, ~66% and 76% of the inner core of the body will respectively exceed solidus resulting in large scale differentiation and formation of Fe-cores. Bodies with very high CAI were recently reported [10]. The early sequestration of CAIs may be responsible for early formation of Fe-meteorites and angrites [1, 11].

References

An investigation of basaltts from the Central Indian Ocean Basin

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Basalts were recovered along with manganese nodules and encrustations from the Central Indian Ocean Basin (CIOB). The basaltts are from the oceanic crusts and from a few seamounts, the latter being the manifestations of propagative fractures that formed from the ancient conjugate crusts of the South East and Central Indian Ridges. Magnetic anomalies (A26-A22) suggest the crust of the CIOB to be 60-52 Ma. Petrologically, the basaltts are aphyric to moderately porphyritic with plagioclase forming a dominance of phenocrysts and microphenocrysts embedded in a glassy groundmass. Pyroxene and olivine occur in lesser amount together with a few opaque minerals.

Bulk-rock analyses indicate that the basaltts from the CIOB are mainly hypersthenic normative (3 – 19% hypersthene). Major element of the CIOB basaltts show a wide range of variation of SiO2 (~46 – 51 wt%) and MgO (~2.8 – 7.14 wt%). FeO (~9 to 17 wt%), TiO2 (1.27 to 4 wt%) and Na2O (2.43 to 4.26 wt%) exhibit an increase for a given MgO concentration. The concentrations of K2O (0.24-1.6 wt%) and P2O5 (0.09-0.31 wt%) in the CIOB basaltts are relatively higher than the general MORB and relatively lower than the K-P type basaltts indicating a slight enrichment of K and P, similar to ferrobasaltic melts. The CIOB basaltts typically have high incompatible contents (TiO2, La = 2.7-16.31 ppm, Rb > 6 ppm) and moderate LREE concentration.

A quantitative major and trace element modeling indicate that most of the variations are attributable to low-pressure fractional crystallisation under low fO2 condition of olivine, pyroxene and Ca-plagioclase. This plausibly led to the formation of Fe-Ti-rich basalt in the CIOB. The decreasing CaO/Al2O3 ratios and relatively constant Sc abundance with decreasing Mg# (55 to 31), supports the above view. The incompatible element ratios (Zr/Nb= 25-166; Y/Nb= 7-63; (La/Sm)_N= 0.58-1.46) are similar to ‘normal’ or ‘enriched normal’ mid-oceanic ridge basalt.

The above investigation of basaltts from the CIOB indicates a similar formation history of magmas from different source regions or alternatively a single magmatic source followed a similar elemental enrichment trend prior to eruption from the ancient South East and Central Indian Ridges.
Phosphorus sedimentation and release processes in a shallow hyper-eutrophic lake, Zeekoevlei in South Africa

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We investigate phosphorus (P) accumulation and release processes in a shallow alkaline hyper-eutrophic lake Zeekoevlei, in South Africa by analysing dissolved phosphate (PO₄³⁻) in waters and sediment pore waters, and organic P (OP), inorganic P (IP), calcium (Ca) and iron (Fe) bound P (HCl-P and NaOH-P respectively) fractions in sediments. Zeekoevlei is suspected for considerable internal P release from P-rich surface sediments that have accumulated from extensive cultural input by seasonally controlled catchment runoff. Absorption and coprecipitation by CaCO₃, planktontic P assimilation and aggregation of Ca-P with planktons control dissolved PO₄³⁻ removal from the water column and its subsequent sedimentation. Moreover, PO₄³⁻ absorption on iron (Fe) oxy-hydroxides contribute to the P absorption process in aerobic lake sediments. Low (10-12) atomic carbon/nitrogen (C/N) ratio indicates algae is the main source of sedimentary organic matter, and lake primary productivity, which is affected by dredging in 1983, controls the OP and IP sedimentation. Significant refractory OP fraction in surface sediments indicate higher recycling of algal-bound P in water and restricts aerobic OP mineralization by benthic bacteria. Low (2-3) Fe/P ratio in surface sediments and high pore water PO₄³⁻ concentration (1.69-4.07 mg L⁻¹) indicate higher P saturation and the fully utilised binding capacity of Fe for P. However, the high carbonate content (~6%) leads to continuous absorption of PO₄³⁻, and results in high P retention in sediments. An upward decreasing concentration gradient of pore water PO₄³⁻ suggests insignificant diffusion-mediated upward transport of P, which is consistent with the above finding. These imply ineffectiveness of internal P release process from the calcareous oxic sediment towards the TP pool in Zeekoevlei.

Kinetic and equilibrium iron isotopic fractionation at high temperature

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Because of a small relative mass difference between adjacent isotopes and because equilibrium fractionation decreases in magnitude with increasing temperature, detection of isotopic fractionation of Fe at high temperature has only recently been explored. Using MC-ICPMS, δ⁵⁶Fe can now be analyzed accurately with precisions of better than 0.05 ‰ (e.g., Dauphas & Rouxel, 2006). Iron isotopic variations at high temperature have been documented in bulk rocks and individual minerals. In some instances, the mechanisms responsible for these variations can be identified.

Subsolidus diffusion. Mullen (1961) first showed that diffusion of Fe in metal could cause isotopic fractionation. During cooling of iron meteorites, growth of kamacite out of taenite is limited by diffusion. Several groups have measured Fe and Ni isotopic fractionation between taenite and kamacite in iron meteorites (e.g., Poitrasson et al., 2005; Horn et al., 2006). Modeling shows that this is best explained by differences in the diffusivities of the isotopes of Fe and Ni during diffusion at temperatures in the range ~450 to 650 °C.

Evaporation and condensation. The kinetic theory of gases predicts that there should be isotopic fractionation during evaporation or condensation, controlled by the degree of under or super saturation of the gas. Experiments of free evaporation of molten FeO and a complicated mixture of oxides show that Fe is indeed isotopically fractionated during these processes (e.g., Dauphas et al., 2004). A zoned metal grain in a chondrite shows correlated zonings for Fe and Ni isotopic compositions (down to ~6 ‰/amu at the core), demonstrating that it formed by condensation (Alexander & Hewins, 2004).

Inter-mineral equilibrium fractionation. Polyakov et al. (2007) showed that measurable equilibrium fractionation between mineral pairs such as pyrite-siderite or magnetite-siderite should exist at temperatures in excess of 500 °C. We measured the Fe isotopic fractionation between magnetite and siderite/pyroxene in BIFs metamorphosed to amphibolite and granulate facies. The measured compositions are in agreement with predictions, validating Fe isotopes as potential geothermometers in regionally metamorphosed terranes.

References
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Carbonation of Ca- and Mg-rich silicates: Experimental investigations and kinetic modeling

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Among the different ways considered to store CO2, the safest one involves the conversion of CO2 to its geologically stable carbonate form. The corresponding reaction (where M is a divalent species):

MxSiOy+(2x-y)(OH)2y+xCO2 ⇌ xMCO3 + ySiO2 + tH2O

is thermodynamically favoured for Ca- and Mg-rich silicates like (ultra)basic minerals (e.g. olivine, serpentine) (Robie & Hemingway, 1995). The efficiency of this method to store large amounts of CO2 essentially depends on the overall reaction rate of carbonation, for which experimental data are scarce.

Recent studies (e.g. Giammar et al., 2005; Huijgen et al., 2006; McGrail et al., 2006) have demonstrated that such a reaction could occur relatively rapidly in hydrothermal conditions. However, kinetic modeling remains absent in most of those investigations.

Our ongoing work both combines laboratory experiments and kinetic modeling, at conditions relevant for geological storage (T=363 K, pCO2 = 25 MPa). Experiments are performed in separated batch capsules filled with monomineral powders and water, introduced in a Ti-autoclave. Different reaction times (from few hours to months) are tested to follow the reaction advancements. Reaction products are identified using SEM, TEM and Raman spectroscopy, and carbonation rates are determined by different analytical methods (Rietveld refinement of X-Ray diffractograms, mass balance, and selective acid attack of carbonates followed by dosage of produced positive ions). These investigations are coupled with kinetic modeling (CHESS, van der Lee, ENSMP, Paris) using data from the literature for each main step of the reaction (silicate dissolution, carbonate precipitation).

We will present our results, focusing on the carbonation of wollastonite (CaSiO3). Then we will discuss some causative factors to explain discrepancies between modeling and our experimental results, such as the general form of kinetic rate laws or armouring effect.

References

Amphibole control in the differentiation of arc magmas

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Subduction-related volcanic rocks are commonly porphyritic, with a typical gabbroic assemblage of plag ± px ± ol. Rock suites from arc volcanoes, can, in terms of major elements, be modelled as due to extraction of this assemblage. However, three observations mitigate against this simple interpretation;
1. Petrographic observations suggest that many of the “phenocryst” phases are not in equilibrium with the liquid in which they were erupted – these phases are, in many cases, more appropriately referred to as antecrysts.
2. A significant amount of crystallisation (microlites, rims on antecrysts) occurs rapidly in response to decompression during ascent, and this material is not efficiently removed/fractionated from the liquid, and
3. Trace element characteristics are difficult to reconcile with simple gabbro fractionation

We compiled REE data from several cogenetic arc suites, and found compelling evidence for a significant role for amphibole in the majority of cases (Fig. 1). A significant decrease in Dy/Yb with SiO2 can only be attributed to amphibole partitioning, either as a directly fractionating phase, or as a residual phase in more complex melting-mixing mechanisms. The implication is that there is a major amphibole–bearing reservoir formed in the arc crust as a result of differentiation of ascending magmas. This reservoir can 1) sequester a fraction of the mantle-derived water from primary magmas, and 2) provide a potentially fertile source for intracrustal melting, producing hydrous silicic magmas.

Note that trends in Fig 1 do not back-project to a common parent, implying that parental compositions are defined by another control (deep early differentiation, possibly with garnet, or mantle source variation with different slab components)

Figure 1. Compilation of differentiation suites from arc volcanoes showing evidence for amphibole fractionation.
The origin of silica-rich Kaapvaal lithospheric mantle
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The Archaean Kaapvaal lithospheric mantle is residual after extensive melt removal but is characterised by high silica content and is often enriched in incompatible trace elements [1]. The timing and nature of the silica enrichment process is not understood partly because interpreting the temporal evolution of mantle xenoliths is complicated by recent interaction with kimberlite. Here we report a combined petrology and in situ major and trace element and mineral Sr-Nd-Hf-Os isotope study of extremely silica-rich and undeformed xenoliths from Kimberley, S.A. Silica enrichment is manifested in two forms: i) orthopyroxene (opx)-rich clots (75% opx, 15% garnet (gnt), 10 % olivine) and veins (5-20 cm) that have mutual gnt and opx exsolution; ii) gnt-rich clots (80% gnt, 15% opx, 5 % ol). Some samples appear recently metasomatised. This process is manifested by clinopyroxene (cpx) and is associated by LREE enriched whole rock patterns with YbN~2, NdN~15. All minerals are in chemical equilibrium and the rocks have isotopic systematics indicating interaction with the host kimberlite. In contrast, Opx and Gnt-clots have “S” shaped REE patterns with YbN~0.5, NdN~10, LaN~0.1 with a maximum at Sm or Nd. Opx-clots have time integrated low Lu/Hf, down to εHf ~15 but variable Sm/Nd ratios, whereas the gnt-clots have time integrated LREE depleted isotopic signatures (εHf + 10). The combined trace element and isotopic data are used to formulate a model for the nature and timing of the silica addition to the Kaapvaal lithosphere.

References

The ion nanoprobe: A new instrument for isotopic and chemical analysis at the few-nanometer scale
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A variety of techniques have been developed or are under development to study the properties of materials at the nm scale, including transmission electron microscopy (TEM) and nm-size x-ray beams. These techniques are unsurpassed for studying the distribution and local environment of atoms on this scale, but are unable to measure isotopic composition. At the µm scale, the secondary ion mass spectrometer (SIMS), commonly known to geochemists as the ion microprobe, is widely used to measure isotopic compositions. The most advanced SIMS instruments can produce isotopic images with 100 nm resolution.

The increase in spatial resolution from the earlier generation SIMS instruments such as the Cameca ims-3f to the latest Cameca NanoSIMS-50 led to important new discoveries, such as the discovery of isotopically anomalous ~500 nm presolar silicates. We plan to build a new instrument that will take another substantial leap forward in spatial resolution, to 5–10 nm. This is perhaps the last such leap, as there are so few atoms in a few-nm analysis spot (a 5 nm diameter sphere of SiC contains only 3200 atoms). In order to make isotopic and trace element analyses at this spatial scale, very high sensitivity is essential. The ionization efficiency in SIMS is typically 10–3, but can be higher for selected elements. The useful yield (ions detected per atom consumed) in SIMS can exceed 1% in only a very few cases. We have developed techniques for laser postionization of ion-sputtered or laser-desorbed/laser-ablated neutral atoms that have much higher ionization efficiency, which results in a remarkably high useful yield (exceeding 20% in the latest generation instrument built by us) and approaching the atom-counting limit. The new instrument will combine a recently developed high resolution liquid metal ion gun, tunable solid state lasers, and an improved time-of-flight mass spectrometer. By analogy with the ion microprobe, a common name for SIMS, we dub the new instrument the “ion nanoprobe”. Development of this instrument will fill a major gap in analytical capability between chemical composition at the nm scale and isotopic composition at the µm scale.

The ion nanoprobe is perhaps best suited to analysis of interstellar and cometary dust returned by the Stardust mission as well as presolar grains in meteorites, where large isotopic variations occur on very fine scales, but a wide variety of applications are envisioned.
Sub-m.y. age resolution for Precambrian igneous events by thermal extraction (TE-TIMS) Pb dating of zircon: Application to progressive crystallization of the 1849 Ma Sudbury impact melt

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Age precision of Precambrian zircon dated using ID-TIMS is usually limited to about 1 m.y. by variable isotopic fractionation in the mass spectrometer and by secondary Pb loss. Thermal pre-heating of cracked and/or altered zircon grains to 1550°C removes most Pb from damaged domains as noted by Kober (1986, 1987), but extraction of primary Pb by evaporation produces relatively small ion beams. Embedding a pre-treated zircon in silica glass by fusion with silica gel on a Re filament allows the primary radiogenic Pb isotopic composition to be measured to high precision on a multi-collector mass spectrometer during thermal extraction of Pb into the silica melt. \(^{206}\text{Pb}\) emission from embedded grains shows a rapid increase at 1600°C to several 100 mv and can be maintained for up to an hour. \(^{207}\text{Pb}/^{206}\text{Pb}\) ages, corrected for common Pb on a cycle-by-cycle basis, generally show a plateau around maximum emission with no systematic increase due to fractionation until near the end of the run. Comparison of TE-TIMS ages on Archean rocks precisely dated by ID-TIMS consistently shows an isotopic fractionation factor of 0.18%/AMU, slightly higher than with ID-TIMS. This new approach has been applied to two phases of the Sudbury impact melt, previously dated at 1850 \(\pm \) 1 Ma by Krogh \textit{et al.} (1982, 1984). TE-TIMS on five single zircon grains from one phase, collected near the northern boundary of the intrusion (Felsic Norite), defines an age of 1849.53 \(\pm \) 0.21 Ma. Six grains from a second phase, collected from the middle of the intrusion on its southern side (Mafic Norite), yielded a younger age of 1849.11 \(\pm \) 0.19 Ma. No difference was found between abraded and unabraded grains from each sample. Errors are 95\% confidence limits and include no error for fractionation. MSWD is 2.0 for both data sets but adding an error of 0.01\% (0.18 m.y.), to account for variability of fractionation, to the age of each grain reduces the MSWD’s to about 1 and results in essentially the same errors for the weighted averages as above. New, less precise ID-TIMS results on abraded zircon from the Felsic and Black Norite agree with TE-TIMS results, with intercept ages of 1849.6 \(\pm \) 0.8 Ma and 1849.1 \(\pm \) 1.2 Ma, respectively. This ca. 0.4 m.y. time interval is longer than expected for passive cooling. It suggests that either the impact melt volume was much larger than previously thought or excavation of the crust resulted in decompression melting and advection of heat from the underlying mantle, which maintained a long-term thermal anomaly beneath the zone of crustal melting.

Stable isotopic evidence of evolving Laramide landscape in the central North American Cordillera

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A growing dataset of stable isotopic records from the western United States is evidence of an evolving landscape during the early Cenozoic. New isotope records from three intraforeland basins of Paleogene Utah are characterized by large (>5‰), diachronous shifts in \(\delta^{18}\text{O}\) values. Combined with previous studies of provenance and paleoflow, these isotopic results are interpreted to reflect changes in hydrology and catchment hypsometry as the basins responded to growing relief in the foreland.

Decreasing isotopic trends indicate an increase in hypsometric mean elevation of catchments feeding each of the studied basins during the Middle and Late Eocene. Along with isotopic trends, evidence of hydrology, sediment provenance and active tectonism supports the development of relief as the subsiding foreland was segmented by Laramide uplifts. Although hypsometry of catchments increased, there are no signs that mean elevation in the foreland increased. Thus, we prefer a model of landscape evolution in which the area of catchments decrease, and sources of water to intraforeland basins are increasingly confined to elevated bounding structures.

The timing and magnitude of isotopic shifts in the studied Utah basins is coincident with the previously observed pattern of similar shifts spreading southward from Montana to southern Nevada between Early Eocene and Oligocene, suggesting that a progression of large-scale topographic development affected both hinterland and foreland. With this study, we increasingly favor an explanation for topographic modification wherein relief grows but mean elevation stays the same or possibly decreases.
Significance of Magmatic epidote in the Azna pluton, Iran

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Magmatic epidote can be a good indicator for the pressure, temperature and original water content of a granitoid body. The Azna syn-tectonic pluton is emplaced within shear zone of the Azna in magmatic-metamorphic belt of Sanandaj-Sirjan. Based on the relationships of Zr + Nb + Ce + Y vs. 10000*Ga/Al suggest an A-type character for these granite. On the tectonic discrimination plots, these granites indicate a within-plate granite character.

The main minerals in the pluton are quartz, plagioclase, microcline-perthite, biotite and phengitic muscovite and the accessory minerals are zircon, allanite, epidote and tourmaline. Plagioclase is as coarse porphyroclast. They do not display any alteration. Biotite is euhedral to subhedral. Biotites are concentrated in the main foliation. Epidote tends to be associated with the biotites; therefore epidote is abundant in the main foliation with biotite. Fine grain epidote crystals are anhedral to subhedral. They occur as faintly to conspicuously pleochroic crystals. Allanite forms cores of some epidote crystals. Generally the epidote crystals are homogenous. Electron microprobe analyses of epidotes from Anza pluton revealed low TiO2 and pistacite content is equal to 0.27.

The lack of alteration of minerals in the rocks suggests that a late vapour phase may have been absent. The textural relations of epidote, biotite and plagioclase as described above, the lack of alteration of minerals and the involvement of epidote in the main foliation show that the epidote is truly a magmatic mineral. Magmatic epidote in a plutonic rock signifies that the rock probably crystallized at pressures of at least 8 Kbar (25-30 km depth) and they must have been removed since emplacement of the pluton.

References

Isotopic and Geochemical characteristics of kimberlite from Raipur and Tokapal, Chattisgarh, Central India

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Four kimberlite fields have been located from Mainpur kimberlite filed (MKF) in Raipur district, Chattisgarh, central India. These Kimberlite fields are Payalikhand, Bahradih, Jangra and Kodamalli. Later Tokapal and Bhejripadar kimberlite fields (TKF) in Bastar district were reported by Geological survey. Kodamalli kimberlite of MKF was intruded in the Late Proterozoic sediments. These kimberlites occur close to the junction of Bastar craton (BC) and Eastern Ghat Mobile Belt (EGMB). Mainpur kimberlite field is located within Bastar craton close to its contact with the granulite terrain of the lower to Middle Proterozoic Eastern Ghts Mobile belts in the east. Based on mineral assemblages and texture it can be classified as hypabyssal facies group I kimberlite.

The concentration of incompatible elements for Kodamalli kimberlite is higher than kimberlite from Tokapal from the same craton. The REE concentration at Kodamalli kimberlite is similar to Bhejripadar and Tokapal. The variation of abundance ratio for Zr/Hf indicates variable intensity of metasomatism by carbonates and suggests that the source magma of the Kimberlite of Kodamalli and Bhejripadar/Tokapal are different and was metasomatically enriched in different degrees prior to kimberlite generation. The Zr/Nb vs La/Yb ratios of Kodamalli and Bhejripadar/Tokapal kimberlites show that the Kodamalli kimberlites have high Zr/Nb ratio and low La/Yb ratios. The plot of Ce/Yb vs Zr/Nb shows that the source rock for Kodamalli kimberlite is different than Bhejripadar and Tokapal kimberlites. The highly fractionated REE distribution (La/Yb >50) in kimberlites indicates that the source lithologies contain garnet and that partial melting occurred in the presence of garnet. The positive anomaly for Ta and Nb in both the kimberlite indicates the mantle source with residual titanite. The presence of Rb anomalies suggests the presence of residual phlogopite in the mantle.

Strontium isotopic data for these kimberlites gives an initial ratio of ~0.7045 at 1100 Ma. Lehman et al. (2002) reported εNd = +11.8 at 1080 Ma for this kimberlite, which is quite different than kimberlite, which is quite different than kimberlite, from Tokapal, Bhejripadar, Majhgawan and Lattavaram (εNd ~+2 at 1080 Ma).

References
Integrated geochemical studies of hydrocarbon in Proterozoic basins

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There are number of unexplored Proterozoic basins for hydrocarbon in India. These basins are characterized by varied geology, age, tectonics and depositional environments. Hydrocarbons generated and trapped beneath the sub-surface seeps to the surface in varying but detectable quantities. Diffusion, effusion, and buoyancy allow these hydrocarbons to escape from reservoirs and migrate to the surface where they are retained in the sediments, diffuse to atmosphere or water columns. Based on these assumptions, surface geochemical prospecting lab has been developed to identify the surface or near surface occurrences of hydrocarbons. The facility includes adsorbed soil gas surveys in light hydrocarbon (C\(_1\)-C\(_4\)), \(^{13}\)C/\(^{12}\)C measurement on C\(_1\)-C\(_4\) and microbial techniques. Surface geochemical research for hydrocarbon was carried out in various in parts of Vindhyan basin, Cuddapah basin, Kaladgi basin, Kutch basin and Jamnagar sub-basin. Soil samples from Vindhyan, Cuddapah and Kaladgi basins were analysed for light hydrocarbon, Carbon isotopic ratio and microbial analyses. Cross plot between C\(_1\)-C\(_2\), C\(_1\)-C\(_3\), C\(_2\)-C\(_3\) show linear correlation which indicates that light hydrocarbon migrated from thermogenic source. Pixler plot (C\(_1\)/C\(_2\) and C\(_1\)/C\(_3\)) plot distinguish the non productive zone from oil/gas producing zone. \(^{13}\)C analyses of C\(_1\)-C\(_4\) suggest thermogenic source for these hydrocarbon. Microbial analyses for MOB and POB also show anomalous concentrations in some of the samples. Integrated geochemical studies in these Proterozoic basins suggest warm area for hydrocarbon exploration.

Lu-Hf and Sm-Nd isotopic study of Martian meteorites: Implications for early differentiation on Mars

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We present a new study of \(^{176}\)Lu-\(^{176}\)Hf and \(^{142}\)Sm-\(^{142}\)Nd isotope systematics in 12 SNC meteorites including 3 nakhlites (Nakhla, MIL03346, Yamato000593), 3 depleted shergottites (SaU008, SaU094, DaG476), 1 intermediate composition shergottite (EETA79001), 4 enriched shergottites (Shergotty, Zagami, Los Angeles, NWA856) and the orthopyroxenite (ALHA84001). The objective is to provide constraints on processes occurring during the early differentiation of Mars and the subsequent crystallization from a magma ocean, resulting in compositionally distinct cumulates. All the shergottites define a mixing trend between a depleted end-member, likely represented by depleted shergottites, and an enriched end-member. Shergottites also plot to the right of a 1:1 line for their calculated time-integrated mantle sources \(^{147}\)Sm/\(^{144}\)Nd vs. measured ratios in lavas. This can be explained by two successive partial melting events that are close in time in the depleted shergottite source. This results in an increased Sm/Nd in the source and in turn produces magmas with Sm/Nd ratios that are greater than time-integrated Sm/Nd ratio inferred from \(^{143}\)Nd/\(^{144}\)Nd. This implies that all the shergottites share a common depleted source and that the enriched shergottites are not corresponding to the enriched end-member of the mixing trend. Shergottites plot to the left of the 1:1 line in a similar diagram using \(^{142}\)Nd/\(^{144}\)Nd. This is because ilmenite is unlikely significant in the Martian mantle, the only other prevalent mantle mineral able to efficiently fractionate these Lu/Hf and Sm/Nd ratios is magnesio-perovskite. This would place the depleted shergottites source in the lowermost Martian mantle, close of the core-mantle boundary. This source may be early cumulates crystallizing from a magma ocean. Acquisition of \(^{142}\)Nd/\(^{144}\)Nd data should give a clearer answer to this problem. Nakhlites are characterized by low \(\varepsilon_{\text{Hf}}/\varepsilon_{\text{Nd}}\) ratios, consistent with a source having experienced ancient garnet segregation.

Finally, Lu-Hf and Sm-Nd systematics of the orthopyroxenite ALHA84001 require a reassessment of the crystallization age of this sample, because a 4.5 Gy crystallization age produces an unrealistically depleted source \(^{147}\)Sm/\(^{144}\)Nd of 0.66 and \(^{176}\)Lu/\(^{177}\)Hf of 0.23. A crystallization age of 3.9 Gy gives more consistent results and is therefore preferred.
Biological versus chemical sulfide oxidation in Beggiatoa inhabited sediment

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We investigated the contribution of metal cycling and biological processes in the oxidation of sulfide in organic-rich marine sediments, covered with Beggiatoa mats. Beggiatoa are large gliding filamentous sulfur bacteria, that can store high concentrations of nitrate in vacuoles. They use their nitrate stores to oxidise sulfide in the 2-4 cm thick suboxic zone, which is their typical habitat. We evaluated the importance of Beggiatoa to chemical oxidation of sulfide, i.e. by metal cycling.

The sulfide oxidation rate by Beggiatoa was quantified from their distribution and cell-specific activity, and by 15N-tracer experiments. Microsensors for H2S, pH, NO3- and O2 were used to characterize the microenvironment and to calculate fluxes of sulfide, NO3- and O2. The sulfide supply into the suboxic zone was determined from sulfate reduction rates and sulfide fluxes from deeper sediments, determined with microsensors.

The sulfide input in the suboxic zone was dominated by a diffusional flux from deeper sediments, while the local production by sulfate reduction was low. The total influx of sulfide was much higher than the sulfide oxidising capacity of the Beggiatoa community. Thus most of the sulfide was removed by chemical processes, mainly binding to Fe(II) and oxidation by Fe(III). This was confirmed by highly characteristic pH profiles, showing a maximum value in the zone where sulfide dissipated. The Fe(II) formed by Fe(III) reduction diffused upward where it was oxidised by Mn(IV), detected by a strong pH decrease. Indeed geochemical analyses showed a distinct Mn(IV) peak in the upper sediments, and the distributions of Fe(II) and Fe(III) confirmed this scenario.

Thus the steep sulfide gradient and high sulfide flux, a typical characteristic of Beggiatoa habitats, is not needed for their metabolic performance. Beggiatoa can glide long distances before nitrate is depleted. We concluded that the free sulfide below the suboxic zone is used as a chemotactic cue by the highly motile filaments to avoid getting lost at depth in the sediment. This means that the distribution of Beggiatoa is a response to- rather than a determinant of the sulfide distribution.

Low-density geochemical mapping in Australia: Pilot projects and outline of a continental-scale geochemical survey

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Pilot projects

Over the past few years, CRC LEME and GA have carried out 4 pilot geochemical surveys aimed at developing and field-testing a low-density sampling strategy adapted to Australian landscapes and climatic conditions. Further, protocols for sample collection, preparation and analysis were developed to ensure quality data were acquired.

The pilot projects were undertaken in the Curnamona region of western New South Wales (NSW) and eastern South Australia (SA), and in the Riverina (southern NSW and northern Victoria), Gawler (central SA) and Thomson (northern NSW) regions. We tested various:

- sampling media (soils, overbank/floodplain sediments, ‘outlet sediments’, groundwater, vegetation),
- sampling depths (‘top’: 0-10 cm, ‘bottom’: a 10 cm interval at ~60-95 cm depth, complete profiles),
- fractions (<2 mm, 2-1 mm, 1000-500 μm, 500-180 μm, <180 μm, 180-75 μm, <75 μm, heavy minerals),
- digestions (total, multi-acid, aqua regia, Mobile Metal Ion Technology®, sequential extractions), and
- analytical methods (INAA, XRF, ICP-MS, GF-AAS, ISE, XRD, PIMA).

The National Geochemical Survey of Australia

Based on lessons learned from the pilot projects, a National Geochemical Survey of Australia (NGSA) project was developed, which recently received funding through the Australian Government’s Onshore Energy Security Initiative. The aim of the NGSA project is to provide pre-competitive data and knowledge to support exploration for energy resources in Australia. The survey will sample sediments at the outlet of ~1400 catchments covering >90% of the Australian mainland, giving an average sampling density of ~1 site/5500 km2. Materials will be collected from 2 depths (0-10 cm and ~60-70 cm) and separated into 2 size fractions (<2 mm and <75 μm). Analysis of these materials, mostly by XRF and ICP-MS, will yield total concentrations for ~60 elements. The project will result in Australia’s first continental-scale, internally consistent geochemical data layer. The data will be useful for an array of applications, such as identifying geological domains likely to host specific uranium and thorium deposit types, and correlating geochemical data with airborne radiometrics data. The NGSA project will run from 2007 to 2011 and will deliver a publicly available geochemical database and atlas on the web.
Reactivity of a rhyolitic glass

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The dissolution mechanism of basaltic glass had been defined by Oelkers and Gisladson (2001), but very little is know about acidic glass such as rhyolitic glass.

Ryolitic glass was processed in a mixed flow reactor ParrTM. As a proxy for the dissolution rate we have used the outlet concentration of Si and Al. The conditions of the experiment was from 40 to 200°C and a pH from 2 to 10.6.

The dissolution mechanism of the basaltic glass is defined by the following equation (1):

\[ r_e = A \exp \left(\frac{E_a}{R} \left(\frac{a_3}{a_3^{0.18}}\right)^{1/\alpha}\right) \]

With A a constant, Ea the activation energy, R the perfect gas constant, T the temperature and ai the activity of i.

Assuming that the dissolution mechanism is the same for both glasses we determined each parameter separately and obtained the following equation:

\[ r_e = 0.031 \exp \left(\frac{-77300}{RT} \left(\frac{a_3^{0.18}}{a_3^{0.18}}\right)^{0.18}\right) \]

The good fit of the computed (eq.2) and predicted data (fig.1) shows that this equation can predict the dissolution rate of the rhyolitic glasses implying that the same mechanism.

Figure. 1: Comparison between the predicted dissolution rate and the rate measured.

Because the dissolution mechanism for the rhyolitic and basaltic glass is the same it is possible to develop a general equation for the dissolution of natural glass.

References


Sr-Nd isotope data on diorite-trondhjemite associations from the central Norwegian Caledonides

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The Trondheim Nappe Complex (TNC) comprises several slightly metamorphosed ca. 435 Ma old leucocratic igneous bodies and dykes. They often have ‘trondhjemitic’ affinity, but not all the leucocratic rocks share the typical characteristics of trondhjemites, such as a high Na/K ratio and strongly depleted heavy REE. The trondhjemitic rocks in the TNC are generally associated with dioritic rocks having mafic to intermediate composition. Since it seems unlikely that this close association in the field is fortuitous, it should be considered a significant pointer to the petrogenesis of the trondhjemitic series. Interest in trondhjemites has been revived because of the similarities to Cenozoic felsic rocks called adakites, which are thought to be melting products of the young, still hot subducted slab. If a similar origin applies to the Phanerozoic and older trondhjemitic rocks, it could help to understand the evolution of subduction-related petrogenetic processes throughout Earth’s history.

A detailed petrographical and geochemical investigation of these TNC felsic trondhjemitic series and associated mafic/intermediate rocks is in progress with the aim to reveal the petrogenetic relationship between the two series. Most of the leucocratic rocks show the pronounced depletion of heavy REE, which is generally attributed to partial melting of eclogitic parent rocks. The absence of negative Eu-anomalies in the REE patterns precludes derivation of trondhjemitic rocks from protracted fractional crystallisation of melts of intermediate composition. The associated mafic to intermediate rocks have REE patterns that are not depleted in heavy REE. They show geochemical characteristics typical of Cenozoic subduction related calc-alkaline series.

In contrast to the differences in major and trace element composition the trondhjemitic and associated mafic rocks have very similar isotopic composition of Sr and Nd. The ‘initial’ (i.e. at a nominal 435 Ma age) \(^{87}Sr/^{86}Sr\) ratios and \(\varepsilon\)Nd values of the greater part of the analyzed samples define an array between \(^{87}Sr/^{86}Sr\approx 0.703\); \(\varepsilon\)Nd= +6 and \(^{87}Sr/^{86}Sr\approx 0.706\); \(\varepsilon\)Nd= -4. The positive \(\varepsilon\)Nd data suggest that a depleted mantle or mantle-derived end-member was involved in the petrogenesis, while the higher \(^{87}Sr/^{86}Sr\) and negative \(\varepsilon\)Nd values seem to imply an additional enriched crustal component. Formation of the trondhjemitic rocks by melting of old crustal material appears improbable. Though it is premature to decide on the most plausible petrogenetic model for the TNC trondhjemites, a viable option is remelting of lower crustal plutonic equivalents of the mafic rocks that have been emplaced together with the trondhjemites at higher crustal levels.
Evaluation of the possibility of uranium 238 series dating for the Pliocene-Holocene basalt

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Evaluation of the degree of disequilibrium of the isotopes of U-series (U238) in recent basalts of Central Mongolia was carried out by means of inductively coupled plasma mass spectrometry (ICPMS).

The basalts of Taryat areal (Khangay, Mongolia) are conventionally dated as belonging to the Quaternary on the basis of paleomagnetic investigations, K/Ar dating and stratigraphic data [1,2]. However, the development of novel procedures of absolute dating of these recent vulcanites is urgent.

Measurements of the isotope ratios U238/U234, U238/Th230, U238/Th232 and U238/U235 were performed with a high-resolution mass spectrometer ELEMENT Finnigan MAT after leaching uranium and thorium from a weighed portion (0.1g) of the crushed rock with concentrated nitric acid under heating. Measurements were carried out in medium mass resolution mode (M/ΔM=4000). This mode allowed ion counting for all the mentioned isotopes, which resulted in a decreased interference of low-abundant U234, Th230 with abundant U238, Th232, the concentrations of which differ by 5 orders of magnitude.

The results show that the degree of modern disequilibrium of Th230 with U238 in the investigated samples is 0.7 to 1.2 for the Pliocene and Holocene basalts.

The observed deviation from the U234/U238 equilibrium, exceeding the measurement error, can be explained by different leaching of uranium isotopes in post-eruptive processes.

The achieved accuracy of measurements allows one to determine isochronous age of these basalts with the relative error of about 15% as a mean.

References
Impact of gold mining on levels of naturally occurring radionuclides in aquatic ecosystems of the Witwatersrand Basin, South Africa

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For more than a century, uraniferous gold ores have been exploited by various mines in the “West Rand” and “Far West Rand” goldfields located in the catchment area of the Wonderfonteinspruit, west-southwest of Johannesburg, South Africa. The long-lasting mining-related discharges of naturally occurring radionuclides from point and diffuse sources into the Wonderfonteinspruit catchment area, which forms the eastern catchment of the Mooi River, result in a complex pattern of radioactive contamination of water bodies, sediments and soils throughout the area. As a consequence of the different sources of radionuclides (mine waters and slimes dams), their different geochemical and transport behaviour in the environment, and variations in the source term (intermittent mine water discharges, infrequent seepage water emission, sporadic erosion from slimes dams after heavy rainfalls) a high temporal and spatial variability of the contamination levels and the activity ratios of the various radionuclides in water and sediments/soils was observed.

Activities measured for the $^{232}$Th decay chain in water and sediment samples are predominantly low and near to natural background levels. In general, the activity concentration levels in surface waters are dominated by $^{238}$U and $^{234}$U, which are in secular equilibrium and in natural ratio with the $^{235}$U activity, and by $^{226}$Ra. At slimes dams, where acidic seepage occurs, secular equilibrium and in natural ratio with the $^{235}$U activity, and by $^{226}$Ra. At slimes dams, where acidic seepage occurs, elevated activity concentrations of $^{210}$Pb and $^{210}$Po in water ponds were encountered, indicating specific impacts of acidic seepage from old mining legacies in the long-term. The activity of sediments and (floodplain) soils is dominated by $^{238}$U decay chain nuclides, exhibiting distinct spatial variations in activity levels and ratios depending on radionuclide source terms and relevant transport processes and environmental conditions.

In the frame of a radiological impact assessment carried out on behalf of the National Nuclear Regulator of South Africa, incremental effective doses (above the natural background) were calculated for members of the public living in the Wonderfonteinspruit catchment area, based on the South African Licensing Guide LG-1032 and IAEA recommendations. Taking into account realistic exposure scenarios and pathways, potential radiation exposures of the public above the effective dose limit of 1 mSv/a were calculated for various of the investigated sites, with maximum effective doses up to some tens of mSv/a.

LA-MC-ICPMS $^{87}$Sr/$^{86}$Sr analysis on tooth enamel – Pitfalls and problems

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LA-MC-ICPMS on human teeth using $^{87}$Sr/$^{86}$Sr to trace intra-individual mobility has been hampered due to the difficulty in generating reproducible radiogenic Sr ratios. Diagenetic uptake of REE into teeth enamel and Krypton in the introductory gases interferes with measurements and are primarily responsible for the analytical difficulties in archaeological samples. Consequently, despite success of LA-MC-ICPMS for biological calcite (Christensen et al. 1995, Ramos et al. 2004, McCulloch et al. 2005), the methodology has not lent itself as readily to analyses of calcium hydroxyapatite.

However, molecular interferences and oxide formation can be eliminated by torch and gas flow manipulation (Foster and Vance 2006), the deviation of $^{84}$Sr/$^{86}$Sr from the natural value of 0.056490 can be used as a qualitative assessment, and the Y intensity can be used as a proxy for REE interferences (e.g. McCulloch et al. 2005). The $^{86}$Kr contribution to the 86 intensity is usually ~1%, and hence can be discounted as a major influence on the normalized $^{87}$Sr/$^{86}$Sr. A further assessment of accuracy and precision is through shark teeth that routinely yield marine $^{87}$Sr/$^{86}$Sr ratios (0.709167 ± 0.00003). Despite these manipulations, our LA-MC-ICPMS data for human teeth consistently show an offset from the bulk solution MC-ICPMS and TIMS, which we attributed to REE concentration heterogeneity within an enamel layer and between those layers combined with the much lower overall concentration of Sr in those samples.

Our data contributes to the understanding of inherent problems in applying LA-MC-ICPMS to biological apatite such as teeth. We also assess the best method for obtaining reproducible $^{87}$Sr/$^{86}$Sr ratios for whole teeth and intra-tooth $^{87}$Sr/$^{86}$Sr variability using LA-MC-ICPMS, MC-ICPMS, and TIMS.

References


Eastern Mediterranean sapropel formation and preservation; Diagenesis versus palaeoceanography

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Organic-rich intervals (sapropels) occur in eastern Mediterranean sediments at an astronomically determined cyclicity, related to relatively humid climatic periods. The intervening, arid periods are characterized by organic-lean sediments, and the deposition of rather high dust fluxes indicated by Ti/Al. The last of such ‘humid periods’ occurred from 10.4 to 5.7 kyr ago, simultaneous with the sustained wet period in the circum Mediterranean area. At the end of this humid period, the rapid increase in aridity (indicated by Ti/Al) coincides with a peak of high Mn-oxide content. This peak in all 30 studied cores occurs in response to a relatively abrupt re-ventilation event, and is confirmed by several other proxies. From the comparison of organic C and Ba/Al it is clear, that in the sediments of all cores, the upper part of the youngest sapropel, S1, has been removed. Following the ventilation event, at 5.7 kyr, oxygen has continued to progressively move downward into the sediment oxidizing e.g. organic C. In line with these observations, microfossil assemblages indicate environmental changes occurring at the lower- and upper S1 boundary of the initial S1 sapropel. From the organic geochemical data it becomes clear that although siliceous microfossils have entirely disappeared even from the unoxidized S1-interval, their ‘signature’ is still there (e.g. diatoms, represented by loliolide). Other marine biomarkers are dinosterol and δ44/42Ca of a few tenths of permil associated with the production of carbonate sediments (Δcalc). It has been proposed that shifts in the concentration of Ca2+ in seawater can be reconstructed from the calcium isotopic composition (δ44/42Ca) of sedimentary calcium carbonate, giving information on past weathering fluxes of Ca2+ to the oceans and atmospheric concentrations of CO2. The 18 million year record presented here of the δ44/42Ca of planktonic foraminifers from ODP site 925, in the Atlantic, on the Ceara Rise, provides an opportunity to critically analyze Ca isotope based reconstructions of the Ca cycle.

δ44/42Ca in this record averages +0.37 ± 0.05 and ranges from +0.21 ‰ to +0.52 ‰. This falls within error of previously published Neogene records based on foraminifers, but is not similar to the record based on bulk carbonates which has values that are as much as 0.25 ‰ lower, especially further back in time. Fairly recent bulk carbonates and planktonic foraminifers (i.e. from core tops), on the other hand, differ only by 0.06 ± 0.06 ‰ (n = 5). The cause of the greater difference in the isotopic composition of the two materials further back in time remains an open question.

Modeling the global Ca cycle from downcore variations in δ44/42Ca by assuming fixed values for the isotopic composition of weathering inputs (δ44/42Caaw) and for isotope fractionation associated with the production of carbonate sediments (Δcalc), has as been commonly done in the past, results in unrealistically large variations in the mass of Ca2+ in the ocean during the Neogene. This suggests that δ44/42Caaw and Δcalc instead fluctuate over time. Indeed, variations of ± 0.1 ‰ in the isotopic composition of weathering inputs or in the degree of isotopic fractionation during the formation of calcareous sediments could entirely account for the observed variations in δ44/42Ca. Ca isotope fractionation during weathering processes, such as has been recently documented, could easily result in variations in δ44/42Caaw of a few tenths of permil associated with climate change. Likewise the differing degree of isotope fractionation associated with aragonite versus calcite formation could drive shifts in Δcalc of several tenths of permil with shifts in the relative output of calcite and aragonite from the ocean. Until variations in δ44/42Caaw and Δcalc over time are better constrained, modeling the mass of Ca2+ in the oceans from Ca isotope curves should be approached cautiously.

Interpreting the Ca isotope record from marine biogenic carbonates

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Computer modelling of organic/biomineral interfaces

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Geologically important minerals such as hydroxyapatite \( \text{Ca}_10(\text{PO}_4)_6(\text{OH})_2 \) and calcite \( \text{CaCO}_3 \) often have a biogenic origin, resulting from exo-skeletons, bones and shells. Unlike inorganic minerals, these biominerals have been grown under controlled conditions within organisms, where organic templates have usually played a crucial structure-directing role, often leading to unusual and thermo-dynamically unfavourable mineral morphologies.

The study of biomineralisation is a rapidly expanding field of research, where computer simulations can contribute significantly to our atomic-level understanding of the processes occurring at the interface between the growing mineral and the organic reagents.

We present a comprehensive computational study of the interaction of surfaces of calcium carbonate (calcite and aragonite) as well as the natural bone mineral apatite with a number of organic molecules that have important growth enhancing or inhibiting effects. We calculate both the energies of the adsorption of the organic molecule to each surface, hence providing a quantitative measure of the strength of interaction to particular surface features, and the surface energies of the adsorbate/substrate system, which allows us to calculate the effect of the adsorbate on the crystal morphology.

For the calcium carbonates, it is found that carboxylic acids often adsorb preferentially to particular surface features, such as growth steps on the calcites surface, leading to asymmetric surface morphologies in agreement with experiment. In addition, the presence of organic adsorbates is found to drastically alter the morphology of the aragonite crystal.

A number of citric acid derivatives are known to affect apatite growth, whereas the citric acid itself is instrumental in its dissolution. Simulation of its adsorption to hydroxyapatite shows a distinct preference of the citric acid to adsorb to the \( \{10\overline{1}0\} \) and \( \{11\overline{2}1\} \), planes compared to the \( \{0001\} \) surface, which affects both the morphology and the growth behaviour of the mineral.

Search for Cr isotopic anomalies in unequilibrated carbonaceous chondrites

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Previous leaching studies [e.g., 1-2] revealed the existence of both negative and positive \(^{54}\text{Cr}\) anomalies in carbonaceous chondrites, with the highest excesses in the CI chondrites (up to 250 \( \varepsilon \)-units) [3]. In such studies, direct mineralogical and chemical information regarding the carrier phase of the isotopic anomalies is lost. The main focus of this work is to find the carrier phase of the \(^{54}\text{Cr}\) anomalies by physically separating different phases from primitive carbonaceous chondrites (e.g., low-FeO and high-FeO chondrules, refractory inclusions, matrix enriched material etc.), to characterize the separated phases by electron probe, and to measure the \( \text{Cr} \) isotopic composition by TIMS.

To assure that the high excesses in \(^{54}\text{Cr}\) found in the CI and CM chondrites also exist in the most unequilibrated chondrites such as the CO3.2 chondrite Kainsaz, we will first carry out leaching studies following the procedures of [1] and [2] before physically separating different chondritic components. Each leachate is measured by atomic absorption to determine the \( \text{Cr} \) content in the leaching fractions before carrying out the \( \text{Cr} \) chemistry and measuring the \(^{54}\text{Cr}\) isotopic composition.

Most of the previous \(^{54}\text{Cr}\) studies were concentrated on CI and CM chondrites. Our study will focus on chondrites from the petrographic subtypes 3.0 to 3.2 as these meteorites have largely avoided aqueous alteration and metamorphic events. It is possible that these secondary processes have dissolved some of the carrier phase(s) of the isotopic anomalies and that leaching studies of the most unequilibrated chondrites may display larger \(^{54}\text{Cr}\) anomalies.

We chose the CO3.2 chondrite Kainsaz because it is a highly unequilibrated fall and because the least altered CO chondrites experienced much less aqueous alteration than the least altered CV chondrites.

References
Geological importance of paleokarsts and neptunian dykes in the Lower Jurassic rocks at the Beytepe village-Çayyolu area (South west Ankara, Turkey)

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The geometric pattern of paleokarsts and the depositional characteristics of their laminated fillings and the development of the Neptunian dykes in Lower Jurassic microbialitic limestone in the study area located 14 km south west of Ankara were investigated by using field observations and examining polished rock slabs and acetate peels.

There are several cross cutting paleokarsts developed several karstification phases in shallow marine limestone of the Bayırköy formation in the study area (Deli 2005). The voids of karsts were filled with pink, laminated peloidal marine sediments. A few conformities were observed among lamina in sediments filling the karstic voids. The synsedimentary Neptunian dykes coexist together with karstic dykes and were filled with the same sediments. In the study area, crinoidal facies with erosional base overlies the microbialitic limestone point that the area were exposed to the atmosphere more than once (Jimenez de Cisneros et al., 1991).

Laminations developed in different lineations and dipping of a single paleokarstic filling and irregularities among laminae in sediments filling the karstic voids. The syngenic Neptunian dykes coexist together with karstic dykes and were filled with the same sediments. In the study area, crinoidal facies with erosional base overlies the microbialitic limestone. Large Neptunian dykes, up to 3 meters, were developed at the upper part of the facies and were filled with red colored mudstone of the Ammonitico Rosso facies (Lower Toarcian, Alkaya and Deli, 1998). Multiphase karstic features developed in the Sinemurian microbialitic limestone point that the area were exposed to the atmosphere more than once (Jimenez de Cisneros et al., 1991).

Laminations developed in different lineations and dipping of a single paleokarstic filling and irregularities among laminae as well as the presence of Neptunian dykes prove that seismic activities were repeated within short periods. Especially the presence of large Neptunian dykes beneath the Ammonitico Rosso facies which is typical for deposits of the Pelagic carbonate platforms (PCP ; Santantonio, 1993) implies that the facies were deposited in a shallow marine pelagic environment resulted from syngenic faulting in the area.

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Non-conservative behaviour of molybdenum in coastal waters

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Introduction
Molybdenum is the most abundant trace metal in ocean water and generally displays a conservative behaviour unaffected by biological activity. However, several authors observed deviations from conservative behaviour, which they attributed to scavenging by MnOx phases, utilisation by plankton, and complexing by organic particles (Head & Burton, 1970; Berrang & Grill, 1974; Yamazaki & Gohda, 1990; Tuit & Ravizza; 2003). In this contribution we postulate a conceptual model for non-conservative behaviour of Mo in coastal waters, which is based on the tight coupling of geochemical, biological, and sedimentological processes (Dellwig et al., 2007).

Results and Discussion
Non-conservative behaviour of dissolved Mo was observed during specific time periods in coastal waters of the Southern North Sea. In July 2005 a loss of about 60% of Mo\textsubscript{Diss} was observed within 36 hours. In contrast, in August 2002 Mo\textsubscript{Diss} revealed a tidal cyclicity with maximum values up to 158 nM at low tide. The decrease in Mo\textsubscript{Diss} was accompanied by Mo enrichments on SPM. Parallel to decreasing Mo\textsubscript{Diss} concentrations Mn\textsubscript{Diss} showed an increasing trend while Mn\textsubscript{part} decreased. Such finding is compatible with the formation of oxygen-depleted zones in aggregates, which provide suitable conditions for the rapid fixation of Mo and parallel release of Mn by chemically and/or microbially mediated processes. This assumption is supported by biological and sedimentological parameters. The production of organic components (e.g. TEP) during breakdown of an algae bloom in July 2005 led to the formation of larger Mo-enriched aggregates, which depleting the water column in Mo\textsubscript{Diss}. After deposition on and incorporation into sandy tidal flats these aggregates are rapidly decomposed by microbial activity. Pore water profiles document that during microbial decomposition of these aggregates, substantial amounts of Mo are released and may replenish and even enrich Mo in the open water column as seen in August 2002.

References
Reconstructing ancient commercial routes between the Roman Empire and the Indian subcontinent via lead isotope ratio analysis

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Ed-Dur is a large coastal archaeological site on the Arabian side of the Persian Gulf. The main occupation phase at this site dates from the 1st century BC until the 2nd century AD. International sea-trade between the Roman Empire and the Indian subcontinent peaked during this period and the many imported products excavated at ed-Dur (Roman glasswork, Indian ceramics, Parthian coins,…) show that also this region was involved in the trade system.

Several metallic objects from ed-Dur with a lead content ranging from trace up to main element level – local coins made from copper/silver alloys, copper base alloy objects, silver rings and bracelets, lead and litharge fragments and a few lead objects of known origin – have been subject to study. After complete sample digestion with quantitative lead recovery, lead was isolated both quantitative and pure using an extraction chromatographic separation based on a lead-selective crown ether (Pb spec™, Eichrom Environment, France). Isotope ratio measurements were carried out using a PerkinElmer SCIEX Elan 6100 DRCplus ICP-MS instrument, equipped with a dynamic reaction cell. Ne was used as a collision gas in the cell in order to obtain a better isotope ratio precision. Finally, the external precision obtained was 0.11% RSD for 207Pb/206Pb, 0.10% RSD for 208Pb/206Pb, 0.09% RSD for 206Pb/207Pb, and 0.2 – 0.3% RSD for the 3Pb/204Pb ratios, where X = 206, 207 and 208. Mass discrimination correction was performed both by standard bracketing using NIST SRM 981 Common Lead and internal correction using Tl; both techniques gave rise to the same result.

So far, 2 samples of known origin can be used as a proxy of lead sources: (i) an ingot found in the Kingdom of Characene, a vassal state from the Parthian Empire, and (ii) a bulla (coin) which is an imitation of a Roman original and originates from India. However, at least one more source needs to be identified to explain the isotopic range of the investigated samples. The provenance of the lead from the sources and the objects investigated will be determined by comparison to an extended database containing lead isotopic compositions from ores and objects from all over the old world.

These and additional results of this study will be presented, along with archaeological conclusions concerning trade relations in the Arabian region at that time.

Comparing GC- and LC-C-IRMS methodologies to quantify formation and turnover rates of microbial-derived soil organic matter

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Amino sugars are the building blocks of microbial cell walls and can be stabilized in the soil after cell death. Their abundance in the soil has been suggested to be a more useful indicator of time-averaged soil microbial responses to land-use or environmental change than the living microbial biomass. Since bacteria and fungi have different cell wall structures, relative abundance of their characteristic amino sugars has been used to assess fungal and bacterial contributions to soil organic matter. However, little is known about the dynamics of fungal and bacterial amino sugar-C. Compound-specific stable isotope analysis forms a powerful tool to quantify production, stabilization and turnover rates of organic compounds. To date, compound-specific stable isotope analysis of non-volatile biomarkers such as amino sugars has only been attempted through gas chromatography – combustion – isotope ratio mass spectrometry (GC-C-IRMS) or GC-MS, which requires derivatization to facilitate GC analysis. Yet, derivatization of amino sugars adds a large number of exogenous carbon atoms with different 13C signature. This necessitates complex 13C corrections which increase the error on the final δ13C values of the amino sugars. A recently developed analytical technology, i.e. high performance liquid chromatography – combustion – IRMS (HPLC-C-IRMS), has enabled the high-precision 13C/12C determination of polar and thermo-labile compounds that can be chromatographically separated in aqueous phase. By avoiding the requirement for derivatization, this technology has greatly broadened the types of biomarkers that can be analyzed in conjunction with stable isotope analysis. In this presentation, an alternative method is described for 13C analysis of amino sugars through HPLC-C-IRMS, and compared with GC-C-IRMS analysis in terms of reproducibility and experimental error. In addition, results will be presented from an incubation study with uniformly labeled 13C-plant residues to quantify formation rates of newly produced amino sugars under laboratory conditions, and to investigate the impact of substrate quality on the turnover of fungal and bacterial residues.
Experimental determination of pyrite dissolution rate in acidic media at 21° to 61°C

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The dissolution of pyrite is important in the formation of acid mine drainage. The dissolution rates of pyrite were experimental determined in the laboratory at 21° to 61°C using short-term batch experiments. The rate experiments were performed on crushed, pretreated and sieved size-fractions of pyrite sampled from Dongguashan large copper deposit in Tongling district, Anhui province, China. Particles of pyrite between 20 and 40 mesh were used at 35°C and between 40 and 60 mesh at 21°, 34°, 52° and 61°C. Dissolution occurred in HCl aqueous solution at pH=2 in contact with air at room pressure. Five to six samples were collected at different reaction time, half to twelve days, in each temperature and were analyzed for iron concentrations using colorometry with precision less than 5%.

The relationship of iron concentration in solution with the reaction time is linear at each temperature, which indicates the pyrite dissolution was at far from equilibrium state. The dissolution rates were calculated by the equation: \( R = \frac{[\text{d}C/\text{d}t] \times [M/A]}{} \), where \([\text{d}C/\text{d}t] \) was calculated in iron concentration-reaction time diagram by linear regression, \( M \) represents the mass of reaction solution and \( A \) is the total geometric surface area of the reaction pyrite particles. The determined dissolution rates are 2.59×10⁻⁹mol·m⁻²·s⁻¹ at 35°C, and 2.12, 3.94, 11.0 and 12.4×10⁻⁹mol·m⁻²·s⁻¹ at 21°, 34°, 52° and 61°C respectively. These slow dissolution rates derived the activity energy of the pyrite dissolution reaction is 40.3kJ·mol⁻¹ by Arrheius equation, which indicates that the pyrite dissolution is a surface controlled process at far from equilibrium state. These results can be used to evaluate the quantity of the dissolved pyrite to the acid mine drainage in Dongguashan large copper deposit.

A crack in the lithosphere cannot make: Geodynamics and mantle geochemistry

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There may be some issues that can be raised concerning the existence of mantle plumes, but one that cannot be ignored is the high rate of magma production far from plate boundaries, and in many cases, beneath thick lithosphere. This is not explained by lithosphere weakness; volcanism occurs where magma is produced by active mantle processes, not where lithospheric weakness “allows” magma to come up. Exceptions to this rule, if any, involve trivial amounts of magma, such as the tiny seafloor volcanoes on the western Pacific seafloor. Adding pyroxenite and water to lherzolite to increase the fertility of hotspot mantle does not remove the requirement for active upwelling and elevated temperature. Hotspot longevity requires that fresh mantle be continually brought into the melting region.

Improving geodynamic models of mantle plumes are allowing more information to be gleaned from their geochemistry. In Hawaii the thick lithosphere allows only the hottest, axial part of the plume to melt. Consequently, the geochemical structure observed is attributable to the base of the mantle – either the CMB or the top of a dense layer; virtually none of the entrained mantle material melts. Some plume components, especially ³He, could come from the core. Another challenge is to deduce plume structure from the volcanic output, which requires models for magma production within the plume as well as magma mixing prior to eruption. These models are still crude, but are helpful for constraining plume structure and source characteristics.

Longstanding issues about plume sources and mantle dynamics still revolve around the contrasts between MORB and OIB geochemistry, the roles of crust-mantle versus intra-mantle differentiation, and the existence of primordial mantle structure. The relative enrichment and heterogeneity of OIB sources is generally identified with recycled lithosphere. The origin of the MORB reservoir is more mysterious, but could be explained as recycled, incipiently-depleted sub-lithospheric oceanic mantle produced as a result of the presence of water in both MORB and hotspot magma sources.
Kinetic isotope effects in snow crystal growth: Lattice-Boltzmann approach

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The fractionation of the major water isotope species (HDO, HDO, H218O) during ice crystal (snow) formation is critical to understanding the global distribution of isotopes in precipitation, and for interpreting ice core data. The morphology of snow crystals is also a subject of continuing interest in physical chemistry and atmospheric science (Libbrecht, KG, Rep. Prog. Phys., 68, 2005). Although it is known that crystal growth rate, which depends largely on the degree of vapor over-saturation, determines crystal morphology, there is no general model to relate morphology to vapor saturation. Since kinetic (vapor phase diffusion-controlled) isotopic fractionation also depends on growth rate, there should be a direct relationship between vapor saturation, crystal morphology, and crystal δ18O and δD.

We use a 2D Lattice-Boltzmann model to simulate diffusion-controlled ice crystal growth from vapor-oversaturated air. The two-dimensional, nine-speed model of Kang et al. (Geophys. Res. Lett. 31, L21604, 2004) was modified to accommodate the specific boundary conditions needed. In the model, “crystals” grow solely according to the diffusive fluxes just above the crystal surfaces, and hence morphology arises only from the initial and boundary conditions. The input parameters are the isotope-dependent vapor deposition rate constants (k) and vapor diffusivities in air (D). The values of both k and D can be computed from kinetic theory, and there are also experimentally determined values of D. The values of k depend on the sticking coefficient (or accommodation coefficient) for ice, which we assume is independent of position on the crystal surface. The ratio D/k is a length (≈ 0.2 to 0.5 µm) that allows us to scale the numerical calculations to atmospheric conditions using a dimensionless Damkohler number: Da = kh/D, where h × h is the size of the 2D calculation domain.

Our calculations confirm that the crystal/vapor isotopic fractionation approaches the equilibrium value, and the crystals are compact (circular in 2D) as the saturation factor approaches unity (S = 1.0). At higher oversaturation (e.g. S = 1.2), dendritic crystals of millimeter size develop on timescales appropriate to cloud processes and the isotopic fractionations are dominated by kinetic effects. The results help clarify the controls on dendritic crystal growth, and the relationships between saturation state, growth rate, crystal morphology and isotopic fractionation. They also show the extent to which crystals are likely to be isotopically heterogeneous.

Late Mesozoic volcanism of the eastern flank of Mongol-Okhotsky orogenic belt (Russia)

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In the end of Mesozoic in frames of Eastern flank of Mongol-Okhotsky orogenic belt the volcanic zones were formed. Morinskaya zone of late Jurassic – early Cretaceous (800 km²) is made by volcanites of basic-acid composition. The age of the rocks is stated by floral remains (Agaphonenko, 2001) and geochronological data by U-Pb method: 120±5 Ma. Selitkanskaya zone of early Cretaceous (6000 km²) is made by volcanites of basic-acid composition. We defined an age of the rocks of the zone (U-Pb) - 101 ± 2 Ma, and by the data (Agaphonenko, 2001) (U-Pb) - 105 ± 2 Ma. Ezop-Yamalinskaya zone of late Cretaceous (2000 km²) is made by tuffs, ignimbrites, lavas of asid composition. Age of the rocks is 95.2±0.7 Ma (Rb-Sr) [1]. The period of the formation of the zones is pretty wide, but their geochemical characteristics are comparable (Fig. 1). They are impoverished by Nb, Ta, Zr, Hf, Sr and enriched with Rb, Ba, K, Th. According to diagrams that are used to state geodynamical situations it turns out that this rocks are the most close to the formations of edge-continental associations, The rocks are characterized by La/Yb=10-32, La/Ta=20-37.

Figure 1. Rocks of volcanic zones: Morinskaya (1), Selitkanskaya (2), Ezop-Yamalinskaya (3).

Conclusions
The geochemical characteristics of volcanites of Eastern flank of Mongol-Okhotsky belt show the presence of the subductional situation under conditions of an activ continental edge during late Jurassic – beginning of late Cretaceous. And the presence of Sr minimum (many authors connect with this a process of the subduction extinguishing) is characterized for the volcanites of the zones and it’s enlargement in the rocks to the beginning of late Cretaceous, may show the slowly coming subductional processes, that extinguish in the beginning of late Cretaceous.

References
Ge/Si fractionation by higher plants: mechanisms and applications to biogeochemical cycles

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In the near surface environment, silica is under both mineralogical and biological control. In order to better understand the sources and cycling of silica in the critical zone we use the ratio of germanium to silicon as a tracer. Uptake by higher plants discriminates against Ge, and plant phytoliths have low Ge/Si ratios. We find consistently low Ge/Si ratios (< 0.5 µmol/mol) in biogenic silica separated from a wide variety of plant groups, including grasses, deciduous and coniferous trees, and ferns. The apparently ubiquitous occurrence of strong discrimination against Ge during uptake of silica from soil solution suggests a fundamental mechanism common to many higher plants. Preliminary SIMS data suggest that control on Ge and Si uptake is exerted along the Casparian strip in the roots of higher plants. These data are consistent with a proposed Si transport mechanism involving aquaporin family proteins across the Casparian strip (Ma et al., 2005). These proteins are known to control transport of small neutral molecules such as glycerol and water, and conformational effects could account for Ge-Si fractionation. The low Ge/Si of biogenic silica can be used to show that labile silica in shallow soils is dominated by biogenic sources. Ge/Si data from tropical sites indicate rapid and extensive cycling of silica through biomass. We find that Si is also strongly cycled seasonally in a NE USA sugar maple forest, with strong net uptake in spring and early summer coupled to transpiration, and release from litter during snowmelt season. Mass balance calculations suggest that a substantial fraction of “labile” Si in forested watersheds in tropical and temperate systems passes through the plant pool prior to export in stream water.

The mode of mantle convection: Exploring the model space and comparing with probabilistic tomography

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A growing number of seismological observations indicate that strong compositional variations are present in the Earth’s mantle. Meanwhile, considerable progresses in numerical modelling of convection have been achieved in the past decade. These include thermo-chemical convection, compressibility, and spherical geometry. Still, the mode of convection of the Earth’s mantle is not well constrained. Important efforts have been made to estimate values of the controlling parameters for the Earth’s mantle by testing various models against available seismological information. Linking convection models and seismological data is a delicate step that requires careful modelling of the thermo-chemical properties of the mantle aggregate. Statistical approaches, which account for all reported sources of uncertainties in thermo-chemical data and modelling, provide the possible ranges of thermo-chemical structure predicted by seismology. Here, we explore the model space of thermo-chemical convection. We run new 3D models of thermo-chemical convection (Figure 1) in which we vary important parameters and properties, including the buoyancy ratio and the volume of dense material, the mode of heating, the spherical geometry, and the presence of a phase transition at the bottom of the fluid. We then test snapshots of these models at different time against existing models of probabilistic tomography (Figure 2).

Figure 1. An example of thermo-chemical convection model. Iso-surfaces represent the fraction of dense particles (green C=0.5) and the non-dimensional temperature (red and blue, contour levels T=0.0375 and T=0.0375, respectively).

Figure 2. Comparison between spherical harmonic degrees 2, 4 and 6 of chemical density anomalies at the bottom of the mantle (2000<z<2891 km) predicted by thermo-chemical convection. (B=0.2, X=10%) and probabilistic tomography as a function of time.
Evidence for stable strontium isotope fractionation during chemical weathering

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The use of a sample–standard bracketing protocol during multicollector inductively-coupled mass spectrometry (MC-ICPMS) enables us to determine the stable isotopic composition of Sr in a variety of materials (rocks & minerals, soils, and water). These variations are reported relative to the standard NBS 987 in the standard delta notation ($\delta^{88/86}$Sr) with an external reproducibility of $\pm 0.06\%$.

We have measured $\delta^{88/86}$Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ of soil parent material (rock, mineral separates) and soils forming a ~150yr chronosequence in the forefield of the Damma Glacier in Central Switzerland. Minerals in the Hercynian granitoid rocks analysed show significant differences (0.3%) in $\delta^{88/86}$Sr, leading to whole-rock $\delta^{88/86}$Sr variations. Such differences are most likely due to postmagmatic events such as the subsolidus unmixing of alkali feldspars, or element remobilisation during a hydrothermal event or during Alpine metamorphism in the presence of fluids.

The $\delta^{88/86}$Sr of surface water tends toward lower values than average watershed lithology and is lower than that of seawater (Fietzke and Eisenhauer, 2006). Temporal variations of ~0.1% are observed and are most likely related to changes in discharge, either due to variations in subglacial water-rock interaction time or in the relative contribution of deep flowpaths to discharge.

The $\delta^{88/86}$Sr values of total soil digestions show a systematic trend from rock-like values (~0.2%) in the youngest soils to higher values (~0.5%) in the oldest. Unlike total soil $^{87}\text{Sr}/^{86}\text{Sr}$, these values cannot be explained by mixing between lithological endmembers, and thus require a preferential loss of isotopically light Sr during weathering, also indicated by the lower $\delta^{88/86}$Sr values observed in surface water. We propose that fractionation during dissolution of feldspars, during precipitation of secondary weathering phases and during biological utilisation are three possible mechanisms for the loss of isotopically light Sr.

This variation in total soil $\delta^{88/86}$Sr, together with heterogeneity in $\delta^{88/86}$Sr of the three main Sr-bearing minerals (plagioclase, K-feldspar, biotite) in granitoid rocks, has implications for studies of relative mineral weathering rates in granitic catchments. The combination of $\delta^{88/86}$Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ data provides a unique solution for three-component mixing, thus obviating the need for simplifying assumptions that are necessary when only radiogenic Sr isotope variations are discussed.

References

Modeling the effect of aging on Deccan Traps weathering and CO₂ consumption

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Basalts weathering account for 30 % of the CO₂ consumption through continental silicate weathering, and may have played a major role in past climatic crises. Since basalts weather rapidly with the subsequent formation of thick soils, the question of the effect aging on weathering rate is crucial. Indeed, in the absence of efficient physical erosion, it can be expected that basalt weathering slows down rapidly with time, thus reducing its impact on the climatic evolution. Here we present the results of a numerical model describing the effect of aging of the rate of weathering of Deccan Traps. The model design is a 20 box-model, based on the structure of the WITCH model. Fresh primary minerals are supplied to the bottom layer through bedrock dissolution, and to top layers as the “numerical” column goes down into the bedrock following chemical dissolution. At each time step, the chemical composition of the downward water flux is calculated within each box, as well as the dissolution of primary minerals and the accumulation of secondary minerals representing the « soil » formation. Both precipitation and dissolution rates are calculated within the framework of Transition State Theory using the best available data issued from laboratory experiments. The model is run for 1 million years until a steady-state is achieved, corresponding to a constant mineralogical composition in each layer and a constant chemical composition of the percolating waters. Calculated elemental ratios in solution are compared to the field measurements, as well as absolute concentrations.

Perturbations are then applied to the model, through the prescribed removal of several boxes at the top of the soil pile, in order to simulate enhanced physical erosion due to external factors, such as anthropic activities. The response of the CO₂ consumption rate to these perturbations is quantified.
The interplay between volcanism, tectonics and hydrothermalism on the Mid-Atlantic Ridge 4-11°S and globally

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Hydrothermalism on the slow-spreading Mid-Atlantic Ridge occurs either on-axis in places where excess volcanism has led to the construction of prominent axial highs (Menez Gwen, Lucky Strike, Turtle Pits, Lilliput) or off-axis in other regions (e.g. TAG, Rainbow, Logatchev, Saldanha). Both on- and off-axis systems appear, however, to draw their heat from similar, magmatic sources.

We present a model to explain the distribution of hydrothermalism on mid-ocean ridges, relating the frequency of volcanic events to the depth of the heat source and to the off-axis distance of the hydrothermal systems. Frequent eruptions produce hot crust and a shallow heat-source – fluids heated by this source exit close to its summit, i.e. on-axis (this is the dominant situation on the EPR, for example, where active off-axis hydrothermalism is almost unknown) and off-axis faults serve as recharge channels. When eruptions are less frequent, the shallow crust cools and hydrothermal circulation is only tapped by deeper-reaching faults related to the axial valley walls; hydrothermal venting migrates off-axis. The cooler the crust (and hence the deeper the isotherms), the farther off-axis venting will occur.

This model has predictive qualities: In areas with no bathymetric or side-scan evidence for abundant, recent volcanism, hydrothermal systems will be located exclusively off-axis. In areas dominated by tectonic spreading, not only will the hydrothermal systems be far off-axis, they will also be separated by large distances along axis due to aspect-ratio constraints. Satellite-based predicted bathymetry can, on the other hand, be used to identify on-axis highs with good hydrothermal potential.

Chemical weathering processes in sub-Saharan Africa: Evaluating controls at different spatial and temporal scales

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New insights into chemical weathering processes across a wide range of different climatic regimes were obtained from a combination of different methods: (i) long-term (> 50 years), high temporal resolution (monthly) records of river water geochemistry at more than 30 different sites and river systems with catchment scales varying from 625 to 650,000 km², (ii) analysis of river bedload material representing contrasting catchment lithologies, for geochemical proxies of chemical weathering intensity and catchment-to-coast geochemical transformations, (iii) geochemical characterization of surface soil samples, collected at ~ 900 km² sampling resolution within the catchments of river systems with ancillary river bedload and river dissolved load data records.

Chemical weathering rates as a function of different controls was evaluated in the context of both long-term and seasonal variations in river geochemistry. The data demonstrates the potential pitfalls associated with deducing weathering rates from once-off sampling surveys and provides important insights into which part of the hydrograph is most advantageous for such sampling strategies. Additionally, comparison with the chemical weathering potential of catchment lithologies and soils was made possible with the analysis of a large number of soil samples, with a new laser ablation q-ICP-MS method applied to powder briquettes, in conjunction with selective leaching experiments. The importance of consideration of the geochemical composition of catchment soils, in addition to that of unweathered bedrock lithologies, when evaluating lithology as a control on chemical weathering characteristics is demonstrated.
Factor analysis interpretation of Geochemical Atlas of Europe data

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Factor analysis was performed on the analytical results of different sample media of the FOREGS-EuroGeoSurveys “Geochemical Atlas of Europe” baseline project (http://www.gtk.fi/publ/foregsatlas/). It was found that the element associations for solid media (subsoil, topsoil, stream sediment and floodplain sediment) are very similar, whereas the pattern for stream water is completely different. This reflects differences in the mode of geochemical dispersion. In each case, the factor structure is little affected by the statistical procedure, indicating that the factors are rather robust.

In the solid media, over 60 determinands are reduced to 7 factors. Straightforward geological explanations can be given for factor 1 (rare earth and alkaline elements), factor 2 (ultramafic and ultramafic rocks), factor 4 (elements of felsic rocks), factor 5 (carbonate versus clastic silicate rocks), and factor 7 (siliciclastics and especially zircon). Factor 3 is related to grain size and inversely to sodium, with Fennoscandia standing out as a region with Na2O rich rocks. Factor 6 groups sulphur, phosphate, total organic carbon and several chalcophile elements typical of human pollution, such as Cd, Hg and Pb. The relative importance of these factors varies, and some interesting differences are apparent between the different solid media. Factors 1, 2 and 4 account for the largest part of the variance and show the most stable patterns.

The factor analysis interpretation of stream water data shows a completely different picture. Factor 2 is related to the general mineralisation of stream water, i.e. all major ions (Cl, SO4, HCO3, Na, K, Mg, Ca, Sr, etc.) have high loadings. Factor 1 is related, among others, to REE, Al, Fe, Zr and dissolved organic carbon, and inversely to pH; it groups acidic samples of low mineralisation, especially well represented in Fennoscandia. Factor 3 groups chalcophile elements such as Pb, Zn, Cd and Cu, and seems to be related to anthropic contamination. Influence of geological substrate is apparent in factors 4 (alkaline rock elements), 5 (W and Mo), and 6 (ultramafic versus felsic elements). Factor 7 is related to Mn, Fe and dissolved organic carbon, and factor 8 to elements such as As, Br, Na and Cl, influenced by salinisation through sea water, saline aquifers, or in the case of the southern Iberian Peninsula, deficient drainage in an arid climate. Factors 1 and 2 carry most of the total variance.

Dust and aerosol pollution from stationary man-caused sources in Novosibirsk city: Geochemical aperiodicities and numerical models

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The main sources of the air pollution in Novosibirsk besides transport are thermal power stations and plant facilities. In the winter time dust which they supplied are accumulated in blanket of snow. In that case, study and estimation aerosol pollution can base on snow survey data.

Snow sample was taken in the regions with man-caused pollution sources and in the regions without it for estimation of background. The level of pollution from each specific anthropogenic source was evaluated by ration average element concentration to average background value of this element. Thus for each element of considering man-caused source pollution level coefficients were calculate.

Concentrations of all analyzed elements in suspended part of snow samples in regions of Novosibirsk thermal power stations № 2 and №3 exceed background values at least at three times. The top concentrations in this region observed for Sb, Ge, Sn, Br, Cd, they are in 10-40 times more then background ones. In the region of Novosibirsk thermal power station № 5 in suspended part of snow samples predominate Br, Se, Mo, I, Sb, Sr. The list pollution level coefficients has Cr and Pb. Differences in emissions chemical composition enplanes various fuel types, thermal power stations № 2 and №3 used Kuznetsk bituminous coal, but heat power plant № 5 used mainly mazut, that verify high Br concentration in it emission.

In suspended part of snow samples in regions of Novosibirsk tin plant observed huge amount of Sn, it concentration in 255 times more then background ones, As - 166 times, Se – 68 times, Cd - 54 times, Sb – 12 times.

Solving inverse task of aerosol transport estimation was applied for forecasting pollution distribution from stationary source. It’s allow to aggregate parameters which can’t be measured (turbulence, particles deposition velocity and est.) and estimate they using natural measuring of pollution concentration in snow blanket.
Sensitivity analysis for a multisurface geochemical modelling approach

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Geochemical models such as surface complexation have been used to successfully describe the leaching of trace metals from different waste matrices. As the model complexity increases different tools need to be used to understand the effect a given input parameter has on the model output. This work extended the multisurface geochemical modelling approach to predict trace metals leaching behaviour in sewage sludge. The NICA-Donnan model was used to incorporate organic matter as a sorbent. The generalized two layer model was used to incorporate iron, aluminium and manganese oxides. Selective chemical extractions were conducted to determine the concentration of available surface sites. The model was tested against pH dependent leaching experiments and isotherm studies.

A sensitivity analysis was conducted to rank the relevance the different input parameters have on the model outcome, as well as to test the model robustness and reliability. The sensitivity analysis was carried out by defining uniform distributions for the input parameters. New sets of input parameters were randomly obtained by sampling the input distributions with a Monte Carlo method; and the model was evaluated. The uncertainty of the outcome was assessed by comparing the median, 5th, 25th, 75th and 95th percentiles from the output with the experimental values. There are different ways to evaluate the effects of the input parameters on the model outcome. One of them is to define best and worst sets of inputs by comparing the output to the experimental value. The best and worst input sets were described in terms of probability distributions and the two probabilities were compared using the Kolmogorov-Smirnov test to determine how likely they are to be the same distribution. This sensitivity analysis shows that the most relevant parameters in this model are solid and dissolved organic matter concentrations, concentration of iron oxides available for sorption, amount of metal available for sorption. Background analytes have different levels of relevance.

Toward calculation of the thermodynamic stabilities of proteins in the deep biosphere

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Microbes that thrive in the deep subsurface and other extreme environments depend for their survival on proteins and other biomacromolecules that are chemically distinct from their counterparts in organisms on Earth's surface. Among the variables that characterize different geochemical environments are oxidation state, hydration state, temperature, pressure, and pH. Although the advantages of a chemical thermodynamic assessment of the relative stabilities of inorganic species as a function of physical chemical variables have long been recognized, such an approach generally has not been used to study systems of proteins and other biomacromolecules. Assessment of the relative metastabilities of proteins as a function of these variables can now be performed, owing to 1) generation of group additivity equations of state parameters for calculating the standard molal thermodynamic properties of ionized proteins at high temperatures and pressures, and 2) the development of a computer software package for calculating the chemical affinities of biomacromolecular formation reactions and displaying predominance diagrams consistent with metastability constraints in systems of biomacromolecules. In this communication we present the results of calculations of the relative metastabilities of orthologous proteins from organisms adapted to different geochemical environments. For example, diagrams representing the relative metastabilities of surface-layer proteins from mesophilic, thermophilic, and hyperthermophilic species of Methanococcus have been generated as a function of oxygen fugacity, temperature, pressure, and pH. The locations of the predominance fields of the proteins correspond with the temperature and other geochemical characteristics of the environments inhabited by these organisms. These findings support the notion that energy minimization in systems of representative proteins provides a thermodynamic driving force for the evolution of biological species, and also provide evidence that a thermodynamic assessment of the relative metastabilities of proteins can be used to predict the physical chemical limits on their occurrence in different environments. Because the current approach takes account of the relative metastabilities of different proteins, it permits explicit assessment of relations between different proteins and the physical chemical characteristics of geochemical environments. Hence, we also discuss calculations of the effects on protein metastability of potential biogeochemical oxidation-reduction buffers which may be composed of mineral or organic species, or both. Continued development of the thermodynamic calculations and integration with experimental observations may contribute significantly to our understanding of the fundamental forces involved in the interaction between microbes and their environments.
Fe isotope fractionation induced by aqueous Fe-siderophore complexes

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The equilibrium Fe isotope fractionation induced by organic ligands was determined by experiments with pH 2 solutions that had coexisting inorganic Fe(III) species (Fe₅⁶) and siderophore complexes, Fe-desferrioxamine B (FeDFOB).

In the experiments, the two differently complexed Fe pools were separated by addition of Na₂CO₃, a method previously applied to separate aqueous Fe(II) and Fe(III) [e.g. 1]. Tests showed that the addition of Na₂CO₃ scavenged the inorganic Fe quickly and effectively, without causing significant dissociation of FeDFOB.

Preliminary experiments using enriched ⁵⁷Fe tracer indicate that isotope equilibration between the ⁵⁷Fe-labelled inorganic species and the isotopically “normal” Fe of the organic species was minor during the 1 s precipitation induced by Na₂CO₃ addition. Although Fe isotope fractionation during precipitation may cause some changes in the isotope composition of the Fe₅⁶, the results suggest that only negligible isotope re-equilibration occurs within the time of the separation, meaning that precipitated Fe faithfully records the Fe isotope composition of Fe₅⁶ and the remaining FeDFOB.

In experiments with starting solutions having δ⁶⁶Fe = 0.76 ‰, desferrioxamine-complexed Fe has δ⁶⁶Fe ~ 1 ‰, whereas inorganic Fe has lighter δ⁶⁶Fe ~ 0.5 ‰. This indicates that co-existing Fe-desferrioxamine B and inorganic Fe complexes have an equilibrium Fe isotope fractionation of 0.5‰ at a temperature of 25 °C. This value is comparable to the kinetic Fe isotope fractionation induced by desferrioxamine-promoted dissolution of hornblende [e.g. 2], suggesting that equilibrium Fe isotope fractionation induced by strongly coordinating organic ligands may fractionate Fe isotopes strongly in seawater, where above 99 ‰ of aqueous Fe is bonded by such ligands.

References


Ocean crust formed from E-MORB overlying an ultra-depleted mantle on Macquarie Island: Implications for mantle heterogeneity

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Macquarie Island (Southern Ocean) is a fragment of young (Miocene) ocean crust and upper mantle uplifted and exposed above sea-level in an entirely intra-oceanic setting, without being obducted onto a continental margin. As such, it is unique in the world and it is generally considered as an important type-locality of oceanic crust and mantle and as a key link between oceanic basement and ophiolites. Several workers have pointed out the similarity between the crustal section on the island and the 'classical' ophiolite sequence. Recent work has, however, shown that the formation history of the island is more complex than originally envisaged.

There is evidence form field relations that the volcanics, dykes and gabbrics were formed during different magmatic episodes and it seems unlikely that the main crustal units are co-magmatic. We have dated the formation of the gabbrics at 9.0-8.6 Ma (U-Pb zircon SHRIMP ages). Secondly, the volcanic rocks on the island are unusual: there are few N-MORB and the majority of the volcanics are strongly incompatible element enriched E-MORB (La/Sm<8). Moreover, our new geochemical data show that the dykes, evolved gabbrics and cumulate rocks on the island are derived from parental melts that range from slightly depleted to enriched MORB, but that they were significantly less enriched (La/Sm<5) than the volcanic rocks on the island, ruling out a co-magmatic origin. Nd isotope data confirm that there is little compositional overlap between the parental melts of the gabbroic rocks (εNd(9Ma)=-7.8-9.3) and the volcanics (εNd(9Ma)=+7.2-8.3).

In addition, we will show that the mantle harzburgites on the island are much more depleted (residue of >20‰ near-fractional melting) than expected from the tectonic setting and slow spreading rate of the Macquarie paleo-ridge system. Their ultra-depleted character is also inconsistent with the thin magmatic crust (<3 km), and with the highly enriched character of the volcanics. This means that these mantle rocks are not the source residue of the magmatic rocks and that their depleted character is the result of an earlier melting episode.

We will attempt to tie these disparate observations into one model for the formation of the oceanic basement section on Macquarie Island. The parental magmas that formed the crust were probably derived from enriched and isotopically distinct lithological heterogeneities within the mantle, with a limited contribution from depleted mantle. Over a short time interval (~1 My), the input of enriched melts increased dramatically due to changes in the magma plumbing system, in the spreading geometry, or in the nature of the mantle material entering the base of the melting domain underneath the ridge system.
Neoproterozoic (~ 850 Ma) subducting in the Jiangnan orogen: New SHRIMP age of the Fuchuan SSZ-ophiolite, South Anhui, China

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The Jiangnan orogen separated the Yangtze continental terrane in the northwest and Cathaysia continental terrane in the southeast of the South China plate, the northeastern boundary of which is marked by the Fuchuan belt, the largest ophiolite block in South China. The Fuchuan ophiolite is represented by two tectonically distinct ophiolitic units: (1) the mantle peridotite unit, mainly composed of massive harzburgites; (2) the lava unit, including pillow lavas and cumulated rocks (dunite – whelrite – gabbro). Massive harzburgites are medium to heavily serpentinized, the high Cr2O3 (0.9-1.3 wt%) abundances of clinopyroxene in about 35% partial melting of a primordial mantle source. The Fuchuan harzburgites formed in the suprasubduction zone (SSZ), and thought as a residue after the subduction of the Jiangnan Ocean started before ~850 Ma. We infer that the Yangtze continental terrane and the Cathaysian continental terrane started to weld together at least before 827–849 Ma, which is consistent with the conclusion described early by Zhao and Cawood [5].

Acknowledgment

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References


Silicon isotope compositions of the underground water, limestone and soil from Karst caves in Guilin City, Guangxi, China

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Silicon isotope variation in hydrosphere catches more attention of geochemists recently. Several studies have been done on silicon isotope compositions of oceanic and riverine water [1,2]. Significant variation of silicon isotopes is discovered in these environments, indicating fine prospects of using silicon isotope to study hydrological processes and silicon circulation. We know that underground water is an important part of hydrosphere. However, no results on its silicon isotope composition have been reported by now.

A silicon isotope study on underground water has been carried out. Some results on silicon isotope compositions of the underground water, limestone and soil from the karst caves are reported here. All samples were collected from Panlongdong and Xiaoyandong karst caves in Guilin city, Guangxi, China.

The δ30Si values of underground water in these two caves vary from 1.4‰ to 1.9‰, with average value of 1.65‰. The δ30Si values of trace silicon in limestone from two caves vary from -0.2‰ to 0.3‰, with average value of 0.05‰. The δ30Si values of soils from these caves vary from -0.5‰ to -0.2‰, with average value of -0.4‰. No silicon isotope datum has been obtained for stalagmite, for its silicon content is too low. These results indicate that in the weathering process of limestone in the karst area, the produced soil tends to be enriched in 28Si and the dissolved silicon in underground water tends to be enriched in 30Si. These observations provide useful information for silicon transportation in continental environment.

References

Different mobility of Nb and Ta along a thermal gradient

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Niobium and Ta have long been regarded as “identical twins” because of similar geochemical behaviors during processes linked to the evolution of the Earth’s mantle. A recent study indicates major Nb/Ta fractionation in subducted slab setting, which was used to interpret the systematically lower Nb/Ta in the continental crust compared to the mantle (Xiao et al., 2006). Here we report an experiment which shows that Ta and Nb are mobile and can fractionate from each other during migration in a temperature gradient.

A homogeneous andesitic powder (AGV-1) along with 4 wt% H2O was sealed in a 20 mm long double capsule, compressed to 0.5 GPa and run in a temperature gradient ranging from 950-350 ºC for 66 days. The run product was analyzed using JEOL 8100 electron microprobe and laser-ablation inductively-coupled-plasma mass spectrometry for major and trace elements, respectively.

The results show large variations in Nb and Ta concentrations as well as Nb/Ta along the temperature gradient. In the matrix of the low-temperature section that contains no melt, the Nb/Ta ranges between 7.5 and 24.8, with supra-chondritic value near the low temperature end and sub-chondritic value at adjacent higher temperature region. More specifically, the highest Ta concentration is observed close to the section where amphibole is present. As the temperature decreases further, the Ta concentration drops quickly to considerably lower than that of the starting material, indicating net transportation of Ta from both low and high temperature ends towards the intermediate temperature region. By contrast, the highest Nb concentration is observed in the lower temperature end, ~3 mm away from the Ta peak. The different migration patterns of Nb and Ta result in the large fractionation of Nb/Ta in the amphibole absent section.

We interpret that variations in Nb and Ta concentration and Nb/Ta to reflect a thermal migration process during which Nb and Ta partition between supercritical fluid and different minerals, likely driven by chemical mobility difference between Nb and Ta. Different thermal migration provides a feasible mechanism to produce lower Nb/Ta in the lower continental crust compared to the upper continental crust.

Formation history of Archaean TTG gneisses in the Taihua complex, Lushan area, central China: in situ U-Pb age and Hf-isotope analysis of zircons

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The Taihua complex is discontinuously exposed along the southwest margin of the North China Carton (NCC). It can be divided into two main rock units, naming quartzofeldspathic gneisses and supracrustal rocks. Among these rock units, tonalite–trondhjemite–granodiorite (TTG) gneiss is the dominant rock type, making up 80% of the total exposure of the Late Archaean basement (Zhang et al., 1985). Zircon grains of TTG gneiss are euhedral, and have oscillatory zones with high Th/U ratios (0.20-1.49), indicating their igneous origin. The LA-ICP-MS zircon U-Pb dating yields age population at 2.8 Ga, representing the TTG magma emplaced at 2.8 Ga. Zircons from gneiss have variable Hf isotopic compositions with 176Hf/177Hf ratios from 0.281021 to 0.281189 and εHf(t) values from +0.68 to +7.09, with a weighted mean of 2.2±0.8. It is suggested that the protoliths of the gneisses were mainly derived from depleted mantle, Correspondingly, their Hf model ages are 2924–3059 Ma (TDM1), with a weighted mean of 2966 Ma. TDM1 model ages, which are calculated using the measured 176Hf/177Hf of the zircon, can only give a minimum age for the source material of the magma from which the zircon crystallized. Therefore zircon Hf isotopic data reveal that crustal component older than 3.0 Ga may exist in Lushan area, and zircon debris of this age have been found.

Acknowledgments

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References

Trace element fractionation during exsolution of garnet from clinopyroxene in an eclogite xenolith from Obnazhennaya (Siberia)

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A large (3 cm) Al-rich clinopyroxene megacryst from a bimineralic eclogite xenolith from Obnazhennaya kimberlite pipe contains 3 sets of garnet exsolution lamellae crystallized in sequence apparently as a result of slow cooling at depth. Thick lamellae (up to 1500 µm, Py38Alm30Gross22) crystallized first and were followed by medium-sized ones (up to 500 µm, Py40Alm27Gross33) and thin ones (50-100 µm, Py34Alm26Gross40). LAM-ICP-MS analysis of the different generations of garnet lamellae indicates the progressive depletion of trace elements compatible with garnet (HREE, Y and Sc) during the course of exsolution (see figure below):

Variation of trace elements in the garnet lamellae and their host clinopyroxene suggests a diffusion-controlled trace element fractionation during cooling and garnet exsolution. The preservation of the fractionated trace element patterns in the exsolved garnets, as well as the diffusion gradients in the host clinopyroxene indicate that cooling and exsolution occurred shortly before the xenolith was entrained by the kimberlite melt.

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Partial melting and melt extraction in Acapulco-Lodran achondrites

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The differentiation of first planetary bodies at the metamorphism-partial melting transition, in the inner solar system, is an important petrological process that can help to understand the first stages of the Earth. This study is based on mineralogical, petrological, major and trace elements, melting models, and microstructural relationships. Mineralogical and modal composition of Lodran display that experienced high temperature (1150-1200°C) and extensive partial melting of silicates (30-35% for melt fraction), metal and sulfides. The silicate melts display dacitic compositions related to the breakdown of Na-Ca plagioclase, clinopyroxene and spinel. Using H or CR chondrites and Acapulco as precursor for Lodranite, melting models can’t explain low-Ca pyroxene abundance. On the other hand, the systematic occurrence of “Fe-rich” olivine (Fa17) as inclusion in low-Ca pyroxene in contrast with large tabular crystal of magnesian olivine (Fa0) support the idea of a reaction between silicate melt with Fe-richest olivine to produce orthopyroxene associated with a reduction process before/during melt extraction. The heat source that initiated the melting was probably the short-lived radionuclides such as 26Al. If we consider the extraction of dacitic melt from Lodranites precursor then it can lead to a heterogeneous thermal evolution of these small bodies. To understand the melt extraction process, we analyse the lattice-preferred orientation (LPO) of silicates, sulfides and metal by EBSD technique. Indeed, mechanical processes must induced deformation and LPO. The result is that any LPO was observed except in troïlite. We can conclude that silicate melt migrate at grain boundaries using surface tension and sulfide melt was interconnected. During cooling, formation of a single troïlite crystal occurs and post-magmatic recrystallisation can explain the preservation of the high LPO in troïlite.
Experimental determination of Ca-Sr distribution between zoisite-fluid and lawsonite-fluid

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The distribution of Sr between a 1 molar (Ca,Sr)Cl2 solution, (Ca,Sr)-zoisite and (Ca,Sr)-lawsonite was determined at 600°C, 2 and 4 GPa. The synthesized crystals of (Ca,Sr)-zoisite and (Ca,Sr)-lawsonite are homogeneous in electron microprobe analysis. The results indicate that Ca2+ can be replaced completely by Sr2+ at the M1 and M2-site in zoisite and at the M1-site in lawsonite. However, Rietveld refinement of the solid run products with site occupation refinement show that the larger M2 site in zoisite is preferred by Sr in the range X_{Sr}^{Zo} 0 – 0.40. Powder diffraction data show a phase transition in the lawsonite solid solution at X_{Sr}^{Law} ≈ 0.24 with a change of the space group from Cmcm to P21/m.

The compositions of the product fluid were analyzed by inductively coupled plasma emission spectrometry. In both the (Ca,Sr)-zoisite-fluid and (Ca,Sr)-lawsonite-fluid systems, Sr fractionates preferentially into the fluid, similarly as at low pressure for Ca-Sr-margarite, anorthite and carbonate (1).

The mixing energies of the solids were calculated using a regular solution model. In the (Ca,Sr)-lawsonite-(Ca,Sr)Cl2 system, ∆µ0 is 4.1 kJ and WlawCaSr = 9.3 kJ. In the system (Ca,Sr)-zoisite-(Ca,Sr)Cl2 the mixing energies for the M2 site were calculated and ∆µ0 is 11.0 kJ and WzoCaSr is –5.1 kJ.

The high ∆µ0 values and, to a much lesser extent, the W_{CaSr} values cause the preferred fractionation of Sr into the fluid. The observed lawsonite and zoisite structures within the solid solution series as well as the moderate values for W_{CaSr} strongly suggest that complete solid solution series exists for (Ca,Sr)-lawsonite and (Ca,Sr)-zoisite.

References

Petrology and geochemistry of Cemilköy Ignimbrite, Cappadocia, Turkey

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In this study, petrological and geochemical characteristics of the Cemilköy ignimbrite, in the Cappadocia region, located in the Central Anatolian Volcanic Province were identified by more detailed examination. The Cemilköy ignimbrite is composed of ash-size volcanic material, normally graded pumices and inversely graded lithic (volcanic and ophiolitic) clasts. Pumices are distinguished from other ignimbrites in the region by a slaty fabric. Mineralogical and petrographical studies show that pumices consist of plagioclases, biotite, quartz, amphiboles and oxide phenocrysts and microcrysts. Predominantly, vitrophyric-porphyrctic fabric is observed in the pumices. Plagioclase phenocrysts are identified as bytownite- oligoclase (An47-19) in composition and they are normally zoned. As a result of geochemical examinations, it has been determined that the Cemilköy ignimbrite is rhyolitic in composition and shows calcalkaline characteristics. The effect of fractional crystallisation process in the formation of the Cemilköy ignimbrite is observed from major and trace element versus SiO2 diagrams. The Cemilköy ignimbrite is enriched with LILE and LREE contents, indicating that not only fractional crystallization process but also subduction and/or crustal contamination processes were effective. A negative anomaly trend of Nb and Ta elements in spider diagrams, the ratio of Ba/Nb>28 (56-77) and the location of all samples in subduction-related volcanic arc granites area in a Rb-Y+Nb discrimination diagram point to the effect of subduction process. As a consequence, Cemilköy ignimbrites appear to have been produced from the magma that derived by partial melting of OIB-like mantle which was enriched by subduction process and also assimilation–fractional crystallization (AFC) process was effected on evolution of these ignimbrites.
Modeling of dehydrogenation of olivine during magma ascent

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Despite the recognised crucial role of H in affecting so many processes and rates of the deep Earth, the actual amount of H contained in Nominally Anhydrous Minerals (NAMs) in the mantle remains unclear. The H content in olivine from mantle xenoliths or megacrysts transported by magmas in different tectonic settings is highly variable from about <1 ppm to ca. 400 ppm H₂O (e.g., Beran and Libowitzky, 2006). This could reflect variable local water contents in the mantle, different transport histories of the olivines and host magma, or a combination of the two. The possibility of H loss from the olivines during magma transport is supported by the experimentally determined H diffusion rates in olivine (e.g., Mackwell and Kohlstedt, 1990) and by the H gradients in natural crystals (e.g., Demouchy et al., 2006). However, much uncertainty remains as to the significance of both, the maximum water contents, and the H profiles, since the effect of the ascent paths and conditions have not been considered, e.g. water saturated vs. undersaturated or multi-stage histories.

Here we present results of a dehydrogenation diffusion model of olivine that clarifies under which conditions of transport times, crystal sizes, and magma decompression paths the H content measured from naturally occurring olivine may reflect the original water content of the upper mantle. We find that even for a grain size of 2 cm, magma ascent rates of > 10 m/s are required to preserve at least most (e.g., 90 %) of the initial water content of an olivine orginated from the mantle. The simulations also show that (i) homogeneous H distribution within naturally occurring NAMs may indicate extensive diffusive loss of H rather than being representative of upper mantle H concentrations as is commonly assumed, (ii) a short stage of a few days in an intermediate magma reservoir prior to eruption completely re-equilibrates the water content with the new low pressure environment, even for crystals several cm in size. The fast rates of ascent required to preserve the highest water contents suggest that the H contents of natural crystals reflect the transport path of their magma rather than their mantle sources.

References

Thermodynamic model for the simultaneous exsolution of two fluids from silicic magmas

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Chlorine is the predominant constituent in magmatic and hydrothermal fluids. From intrusive to shallow epithermal settings the salinity and composition of hydrothermal fluids changes dramatically and this is partly due to the subcritical phase separation in the H₂O-NaCl system. It is still unclear (1) what is the salinity of exsolving magmatic fluids, (2) whether one or two fluid phases simultaneously separate from the magmas, and (3) how analytical data from melt inclusions can be linked to fluid chemistry or be used to monitor the devolatilization paths. We propose a new thermodynamic model for chlorine in silica-rich melts that is based on Darken’s formalism for solute in a multicomponent solvent. Thermodynamic properties of NaCl are related to the molten-salt standard state via the increment, I_{NaCl} (kJ) = 11 + 0.03 T(K) - 1.33 p(kbar), which was calibrated by experimental data on the chlorine solubility in granite melts. Interaction between NaCl and H₂O in the melt structure is defined by the regular solution parameter, W_{NaCl,H2O} (kJ) = -53 + 0.04 T(K) + 2.67 p(kbar). Properties of the H₂O-NaCl-KCl fluids are described by the Kosinski-Anderko-Pitzer equation of state. Phase equilibrium computations in the granite-H₂O-C12O3 space reveal existence of a temperature minimum at 5.4 wt. % H₂O and 0.13 wt. % Cl in the melt (at 200 MPa) where very small changes in the melt Cl/H₂O ratio produce large variations in the fluid salinity. At subcritical conditions, the thermal minimum becomes an invariant point (Cl/H₂O = 0.037 at 100 MPa) where all differentiation paths of chlorine-bearing granitic magmas terminate by simultaneous saturation with the vapor and brine. Here the Cl and H₂O concentrations in the melt remain invariantly buffered despite the fact that the largest amount of fluids is produced at this stage. The thermodynamic model demonstrates that: (1) experimental data require only minor deviations from mixing of halide and aqueous components in the melt, i.e., the trends of chlorine and water solubilities are largely related to non-ideal activity-composition relationships in the aqueous fluid, (2) natural silicic magmas with Cl/H₂O < 0.04 first saturate with a low-density aqueous vapor and subsequently exsolvoc concentrated brines at the solids; decompression favors vapor saturation whereas crystallization promotes brine separation, and (3) realistic predictions of metal to hydrothermal fluids must consider both the melt-brine and melt-vapor partitioning. It remains to be understood whether the “vapor-then-brine” mechanism of fluid saturation in the shallow-level magma bodies promotes the vapor-mediated metal transport or it leads to metal enrichment in the melt up to high degrees of fractionation, followed by partitioning to late-stage brines. The new thermodynamic model offers the missing link between the melt and fluid chemistry in crustal magmatic reservoirs and it can be used in quantitative modeling and interpretation of devolatilization and ore-forming processes.
Dissolved quartz in supercritical water: Insights from ab initio molecular dynamics simulations

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We have carried out ab initio molecular dynamics (AIMD) simulations of \(\text{SiO}_2\) in supercritical water at temperatures of 900 K and 1200 K and a pressure of 1.5 GPa at concentrations of 5 and 16 wt% [1]. The different polymeric forms monomer (\(\text{SiO}_4\text{H}_4\)), dimer (\(\text{Si}_2\text{O}_7\text{H}_6\)), and trimer (\(\text{Si}_3\text{O}_{10}\text{H}_8\)) are found to be stable during the 10 ps time span of the simulations. A Raman spectrum recorded of the \(\text{SiO}_2/\text{H}_2\text{O}\) fluid in a diamond-anvil cell, comparable to spectra presented in the literature [2-4], has been compared to the vibrational spectra obtained from the AIMD simulations by Fourier transform of the velocity autocorrelation function. Determination of relative monomer and dimer concentrations from the relative intensities of the Raman bands is found to be problematic as both species contribute to the most intense band [1]. The mechanism of dimerisation and the associated free energy profile along the reaction coordinate have been obtained using coordination-constrained AIMD together with thermodynamic integration [5-7]. The calculated relative free energies of monomer and dimer suggest that both species should coexist at high P, T conditions.

References

Characterization of carbon materials in metasediment hosted gold deposits (NW Portugal) by micro-Raman spectroscopy

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Introduction
Micro-Raman spectroscopy (MRS) is a powerful technique used for the characterization of dispersed carbon materials (DCM) in metasediments, giving information about their evolution during metamorphic process (graphitization).

The aim of this study is to characterise the DCM by MRS in order to estimate the maximum P-T conditions reached during regional metamorphism.

Results
Using a Labram Dilor-Jobin Yvon spectrometer attached to an Olympus microscope and an excitation of 633 nm lines of a He-Ne laser, MRS analyses were performed on samples from metasedimentary rocks of borehole cores obtained during an exploration survey at Três-Minas roman open-pits. The criterion of sample selection was the presence of non-outcropping black-carbonate lithologies. Four samples were studied and ten Raman spectra were recorded for each sample.

The first-order Raman spectrum of DCM exhibit a graphite G band at around 1580 cm\(^{-1}\) and defect bands D2 around 1616 cm\(^{-1}\) and D1 around 1332 cm\(^{-1}\). For the second-order spectrum a symmetric S1 band and a broad S2 band appear near 1700 cm\(^{-1}\) and 1900 cm\(^{-1}\), respectively (Fig.1).

Figure 1: Representative Raman spectra obtained for DCM at Três-Minas.

After the calculation of the Raman parameters for the different first-order Raman spectrum and using Beyssac et al. (2002) graphite geothermometer in order to estimate the peak temperature of metamorphism the obtained temperatures are in the range of 360 to 490 °C.

This data will be further compared and constraint with others geothermometers, fluid inclusion and mineral assemblages.

References
Specific gas composition of the adsorbed form in impactites of the diamond-bearing Mongolian astropipes

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The new methodics
At present scrutiny of the adsorbed form of gas in rocks of diamondiferous provinces is new acknowledgement of an elaboration and sampling of the intraditional prospecting methodics.

The new results
According to Dorjnamjaa et al. (1) the Agit Khangay, Khuree Mandal Tsenkher, and Bayan Khuree diamond-bearing ring impact astropipe structures are established for the first time in Mongolia. These astropipes are wonderfully-preserved from erosion and active denudation, and characterized by both well natural exposures and diversity of different impact-derived and shocked magmatic rocks and minerals. The Agit Khangay astropipe is the most detailed studying meteorite structure.

The Agit Khangay astropipe in western Mongolia was formed at the Permian granite massive. The crater’s total diameter is about 10 km and filled with shattered and shocked granite (agizit). Most panned samples and hand specimens contain microdiamond of octahedron habit, gold, platinum, moissanite, pyrope, rhenium, coesite, khamarabaevite (TiC), graphite-2H, etc.

Conclusions
The adsorbed form of gas in the Mongolian astropipe impactites (Agit Khangay-sample 32/99, Khuree Mandal-sample 58/03, Bayan Khuree-sample 17/03) has been compared with gases of analogous form in volcanic rocks of modern (Volcano Gorelii, Kamchatka) and ancient (Maikhant-sample 25/04 and Zuun Busluur-sample 36/04., volcanoes, Dariganga plateau, Mongolia) eruption and kimberlite pipes (Victory-1, Shandun province, China).

Detailed geological and gas-geochemical investigations shows diamondgenesis is the expression of the collision of the lithospheric mantle with meteor impact collsaps explosion process. The essence of the phenomenon is mantle manifestation and plume of the combined nuclear-magma-palingenesis interaction.

References

Statistical determination of geochemical data to evaluate Oelberg-basalt as a geochemical reference material

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Modern geochemistry allows very accurate and precise measurements, however the critical part is still the sampling. On the basis of statistical observations unaltered-tertiary basalt in the Northern Hessian Depression, Germany from a quarry of the German Basalt – Corporation are analysed. The aim of this study is to evaluate this alkali-olivine basalt from the Oelberg/Hessisch Lichtenau for its potential as being geochemical reference material. Hence, the samples are taken systematically by hand over a 500 m long profile in a distance of 5 to 10 m and of 5 kg each. Furthermore, from the operatingresher of the quarry of different fractions are taken as well for random sampling.

Besides macroscopically and microscopically petrographical investigations of each sample selected phases (xenoliths, crystalline and glassy matrix) are studied in detail by EMP. In addition to phase analyses by EDX on selected mineral separates some bulk analyses were performed. For the bulk rock chemistry the samples were crushed in steel crushers and milled down to fine powder of <125µm in an agate mill. After each step the sample are controlled for impurity, stepwise minimized and homogenised. All samples are analysed for major and minor element concentrations by XRF using smelting tablets. Minor and trace elements are studied by ICP-OES and ICP-MS. The measurements are performed as repeat determination. To control the accuracies and precision of the measurements reference material were analyses in addition (BHVO-1 and BB). The BB is an in-house reference basalt from the University of Göttingen (BB) from the Northern Hessian Depression.
Thermal stability of soil organic matter pools under elevated CO₂ and their turnover times calculated by δ¹³C and δ¹⁵N values

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Various SOM fractionation approaches (density, particle size, chemical extractability etc.) have been applied to estimate C and N turnover rates in SOM pools. The thermal stability of SOM coupled with C and N isotopic analyses has never been studied in experiments with FACE. We tested the hypothesis that the mean residence time (MRT) of SOM pools is inversely proportional to their thermal stability. Soil samples from FACE plots under ambient (380 ppm) and elevated CO₂ (540 ppm; for 3 years) treatments were analyzed by thermogravimetry (TG) coupled with differential scanning calorimetry (DSC). Based on TG, five SOM pools were distinguished. Soil samples were heated up to the respective temperatures and the remaining soil was analyzed for δ¹³C and δ¹⁵N by IRMS. Energy consumption and mass losses in the temperature range 20-200°C were mainly connected with water volatilization. The maximum weight losses occurred from 200-310°C. δ¹³C values of SOM pools under elevated CO₂ treatment showed an increase from -34.3‰ (20-200°C) to -18.1‰ (>480°C). The incorporation of new C and N into SOM pools was not inversely proportional to their thermal stability. SOM pools decomposed at 20-200 and 200-310°C had 2% and 3% of new C, with a MRT of about 60 years. The pool decomposed between 310-400°C had 22% of new C, with a MRT of 12 years. The amount of fertilizer-derived N decomposed at 20-200°C had 22% of new C, with a MRT of 149 years. In contrast, the pool decomposed above 480°C had only 0.5% of new N, with a MRT of more than 400 years in soils under both treatments. Thus, the separation of SOM based on their thermal stability was not sufficient to reveal pools with contrast turnover rates of C and N.

The timescale of sediment transport in a small tropical watershed

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How fast are sediments produced, stored and transported in a watershed? This question has important implications for understanding the transfer of carbon, nutrients and pollutants from their continental sources to the oceans. Sediment transport times can be inferred indirectly through the measurement of erosion rates, however uranium-series isotopes have the great advantage of providing a direct measurement of the residence time of sediments in a catchment. Most previous studies have focused on large basins (e.g. Amazon [1,2], Mackenzie [3]), yielding important insights on timescales of sediment transport and chemical weathering. However, the provenance and path of sampled sediments are not well-constrained. In this study, we chose to focus on small catchments (less than a few km²) to quantify how much time sediments reside in a tropical watershed where landslides are the dominant agent of physical denudation.

The study area is located in the rainforest of the Luquillo Mountains, Puerto Rico. River suspended and bedload sediments have been analyzed for ²³⁸U-²³⁴U-²³⁰Th and ²²⁶Ra isotopes. Assuming that sediments have followed a single, continuous weathering evolution since their production from the bedrock, we inferred that the time elapsed between the onset of bedrock weathering and export of sediments out of the catchment is 100 – 200 years. This constrasts with previous estimates for rivers around the world (1,000 – 500,000 years [1-4]) and is best explained by the landslide-dominated nature of erosion in this region, which delivers to the river weakly weathered soil particles.

Soil profiles will also be studied in order to understand the rate of development of the weathering profile in this region and how physical erosion and sediment transport relate to weathering profile evolution.

References
Geochemical Segmentation of the Pacific Antarctic Ridge

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Samples collected during the PACANTARCTIC 2 (PAC2) cruise fill a sampling gap from 53° to 41° S on the Pacific Antarctic Ridge (PAR). Therefore it becomes possible to have a picture of the geochemical variations along the PAR from 65°S to the Juan Fernandez microplate.

PAC 2 data together with a compilation of published Sr, Nd, Pb, Hf and He isotopic analyses show geochemical variations related to first order tectonic discontinuities. One example occurs at the Eltanin fracture zone. Another example is within the PAC2 study area at 50°S where a major transform fault, Menard TF, marks the boundary between two geochemical domains. To the south of Menard TF, trace element and isotope ratios are depleted and more variable than to the north where the variations are more subdued and the geochemical parameters indicate a more enriched source. These geochemical variations reveal large-scale chemical and morphological divisions of the Pacific mantle.

At a smaller scale, the regular sampling of the different segments, limited by overlapping spreading centers along the 53–41°S ridge section, shows regular variations in geochemical parameters. Most of the 100–260 km long segments are depleted with \( \text{Nb/Zr}_N < 1 \). The centers of the segments have higher \( \text{Nb/Zr}_N \) and more radiogenic Sr isotope ratios than the segment ends where the ridge becomes less robust. This small-scale geochemical segmentation together with observed variations of geophysical parameters suggests small-scale mantle flow below the ridge. However, this regular small-scale variation is locally affected by the presence of nearby off-axis volcanoes which define a pseudomicroplate. The consequences at the ridge axis are both morphological and geochemical. They are revealed by a slight change in the ridge axis direction associated with atypical geochemical signatures of the ridge basalts. Kinematic reorganization of the Pacific Antarctic plate boundary is likely responsible for these features.

Isotope evidences for the origin of Cape Verde oceanic carbonatites

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Carbonatite rocks are found on every continents, except Antarctica. However, their occurrence in an oceanic setting is very rare and oceanic carbonatites have been reported only at the Cape Verde and Canary archipelagos. More precisely, they have been found on five out of ten islands of the Cape Verde archipelago, and on only one (Fuerteventura) amongst seven islands of the Canaries.

Geochemical studies based on stable, radiogenic and noble gas isotope systematics have led to the general consensus that parental magmas to continental carbonatites originate in the mantle. For oceanic carbonatites, their mantle origin is not debated either. They have been associated with the mantle plumes at the origin of the Cape Verde and Canary archipelagos (Hoernle et al., 2002; De Ignacio et al., 2006).

Here, we report new Sr-Nd isotope data, as well as major- and trace-element contents measured on 15 Cape Verde carbonatites (whole-rock samples and separate phases) collected on the islands of Brava, Fogo, Santiago and São Vicente. We discuss the relationship that exists between isotope data and the geographical location of carbonatites in the Cape Verde archipelago. That way we determine the best representative isotopic composition of the carbonatites parental magmas (pristine melts) and focus on the comparison between distributions of (i) carbonatite chemical compositions and (ii) basaltic rocks of the Cape Verdes. Finally, we discuss two alternative models for the origin of carbonatites: (1) partial melting of a HIMU-like Cape Verde plume component; and (2) plume-induced melt generation within carbonatitic metasomatized oceanic lithosphere domains.

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References
Geochemical interactions between nitroaromatic (TNT) and nitramine (RDX and HMX) explosives and sediments

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Training with artillery, mortars, hand grenades and small arms containing nitroaromatic (e.g., TNT) and nitramine (e.g., RDX and HMX) explosives is common at military training installations worldwide. Adsorption and transformation reactions of explosives are sensitive to the composition and geochemical conditions in the soils and sediments onto which they are deposited. Thus the geochemical relationships between training range sediments and explosives affect range sustainability, environmental stewardship and site remediation options. Our work addressed fundamental relationships between soil and water geochemistry and explosives degradation through two laboratory experiments.

First, we quantified the breakdown of TNT, RDX and HMX in surface waters containing different concentrations of sediment and dissolved organic carbon. Samples spiked with 10 different explosives and explosives breakdown products were sampled over 85 days and the explosives and breakdown products were measured. We found that the presence of either dissolved organic carbon or fresh mineral surfaces promoted the breakdown of nitroaromatics TNT, 1,3,5-trinitrobenzene and tetryl. RDX and HMX concentrations remained stable in all samples as expected. Concentrations of all explosives phases remained constant in 18Mohm-cm control water throughout the exposure period suggesting that either an organic substrate or a mineral surface is required to facilitate explosives transformation or breakdown.

In a second aspect of the study we investigated the interaction between explosives and freshly fractured mineral surfaces to assess the effects of detonation shock on the interactions between explosives species and sediments. Three different surface sediment samples were crushed with a 50,000 psi steel plate to simulate blast fracturing. Uncrushed “pristine” sediments were sieved using size fractions similar to the crushed samples. Column and batch experiments using waters spiked with TNT, HMX and RDX were applied toward investigating the reactive transport of explosives through the crushed versus pristine sediments. Grain surface morphology was examined by scanning electron microscopy. TNT in some of the columns comprised of fractured sediment showed greater retardation compared to the columns with pristine sediment suggesting that TNT is adsorbed or preferentially transformed on fresh mineral surfaces.

Electrolyte-promoted demineralization of biogenic, vitreous, and crystalline silica: A density functional investigation

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The dissolution of amorphous and crystalline varieties of SiO2 is an integral part of the global biogeochemical cycle of silicon. Nanoparticulate biogenic silica produced by marine phytoplankton and terrestrial plants are of particular interest because their enhanced reactivity and abundance make them important sources and sinks of dissolved silicon in natural environments. Low concentrations of major solutes have been shown to enhance the rate of silica dissolution by up to a hundred times. Recent experimental results on Q3-terminated (100) surfaces of quartz, show that the presence of dissolved electrolytes triggers a crossover in the dominant dissolution mechanism from defect assisted dissolution and simple step retreat, to nucleation of vacancy islands. However, the underlying reaction mechanism remains poorly understood (Dove et al., 2005).

The specific effects of group II metal cations (Mg2+, Ca2+, Sr2+, Ba2+) on the energetics of Si-O bond hydrolysis have been investigated with density functional methods (B3LYP) and a relatively large neutral silica cluster (H13Si6O16). Reactant, product, and transition states for Q3 to Q2 hydrolysis in the presence and absence of the afore-mentioned cations have been determined with all electron (6-31G(d)) and effective core potential (SDDALL) Gaussian basis sets. The free energy of activation for Q3 to Q2 Si-O bond hydrolysis was determined to be approximately 5 kJ/mol lower for Ca2+ than Mg2+ at the 6-31G(d) level. Similar calculations for Ca2+, Sr2+ and Ba2+ using the SDDALL basis set yielded similar molecular geometries to the all-electron results, and free energies of activation for Sr2+ and Ba2+ that are ~10 kJ/mol and ~15 kJ/mol lower than for Ca2+ respectively. These results are consistent with experimental results which show that these cations increase the maximum rate of silica dissolution in the order Mg2+ << Ca2+ << Sr2+ << Ba2+. Although these calculations successfully reproduce the relative rates observed in the presence of these cations, they also predict that the rate of Si-O bond hydrolysis should be faster in the absence of electrolyte, which is contrary to experiment. To address this issue, supplemental calculations are being performed to determine how the incorporation of surface charge into the model will affect the energy landscape and mechanism of Si-O bond hydrolysis.

References

The oxidative breakdown of PAHs by manganese oxide tailings

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Introduction
The Kalahari Manganese Field, situated in the Northern Cape province of South Africa, represents the largest body of Mn ore in the world holding up to 80% of the world’s Mn reserves. As a result of ore extraction processes, large quantities of fine, relatively pure Mn oxide tailings are generated. Despite being classified as a ‘waste’ the tailings material could be a valuable source of ‘slow-release’ oxidising capacity for the treatment of organically contaminated soils. Manganese oxides are one of the most powerful oxidants in terrestrial geochemical systems. They are involved in redox cycles in soils and waters, which are essential to nutrient cycling, humification, contaminant fate and mobility.

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous contaminants which are not easily biodegraded, largely as a result of their very low water solubility (Zhang et al., 1995), and thus persist in soils and waters. There have only been limited studies conducted on the oxidation and degradation of PAHs by Mn oxides (Mihelcic and Luthy, 1988). In the present study the Mn oxide tailings materials were reacted with anthracene, one of 16 PAHs appearing on the USEPA priority contaminant list.

Discussion and conclusions
The results obtained using UV-visible spectrometry and gas chromatography mass spectrometry show anthracene is being oxidised to anthraquinone on the surface of the Mn tailings materials under certain environmental conditions. This is thought to be one of the few reported cases of anthracene oxidation by natural minerals.

References

Processes in early planetesimals: evidence from ureilite meteorites

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Ureilites are primitive ultramafic achondrites composed largely of olivine and pigeonite, with minor augite, carbon, sulphide and metal. They represent very early material in the history of the Solar System and form a bridge between undifferentiated chondrites and fully differentiated asteroids. They show a mixture of chemical characteristics, some of which are considered to be nebula-derived (e.g. a negative correlation between Mg/Fe and Δ¹⁷O that resembles that of the ordinary chondrites but at lower Δ¹⁷O values) whereas others have been imposed by asteroidal differentiation. Carbon isotope data show a striking negative correlation of δ¹³C values with mg# in olivine. δ¹³C also correlates positively with Δ¹⁷O, and therefore this isotopic variation was probably also nebula-derived. Thus, oxygen and carbon isotope compositions and Fe-Mg systematics of each monomict ureilite were established before differentiation processes began.

Heated by decay of short-lived radioactive isotopes, the ureilite asteroid started to melt. Metal and sulphide would have melted first, forming a Fe-S eutectic liquid, which removed chalcophile elements and incompatible siderophile elements, and basaltic melts that removed Al, Ca and the LREE. Several elements show different abundances and/or correlations with Fo content in olivine, e.g. carbon shows a positive correlation in ferroan ureilites, and a weak or even negative correlation in more magnesian compositions. HSE such as Os and Ir also show different distributions, i.e. ureilites with Fo < 82 have very scattered Os and Ir concentrations, which reach high values, whereas ureilites with Fo > 82 tend to have much less scattered and overall lower Os and Ir abundances. A similar change in elemental behaviour is shown by the Fe-Mn relations in ureilite olivines: those with Fo contents < 85 show a good negative correlation, whereas those with Fo > 85 show much greater scatter.

This suggests that a major change affected the parent body at a time when melting had reached relatively magnesian bulk compositions. We consider that this event may have been a “hit and run” collision in which the ureilite parent body collided with a larger object. During the collision, the ureilite mantle broke up catastrophically but re-accreted in a jumbled state around the still-intact core. Mg-rich basaltic melts that were in the process of being formed at the time of break-up were retained in part as melt clasts that re-accreted to the regolith and are found in polymict ureilites.
Introduction
Recently, a new group of P-rich Fe-Ni sulfides has been reported from CM2 chondrites (e.g. Devouard and Buseck 1997, Nazarov et al. 1999, 2001). Lauretta et al. (1998) reported in run products of sulfidation of kamacite also a P-rich phase, in addition to the mixture of barringerite monosulfide solid solution with pentlandite. P-rich sulfides are very fine-grained and their reliable phase description is very difficult. Therefore, we opted for a study of phase relations in the ternary system Fe−P−S using the evacuated silica tube method. Reaction products were examined by X-ray powder diffraction, reflected-light microscopy and by electron microprobe.

Results and discussion
From the phase diagram in Figure 1 it is obvious that in the metal-rich portion of the system at 800°C, the following univariant assemblages are stable: Fe + FeS + Fe3P, FeS + Fe3P + Fe2P and FeS2 + FeS + Fe2P.

Figure 1: Phase relations in the metal-rich part of the Fe-P-S system at 800 °C.

The results of sulfidation and phosphidation experiments in the Fe-P-S system are displayed in Figure 1. Fe3P sulfidates through Fe2P+FeS to FeS +FeS2 +Fe3P (1) and FeS phosphidates to FeS2 +FeP (2). The P content in pyrrhotite from the univariant assemblage FeS2 + FeS + Fe2P at 800°C is in the range 0.01-0.02 wt.%. On the contrary, P content in natural phosphorite Fe-Ni sulfides is higher and ranges between 1.1 and 7.2 wt.%. (Nazarov et al. 1998 and 2001). Clearly, additional experiments and crystal-chemical analyses are needed to explain this discrepancy. Barringerite occurring in association with P-rich Fe-Ni sulfides could likewise be a product of phosphidation or sulfidation.

References
Element transfer through the Kurile convergent margin

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We have recently conducted a detailed geochemical investigation (including selected trace elements and Sr-Nd-Pb-Hf- and Be-isotope ratios) of the incoming crust (sediments and AOB) and across the wide (volcanoes ~115-200km above slab depth), active Kurile arc in the NW Pacific to address 1) the changing nature of the slab component with depth and 2) element cycling via the subduction “factory.” Initial results indicate the pre-subduction mantle is a mixture of Pacific and Philippine Sea Plate types and melting processes largely explain systematics of immobile, incompatible trace elements in VF and BVF lavas. The behaviour of highly fluid-mobile trace elements is contradictory and is better explained by multistage processes operating beneath the arc.

The agent of mass transfer appears to change from aqueous fluid beneath the volcanic front to melt-like and solute-rich fluid beneath the deeper regions of the arc, which is demonstrated by: 1) the strong VF→BVF decline in highly soluble fluid mobile elements when melting effects are minimized (e.g., B/Be, B/Nb, Cs/Th, Pb/Ce), 2) these ratios are often higher in the VF than the bulk incoming crust, and 3) enrichments in sediment-derived cosmogenic ¹⁰Be (t₁/₂=1.5My) in BVF lavas that are equal to those in the VF-despite longer transit times. ¹⁰Be recycling (flux out / flux in) is estimated at ~17%, to which additional elements are compared. Cross-arc trends coupled with previously well-characterized Wadati-Benioff zone and mineral stability studies allow inferences about the pressure and temperature conditions at the slab-surface (e.g., exploiting the contrasting fluid and melt partitioning behaviours of Be and B in primary sedimentary host white mica) with extensions to thermal and geodynamic models. Geochemical flux estimates clarify longer-term evolution of the crust-mantle system.

Fluid properties at high P and T – What are they good for?

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The knowledge of accurate physical and chemical fluid properties at high pressures and temperatures is the key to a quantitative understanding of many geochemical processes. Recent simulation studies have demonstrated that the physical evolution of hydrothermal systems is largely controlled by the non-linear dependence of fluid properties such as viscosity, density and heat capacity on temperature, pressure, and composition. Using simplified fluid properties in a simulation will obscure and sometimes completely suppress important phenomena observed in natural systems. Typical examples from mid-ocean ridge type hydrothermal systems and ore-forming magmatic-hydrothermal systems will be discussed.

A major problem for understanding the geochemical evolution of these systems is the lack of accurate, experimentally determined thermodynamic data for many geochemically important fluid systems at high temperatures and pressures. Moreover, for the near-critical region as well as for phase-separating complex fluids, no thermodynamic formalism is currently available that allows the accurate description or even prediction of thermochemical properties. Current models for standard (infinite dilution) thermodynamic properties such as HKF/Superc fail in this region as do Gibbs Free Energy-based activity models for solutions with finite concentrations. To overcome these limitations, geochemists have more recently moved into theoretical and experimental fields that have little to do with a traditional view of geochemistry including combined quantum chemical calculations and mass spectrometric stability determinations of cluster ions, combined molecular dynamics simulations and EXAFS determinations of ion solvation, and theoretical studies linking these molecular-scale determinations to macroscopic thermodynamic fluid properties. The presentation reviews a few of these recent studies and gives an outlook how these approaches may eventually lead to a quantitative formalism for fluid properties at high temperatures and pressures.
Linkage between Hg(II) pore water speciation and MeHg production in contaminated sediments

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Introduction
The formation of toxic and biomagnifying mono methyl mercury (MeHg) in sediments has been proposed to be largely controlled by a passive uptake of dissolved, neutral Hg-sulfides in sulphate reducing bacteria. We have studied relationships between the concentration of dissolved neutral Hg-sulfides, modeled by equilibrium speciation calculations, and specific methylation rate constants (Km. day⁻¹), as well as concentrations of MeHg (µg kg⁻¹), in sediments contaminated by Hg from the pulp and paper industry.

Materials and Methods
Sediments were sampled at seven sites in Sweden, covering a range of environments differing in salinity, total Hg concentration, annual air temperature sum, and organic matter content and quality. The potential methylation rate was determined by addition of isotopically enriched ²⁰¹Hg(II) followed by incubation at 23° C under N₂(g) for 48 h. Pore water Hg(II) speciation was modeled using measured concentrations of pore water Hg(II), pH, inorganic sulphides, halides and dissolved organic matter. Formation of HgS(s) and mixed Hg/FeS(s) was considered independently by Hg EXAFS and S XANES.

Results and Discussion
The sum of dissolved neutral Hg-sulfide species [Hg₃(SH)₂]²⁻(aq)] + [HgS₂⁻(aq)] was significantly, positively (p<0.001, n=20) correlated to Kₘ at depths of 5-100 cm in brackish water sediments. In contrast, total Hg, total Hg-sulfides or Hg(SR)₂ (aq) in pore water gave no significant relationships with Kₘ. In two sets of freshwater sediments, both neutral Hg-sulfides and total Hg (because of an autocorrelation) gave significant relationships with Kₘ. Furthermore, the sum of neutral Hg-sulfides in pore water was significantly, positively correlated to total sediment MeHg (µg kg⁻¹) in brackish waters (p<0.001, n=23), in southern, high-productivity freshwaters (p<0.001, n=20) as well as in northern, low-productivity freshwaters (p=0.048, n=6). Our results confirm findings from laboratory experiments that concentrations of dissolved neutral inorganic Hg-sulfide species largely control Hg methylation rates, as well as accumulated MeHg concentrations, in contaminated sediments.

References

Archean granites from the Rum Jungle Complex, Australia

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The 2.55 Ga Rum Jungle Complex (RJC), N Australia, comprises two Archean basement cores, the Rum Jungle and the Waterhouse domes that are surrounded by ortho- and paragneisses of the Palaeoproterozoic Pine Creek Orogen (PCO). The RJC predominantly comprises granite, syenite, quartz-monzonite, and quartz-monzodiorite intruding earlier schists and BIFs. A large number of uranium and base metal deposits have been discovered in black pelites of the PCO neighbouring the granitoid bodies.

Perthitic K-feldspar and quartz are the main minerals present in the granitoids, accompanied by variable amounts of plagioclase (An₀₂₃), magnetite, relict biotite, and accessories such as zircon, monazite, titanite, allanite, apatite, and ilmenite. Most of the samples underwent major post-emplacement mineralogical changes, e.g., formation of white mica at the expense of feldspar, replacement of titanite by rutile, and formation of biotite rims (X_Mg: 0.45-0.53) around magnetite. A pervasive alteration is characterised by sulphide mineralisation, chloritization of biotite and white mica, marlization of magnetite, formation of tourmaline, muscovite, and thoro-silicates along micro-shear zones.

The major element data of the granites show well-defined fractionation trends, involving a negative correlation of Si with Ti, Fe, Mg, Ca and P, whereas K increases in the same direction. The granitoids are metaluminous to peraluminous and alkalic to alkali-calcic in composition, the X_Mg is 0.45-0.53, suggesting that they were derived from the same parental magma. Remarkably, they have conspicuously high Th (8.6-123.3 ppm) and U (2.9-39.9 ppm) compared to the average Upper Crust. All samples, except three highly altered granitoids, can be defined as I-type granites (ASI 0.9-1.1).

Post-emplacement deformation and alteration are associated with secondary, low-salinity (0-14 wt.% NaCl equiv.) to high-salinity fluid inclusions (15-38 wt.% NaCl equiv.) in magmatic quartz that display generally moderate homogenisation temperatures (107-384°C and 81-392°C, respectively). High-salinity inclusions also comprise minor gas-rich mixed H₂O-CO₂ inclusions. All fluid inclusions contain a variable number of presumably accidentally trapped solid inclusions. The fluids are suggested to have been derived by de-wetting of metasediments of the PCO and to be modified by fluid-rock interactions during transport and metamorphism of the RJC and PCO at c. 1.8 Ga. This process might also be responsible for the formation of U and ore deposits in the vicinity of the RJC.
The geochemical characteristics of molybdenum ore deposits in east Qinling orogenic belt, north China

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Introduction
The molybdenum mineralization district in east Qinling orogenic belt is tectonically located in the south edge of north China Craton, where a series of molybdenum ore deposits are discovered. These ore deposits retain the largest capacity of molybdenum in China. The most important mineralization of these molybdenum ores is porphyry type genetically forming with the Yanshan granites (Mesozoic) in Qinling orogenic belt. In this study, both the granitic samples and molybdenum ore samples are collected for detailed geochemical analyses to focus on the genesis of these molybdenum ore deposits.

Experiment and Results
Major elements, trace elements and REE are determined by XRF, ICP-AES and ICP-MS, respectively. The major elements that the samples are alkali granite and syenite-granite, which are formed in an anorogenic, syn-collisional or postorogenic environment. The chondrite normalized spider diagram and the MORB normalized diagram for the trace elements of the samples are both similar to that of the upper continent crust. The total REE amount is 32.1-251.4ppm, with an average 113.3ppm. The highest δEu anomaly is 1.7, while most of samples are less than 1 (with an average value of 0.67). The Re-Os ages of molybdenum ore give 144.8 ~ 132.40 Ma (Li et al, 2005), resembling the same period of massive Yanshanian granitic intrusives, indicating that the metallogenesis of these molybdenum deposits are relevant to the Mesozoic magmatic activities in east Qinling orogenic belt. In fact these ore deposits are associated with the small medium-sized acidic intrusives.

Acknowledgments
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References

The geochemical characteristics and its tectonic backgrounds of the Lower Silurian flysch sandstones in North Qilian orogenic belt

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The North Qilian orogenic belt is an elongated unit situated between the North China plate in north and Qaidam plate in the south. The lower Silurian Angzanggou Formation is distributed in Zhenglu, Cuijiadun sections in the eastern sector of the orogenic belt. Angzanggou Formation is dominated by clastic deposits, which is typical turbidite deposit of flysch facies. Sandstones collected from Zhenglu section consist of SiO2 ranging from 61.83% to 69.90% and Fe₂O₃*+MgO(3.83—4.98), Al₂O₃/SiO₂(0.13—0.17), K₂O/Na₂O (0.89—1.35), Al₂O₃/( CaO+Na₂O ) (0.81—2.76). The provenance analyses and tectonic setting distrimination indicate that the terrigenous materials come from the active continental margin and orogenic belts. Sandstones collected from lower part of Cuijiadun section consist of Fe₂O₃*+MgO(5.03—5.11), Al₂O₃/SiO₂(0.12—0.14), K₂O/Na₂O(0.43—1.26), Al₂O₃/( CaO+Na₂O ) (2.21—3.53). The upper part of Cuijiadun section consist of Fe₂O₃*+MgO(15.6—17.63), Al₂O₃/SiO₂(0.24—0.28), K₂O/Na₂O(0.25—0.85), Al₂O₃/( CaO+Na₂O ) (0.98—1.42). The provenance analyses indicate that the lower part of the turbidite is mainly derived from a mixed provenance between ancient orogenic belt of Alashan Plate to the north and active continental margin to the south.The upper part come from the eroded mid-basic igneous rocks implying an environment of back-arc basin.

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Lead(II) desorption from goethite mediated by hydroxamate ligands

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Introduction

Siderophores are low molecular weight organic molecules secreted by plants and micro-organisms in response to Fe stress. More than 400 siderophores have been isolated, the majority of which possess either catecholate or hydroxamate functional groups. With stability constants commonly exceeding 10^{30}, siderophores are considered to have higher affinities for Fe(III) than for any other major or trace element dissolved in soil solution. Despite the abundance, ubiquity and structural diversity of siderophores in both terrestrial and aquatic ecosystems, their possible role in Pb mobilisation has received only brief attention. Here we show that three hydroxamate siderophores solubilise lead(II) chemisorbed to an iron(III) oxide adsorbent, significantly increasing the bioavailability of this toxin.

Methods

Goethite [α-FeOOH], prepared by standard methods and identified by X-ray diffraction, gave a specific surface of 36 m² g⁻¹ as determined by N₂ multipoint BET analysis. Adsorption experiments were performed aseptically using a batch method with a goethite concentration of 1.0 g l⁻¹ and an ionic strength of 0.01 M NaClO₄. Soluble Pb and Fe were measured between pH 3 and 8 by first adding Pb (10 µM) and then siderophore (10, 20, or 40 µM) to the goethite suspension. Following 20 h reaction, Pb and Fe in solution were measured by ICP-MS (Pb detection limit ≈ 0.1 ng g⁻¹) and ICP-AES, respectively.

Results

The efficacy of Pb desorption varied with siderophore type and generally increased with pH and siderophore/Pb molar ratio. A trihydroxamate siderophore, at pH 6.5 and a siderophore/Pb molar ratio of 4, solubilised nearly 25% of the total sorbed Pb. In the presence of 10 µM ferrichrome, Pb adsorption largely mimicked that for the siderophore-free system, whereas significant amounts of Pb were desorbed with 20 µM ferrichrome at pH > 5.5. Rhodotorulic acid was the least effective Pb chelator, requiring 20 µM to desorb detectable amounts of Pb.

Isotopic tracing of water filtration in oxidizing, fractured porous media

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The Krasnokamensk area, SE Siberia, Russia is known for its rich ore deposits. The Tulukuevskoe U deposit is hosted in Mesozoic (135 Ma) welded tuffs that are characterized by tectonic faulting, hydrothermal-metasomatic alteration, and oxidizing transformation. Further to environmental impacts caused by open pit mining, the migration of U from the ore body into the wall rocks and to the underlying aquifers is of particular interest for nuclear waste management purposes. Using the Tulukuevskoe open pit as a natural analogue, the conditions under which U can be mobilized, transported and precipitated are being investigated.

In this context the dynamics of isotope (¹⁸O, D) composition of meteoric water filtering through the fractured-porous media was studied. We monitored 9 water locations for 7 years.

Figure 1: δD for meteoric water filtering through fractured-porous media of the Tulukuevskoe U deposit

We also studied the ⁸⁷Sr/⁸⁶Sr and chemical composition of waters. The same type of analysis was performed for rain and snow precipitation. To explain the results obtained, the integration of water isotope parameters inside the fractured-porous media was modeled for many-years type of monitoring. The model calculations show that the mean extent of water filtration is from 2 to 3.5 years for the various watersampling locations.

The model calculations based on δD behavior gave more realistic results, than those based on δ¹⁸O behavior. The oxygen isotope composition of infiltrating water obviously could be altered by oxidation and carbonatization of the media. ⁸⁷Sr/⁸⁶Sr data supported this interpretation.
Searching for the perfectly removable, ultrabasic and dense lower crust

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The two main lines of thinking concerning lower crustal recycling into the mantle are mass balance-related; one is “mechanical”, and comes from shortening estimates in compressional orogens, the other is “chemical”, and is driven by the realization that the continental crust is too silicic to be produced directly by mantle melting. The first line of reasoning can be directly applied to specific mobile belts on Earth, whereas the second remains plagued by our inability to decipher the rate of continental growth through time and thus is difficult to connect to specific orogenic styles. The discourse on tectonic recycling of lower crustal crust into the mantle is plagued by the misconception that “founding of dense, eclogitic material (that is) produced during continental orogenesis … at the base of the crust”, as stated even in the overview for this session. The statement does vaguely imply that solid-state, metamorphic processes in overthickened orogenic crust lead to eclogite facies formation and potentially to subsequent convective removal. However, there is no reason why thickening-related eclogitization (although perfectly plausible) would segregate a felsic upper crust from a mafic-ultramafic lower crust. Instead, subduction-related arc environments are the only realistic settings in which felsic crust can be segregated, because magmatic differentiation operates in corroboration with shortening. Unfortunately, the most cited paper addressing removal of the deepest arc petrologic crust deals primarily with the architecture of ISLAND arcs (mafic rocks, garnet-free pyroxenite residues). Lower crustal delamination in island arcs has neither any significance on continental formation nor any relevance to mechanical mass balance issues mentioned above. Instead, I will argue that transitional or continental arcs are the perfect environments for differentiating felsic crust from a garnet-rich residue that is likely to be recycled in the mantle.

References

Uncertainty of Hf isotope analysis in zircon using LA-MC-ICPMS techniques: Full disclosure

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In-situ Hf isotope measurements of zircon by laser ablation (LA) MC-ICPMS coupled with in-situ U-Pb geochronology by SHRIMP or LA-ICPMS is a potentially powerful technique because both tracer and age information can be determined from small zircon domains. The uncertainties inherent in zircon LA-Hf isotope analysis, however, can be considerable and all must be accounted for in order to assess these data in the context of Hf isotope data determined on chemically purified solutions.

In order to assess precision and accuracy associated with LA-MC-ICPMS zircon Hf analysis we analyzed 7 zircon standards (91500, QGNG, Temora, Peixe, R33, FC-1, and 94-35) during separate analytical sessions. Hf isotope measurements were made using a ThermoFinnigan Neptune MC-ICPMS with a New Wave 213nm Nd-YAG laser. A large source of analytical uncertainty in LA-Hf isotope analysis comes from the interference corrections on mass 176, principally from $^{176}$Yb. Mass bias for Yb was exponentially corrected assuming: (1) $\beta_{\text{Yb}} = \beta_{\text{Hf}}$ and (2) $\beta_{\text{Yb}} = x \beta_{\text{Hf}}$, where $x$ is determined by normalizing to a standard and subsequently applied to the “unknowns”.

Internal precision for individual analyses averaged $\sim 1 \, \varepsilon_{\text{Hf}}$ unit (2$\sigma$, SE). External precision of each standard during an analytical session ranged from 0.4-1.1 $\varepsilon_{\text{Hf}}$ units (2$\sigma$, SD, n=6). Between analytical sessions, however, the spread of the session means range over 1.5 $\varepsilon_{\text{Hf}}$ units, with one Yb rich zircon sample (R33) varying by $> 4 \, \varepsilon_{\text{Hf}}$ units. Accuracy of the LA Hf analyses (compared with solution Hf analyses) varied depending on the Yb correction method. For method 1, session averages for 5 samples were accurate within $\sim 1$ $\varepsilon_{\text{Hf}}$ units, but Peixe was several $\varepsilon_{\text{Hf}}$ units low and R33 was $\sim 3 \, \varepsilon_{\text{Hf}}$ units high. Method 2 improved accuracy for R33 (high Yb/Hf) but had little affect on accuracy of Peixe (low Yb/Hf).

Potential sources for variations in precision and accuracy for LA Hf isotope analysis include matrix effects and oxide interferences from Dy or Gd. For initial $^{176}\text{Hf}^{177}\text{Hf}$ ratios a large source of potential error comes from uncertainty in the age, particularly for old zircons. This is not due to the radiogenic correction of the initial $^{177}\text{Hf}^{177}\text{Hf}$ ratio, which is quite small, but in the CHUR reference, which varies by over 2 $\varepsilon_{\text{Hf}}$ units/100 m.y. Regardless of their sources, all uncertainties associated with LA-MC-ICPMS zircon analyses need to be incorporated into the errors reported on $^{176}\text{Hf}^{177}\text{Hf}$ ratios. These several $\varepsilon_{\text{Hf}}$ unit uncertainties may not be an issue where large variations in $^{176}\text{Hf}^{177}\text{Hf}$ are expected (e.g., detrital zircons), but they put limitations on applications where small variations in $^{176}\text{Hf}^{177}\text{Hf}$ are significant (e.g., constraining crust-mantle evolution).
Molecular and compound-specific stable C isotope investigation of the fate of dung C in a temperate grassland soil

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Establishing the potential of soils to sequester C and elucidating the mechanisms whereby this is achieved is vital in order to understand the capacity of terrestrial ecosystems to act as sinks for anthropogenic C. Significant quantities of cattle dung are applied to temperate grassland annually and traditional long-term use of manures as soil improvers has been proven to increase SOM (Haynes and Naidu, 1998). This project applied molecular and compound-specific stable C isotope methods to investigate the fate of cow dung in a temperate grassland soil, utilising the Δ13C(con-trt) values of compounds from natural abundance 13C-labelled C4 dung (δ13C = -12.6‰) and C3 soil (δ13C = -30.3‰). The 0-5 cm horizon of dung-treated soils were sampled at 0, 7, 14, 28, 56, 112, 224 and 372 d. Bulk δ13C values estimated that a maximum of 12% dung C was incorporated at 56 d (Dungait et al., 2005) with compound-specific determinations estimating that 19% dung C was incorporated at this time. Differences between degradation rates of major organic components of C4 dung were revealed. C4 dung comprised 80% carbohydrate, 5% lignin and <1% lipid. Percentage incorporation of xylose accounted for 10% dung C at 56 d, compared with 3% for glucose; significant concentrations of dung carbohydrates remained in the soil at the end of the experiment. Dung-derived lignin 4-hydroxyphenols displayed a range of degradation rates in the soil, but appeared to be more labile than expected and did not contribute significantly to dung-derived C later in the experiment. Faecal biomarker 5β-stanols and free fatty acids suggested that concepts of recalcitrance might not rely on individual chemistry but on the potential of certain compound classes to escape degradation or leaching; very long chain fatty acids were appeared to be the most resistant dung compound class.

References

Investigation of the ‘Trigger Molecule Response’ using 13C stable isotope probing of microbial membrane fatty acids

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The ‘Trigger Molecule Response’ is a hitherto unrecognised mechanism in soil microorganisms that provides a strategy for survival in a relatively substrate-poor environment. Previous respiration experiments have shown that the additions of ‘trigger molecule’ concentrations of low molecular-weight compounds to soils induce two- to five-fold greater expenditure of energy by the soil microbial biomass than that provided by the added substrate (De Nobili et al., 2001). Thus, we investigated the hypothesis that soil microorganisms maintain metabolic alertness in anticipation of a food event through application of 13C-labelled substrates at ‘trigger molecule’ concentrations, using compound-specific 13C isotope analysis of microbial biomarker PLFAs (Evershed et al., 2006). This paper presents results from recent experiments with soils from Rothamsted Classical Experiments that show: a) significant increases in the δ13C values of individual PLFAs without significant increases in abundance at four concentrations (0, 25, 83 and 416 µ 13C g-1 soil) after 120 h, and, b) differential uptake of 13C over a 240 h time course in individual microbial PLFAs extracted from soils treated with 15 µ 13C g-1 soil. Additional evidence for the ‘Trigger Molecule Response’ from concurrent experiments using CO2 respiration, nucleic acid and RNA-SIP methodologies will also be discussed. The significance of these findings in the context of the role of the soil microbial biomass in C cycling in soils will be considered.

References
The Dolomites of the eastern Southern Alps were formed from the Permo-Triassic sedimentary cover of the South Alpine unit that was slightly deformed in the Tertiary. The different parts of the Dolomites have suffered Alpine deformation two times, and the shortening process is actually still active along the southernmost thrusts. The direct dating of the deformation is possible only in the southern zones, where sediments are involved in the thrusts, whereas in the northern areas no or rather scarce geological evidences on the timing of structural evolution exist. The isotope geochronological dating is difficult due to lithology of the sedimentary successions, areas no or rather scarce geological evidences on the timing of shortening process is actually still active along the southernmost thrusts.

In order to constrain structural evolution of the area, we applied low temperature thermochronology [apatite fission track (AFT) and apatite (U-Th)/He (AHe) dating methods] on the Triassic volcanic dikes and tuff horizons. The AFT ages are ranging between 210 and 6 Ma. The oldest ages indicate the presence of slightly reset areas and date the exhumation of some structural blocks to be Late Miocene. The AHe ages are younger than the AFT ages in each sample. In the western Dolomites, where the Neogene thermal reset is not detected by the AFT thermochronometer, the AHe ages show Late Miocene reset due to the lower closure temperature of the later method. Inferring from the significant contrast between the AFT and AHe ages we conclude that the dated stratigraphic horizons were deeper than the total reset depth of AHe method but shallower than the reset depth of the AFT method between the Late Triassic and Late Miocene. We suppose that beyond the general Miocene uplift of the Dolomites mainly the displacements along the Stava line and Schio-Vicenza fault or Bassano thrust are responsible for the exhumation of Passo Feudo and Recoaro area, respectively.

Data handling, outlier rejection and calculation of isotope concentrations from laser ICP-MS analyses by PEPITA software

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The raw output data of laser ICP-MS analyses are composed of high number of ion counts registered in time. The handling of these huge matrices and the expression of trends, isotope ratios and finally the concentrations is a rather time consuming procedure. We have created a data handling system and an evaluation software (for Windows) that stores the necessary background information, and performs several outlier tests and the computations for the concentrations.

The composition of the standards, measurements on standards and the used dwell-times are stored in different files. The blank counts can be extracted from the data files or from separate 'blank files'. The computation starts with the selection of internal standard isotopes. Then PEPITA investigates the compatibility of the files and warns if one or more isotopes are not present in all kind of input files. The preferred time slices for the calculation of the isotope concentrations can be extracted graphically from a time/cps plot. The raw data or the cps values normed by the counts of the internal standard can be tested for outliers.

The time slices show always some fluctuation of the cps values, and the experiments frequently contains spikes, which appear only in single time slices. These individual data can seriously bias the average count, especially when the count rate is low. PEPITA offers three methods to visualize and/or reject the extreme values. (1) The minimum and maximum values detected by the record of an isotope can be highlighted. (2) The Grubbs outlier test indicate the probability that the highest or lowest value belongs to the rest of the population. (3) The user can specify how many relative standard deviation can be tolerated for the individual data points. The extreme values (e.g. having more than 4 rel. std. dev., which is rather probably a 'technical outlier') can be rejected and this procedure can be consequently repeated for all processed files.

The software exports into files or pastes to the clipboard the results in the following order: (a) list of files, time slices used, rejection algorithm and criterion, (b) average concentrations, limit of detection and other statistical parameters, (c) concentrations and errors in time slices (d) warning in case of incompatible files.

PEPITA is freeware, downloadable from:
http://www.sediment.uni-gottingen.de/staff/dunkl/software/pepita.html
Isotopic zonation in zircon as a recorder of progressive metamorphism

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Zircon and garnet share some common traits: both are typical metamorphic phases in granulites; both are important sinks for heavy REEs; and both tend to preserve complex compositional zoning that reflects growth behaviour during high-temperature metamorphism. Whereas growth stages recorded in garnet porphyroblasts are widely used to characterize stages along a metamorphic P-T path, zircon tends to be treated as a single stage mineral, with growth (and consequently age estimates from U-Pb isotopic dating) tied to a poorly defined thermal maximum. This is in contradiction to the complex zoning commonly seen in metamorphic zircon grains, especially those in metapelitic migmatites. Such zoning can be understood through the same methods by which garnet is studied; i.e. compositional mapping and micropetrographic relationships. Zircon grains from metapelite samples of the granulite-grade Lützow-Holm Complex of east Antarctica show a complex range of textures and ages. Whereas previous SHRIMP ages from zircon grain separates concentrate around 530-550Ma, and were interpreted as timing peak metamorphism, further detailed analysis yields a spread of age estimates from 500 to 630Ma. In-situ analyses of zircon inclusions in garnet porphyroblasts reveal a stage of U-rich zircon growth at c.600Ma, with flat HREE-MREE profiles indicating prograde growth in the presence of garnet. Zircon preserved in a garnet megacryst from felsic pegmatite that fills boudin necks in a metapelitic layer show multiple stages of growth (Fig.), with c.600Ma flat H-MREE (garnet-equilibrated) cores, c.570Ma rims with outward steep to flat H-MREE growth zoning, and resorption prior to incorporation in the garnet megacryst and crystallization of the felsic pegmatite at c.550Ma. Although the 100Ma spread of zircon ages could be interpreted as recording separate metamorphic events, the textural and chemical associations between zircon, garnet and felsic melt suggests that zircon growth was progressive through a prolonged metamorphic event, and that a large proportion of zircon growth at 530-550Ma occurred during retrograde rather than peak metamorphism.

A bacterial model for studying interactions between microorganisms and CO₂ injected in the subsurface

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Geological storage of CO₂ in the subsurface will likely become an important industrial process since it is an option envisaged to mitigate the increase of atmospheric CO₂ in the coming decades. The potentialities of some subsurface microorganisms to induce CO₂ mineralization into carbonates could strongly enhance the stability of the CO₂ containment or could also have adverse effects on the injectivity. In order to study this process, we have carried out experiments of biotransformation of CO₂ into solid carbonates using Bacillus pasteurii, an ureolytic model strain. The strain was inoculated in an artificial ground water based on the composition of actual deep groundwaters from the basin of Paris, France. Experiments were performed in a specially designed circulation cell. The complex pH evolution, induced by the strain in the artificial groundwater, could be modelled using the geochemical software Chess 3.6, from Ecole des Mines de Paris, including enzymatic kinetics of ureolysis, kinetics of gas-solution transfer, and rate of calcite precipitation. Alkalization due to the enzymatic hydrolysis of urea, part of which was shown to occur by extracellular processes, reached a plateau once a dynamical equilibrium was established with the rate of CO₂ transfer into the aqueous solution. Calcite precipitation induced a decrease in pH as well as a strong cellular mortality due to nucleation of carbonates on bacteria followed by the embedding of cells within the carbonate crystals, as evidenced by SEM, X-ray synchrotron imaging and TEM studies. The implications of this model for CO₂ biomineralization in subsurface environments are finally discussed in the light of subsurface metabolisms, which might often imply local pH increases (e.g. dissimilatory sulphate reduction).
FT-IR spectroscopic study in plants from contaminated mining sites

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The roots and above ground parts of three different plants species (Cistus Ladanifer, Juncus efusus and Scirpus holoschoenus) collected in contaminated mining sites of Iberian Pyrite Belt were chemical analysed. Concentrations of toxic metals (Cu, Pb, Zn) were found higher in both Juncus efusus and Scirpus holoschoenus especies than Cistus Ladanifer. The concentration values of toxic metals determined in roots in the firsts plants species are: Cu 352 -519 mg.kg⁻¹, Pb 169 – 568 mg.kg⁻¹, Zn 212-563 mg.kg⁻¹. Both Fe and Mn concentrations increase, as toxic metals concentrations increase.

FT-IR technique was used for evaluation of the type of organic and inorganic complexes in plants. The analyses were carried out on drying and low ashing temperature material of different parts of each plant.

Slightly differences regarding to organic complexes were observed in FT-IR patterns. Strong stretching bands attributed to C–H (2923; 2850 cm⁻¹) and C=O (2360; 2340 cm⁻¹) were found for each part of studied plant. Salts and fatty acids are observed at 1620 cm⁻¹, 1536 cm⁻¹ and strong saturated fatty acids occur at 1700 cm⁻¹. A slight broadening band at 3400 cm⁻¹ is attributed to OH⁻ stretching band. Bands associated with H₂O (1630 cm-¹ bands) are more expressive in the roots and stems. No H₂O bands were identified in the upper part of plants.

However, strong differences in inorganic complexes were observed between the roots and above ground parts of plants species analysed. Molecular vibrations associated with inorganic complexes were related to the stretching modes of the S–O bonds show characteristic absorption bands at 1250 – 1000 cm⁻¹. Probably, these bands are characteristics for sulfate adsorption on Fe-oxyhydroxides. The presence of S–O bonds suggests that some mechanisms of detoxification of metals in plants consist in the precipitation of metals as sulfates. A strong band at 669 cm⁻¹ attributed to anhidrite occur mainly in leaves and stems.

The organics acids and S–O complexes may act as chelating agents in the transporte of metals in plants allowing the accumulation of metals in plants.

Distribution and speciation of mercury in the Curuai floodplain lakes and role of the water exchanges with the Amazon River, Brazil

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The role of the channel-floodplain interactions in the biogeochemical cycle of mercury in the Amazon basin is still poorly documented. It appears that floodplains can act as an important sink of sediments and Hg associated with fine particles. The main objective of this work is to study the distribution and the speciation of Hg in the Curuai floodplain lakes system (3800 km²) in the Middle Amazon.

The sediment inputs in these floodplain lakes occurs during the rising stage of the Amazon R., from January to May. In most of these lakes, the maximum Filtered-Hg and F-CH₃Hg concentrations are observed during the rising water stage, varying from 27.6 to 51.6 pM and 0.12 to 1.66 pM respectively, that coincides with the F-Hg input of the Amazon R. The dry season, when most of the lakes are isolated from the mainstream, is characterized by low F-Hg concentrations. This can be explained by the formation of Hg° from Hg ²⁺ reduction and its volatilisation induced by wind waves. On the contrary, the highest P-Hg concentrations are observed during the dry season (47 to 478 pM) due to the elevated TSS content associated to the re-suspension by the wind of the bottom sediments in shallow water lakes (~50cm) and by the fish and invertebrates bioturbation. The negative correlation between the partition coefficient of Hg (Kₐₐ) and the TSS content confirms the Hg complexation on OM-fine particles during its transfer in the floodplain system. The water and sediment storage in the floodplain lakes favors biogeochemical processes, like reduction, volatilization, adsorption and re-suspension of Hg in surface waters.
Provenance and fates of the REEs and heavy metals in the suspended particulate matter off Luzon shelf in the South China Sea

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The study establishes the provenance of the suspended particulate matter (SPM), collected in the upwelling area at a water depth of 1,200 m off Luzon shelf using sediment traps during eleven sampling periods. The shale-normalized REE patterns of the SPM correlate with those of the volcanoclastic sediments of the Amburayan and Abra Rivers in NW Luzon, establishing their mutual provenance. These river systems drain Cu mine areas.

Knowing their mutual sourcing, we tried to correlate the REEs and heavy metals with the host matrices to ascertain their fates. The REEs, known to be chiefly geogenic, do not correlate with the heavy metals, such as Zn ($R^2 = 0.002$), Pb ($R^2 = 0.020$), and Cd ($R^2 = 0.085$), which are mine-derived. Cu, on the other hand, correlates fairly with the REEs, but not with the other heavy metals.

Cd is hosted by the Mn oxides, whereas, Zn and Pb have strong affinity with the clay minerals, especially smectite. These heavy metals take on soluble form when released from their sources and favor matrices that bond them as adsorbed or exchangeable cations. In contrast, the REEs are associated with the lithogenics and the organic matter. The same association is exhibited by Cu with the lithogenics, which is largely controlled by the presence of chlorites.

Though mutually sourced, the above geochemical scenarios for the REEs and the heavy metals establish that they share only the same provenance but not geochemical behavior once they are released from their source rocks. When released anthropogenically by mine activities or, geogenically, by weathering, the heavy metals become significantly more available for uptake, whereas, the REEs are more strongly bound by their particulate hosts.

The reactivity of raw and incinerated mammalian bone in the presence of aqueous metals

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The production of meat generates a range of by-products including meat and bone meal, the use of which, in applications such as animal feeds, has become severely restricted, due to possible contamination by pathogens (e.g. BSE). The material has to be incinerated and then disposed of in landfills, unless other applications are found.

Raw bonemeal has been previously used in the remediation of metal contaminated soils [1]. Thermal treatment of this material to remove the organic matrix has been suggested in order to increase its reactivity and eliminate pathogens. The purpose of the work presented here was to investigate metal removal capacity of both incinerated and raw bonemeal with a view of a potential application of this waste by-product in wastewater/acid mine water remediation.

Raw and incinerated bonemeal at temperatures ranging from 725-850ºC (as supplied by industry – PDM Group) were reacted with 1000 mg/L solutions of Pb, Zn and Cu. Synthetic HAP was used as a control. Metals in solution were measured using ICP-AES while the solid residues were characterised using analytical SEM, FT-IR and XRD.

Synthetic HAP outperformed both raw and incinerated bonemeal in the removal of all metals except for Pb. HAP removed 95% Pb, 86% Cu and 80% Zn. Both raw and incinerated bonemeal removed 99% of Pb. However, Zn and Cu were only eliminated from solution by 60% by the raw bonemeal and by 18% for Cu and below 10% for Zn by the incinerated bonemeal. Metal phosphates formed as a result of Pb, Cu and Zn reaction with HAP, as indicated by SEM analysis. In samples of raw and incinerated bonemeal only phosphates of Pb were found.

Incineration of bonemeal at high temperatures (700-850ºC) reduces its removal capacity for Zn and Cu, indicating a different removal mechanism to that of Pb, which appears to be always by precipitation of Pb phosphates. Incinerated bone has a strong pH buffering capacity and thus may prove effective in remediation of acid mine waters – leaching columns tests are now carried out to investigate this further.

References
Variscan potassic-alkaline magmatism in Stara planina, Bulgaria – Composition, source and geodynamic significance

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Three Variscan potassic-alkaline plutons: Svidnya, Buhovo-Seslavtzi and Shipka outcrop in Western and Central Stara planina, Bulgaria. The rocks intrude Silurian, Ordovician and Devonian metasediments. The existing isotopic data indicate an emplacement age between 340-320 Ma for Svidnya, the first TIMS results on zircons for Buhovo-Seslavtzi yield 352±22 Ma.

The plutons have essentially intermediate monzonite - syenite composition, with minour amounts of granite. The metaluminous intrusive varieties predominate, but in the three plutons magmatic activity terminates with the separation of strongly peralkaline dyke residue. The peralkaline dyke rocks are of quartz syenitic and granitic composition and contain sodic-calcic and sodic pyroxenes and amphiboles. The rocks have pronounced potassic character, with K2O in the range 5.49 – 11.04 wt.%, and very high LILE and Th – U contents. Synchronous with the peralkaline tendency the contents of HFSE and REE increase.

Preliminary isotopic results show that the rocks have isotopic signature plotting in the enriched quadrant of Sr-Nd isotope systematics. 87Sr/86Sr and 143Nd/144Nd for Svidnya pluton are 0.709 – 0.712 and 0.51192 – 0.51194 respectively. For Buhovo-Seslavtzi 87Sr/86Sr is 0.709 and 143Nd/144Nd is 0.51191 – 0.51188, coupled with εHf from -3.8 to -5.2. Concordant with the moderate enrichment in incompatible elements Shipka pluton shows less enriched composition: 87Sr/86Sr is 0.705 and 143Nd/144Nd is between 0.51215 and 0.51217.

The rocks present fractionated trend of distribution of REE with La/LuN: 23 (Svidnya) and 17 (Buhovo-Seslavtzi), which features are consistent with the presence of residual garnet in the source. The rocks from Shipka have less fractionated trend with La/LuN: 10 which implies on the presence of residual spinel in the source. Low rate melting of enriched mantle is the probable mechanism for the magma generation of this Variscan association.

The very high K2O and the dominance of LILE, Th and U over HFSE indicate significant crust – mantle interactions and involvement of crustal materials into the mantle. The potassic rocks asssociate with S and I type granitoids and this fact is in favor of the orogenic character of the whole Variscan magmatism in Stara planina, Bulgaria. The rocks have isotopic fabrics and are formed after the main orogenic events.

Controls on major and trace element zoning in hydrothermal garnet

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Garnet from the Navachab gold deposit, Namibia, records complex zoning profiles that reflect the alteration history during mineralization. The deposit is situated in the Southern Central Zone of the Damara Orogen, a typical low-P metamorphic terrane. It is hosted by late Proterozoic shelf sediments that are dominated by marbles and calcisilicate rocks, consisting of highly variable proportions of Cal, Cpx, Kfs, An and Qtz. The P-T conditions of formation have been estimated at c. 550-600°C and 2-3 kbars, consistent with the low-P regional metamorphism in the Damara belt.

The garnets investigated in this study are from a massive “replacement-style” sulfide lens and associated alteration zone. Hydrothermal alteration was mainly driven by an increase in bulk rock Mn, Si, and Fe. Two types of alteration can be distinguished that are interpreted to have formed contemporaneously: one dominated by Gt-Cpx-Kfs-Qtz, the other one mainly consisting of Gt and Bt. Textural analysis, coupled with detailed mineral-chemical investigations reveal two distinct garnet generations, and a two-stage growth history.

Stage I garnet usually forms the cores of individual porphyroblasts, and is highly enriched in spessartine. It commonly records a classic bell-shaped zoning profile, in which the XMn progressively decreases from core to rim. This type of zoning profile formed during pervasive hydrothermal alteration, leading to the progressive depletion of Mn in the fluid.

Stage II garnet overgrows the early garnet, and is best-developed in zones of intense fluid-rock interaction. Most of the major and trace elements (including the REE) were mobile at this stage. Stage II garnet is Ca-rich, and records variable zoning patterns that are controlled by the permeability in the different alteration zones. In the Gt-Bt alteration, stage II garnet is characterized by µm-scale oscillations. The oscillations document the episodic supply of fluid in zones of strongly reduced permeabilities. In high-permeability zones, such as the massive sulfide lens, the compositional variations are more progressive, suggesting a rather constant fluid supply in these units.

The garnet zoning pattern are related to different stages during the development of the hydrothermal system. They document the complete history of initial fluid-rock interaction during the onset of pervasive hydrothermal alteration, subsequent fluid pressure built up towards critical values, and final hydraulic fracturing in zones of high fluid pressures. There is no evidence for changing P-T conditions during garnet growth.
Low-Ca pyroxene relics in drilled basalts from EPR crust (IODP Site 1256D)

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It is well-accepted that under fast-spreading ridges the differentiation of primitive MORB into the upper volcanic, and the lower plutonic crust proceeds in crustal magma chambers. Thus, it is to expect that those phases which are fractioned in the magma chamber should also be found as phenocrysts in the erupting melts, at least from time to time. This is general valid for olivine, plagioclase, and clinopyroxene, but not for orthopyroxene. This is expressed in the "orthopyroxene paradoxon" meaning that orthopyroxene is often present in the gabbroic rocks of the plutonic crust from fast-spreading ridges (e.g., from Hess Deep and Garrett Transform fault), but not in the corresponding basalts of the upper crust.

We studied basalts and gabbros from the IODP (Integrated Ocean Drilling Program) Site 1256D in the eastern Pacific where 15 Ma old crust was formed at the EPR (East Pacific Rise) under superfast conditions (Wilson et al., 2006). Here, the Expeditions 309 and 312 deepened Hole 1256D initiated by Leg 206, drilling through lavas, the underlying sheeted dike complex, and into gabbroic rocks, providing the first penetration of the dike-gabbro boundary in intact ocean crust. Many of the gabbros bear orthopyroxene both as poikilitic and as prismatic crystals implying that orthopyroxene saturation was reached during differentiation. However, up to now, orthopyroxene was not recorded as phenocryst or matrix mineral in the corresponding dikes, sheet flows and pillow basalts above the gabbro/dike transition. Therefore, the first observation of low-Ca pyroxene in the volcanic section of the 1256D drill core is of significance.

Low-Ca pyroxene was detected as relics in matrix clinopyroxenes in several samples from the uppermost sheet flows of Leg 206. They appear as strongly disrupted, often cloudy patches in intensely zoned matrix clinopyroxenes. Since they show relatively high CaO contents (4-5 wt%), these pyroxenes correspond in composition to typical pigeonites. Their Mg# (MgO/(MgO+FeO)*100; molar) vary between 75 and 82, and are generally slightly higher compared with the rimming matrix clinopyroxene. This implies that the magma which generated the low-Ca pyroxene was more primitive than the later one producing the matrix clinopyroxene, which contrasts with the general observation that orthopyroxene is more stabilized in evolved MORB systems than in primitive (at shallow pressures). The textural features of the low-Ca pyroxenes suggest that partial melting reactions proceeded instead of simple resorption by a later magma.

References

Individual particle analysis of urban aerosols in the Rhein-Main area

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Epidemiological studies have shown a correlation between aerosol concentration in the ambient air and mortality. Adverse health effects seem to be better correlated with the surface or the number as with the mass of aerosol particles inhaled. Therefore individual particle analysis techniques provide very valuable additional information to the conventional performed mass concentration measurements (Pm).

In the years 2003 and 2004, size-resolved aerosol particle samples in the size range 0.1 – 10 µm aerodynamic diameter were collected at an urban background station in Mainz, Germany. Size, morphology, chemical composition and mixing state of more than 5400 individual particles of seven selected sampling days were analyzed in detail by scanning electron microscopy and energy-dispersive X-ray microanalysis. In addition, transmission electron microscopy, aerosol mass spectrometry and atomic force microscopy were applied to obtain further information about the mixing state of the particles. The fine particle fraction (diameter < 1 µm) is always dominated by complex secondary aerosol particles (≥ 90 % by number) independent from air mass origin. These particles are complex internal mixtures of ammonium and sodium sulfates, nitrates, and organic material. Between 20 and 40 % of the complex secondary aerosol particles contain soot inclusions. The composition of the coarse particle fraction (> 1 µm diameter) is strongly dependent on air mass history with highly variable abundances of complex secondary aerosol particles, aged sea-salt, silicates, silicate-mixtures, calcium sulfates, calcium sulfate/carbonate mixtures, calcium nitrate/carbonate mixtures, biological particles, and external soot.

The dominance of complex secondary aerosol particles shows that reduction of the precursor gases has to be a major goal for successful reduction strategies for PM10. Additionally, because of the carcinogenic potential and the frequent occurrence of soot inclusions within secondary aerosol particles, the reduction of the soot component has to be an important goal.
Evaluation of oxidation state and potential for bio-signatures in Fe-bearing minerals in deep-sea minerals using spectroscopic approaches

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X-ray absorption spectroscopy has proven to be a useful way of examining the chemical state of various elements in Earth materials. Iron is the most abundant redox-active element near the Earth’s surface, and is particularly abundant in oceanic rocks and minerals and biological mats that occur in hydrothermal systems. Basalt is the dominant extrusive rock that comprises the ocean crust, and is approximately 10 wt % FeO, principally as Fe(II). Hydration and oxidation of basalt during water rock reactions produces clay minerals and oxides of variable composition, crystallinity, and oxidation state on the surfaces of basalt. Sulfide minerals, such as pyrite (FeS₂) that precipitate at hydrothermal vents also undergo alteration reactions that produce Fe(III) minerals. We are using XANES (X-ray absorption near-edge spectroscopy) to examine Fe-bearing rocks and minerals from the deep sea. Our objectives are two-fold: 1) test our ability to discriminate Fe(II) from Fe(III) in rocks and minerals from the seafloor; to discriminate between Fe(II) and Fe(III) we are using a new method is proposed which is usable with only ordinary levels of energy resolution, signal/noise, and energy calibration accuracy. 2) Examine the range of natural Fe(III)-bearing minerals occurring in the deep sea in order to determine if biological activity produces a distinct signature in the short- and intermediate-range order.

The Loihi Seamount microbial observatory: An extremely common deep-sea habitat for Fe-oxidizing bacteria

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Loihi Seamount is a seismically active submarine volcano that represents an emerging Hawaiian island. Hydrothermal fluids are emitted at the summit, in vicinity to the pit craters, and at more diffuse sites long the flanks of the seamount, even down to the seamount base (5000 meters). Since discovery of this seamount a prominent microbial group that has been recognized and play prominent roles in biogeochemical cycles on the seamount are the neutrophilic iron oxidizing bacteria (FeOB). FeOB habitats include the hydrothermal vents, which range in temperature from ambient (~)°C) to about 55°C presently. The composition of the fluids at Loihi is largely dictated by magmatic degassing and consequently are enriched in carbon dioxide and Fe(II) and are depleted in sulfide by comparison to other deep-seam marine hydrothermal venting habitats. Previous studies have established that FeOB play a major role in Fe oxidation and Fe oxide deposition at the site; these processes may serve as modern analogues to past major Fe oxide depositional settings. Our ongoing studies are evaluating the communities mediating Fe oxidation, the physiology of FeOB, and the biomineralogy of Fe oxides formed by FeOB. Other habitats occupied by FeOB among other microbial groups include the bare rock of the volcano itself, theollitic basalt that undergoes hydration and oxidation reactions in the presence of oxidizing seawater, and rock that interacts with hydrothermal fluids that are being emitted. Ongoing studies are looking at the biogeochemical roles epilithic and endo-lithic microbial communities play in mediating water-rock alteration reactions on basalt surfaces.
**U(VI) and Eu(III) interaction with pyrite (FeS₂)**

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The mechanism of U(VI) and Eu(III) interaction with pyrite was studied by solution chemistry and X-Ray Photoelectron Spectroscopy (XPS). Pyrite dissolution under anoxic conditions leads to the production of sulphoxyanions and ferrous iron, which in turn is sorbed at the pyrite surface. This sorption was confirmed by isotopic dilution. U(VI) is in competition with Fe(II) for adsorption on sulfur sites. This sorption is maximum at pH ≥ 5.5. Co(II) and Eu(III) are also sorbed on pyrite surface at pH ≥ 5.5, confirming that sorption on pyrite does not necessarily result from a redox reaction.

When [U]₉₆h is below 4 10⁻⁹ mol g⁻¹, a redox reaction occurs at the pyrite surface and leads to the formation of reduced uranium and elementary sulphur. Iron remains at oxidation degree +II during the whole process. The formation of these solid products tends to passivate the pyrite surface as the redox reaction is no longer observed when the amount of sorbed U increases. The surface is saturated for [U]₉₆h = (3.4±0.8) 10⁻⁷ mol L⁻¹. The sorption at [U] > 10⁻⁹ mol L⁻¹ can be modelled by a Langmuir isotherm with a sorption constant equal to 8 10⁻⁷ L mol⁻¹.

At higher uranium (VI) concentration, a redox reaction between U(VI) and Fe(II) occurs. This reaction produces a U(IV)-U(IV) mixed (hydr)oxide, U₄O₉(s), and iron (III) (hydr)oxide, such as maghemite (γ-Fe₂O₃(s)), which can in turn participate to U(VI) adsorption.

**Comparison of estimates for Andean Plateau formation from thermochronology and stable isotope paleoaltimetry**

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Quantifying the timing and rates of central Andean mountain building and plateau formation have previously been limited by (1) sparsely available age constraints on the timing of deformation, and (2) a lack of constraints on the elevation history of the plateau. We address these limitations with 52 new low-temperature thermochronometer ages, and stable isotope paleoaltimetry results of Garzione et al (2005) and Ghosh et al. (2006). Thermochronometer samples were collected across two 200-300 km long transects in the northern (~15ºS) and southern (~19ºS) Bolivia thrust belt. We assess the consistency of interpretations of plateau formation from these two approaches.

We interpreted thermochronometer cooling ages along each transect to constrain the timing of deformation in different tectonic zones across the Andes. Results suggest a consistent chronology of deformation in northern and southern Bolivia. We find: (1) deformation initiated ~40 Ma along the plateau margin (Eastern Cordillera) with distributed exhumation across the entire thrust belt since about ~15 Ma, (2) deformation in the eastern part of the thrust belt (Subandean Zone) initiated by ~25-10 Ma, (3) shortening rates across each transect have been similar and decelerated over the last ~20 Ma, and (4) development of the Andean Plateau analogous to it’s modern width (but unknown elevation) occurred by ~20 Ma (Barnes et al., 2006).

In comparison, paleoaltimetry results suggest a 3.7 ± 0.4 km increase in plateau elevation between 10.3-6.7 Ma. Plateau rise is suggested to have increased deformation in the Subandean Zone over this time interval. The retention of a dense mantle root below the plateau could account for the plateau remaining at a low elevation for ~10 Ma after the thermochronometer data suggest its modern width formed. However, the steadiness of shortening rates across the thrust belt since ~20 Ma, as well as the initiation of Subandean deformation predating plateau rise by up to ~10 Ma draws into question the consistency of these two approaches. Work in progress is evaluating if temporal variations in atmospheric temperature and moisture source could account for the appearance of a low-elevation plateau prior to 10.3 Ma from stable isotope techniques.

**References**


Multilayer fixation of dissolved phosphate on natural calcites derived from sorption experiments

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The predominance of different phosphate fixation mechanisms on natural calcite were studied in short-term batch experiments varying in hydrochemical conditions and physical properties of calcites. The fixation mechanism is crucial for the efficiency of sediment capping with calcite as an active material to reduce phosphate flux from anoxic sediments into the water column of eutrophic lakes.

Depending on the specific surface area of the applied calcite (SSA_Cc) as well as on the dissolved phosphate concentration different processes are indicated by sorption isotherms. Low P-concentrations (10 - 30 µmol L⁻¹) in the solution together with a small SSA_Cc (1 - 4.3 m² g⁻¹) lead to logarithmic shaped isotherms, indicating that adsorption processes are predominant. The same shape of isotherm can be achieved if both P-concentration (400 µmol L⁻¹) and SSA (67 m² g⁻¹) are high. Both cases result in a SSA_Cc/P-ratio of 0.1 to 0.2. Low P-concentrations (30 µmol L⁻¹) in connection with a large SSA_Cc (67 m² g⁻¹) as well as high P-concentrations (100 - 200 µmol L⁻¹) and low SSA_Cc (1 - 4.3 m² g⁻¹) result in sigmoidal shaped isotherms. The calculated SSA_Cc/P-ratio for both cases is > 1.8 and < 0.02, respectively. Depending on the residual P-concentration in solution, the sigmoidal shaped isotherms can be divided into three sections indicating different processes responsible for the P-fixation on calcite surfaces. Adsorption prevails in equilibrium with lowest residual P-concentrations. The inflection of the isotherm at moderate residual P-concentrations suggests that precipitation and transformation of Ca-P-compounds becomes dominant. This is supported by characteristic Ca/P-ratios for different Ca-P-compounds, e.g. β-Tri-Calcium-Phosphate, Octa-Calcium-Phosphate. The last section, with highest residual dissolved P-concentration, shows a logarithmic form, which can be attributed to adsorption onto the newly formed Ca-P-surface. Our results indicate that the P-fixation onto calcite is as multilayer process.

In addition, calcite saturation of the solution has an implication on the precipitation process. Subsaturation leads to partial dissolution of calcite followed by heterogeneous nucleation of Ca-P-compounds whereas supersaturation is followed by precipitation via solid solution formation.

Petrography, geochemistry and isotope characteristics of authigenic carbonates from the Mid-Atlantic Ridge

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Although much work focused on sulphide mineralogy of active hydrothermal systems hosted in ultramafic rocks, little is known about the genesis of authigenic carbonates found in these settings. Serpentinization of peridotites at mid-ocean ridges leads to the formation of carbonates. The hydrolysis of peridotite minerals results in an increase in pH. The high alkalinity favours the precipitation of calcium carbonate. Almost 20% of the ocean crust consists of ultramafic rocks. The formation of carbonates in ultramafic rocks may consequently represent a major CO₂ sink in the global carbon cycle. Yet, the geochemical parameters of carbonate formation in ultramafic systems are poorly understood.

We analyzed serpentinite-hosted carbonates, sulphide-hosted carbonates, and dolomite hosted in red jasper from the Logatchev hydrothermal field. The unusual dumbbell-shaped crystal aggregates of dolomite represent the first observation of dolomite in a hydrothermal environment. From the Gakkel Ridge serpentinite-hosted carbonates have been studied. Most serpentinite-hosted carbonates are isopachous and botryoidal aragonite. Occasionally, microcrystalline aragonite is predating these cements. The paragenetic sequence of the sulphide-hosted carbonates is represented by (1) micrite, (2) botryoidal and isopachous aragonite and (3) clotted micrite. Our observations reveal that carbonate formation is not a single event during late-stage seafloor alteration. δ¹⁸O values of the serpentinite-hosted carbonates range from −20.0 to +5.3‰, those of the sulphide-hosted carbonates range from +1.3 to +4.2‰. Dolomite in the red jasper exhibits δ¹³C values from −9.2 to −7.0‰. δ¹³C values of sulphide-hosted carbonates vary from +2.5 to +3.6‰, those of dolomite dumbbells range from +2.6 to +3.0‰. δ¹³C values of the serpentinite-hosted calcite that formed at high temperatures range from −5.8 to −5.5‰, reflecting a signal of mantle CO₂. The δ¹³C values of the serpentinite-hosted aragonite range from −1.6 to +2.7‰, which are typical for marine carbonates. We suggest that δ¹³C values of +3.0‰ and higher found for carbonates in serpentinites may reflect a partial contribution from methanogenesis. This hypothesis is supported by high Fe contents in these carbonates. Chondrite-normalized REE+Y patterns of the dolomite dumbbells are characterized by (1) a negative Ce anomaly, (2) a positive Eu anomaly, and (3) a slight enrichment of HREE. The negative Ce anomaly of the dolomite dumbbells indicates formation from oxic waters.
Denudation rates in NE-Iceland. Evolution of a steady state model of erosion

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This study critically assesses the temporal sensitivity of a steady state model of erosion that has been applied to various chemical and mechanical weathering studies worldwide. The model assumes a geochemical mass balance between the initially unweathered rock of a drainage basin and the weathering products (Gaillardet et al., 1995).

The model was applied on 89 samples of river dissolved and suspended matter collected during 1998-2002 from five basaltic glacial river catchments in NE-Iceland. The steady state model of erosion was sensitive to the seasonal changes of the dissolved constituents in the rivers. However, the measured and modelled results are within the error of the method. The modelled concentrations of the suspended inorganic matter were most consistent to the measured ones, when the average annual chemical composition of the dissolved- and the suspended matter was used in the modelling (figure 1).

These results validate the use of a steady state model of erosion in estimating the denudation rate at a catchment scale. Best results are gained when samples are collected at close to average dissolved loads of the rivers.

References

Dehydration processes determine fO2 of arc and intraplate magmas

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Chromite inclusions within early-crystallised olivine phenocrysts (Fo>85 mol%) in most arc lavas have lower Fe2+/Fe3+ ratios than similar inclusions from MORB. This can be calculated to reflect a higher oxygen fugacity (ΔFMQ>+2) in the source region of arc magmas compared to the source of MORB (ΔFMQ <+1). This higher oxygen fugacity in arcs is likely related to the “subduction component” added to the asthenospheric, MOR-like mantle. Aqueous fluid by itself is a very inefficient medium to increase the mantle’s oxygen fugacity, so it has been proposed that Fe3+-bearing melts are involved (Frost and Ballhaus, 1998). However, not all arcs show influence of a slab-derived melt.

We propose that the observed higher oxygen fugacity in arcs is related to the dehydration of serpentinites, formed in either the downgoing slab or the forearc mantle. Serpentinisation involves the hydration and oxidation of olivine and pyroxene, and generation of serpentine, magnetite, ± brucite, H2 ± CH4 (Frost, 1985). Serpentinites release their water into the sub-arc mantle by formation of olivine and orthopyroxene at ~2-3 GPa and 700-750ºC. Olivine is always more iron-rich than its equilibrium serpentine (Evans, 2004) and neither olivine nor orthopyroxene can accomodate Fe3+, so ferric iron from magnetite needs to be reduced to be incorporated into these minerals. This reaction will liberate oxygen that is carried into the mantle wedge with the aqueous fluid, explaining the high oxidation state of the sub-arc mantle.

Dehydration of the similarly oxidised metabasaltic portion of the subducted slab leads to the formation of an eclogitic mineral (cpx-gt) assemblage, which does not discriminate against Fe3+ in the same manner as ol-opx. This material is subducted into the deep mantle, and recycled to form OIBs. This model agrees with the oxygen fugacity of OIBs being intermediate between that of MORBs and arcs.

References
**Biominerals, proxies, vital effects, and ocean palaeochemistry**

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Successful reconstruction of the physics, chemistry and biology of past oceans from marine biominerals requires the fusion of several strands: understanding the physical basis of trace element and isotopic incorporation, modelling, empirical calibrations, analysis of natural systems, critical evaluation of the PCF, evidence by application, high resolution records, new developments. Focussing chiefly on O, C, Mg and B of planktonic and benthic foraminifera, recent work will be presented that gives insights into the biomineralisation process (vital effects), how conflicting results from proxies may be reconciled, and on changes in ocean temperature, carbonate ion saturation and hydrography over glacial-interglacial periods.

**High-pressure mineral inventory in the Ries crater, Germany: A window to phase transformation processes in planetary interiors**

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**High-pressure mineral inventory**

The impact event that created the Ries crater in the Swabian Alb 14.7 My ago induced high-pressure phase transformations in minerals in the crystalline basement. These inversions include quartz to coesite and stishovite, graphite to diamond (El Goresy et al., 2001a), rutile to two new dense and ultradense polymorphs of TiO2 (El Goresy et al., 2001b; El Goresy et al., 2001c). In situ study of these high-pressure polymorphs is a key method in uncovering critical parameters that promoted and controlled the high-pressure mechanisms of phase transitions, possible back transformations and in conducting a more realistic estimate of the equilibrium shock pressures in natural events.

**Results and discussion**

We successfully in situ localized quartz-coesite, graphite-diamond, and rutile to orthorhombic (space group Phen) and to the monoclinic polymorphs (space group P2/c) inversions. Quartz-coesite inversion is preferably localized at the grain boundaries to neighboring denser minerals. Raman mapping revealed the presence of coesite intergrown only with undeformed quartz thus indicating partial back inversion of coesite or plausibly complete back inversion of stishovite to quartz. Graphite/diamond inversion is never complete (<60%) and is localized exclusively at the graphite/garnet interface as a result of the high difference in shock impedance. The petrographic settings of the two new TiO2 dense and ultradense polymorphs with their parental rutile also indicate the crucial importance of phase boundary settings in accomplishing the phase transitions. Grafhite/diamond and rutile to the both dense orthorhombic and the ultradense monoclinic polymorphs are encountered in graphite-bearing garnet-cordierite-sillimanite gneisses and their coexistence allows to constrain the equilibrium shock pressures to be definitely < 28 GPa and the post-shock temperature < 200°C.

**References**

El Goresy A. et al. (2001c) *Science*, 293, 1467-1470.
Trace element data and fluid regime during HP-LT metamorphism of basic rocks, Ile de Groix, France

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Trace element contents in whole-rock samples and minerals of the metamorphic rocks of the Ile de Groix - part of a Hercynian HP/LT metamorphic belt - were analyzed in massive and banded eclogites and blueschists. Geochemical data indicate that the protoliths of the massive lithologies represent MORB-type basalts. The banded lithologies are of volcano-sedimentary origin.

Trace elements contents for metamorphic assemblages were determined by LA-ICP-MS. GR03 is a banded blueschist containing an assemblage of grt-ep-Fe3+ rich gln-pheng-rt-mt-volcano-sedimentary origin.

The comparison of massive and banded rocks indicates that the massive rocks were less affected by the fluid/element transfer than the banded rocks. Epidote in massive eclogites is REE enriched compared to the bulk rock. The distribution of REE in epidote is highly variable in all rock types. This seems to be constrained by the local equilibria associated with the appearance and disappearance of new stable mineral phases (garnet, apatite or titanite) during the various stages of metamorphism. We suggest that the massive rocks were less rich in fluid components before the onset of high-P metamorphism, and that during fluid escape the REE mostly remained trapped in the newly forming mineral phases.

Reference

Diffusively driven Li isotope fractionation

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The cycling of Li at the Earth’s surface results in marked isotopic fractionations (~40%) that lead to the subduction of isotopically heavy Li. This scenario suggests that Li isotope ratios should provide a distinctive tracer of subducted components in oceanic basalts. Such promises are based on the tacit assumption of equilibrium, in which only low temperature processes can significantly fractionate stable isotopes. However, several recent experimental and observational studies have highlighted that Li isotopes are readily fractionated in magmatic processes by diffusion. In order to use Li isotopes as a tracer of recycled material it is thus critical to understand the role of diffusion on Li isotopes at different length scales.

We have examined Li isotopic profiles in phenocrysts of lava flows. Except in glassy samples, we commonly find zoned crystals. Such isotopic zoning appears to be the natural consequence of cooling, during which the partition coefficient of Li in phenocrysts increases. We have reproduced the forms of isotopic profiles in a self-consistent model driven only by cooling. Deriving absolute cooling rates depends on several parameters which are currently poorly constrained (e.g. the diffusivity of Li in olivine), but the data plausibly imply temperature drops of a few hundred degrees in hours.

The influence of diffusion on the Li isotopic composition of a whole lava flow, rather than its redistribution during final cooling, is more difficult to determine. The general over-lap of (unzoned) olivines from peridotite xenoliths with many mantle derived melts suggest that whole rock compositions are not ubiquitously fractionated by diffusion. As an empirical assessment of possible diffusively driven differences in bulk Li isotopic compositions, we have analysed a suite of samples from the East Pacific Rise (9-10°N). These samples show near homogeneity in long-lived radiogenic isotope tracers but contrasting U-series disequilibria, suggesting their derivation from different depths of the melting regime. This should give rise to differential chemical gradients between the melts and mantle through which they finally ascend, potentially driving different diffusional loss of Li. Although the sample suite shows a significant range in δ7Li related to disequilibrium, its magnitude is small (0.7‰), suggesting that the role of diffusion in influencing these lava compositions is minor.
Consideration of formation buffering potential and reactive mineral availability pertaining to geological storage of carbon dioxide

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One promising strategy for decreasing CO₂ emissions to the atmosphere is carbon capture and storage in deep saline formations. Modelling efforts and the experimental measurements that support these efforts are critical to determining the fate of injected CO₂. The focus of this work is CO₂-water-rock interactions as they pertain to formation buffering potential and reactive mineral availability. In addressing formation buffering potential, PHREEQC was used to model pH evolution in siliciclastic and carbonate rocks. The initial mineral and formation water compositions were determined from analyses of core samples and brines from several formations in the Alberta sedimentary basin in western Canada. Simulation parameters correspond to injection conditions of 50°C, CO₂ pressure of 100 bar and high ionic strength. The aim of this modelling is to evaluate host formation mineralogy based on the ability to buffer the acid created by CO₂ injection.

Our second goal is to better define mineral abundance and availability in siliciclastic sedimentary rocks, to support the development of relationships for upscaling reactive transport. Energy dispersive X-ray spectroscopy and back-scattered electron microscopy were used to identify minerals and characterize the spatial distributions of potentially reactive minerals in thin sections from the Alberta Basin. Minerals of mean atomic mass greater than quartz, which include those that are reactive under acidic conditions, occur as entire grains in sandstones and shaly sandstones. Kaolinite is found to cement quartz grains and line pore spaces, decreasing primary porosity and obscuring contact between pore fluids and reactive minerals. There is less kaolinite in conglomerate sandstones but reactive minerals are sparse and typically found as inclusions, thus limiting their contact with pore fluids. The sandstone specimens have between 1% and ~5% reactive minerals, but these estimates of mineral abundance overestimate the percentages of reactive minerals accessible to pore fluids by as much as a factor of five. Incorporation of these results into reactive transport models will allow for more accurate representation of formation reactivity with injected CO₂.

Reactive transport and pore-size controlled solubility in porous rocks

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Nano-scale pores in sediments and soil can modify the effective solubility of minerals, allowing highly supersaturated fluids to exist within the porous medium; this mechanism suggests that precipitation or dissolution can occur when fluid flows from small pores into larger ones, or vice versa. Pore-size controlled solubility (PCS) is a process which stems from the surface tension associated with crystals growing in rigid pores. In many ways analogous to the capillary pressure at a liquid-vapor interface within a pore, this surface tension gives rise to an excess pressure within the crystal, which can be related both to solubility and pore size. Here, we demonstrate how PCS can be incorporated into continuum equations for fluid transport and porosity evolution in simple porous media. Using numerical simulations, we demonstrate that the PCS mechanism can account for the filling of large pore spaces during transport through a heterogeneous rock matrix and represents an effective mechanism for fracture mineralization. In addition, evidence for PCS from scanning electron microscope (SEM) analyses of sedimentary rocks is also presented.
A micrometeoritic "volcanism" in the early thermosphere

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Our scenario, "EMMA" (Early Micrometeorite Accretion), describes the formation of the Earth's atmosphere through the destruction of volatile-rich micrometeorites during their frictional heating in the thermosphere [1]. We recently improved EMMA by taking into account: (i) measurements of the C, N and S contents of Antarctic micrometeorites (AMMs) [2, 3]; (ii) studies of the Wild 2 cometary grains showing that AMMs could have a cometary origin [e.g., 4]; and (iii) studies of unweathered AMMs recovered from ultra-clean snow in Central Antarctica [5].

About 99% of the AMMs are related to the volatile-rich hydrous-carbonaceous chondrites. The Earth's atmosphere has a "micrometeoritic-like" composition: the average values of D/H ratios and the Ne, N₂, H₂O and C contents of a few hundreds of AMMs are similar to that of the ~2 x 10^24 grams of the Earth's atmosphere that formed about 4.4 Ga ago. This micrometeoritic "purity" of the Earth's atmosphere can be most simply interpreted if the Moon forming impact blew off most of the complex pre-lunar atmosphere at a time when the young Earth was already mostly degassed.

This similarity also suggests that the composition of the micrometeorite flux was invariant with time since the formation of the Moon. This invariance yields a simple accretion formula to estimate the total amount, Mₘ, of any given species, A, deposited on the Earth by the degassing of AMMs during their atmospheric entry after formation of the Moon:

\[ Mₘ \sim \frac{[A(\%) / 100]}{\Phi} \times \Phiₘ \]

where, \( \Phiₘ \) is the integrated mass flux of micrometeorites since the formation of the Moon, and \( A(\%) \), the wt.% of specie A in AMMs. We derived three independent estimates of \( \Phiₘ \) by taking into account: (i) measurements of the C, N and S contents of Antarctic micrometeorites (AMMs) [2, 3]; (ii) studies of the Wild 2 cometary grains showing that AMMs could have a cometary origin [e.g., 4]; and (iii) studies of unweathered AMMs recovered from ultra-clean snow in Central Antarctica [5].

References

Characterization of the silicon isotopic composition of the terrestrial biogenic output from a boreal forest in Northern Sweden

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During the last decade, the potential plant impact on the biogeochemical cycle of Si via the large terrestrial biogenic Si reservoir formed by vegetation has attracted considerable interest. It has been concluded that the release of silicic acid from dissolution of soil phytoliths might exceed the Si mobilized by weathering of Si-containing primary minerals, which implies that the biogenic contribution to the total content of Si in the soil profile must be considered in weathering studies.

Information about Si isotopes can potentially be used for differentiation between relative contributions from biogenic and mineral sources in natural waters, soil solutions and plants. This would, however, require thorough characterization of the terrestrial biogenic Si reservoir, a task that received somewhat limited attention to date.

The aim of the present study was to characterize the Si isotopic composition of a boreal forest, with bedrock consisting of dolomitic limestone, in Northern Sweden. Representative biomass from the forest area exhibited a surprisingly homogenous Si isotopic composition, ranging from \( \delta^{29}\)Si (~0.14 ± 0.05)‰ (2σ) to (0.13 ± 0.04)‰. Further, a change in the Si isotopic composition of (+0.39 ± 0.04)‰ has been detected in Leymus arenarius, indicating predominant accumulation of heavier isotopes from spring to autumn.

Recent studies of Si isotopic composition in plants have focused on the root uptake of dissolved silicic acid as the only Si accumulation path. Results acquired during the present study provide compelling evidence to suggest that exogenous Si is also incorporated in the surface structure of the plant material. A surface contribution in excess of 5% of the total Si would introduce a significant shift in the bulk isotopic composition (~0.1‰) assuming that the exogenous material differed by 2‰ from the biogenic Si. This strongly suggests that the surface contribution must be carefully considered during in situ uptake studies.

References
Intragranular replacement of chlorapatite by hydroxyapatite during scapolitisation

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Intragranular replacement of chlorapatite by hydroxyapatite is studied in the Ødegården metagabbro, Bamble sector of south Norway. The Ødegården metagabbro is pervasively scapolitised in a 1.5 km long zone of 50-100 m thickness, forming a rock composed of Cl-rich scapolite + rutile + apatite ± edenite ± phlogopite ± enstatite ± diopside. The magmatic apatite is non-porous and homogenous in composition with a Cl-content of c. 2 wt%. Scapolitisation transforms apatite during multi-stage replacement reactions: I) The magmatic apatite was transformed to chlorapatite with Cl-content of 6.5 wt%. II) A secondary replacement reaction transforms the chlorapatite to porous hydroxapatite with only minor Cl (Fig. 1), and is correlated with a hydration of enstatite to talc. The observed compositional zoning in apatite is consistent with observations of apatite from pegmatites cutting the Ødegården metagabbro (Harlov et al. 2002). The observed changes in Cl-content of apatite is interpreted to reflect the fluid evolution and the propagation of metasomatic fronts through the gabbro. The reaction mechanism of chlorapatite to hydroxyapatite is studied by energy-filtered transmission electron microscopy (TEM). A TEM-specimen across the replacement interface was prepared using a focused ion beam apparatus (FIB). The diffraction pattern is similar in the chlor- and hydroxyapatite parts of the crystal. The results are consistent with replacement by a coupled dissolution-reprecipitation mechanism during metasomatism.

Figure 1: Chlorapatite (light grey) partly transformed to hydroxyapatite (dark grey).

Dissolution from a CO2 lake

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If liquid CO2 is stored as a dense "lake" on the deep ocean floor, it is expected to dissolve in seawater. A similar situation may occur if CO2 is dissolved from a saturated benthic boundary layer caused by a potential leak of geological stored CO2. Due to ocean currents and turbulence the net rate of release may increase by several orders of magnitude compared to molecular diffusion. However, density stratification induced by dissolved CO2 will tend to reduce vertical mixing. This scenario has previously been modelled in two dimensional domain (e.g. Fer & Haugan, 2003; Haugan and Alendal, 2005). There has also been a three dimensional study (Enstad et al. 2006) using the MIT general circulation model (http://mitgcm.org). Recently the MITgcm model has been coupled with the General Ocean Turbulence Mode (http://gotm.net/), and this model is used to simulate the lake option. The new vertical turbulent mixing scheme takes into account density effects, and should give more realistic results for the CO2 plume than constant eddy diffusivity models. The introduction of a third direction gives qualitatively different results for the spreading of the CO2 plume than previous two dimensional results. Among the results we also show the hit rates of a passive tracer passing through the domain.

References

Reference
Development of the high precision measurement of mercury species isotopic ratios by GC-MC-ICP-MS and its validation with two other analytical approaches

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Development of the novel technique
Mercury is transformed by microorganisms into organic forms, mainly CH$_3$Hg ($\text{MeHg}^+$) and (CH$_3$)$_2$Hg (di-MeHg), which are highly toxic and volatile. Hence, two most abundant Hg species in the environment are Hg$^{2+}$ and MeHg. Since gas-chromatography (GC) is one of the easiest approaches to separate this species on-line, with relatively simple sample preparation, we have estimated the suitability of the GC hyphenation with MC-ICP-MS for the precise isotopic analysis. A new protocol for the simultaneous measurement of isotopic ratios in Hg species was developed.

Validation of developed method versus other techniques
Two other analytical approaches cold-vapour generation (CVG) and continuous nebulization (CN) were chosen as reference techniques to validate the measurement of isotope ratios by GC-MC-ICP-MS. Analytical performances of these three techniques were compared, and precision for the different techniques are compared in the table below. Optimisation of the integration approach of the transient signal and GC parameters provide a suitable precision for the Hg isotopic analysis in environmental samples.

<table>
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<tr>
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Conclusions
When analysing real-world samples for Hg species isotopic analysis, preliminary sample preparation for both CVG and CN are very time- and labour-consuming in comparison with GC, while GC has a higher precision of the measurements. The precision of the GC-MC-ICP-MS measurement can be improved if a preconcentration step is applied before injection into the GC.

Stress-induced redistribution of Y and HREE in garnet during high-grade polynmetamorphism

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Almandine garnet (Alm$_{62.6}$Pyr$_{11.4}$Sp$_{8.4}$And$_{6.5}$Grs$_{4.0}$) exceptionally rich in Y$_2$O$_3$ (1.8-2.3 wt%), Sc$_2$O$_3$ (0.11-0.23 wt%), HREE$_2$O$_3$ (1.9-2.3 wt%) and Na$_2$O (~ 0.3 wt%) occurs in Precambrian quartzofeldspatic granulites ($T$ ~ 860 °C) on Hisarøya, Western Gneiss Region, Norway. The granulites were partially reequilibrated to eclogite- ($P$: 14.9 ± 1.3 kbar, $T$: 649 ± 67 °C) and amphibolite-facies assemblages during the Caledonian Orogeny. The high Y and HREE concentrations allowed quantitative analysis and imaging of element distribution at the spatial resolution of EMPA. The granulite-facies garnet is overgrown by Caledonian garnet with Y$_2$O$_3$ and HREE$_2$O$_3$ both below 0.1 wt%. The granulite-facies cores are reequilibrated to lower Y$_2$O$_3$ and HREE$_2$O$_3$ in an outer zone, typically ~ 4 µm thick, (both Y$_2$O$_3$ and HREE$_2$O$_3$ ~ 1.2 wt%), and along internal deformation structures including microfaults with horsetails, en-echelon bands and splaying features around the tip of fractures (Y$_2$O$_3$ and HREE$_2$O$_3$ ~ 1.8 wt%). Locally, the internal reequilibrated zones, typically 10-20 µm across, have shoulders with higher Y and HREE (~ 2.9 wt%) than in the original garnet, suggesting closed-system behaviour for these elements. In addition, the garnet locally displays a m-scale complex mesh-like pattern with high and low HREE and Y bands, possibly related to straining. All features indicate ineffective Y and HREE diffusion under the present P-T conditions. Two charge-balancing mechanisms account for Y and HREE incorporation: (1) the YAG substitution involving incorporation of Al into the tetrahedral site is dominant in the granulite-facies garnet, and (2) coupled substitution with Na into the dodecahedral site is increasingly important during high-P reequilibration. The internal closed system reequilibration of the granulite-facies garnet may be due to stress concentrations build up in relic garnet during the eclogite-facies event. Possible mechanisms for reequilibration are discussed.
Petrogenesis of the basic volcanism behind the volcanic front (Cinotepeque range, El Salvador)

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Most of Quaternary volcanic activity in El Salvador is concentrated to 5 major volcanic centres, forming part of the volcanic front (VF), directly related to the subduction of the Cocos Plate under the Caribbean Plate. A volcanologically distinct volcanic province is represented by diffuse clusters of subrecent cinder cones and small shield volcanoes behind the volcanic front (BVF). While geochemistry of the prominent BVF zone, situated in the Ipala transtensional Graben along the Guatemala–Salvadorian border, has attracted much attention, the minor Quaternary BVF field in the central El Salvador has been little studied so far. This zone of 30 individual volcanic bodies extends from the Boquerón Volcano (VF) c. 20 miles N, as far as the N–S trending horst of the Cinotepeque Range (Rapprich & Hradecký, 2005).

Compositional data available for the Cinotepeque area correspond to a suite of fairly fractionated subalkaline basalts and basaltic andesites (mg# < 55, Cr < 149 ppm and Ni < 56 ppm). Characteristic is steep increase in K2O with increasing differentiation (SiO2). Identical trend is observed in the lavas from Boquerón and, to some extent, the Ipala Graben (data of Carr, 2003). Similar behaviour may be demonstrated also for the other LILE. In the SiO2–FeOtot/MgO plot, the whole series falls within the Fe-rich, “tholeiitic” field. On the other hand, the K2O increase in lavas from the more remote VF edifices is much slower and their FeOtot/MgO significantly lower, typical of normal calc-alkaline rocks.

In spite of similarities of BVF and adjacent VF volcanoes, there are also differences. At the given SiO2, the BVF lavas have higher MgO, lack the negative Eu anomaly, and show lower LILE/HFSE ratios indicative of diminishing subduction fluid involvement (Ba/La > 43). Similar pattern was reported previously also from the Ipala area.

Compositional trends in main oxides of the Cinotepeque lavas can be modelled by up to 40% fractional crystallization (plg 40%, augite 35%, olivine 20% and magnetite 6%). The enrichment in incompatible elements requires comparable degrees of fractionation. The variation in silica contents in the BVF lavas is limited. Clearly the SiO2 content of the fractionating assemblage (43.6 %) was too similar to the most primitive lavas (49.7 %) to produce acid magmas.

References


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Geochemistry of an actual Fe-sulfides formation from Acisu district, Karsanti, Adana, Turkey

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The aim of this study is to elucidate the geochemical characteristics of the Acisu district actual Fe-sulfides (pyrite/marcasite) formation (Karsanti, Adana, Turkey). Around this mineralization, Upper Cretaceous ophiolite is cropped out and Paleozoic and Mesozoic aged sedimentary rocks are trusted over it. The Fe-sulfide occurrence is approximately 25 m length, 5 m width, and 3 m depth in diameter. The paragenesis comprises marcasite, chalcopyrite, quartz, hematite and calcite/dolomite. Approximately 0.5 l/s hydrothermal water (pH=4-6 and T=40-45°C) is going out to surface as a spring. Total sulfur concentration of the is 200-250 µM. It is known that Ti, Ni, Co, Mn, Zn, Pb, Ge, Cd, and As contents and Co:Ni ratio of the pyrite/marcasite are permit to distinguish them sedimentary, high and low temperature occurrences (Huston et al., 1995; Temur et al., 2006). Fe and Sb contents in the ore showed positive correlation, against to strong negative correlation of Fe and SiO2, Al2O3, CaO, MgO, Sr, U. Wide ranges in concentrations of Cd, Cr, and Zn characterize the mineralization. The samples contain low Ag (12 ppm), As (26 ppm), Ni (14 ppm), Sr (1.4 ppm), Y (0.25 ppm), versus high Cu (9600 ppm), Mo (23 ppm), Pb (120 ppm), Se (86 ppm). Based on cluster analysis, four main groups can be clearly distinguished. These are the main oxides group (SiO2, CaO, MgO, Al2O3, Sr and U) respecting enrichment of these element against to Fe; the iron-sulfide group (Fe, Sb, LOI and TOS) representing of the main marcasite mineralization; the chalcophile elements group (Zn, Cd, Hg, Ga, Ag and Cu) reflecting a mineral accumulations by sulfo-salt in solution; and the Co-Cr group (Co, Bi, Se, As, Cr, Y, and Au) representing contamination by ultramafic wall rock. On the triangular diagram of (Sr-Sb-Zn) and (Sr-Co-Zn), three mineralization types can be deviated from each other as: (1) pure marcasite; (2) marcasite which contains rich lattice stoichiometric substitutions; (3) marcasite which contains rich other sulfide minerals.

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Calcification in hermatypic corals is based on direct seawater supply to the biomineralization site

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Corals are major CaCO₃ producers the ocean and their skeletons contain a unique archive of paleo-environmental information based on their isotope and trace element composition. The physiological process of biomineralization in corals, however, is not well understood, thus limiting our ability to predict their resistance to global changes, and lowering the reliability of paleo-environmental reconstructions. We investigated the biomineralization processes in the hermatypic coral species *Pocillopora damicornis* and *Stylophora pistillata* using fluorescent dyes with laser confocal microscopy. Colonies growing flatly on glass Petri dishes and small colonies completely covered with tissue (microcolonies) allowed direct in vivo microscopic observations on the actively growing crystals at the calcification site. The fluorescent cell impermeable dyes Calcein and FITC-Dextran which were added to seawater were incorporated to the aragonite skeletons of micro-colonies during short incubations of several hours. This suggests direct seawater supply into the calcification site. The seawater probably passes through the calicoblastic epithelium in narrow paracellular pathways between cells. The size of these narrow pathways is probably between 20 nm and 1 µm based on the incorporation of fluorescent plastic spheres into the growing skeleton of micro-colonies. Previous studies demonstrated the involvement of membranal Ca²⁺ channel and Ca-ATPase in the calcification process of corals. We propose that in addition to the activity of these channels and pumps, Ca²⁺ and CO₃²⁻ ions are supplied to the calcification process directly with the seawater. The activity of Ca-ATPase may be very important to elevate the pH of the seawater at the calcification site, thus increasing the CO₃²⁻ and facilitating diffusion of inorganic and respiratory CO₂(aq) into the calcification site. Our findings explain both the high sensitivity of corals to ocean acidification and their high fidelity in recording paleo-environmental proxies of ocean chemistry.

Environmental pollution originated from open dumping of solid waste in the cities of Eastern Black Sea

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Almost all municipalities dispose and discharge their wastes and wastewaters into the shallow sea water and the coast, mostly without treatment and outfall systems in the countries on the Black Sea coast. About 450-500 tons solid waste is generated in a day and more than 70 percent of solid waste having high organic and inorganic strength is disposed to the open dumps, land, sea and the rivers in the coastal cities of the Eastern Black Sea Region, Turkey. In the coastal cities of Eastern Black Sea Region, collection and transportation stage of solid wastes are generally well organized, but not disposal of municipal, industrial and agricultural wastes. All municipalities and industrial factories have disposed their solid wastes with together hospital and hazardous wastes to the nearest lowlands and river valley or directly into the sea environment without any prior treatment. This solid waste management strategy applied for a long time has threatened environmental health. Due to these solid waste and wastewater management strategies, coastal cities of Eastern Black Sea are faced with serious environmental and administrative challenges in recent years. In this study, an overview of the current solid waste management situation in Eastern Black Sea Region and provides a brief discussion of the future challenges are analyzed, the environmental, technical, social goals are discussed.

References
Nanonuggets and their implication for core formation

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The Platinum group elements (Ru, Os, Ir, Pd, and Pt) together with Au and Re are defining the geochemical group of the highly siderophile elements (HSE) based on their 1 atm extremely high metal/silicate partition coefficients ($D_{\text{metal}} > 10^5$). In consequence, these elements are present in very low absolute elemental concentrations in the Earth’s upper mantle ranging from 0.3 ppb for Re to 8 ppb for Pt.

However, two startling observations led to the “enigma of the overabundance of the HSE” in the Earth’s upper mantle [1]. First, according to their extremely high metal/silicate partition coefficients at 1 atm, all HSEs should have been stripped entirely into the Earth’s core by the Fe-rich liquid forming the Earth’s core, resulting in unmeasurable low concentrations left in the mantle. Second, their elemental abundances show interelement ratios which are similar to what is observed in CI chondritic material.

The development of new analytical techniques made accurate HSE concentration determinations in basaltic, ultramafic and synthetic samples possible, and in consequence, stimulating fundamental experimental investigations of their partition behavior between metal, silicate and sulfide phases.

LA-ICP-MS techniques revealed another exciting feature of the HSE geochemical behavior: the so-called Nanonugget formation problem, mostly observed at very low oxygen fugacity conditions. At present it is under debate whether these Nanonuggets are intrinsic features of HSE solubility in silicate melts [2], contaminants [3] and, therefore, non-representative for its natural equilibrium solubility, and/or simply quench products. Including or excluding Nanonuggets during the elemental concentration determination procedure alone can account already for two to 3 orders of magnitude regarding their metal/silicate partitioning behavior. The clarification whether Nanonuggets represent the true solubility of an element, or are contaminants which, in consequence, have to be excluded from the concentration determination needs fundamental investigation.

In this paper, we present the latest results on our study on the formation and existence of Nanonuggets in Re, Os, Pt, Rh, and Ir containing experiments and discuss their influence on metal/silicate partitioning during core formation scenarios.

References

Werner Schreyer's experiments on synthetic B-rich high-pressure tourmalines and micas

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Recently Werner Schreyer worked on the synthesis of B-rich mica (boromuscovite) and Al-rich tourmaline (olenite). He published many interesting papers with his colleagues, resulting from high-pressure experiments in Bochum. Olenites, where [4]B substitutes for up to ~2 apfu Si, were synthesized at PT-conditions in the range 10-40 kbar/450-700°C [1]. Like excess-B in olenites, B in boromuscovite is favoured by high pressures and low temperatures. Schreyer was also involved in investigations on natural olenite with [4]B up to ~1 apfu, from Koralpe, Austria [2-3] and from Kola Peninsula, Russia [4]. The unique pegmatite in the Koralpe, which contains B-rich olenite and muscovite may also have formed at relatively high pressures and low temperatures [5-7]. Pure endmember boromuscovite was found to be stable only at 500°C, >5 kbar and at 750°C, >10 kbar, up to 50 kbar [8]. Experimental incorporation of [4]Al extends the high-pressure stability field of boromuscovite to lower pressures [9]. We suggest a similar situation for B-rich olenite: the amount of [4]B may be pressure dependent but the stability field may be extended to lower pressures when significant amounts of [4]Al are present, as in the olenite from Koralpe. Future search for boron in muscovites and in tourmalines should be focused in high-pressure environments. Werner Schreyer’s unique contributions in experimental metamorphic petrology and mineralogy together with his theoretical models should invite petrologists and mineralogists to conduct future work in this interesting field.

References
Molybdenum speciation in anoxic aquatic systems: HPLC-ICPMS determination of molybdate and thiomolybdates.

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Dissolved molybdenum in fresh and marine waters is essentially under molybdate form. Though adsorbed on manganese oxides or complexed by natural organic ligands in specific conditions, molybdate is not very reactive. In anoxic condition, molybdenum can be strongly associated with colloidal organic matter [1]. When sulphide is present, transformation of molybdate to thiomolybdates (MoO_xS_{4-x}) has been proposed to explain Mo precipitation in euxinic water column and sediment Mo enrichment. Such pathway is validated in laboratory [2] but thiomolydates are not yet detected in natural aquatic samples. Here we present a new method that will allow to fulfil this objective: HPLC-ICP-MS protocol is further discussed and apply to lake Pavin samples (a permanently anoxic, sulphide rich crater lake). Molybdate is separated from tetra-thiomolybdate within 15 minutes (fig 1) with optimal conditions.

References

Mass independent fractionation of Hg isotopes during evaporation and condensation processes

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We measured mass independent isotope fractionation during experimental evaporation of liquid metal mercury. Recent revision of the theory of first-order mass dependent fractionation by Bigeleisen (1996) introduced nuclear field shift effects as the cause of mass independent fractionation. In equilibrium conditions, Schauble (2007) calculated the proportions of mass dependent and nuclear volume dependent isotope fractionation between several species of mercury relative to metal mercury vapour. We suggest that nuclear volume dependent isotopic fractionation can occur during evaporation and condensation of Hg.

Different sets of experiments were performed: 1) Hg liquid-vapour equilibrium between 0 and 25°C, and 2) evaporation of liquid Hg under vacuum conditions varying i- the fraction of liquid Hg evaporated at 22°C and ii- the temperature of evaporation (20°C to 100°C). Isotopic compositions were measured by generation of mercury vapour (SnCl2) coupled with an MC-ICP-MS. For the equilibrium experiment, we report \( \Delta^{202/198} \text{Hg}_{\text{liq/vap}} = 0.8 \pm 0.3\% \) on the range of temperature. Results from the vacuum experiments fit perfectly to a Rayleigh distillation system and indicate \( \alpha^{202/198} \text{Hg}_{\text{liq/vap}} = 6.5 \pm 0.3\% \) at 22°C, different from the kinetic theoretical value of 10.1%. Isotopic fractionation between liquid and vapour Hg decreases with temperature to reach close to 0% at 100°C. This suggests that both kinetic and equilibrium processes are involved.

The relationship between \( \delta^{202/198} \text{Hg} \) and \( \delta^{199/198} \text{Hg} \) of vapour Hg in equilibrium with liquid Hg indicates that more than 90% of the total fractionation is explained by nuclear volume processes, while only 15% is required for vacuum experiments at 22°C. This proportion increases exponentially with temperature, as the importance of equilibrium increases over kinetic processes. These results suggest that liquid-vapour equilibrium isotopic fractionation is mainly nuclear volume dependent, whereas kinetic fractionation is mass dependent.

Fly ashes from a waste combustor reflecting progressive Hg condensation (300°C-200°C) did not show mass independent isotope fractionation, suggesting a dominance of kinetic fractionation during Hg condensation.

References
Mineralogy and alteration of fly ash from secondary Pb metallurgy

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The mineralogy and solubility of fly ash and air-pollution-control (APC) residues from a secondary lead (Pb) smelter have been studied on samples from the Příbram smelter, Czech Republic, recycling car batteries, with the emphasis on their potential environmental effect. The X-ray diffraction analysis, scanning and transmission electron microscopy and electron microprobe were used for this investigation. The presence of dominant anglesite (PbSO4) and laurionite (Pb(OH)Cl) was observed in a sintered residue from after-burning chambers (800-1000°C). Low temperature Pb-bearing phases, such as KCl·2PbCl2 and caracolite (Na3Pb2(SO4)3Cl), were detected in the major APC residue from bag-type fabric filters. The formation of anglesite, cotunnite (PbCl2), (Zn,Cd)2SnO4 and (Sb,As)2O3 was observed during the sintering of this APC residue at 500°C in rotary furnace (Ettler et al., 2005a).

The 720-hour leaching test on filter residues indicated rapid release of Pb and other contaminants. Caracolite and KCl·2PbCl2 are significantly dissolved and anglesite and cotunnite form the alteration products, as was confirmed by mineralogical analysis (XRD, TEM/EDS) and PHREEQC-2 modelling (Ettler et al., 2005a,b). The observed Pb-bearing chlorides have significantly higher solubility than anglesite and, following emission from the smelter stack, can readily dissolve, transferring Pb into the environmental milieu (soils, water, inhabited areas). As a result, only anglesite as an alteration product was detected by X-ray diffraction analysis in soil horizons highly contaminated by Pb smelter emissions (Ettler et al., 2005c).

References


Synchrotron studies of RbBr-bearing solutions ± CO2 in synthetic fluid inclusions

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Salt- and CO2-bearing solutions are common in geological environments, yet the consequences of interactions between these components remain unclear. XAS studies of corundum-hosted synthetic fluid inclusions that contain RbBr -CO2-H2O solutions have shown that: 1) Br exhibits a strong pre-edge peak in CO2-bearing solutions at temperatures between 25 and 150°C. The pre-edge feature is similar to that shown by covalently bonded Br, but observed and calculated concentrations of covalent Br-bearing compounds (HBr, Br2, CH3Br) are vanishingly small. An alternative possibility is that CO2 contributes to a charge delocalisation on the solvated Br ion that confers some covalent character to bromine-solute interactions; and 2) Rb EXAFS at temperatures to 650°C and pressures to 0.6 GPa are consistent with a decrease in the number of waters of hydration and Rb-nearest neighbour distances with increasing temperature and pressure. This result is consistent with those of previous workers. The presence of CO2 in concentrations of up to X(CO2) of 0.1 is not observed to have a significant effect on either the number of nearest neighbours or ion-solute differences. However, the possibility that CO2 affects salt speciation by inducing an increase in ion association, cannot be eliminated. Simulations show that a significant increase in the number of Rb-anion nearest number pairs would be difficult to detect by this method.

Overall, the presence of CO2 is shown to affect the local environment of salts in solution, at least at low temperatures. Complementary methods are required to determine the magnitude and consequences of CO2-induced changes in fluids at higher temperatures and pressures.
Non-biological fractionation of Ca isotopes in soils of the Atacama Desert, Chile

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Stable Ca isotopes hold great potential for weathering studies, but their successful interpretation will require improved understanding of processes that fractionate Ca isotopes in terrestrial surficial environments. It has been demonstrated that both biotic uptake and abiotic precipitation fractionate Ca isotopes. To consider abiotic effects in a natural context, we measured Ca stable isotope ratios ($\delta^{44/40}$Ca) in an ancient (2My), nearly abiotic, hyperarid soil in the Atacama Desert. The primary source of mobile Ca in this soil is atmospheric deposition, and the primary mechanism of isotopic fractionation appears to be precipitation of sulfate and carbonate minerals. Most of the accumulated Ca in the upper meter of this soil (2.9 kmol m$^{-2}$) is present as sulfates (2.5 kmol m$^{-2}$). Sulfate-associated $\delta^{44/40}$Ca$_E$ values (vs. bulk Earth) increase with depth (1.4 m) from a minimum of -1.91‰ to a maximum of +0.59‰. Linear correlation between sulfate-associated $\delta^{44/40}$Ca and sulfate-$\delta^{34}$S indicates a $\delta^{44/40}$Ca fractionation factor of -0.4‰ in CaSO$_4$. The overall depth trend in Ca isotopes is reproduced by a transport model that considers repeated small and infrequent rainfall events. The lowest Ca isotope values occur at shallow depths and are reproduced by a Rayleigh model, using measured soil Ca concentrations and the Ca fractionation factor predicted by the relationship with S isotopes. This indicates that the primary mechanism of fractionation in CaSO$_4$ is incremental and effectively irreversible precipitation with downward transport during repeated small rainfall events. This work demonstrates that significant inorganic Ca isotope fractionation in terrestrial settings can be a function of transient conditions of water supply, solution chemistry, and dissolved transport. These conditions are ubiquitous in weathering environments and should be considered in the interpretation of Ca isotope values.

Numerical modeling of continental plate retreating and crustal recycling

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Numerical experiments of oceanic subduction followed by continental collision reveal continuous subduction of the downgoing plate. When the continental plate arrive to the trench, slab pull and ridge push forces drag it into the mantle. When slab pull overcomes plates coupling, the subducting plate detaches from the upper one and starts to retreat. Relatively buoyant mantle astenosphere wedges between the two plates facilitating the continental plate retreating process. The upper crust is scraped off by the astenosphere and thrust over the pro-foreland; on the other hand, the lower crust is dragged into the deep mantle with important consequences for crustal growth models. Models with a weak lower crust exhibit a complete delamination of the lithospheric mantle from the continental crust. At the surface, we have development of a system characterized by two different tectonic regimes: the pro-foreland is dominated by compressional tectonics, while backward crustal thinning is evidenced by very low depth astenospheric mantle. The Western Mediterranean formed from the Oligocene times with a mechanism supposedly analogous to our models. We try, therefore, to compare our results with an extensively studied belt of this area, the Appennines. The geological record and geophysical data show indeed interesting similarities with the models, supporting the idea that the Western Mediterranean is the result of a retreating oceanic and, ultimately, continental plate.
Mineralogy and Nd and Pb isotope signatures of clay-size fraction of northern North Atlantic sediments during the Holocene and Late Glacial: Implications for the inception of modern deep circulation pattern

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The production rate of North Atlantic Deep Water (NADW) is a critical component of the high-latitude ocean-climate system. Here we analyse the mineralogy and Sm/Nd and Pb isotope signatures of the clay-size fraction of four sediments cores collected in Labrador Sea and adjacent basins. Clay composition and their isotopic ratios bring information on the origin of particles driven by deep currents. Our aim is to monitor deep current variability through the Holocene and the Late Glacial.

The cores are located along gyres of NADW components in the NW North Atlantic. In the Iceland basin, cores MD99-2254 (2440 m deep, on the eastern side of the Bight Fracture Zone) and HU91-045-091 (3870 m deep on the western side of the Charlie Gibbs Fracture Zone) are used to document water outflow originating from the Norwegian Sea. In the Labrador and Irminger seas, cores MD99-2227 (3460 m deep, off Southern Greenland) and HU91-045-080 (3024 m deep, on the western side of the Charlie Gibbs Fracture Zone) illustrate conditions along the pathway of the Western Boundary UnderCurrent that carries NADW masses in their deep Labrador Sea gyre.

Based on sedimentary mixings of four regional end-members, our isotopic dataset emphasizes several main changes in the relative contribution of the two major components of North Atlantic Deep Water, i.e. the North East Atlantic Deep water (NEADW) and the Danmark Strait Overflow Water (DSOW) throughout the last 12 kyr, and especially during the Late Holocene.

An innovative tool for in situ monitoring of Fe and associated trace metal mobilization in soils

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Iron (III) oxides are common mineral components of soils, sediments, aquifers and geological materials. Trace metals associate with Fe (III) oxides as adsorbed or co-precipitated species and, consequently the biogeochemical cycles of Fe and trace metals are closely linked. Therefore, the sorption and redox chemistry of Fe (III) oxides have been widely studied because of recognition that they control water chemistry and contaminant behaviour in near-surface geochemical systems. However, most previous experimental approaches, set up to study the in situ evolution of such oxides through redox alternations within soils, suffered from drawbacks related to the disturbance of the soil system during the recovery of the Fe oxides. The aim of this study was to design and test a new tool for the in situ monitoring of Fe and associated trace metal mobilization within soils and for tracking the potential changes of mineralogy of the Fe solid phases. Fe oxides characterized by various (i) mineralogical phases (ferrihydrite, lepidocrocite and goethite) and, (ii) associated co-precipitated trace metals (Cd or As) were directly precipitated on little (2-cm-side square) striated polymer supports. These plates were inserted both in laboratory soil columns under anaerobic conditions and, in three different soil horizons (organic-rich, albic and redoxic) belonging to a wetland located in the western part of France. The pedo-climatic setting and the hydrological and geochemical behaviour of this long-term surveyed wetland is well known. Reductive conditions allowing Fe oxides to dissolve when soils are waterlogged occur annually during the winter season.

The polymer supports were unaltered through time, suggesting that this technique can be safely used to study Fe oxide evolution. Fe amounts were quantified by XRF before and after incubation. The evolution of Fe oxides was also observed by SEM and characterized by XRD. Over a period of three months during the winter season, 69% of ferrihydrite and 15% of lepidocrocite were dissolved while the more crystallized goethite remains unaltered. SEM observation coupled with XRD showed that new iron sulphide and oxide phases precipitated on the polymer supports. Moreover, SEM observation showed that the supports were highly colonized by bacteria and biofilms suggesting that micro-organisms played a key role in the occurring mineralogical changes as well as in the Fe and associated trace metal release. Further studies dedicated to the identification of both the involved bacteria consortium and the secondary mineralogical phases as well as, kinetic study of metal release in solution will be undertaken.
Oxynitride glass-ceramic microstructures
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Oxynitride glass-ceramics attract an interest, not only because of their improved mechanical properties and refractoriness compared with oxide glass-ceramics, but also because of their presence as an intergranular microstructure in liquid phase sintered silicon nitride based ceramics. This intergranular microstructure is a result of the oxynitride liquid phase sintering medium required for densification. A tailored starting powder composition containing a combination of metal oxide and nitride additives that would form an oxynitride glass-ceramic may result in a liquid phase sintering medium that is readily crystallized after densification leaving a minimum of residual glass.

This presentation will focus on B-phase, which is a five-component phase, and its incorporation into the intergranular regions of silicon nitride ceramics. B-phase glass-ceramics may be fabricated through the nucleation and crystallization heat treatment of nitrogen rich parent sialon glasses with composition \((\text{e/o}) 35\text{R}:45\text{Si}:20\text{Al}:83\text{O}:17\text{N}\), where \(\text{R} = \text{Er, Yb, Y or a mixture of Y and Yb}\). The element \(\text{R}\) determines the degree of crystallization, and it has been shown that a virtually fully crystalline, single-phase, glass-ceramic may be obtained with \(\text{R} = \text{Y}\).

References

Water diffusion in trachyte and phonolite melts
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Knowledge on water diffusivity in silicate melts is required for modelling degassing of magmas and magma/fluid interaction. Water diffusion in trachytic and phonolitic melts was investigated in a piston cylinder apparatus at pressure from 5 to 25 kbar, at 1300°C and for durations of 0 to 300 s. As starting materials we have used synthetic analogues of potassium-rich trachyte from the Phlegeran Fields, Italy and potassium-rich phonolite from Laacher See, Germany. Hydrous glasses were produced by fusion of glass powder plus water for 20 h in AuPd capsules in an internally heated pressure vessel at 1200°C and 4 kbar. In diffusion couple experiments two cylindrical halves with different water contents (nominally dry to 5.5 wt%) were combined. Water concentration profiles were measured by Fourier transform infrared microspectroscopy using the peak heights of combination bands of OH and H\(_2\)O in the near-infrared. The obtained total water profiles are asymmetric, very steep in the half with low water content but more extended into the water-rich half. Water diffusion coefficients were calculated from the total water profiles by the Boltzmann-Matano analysis and/or numerical fitting. In case of phonolite melts fitting of the profiles indicate that the water diffusivity is proportional to the total water content.

In a first experiment at 1325°C, 15 kbar for 5 min combining phonolitic halves containing 0 and 5 wt% H\(_2\)O we determined a water diffusivity of \(7.7 \times 10^{-11}\) m\(^2\)/s at 1 wt% H\(_2\)O, similar as found by Freda \textit{et al.} [1] for trachytic melts at 10 kbar, but about 0.7 log units faster than in rhyolite (Zhang and Behrens 2000, [2]). Effects of pressure and temperature on water diffusion are discussed.

References
The role of Mn oxides on the geochimical cycle of chromium: a field study in New Caledonia

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Chromium is naturally released in the environment upon weathering of ultramafic rocks containing Cr3+-bearing minerals [chromite FeCr2O4, magnetite Fe3-xCrxO4, olivine (Mg,Fe)2-xCrxSiO4 or pyroxene (Ca,Mg,Fe)1-xCrxSiO3]. In surface conditions, chromium occurs under two main redox states (Cr3+ and Cr6+), the former being much less soluble, bioavailable and toxic than the latter (Anderson, 1989). Several laboratory studies have shown that Cr3+ ions could be oxidized to Cr6+ ions by Mn oxides (Fendorf and Zasoski, 1992; Silvester et al., 1995; Weaver and Hochella, 2003), which suggest that the concomitant occurrence of chromium and Mn oxides in soils could be hazardous. Although few field studies already addressed the question of the mobility and bioavailability of chromium in naturally Cr-enriched soils (Neel et al., 2007; Garnier et al., 2006; Becquer et al., 2003), only one (Cooper, 2002) focused on the role of Mn oxides on these geochemical parameters.

The present study, which is supported by the French ANR-ECCO program, aims at increasing our knowledge on the actual role of Mn oxides on the geochemical cycle of chromium in soils developed upon weathering of ultramafic rocks. To reach this goal, soil samples were collected along a 60 m core drilled across a weathering sequence in New Caledonia. Chemical and mineralogical analyses along this sequence indicate the occurrence of a saprolitic unit (ultramafic rocks more or less altered) at the bottom. This unit is overlaid by a first lateritic unit containing goethite, hematite and chrome and particularly enriched in Mn oxides (asbolan), which is itself overlaid by a second lateritic unit containing no Mn oxides. XANES analysis allowed detection of significant amounts of Cr6+ (up to 20 wt% of total chromium) in the unit containing Mn oxides whereas no oxidized chromium could be detected in the other units of the drilling core. These results strongly suggest that the reactivity of Cr3+ with Mn oxides observed in laboratory experiments is effective in soils and that these Mn oxides actually play a key role on the redox state of chromium, and in turn, on the geochemical cycle of this element in surface environments.

Constraining reaction rates in marine carbonate sediments using reactive transport modeling: Investigating the effects of diagenesis on Sr, Ca, and Mg

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Numerical modeling, in conjunction with pore fluid chemical and isotopic measurements, can be used to deduce mineral dissolution and precipitation rates in natural systems. The current study reports calcite recrystallization rates for a marine sedimentary section (ODP Site 807A, Ontong Java Plateau). The rates are constrained by Sr isotopes (87Sr/86Sr), which are sensitive at multi-million-year time scales, and Ca isotopes (δ44Ca), which are sensitive at time scales of tens of thousands of years. Recrystallization rates for sediments that are older than 2 Ma are ~0.2 to 2 %/Myr, which are similar to those reported in previous studies for other locations. However, reaction rates deduced for relatively young (~< 2 Ma) carbonate sediments using Ca isotopes are significantly faster (30 to 40 %/Myr), indicating that the approximate inverse age dependence of recrystallization rate extends to carbonate sediments as young as 0.1 Ma.

Rapid rates of recrystallization in relatively young carbonate sediments have implications for the fidelity of elemental and isotopic proxies of past climate and ocean chemistry. Recrystallization may change the original elemental and/or isotopic composition of carbonate, complicating attempts at paleo-reconstructions. The current study presents model results that describe the effects of diagenesis on the Sr/Ca and Mg/Ca elemental ratios, as well as the Ca isotopic composition, of marine carbonates. Using the reaction rates constrained by Sr and Ca pore fluid geochemistry, we use numerical models to estimate that up to 25 to 30% of the initial Sr and Mg in the solid phase may be lost during diagenesis. This conclusion is different from that inferred from the Sr isotope data only. The pattern of loss is dependent on the sedimentation history, so that loss is not constant throughout the column. If there is no externally imposed advection in the sedimentary column, then Ca isotopes are not significantly modified by diagenesis. Given the upper limit of reaction rates determined at 807A, the δ44Ca of the bulk carbonate sediment is altered by no more than +0.15‰. The small degree of diagenetic alteration is due to the fact that Ca is a major element in calcite, as opposed to the trace constituents Sr and Mg. Finally, diagenesis is not likely to account for the fluctuations observed in the seawater Ca isotope curve over the Late Cenozoic that is derived from measurements of bulk carbonate sediments.
Geochemical records of anthropogenic change: lake sediments and peat bogs

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Radiometrically dated cores of sediments from freshwater lakes and of peat from ombrotrophic bogs have been used to reconstruct the history of heavy element deposition arising from humankind’s activities over the past few thousand years. The historical records so obtained for lead, by far the most studied element, are probably the most convincing, with confidence augmented by the corroborative use of source-related stable lead isotope variations and by correspondence with independently derived records, for example from ice cores and archival herbarium mosses. Yet the bottom sediments of freshwater lakes and the living/decaying vegetation and peat of ombrotrophic bogs are dynamic systems with potential for perturbation of historical pollution records through remobilization and redistribution of elements as a consequence of inter-related physical, chemical and biological processes. The natural diagenetic enrichment of arsenic, in association with redox-sensitive iron, sometimes observed in the solid and solution phases of near-surface layers of lake sediments, and the vegetative recycling of nutrient manganese in peat bog surface plants are but two examples. Site-specific conditions, as well as element-specific processes, can be important in the case of both lakes and peat bogs and comparative studies of the two systems, where geographically possible and appropriate, may be additionally revealing. The authenticity of historical records in lake sediments and peat bogs depends also upon the accuracy of radiometric dating techniques, such as those based upon naturally occurring $^{210}$Pb, nuclear fallout $^{137}$Cs and $^{241}$Am, and ‘bomb’ and cosmogenic $^{14}$C, each with its own strength and weaknesses, and the current need for routine application of additional methods (e.g. $^{32}$Si) with half-life (~140 y) intermediate between those of $^{210}$Pb (22.3 y) and $^{14}$C (5730 y).

Dynamics and internal structure of a mantle plume conduit

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Plumes are often thought of as thermal structures, the key parameter being their excess temperature with respect to the surrounding mantle, while the associated velocity field is frequently neglected. However, in order to understand the structure of a plume conduit and the internal distribution of geochemical heterogeneities we change perspective and focus on velocities and strain rates. Like the hands of an invisible sculptor, velocity gradients constantly modify the shape of heterogeneities rising in the plume conduit.

Numerical simulations of a vigorous thermal plume provide a high resolution velocity field that is used to advect deep-seated passive heterogeneities. Our first objective is to investigate the relation between initial length-scales of heterogeneities across D'' and the length- and time-scale of geochemical variations induced in the plume conduit. We also explore dynamical differences between the central and peripheral part of the plume conduit, and calculate the strain rate $\varepsilon_{rr}$, the buoyancy flux and the elongation as a function of radial distance from the plume axis. Our results clearly show that most of the plume buoyancy flux occurs in highly sheared parts of the conduit.

We then concentrate on a 'Hawaiian' plume sheared by a fast moving oceanic plate. Our fully three-dimensional numerical model allows us to study the flow trajectories inside a sheared plume conduit and the deformations undergone by passive heterogeneities. Although our approach is simplistic, we consider the lifetime of a volcano carried by the plate over different parts of the plume conduit and we investigate the relation between heterogeneous structures in the mantle and the spatio-temporal geochemical variability registered by the volcano.
Isotopic evidence for mid-Archean anoxia

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The presence of nonzero $\Delta^{33}$S and $\Delta^{36}$S in the Archean and earliest Paleoproterozoic sedimentary rock record is considered to provide the strongest line of evidence for an anoxic early atmosphere. Low atmospheric oxygen is required both for production and transfer of the signal to the geologic record (Farquhar et al., 2000; Farquhar and Wing, 2003, 2005; Pavlov and Kasting, 2002). Temporal trends of sulfur isotopes in the Archean record reveal periods of large amplitude non mass-dependents signals (Early and Late parts of the Archean), and others when the signal was attenuated (Middle Archean) (Ono et al., 2003; Ohmoto et al., 2006), and some workers argue that this interval lacks a non mass-dependent signal and records an early, transient oxygenation of Earth’s atmosphere (Ohmoto et al., 2006).

We have investigated this interval and present new analyses of samples from the mid-Archean record (ca. ~2.8 and ~3.0 billion years ago (Gya)) that demonstrate the presence of an unambiguous non mass-dependent signal and is inconsistent with an oxygenated mid-Archean atmosphere. Our results for $\Delta^{33}$S and $\Delta^{36}$S indicate however that the character of the non mass-dependent signal is different for this interval in Earth history and provides evidence for changes in the pathways for non mass-dependent chemistry in this interval. This may reflect a change in the chemical composition of the atmosphere and may also be related to the observation of an attenuated $\Delta^{33}$S signal at this time.

References

Uptake of heavy metals, and arsenic by an aquatic plant in the vicinity of the abandoned Ervedosa tin mine (NE Portugal)

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This paper focuses on the uptake of heavy metals, and arsenic by an aquatic plant (Ranunculus peltatus Schrank) growing in the Tuela river in the vicinity of the abandoned tin mine of Ervedosa in the north region of Portugal. At mine, tin-bearing quartz veins with cassiterite and sulphides were exploited for tin (Sn) and arsenic trioxide (As2O3), until 1969. The waters at the mining site are affected by AMD, with high iron reduction and that is suggested to be associated with oxides and benthic ferrous Fe that is produced by dissimilatory iron reduction and that is suggested to be associated with enrichments in Fe/Al in the Gotland Deep, as Lyons and Sevavermann, 2006b, implying that negative Fe isotopic signatures could be characteristic for euxinic sediment deposition. Enrichments in Fe/Al can be explained by transport of reactive Fe from the shelf to the euxinic basin where it is transferred to the sediment by pyrite formation in the water column (e.g. Raiswell and Anderson, 2005). This is supported by pyrites with mean δ56Fe values of -1.1 ± 0.2 ‰ in the Gotland Deep. Reactive Fe is derived from oxides and benthic ferrous Fe that is produced by dissimilatory iron reduction and that is suggested to be associated with negative δ56Fe values (Severmann et al., 2006b). Therefore, our data support the suggestion of Lyons and Severmann (2006) that Fe isotopes can be used to fingerprint the Fe enrichment process by shelf to basin shuttling of Fe. If negative Fe isotopic signatures are characteristic for euxinic sediment formation, widespread euxinia in the past might have shifted the Fe isotopic composition of the ocean towards more positive δ56Fe values.

Table 1- Elemental concentrations in water and plant samples (water in µg/l and plant in mg/kg dry wt).

<table>
<thead>
<tr>
<th>Samples</th>
<th>As</th>
<th>Co</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water 1</td>
<td>0.56</td>
<td>37.1</td>
<td>49.1</td>
<td>0.60</td>
<td>118</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Plant 1</td>
<td>8.47</td>
<td>7.96</td>
<td>37.6</td>
<td>21.1</td>
<td>4.46</td>
<td>78.6</td>
<td>0.40</td>
</tr>
<tr>
<td>Water 2</td>
<td>0.63</td>
<td>38.7</td>
<td>23.3</td>
<td>13.7</td>
<td>225</td>
<td></td>
<td>3.15</td>
</tr>
<tr>
<td>Plant 2</td>
<td>6.36</td>
<td>18.4</td>
<td>103</td>
<td>50.8</td>
<td>3.10</td>
<td>268</td>
<td>13.8</td>
</tr>
<tr>
<td>Water 3</td>
<td>0.60</td>
<td>16.2</td>
<td>32.5</td>
<td>0.71</td>
<td>147</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>Plant 3</td>
<td>73.8</td>
<td>66.7</td>
<td>342</td>
<td>108</td>
<td>7.56</td>
<td>1440</td>
<td>57.9</td>
</tr>
<tr>
<td>Water 4</td>
<td>0.30</td>
<td>0.64</td>
<td>13.3</td>
<td>1.78</td>
<td>1.65</td>
<td>142</td>
<td>0.17</td>
</tr>
<tr>
<td>Plant 4</td>
<td>20.2</td>
<td>36</td>
<td>156</td>
<td>66.5</td>
<td>3.43</td>
<td>879</td>
<td>31.6</td>
</tr>
</tbody>
</table>

The analytical data obtained (Table 1) demonstrate low pollutant concentrations in fluvial water. However, the trace elements are considerable concentrated in the plant samples. The heavy metal, and arsenic concentrations in the plants exceed the corresponding concentrations in the habitat (water) by tens of thousand times. Concentration factor (CF), as a ratio of a chemical element content in plants (Cp) to its content in the corresponding habitat (Cph), was used to estimate the extent of heavy metals, and arsenic concentration by plants (CF=Cp/Cph).

The plant studied can be used to decrease the heavy metals, and arsenic amounts into the aquatic environment affected by acid mine drainages. On the other hand, this aquatic plant can enter the food chains, presenting a potential danger for animal and human health.

Iron isotope variations in Holocene Baltic Sea sediments

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Sediments from the Gotland basin in the Baltic Sea display variations in their bulk Fe isotopic compositions from -0.27 ± 0.09 ‰ to +0.21 ± 0.08 ‰ for δ56Fe (differences in 56Fe/54Fe relative to the IRMM-14 standard). Deposits formed in freshwater with oxygenated bottom water before ~8000 years B. P. display identical Fe isotopic signatures as oxic marine sediments and igneous rocks. In contrast, samples from the more recent brackish water and periodically euxinic units have significantly lighter δ56Fe values by ~0.2 ‰ on average (6 samples). Data for Fe/Al provide additional information about the cause for the shift in Fe isotopic compositions.

Enrichments in Fe/Al are characteristic for euxinic sediment deposition and can be used as a paleoredox proxy (e.g. Lyons and Severmann, 2006). Negative δ56Fe values are associated with enrichments in Fe/Al in the Gotland Deep, as has also been reported from the Black Sea (Lyons and Severmann, 2006; Severmann et al., 2006a), implying that negative Fe isotopic signatures could be characteristic for euxinic sediment deposition. Enrichments in Fe/Al can be explained by transport of reactive Fe from the shelf to the euxinic basin where it is transferred to the sediment by pyrite formation in the water column (e.g. Raiswell and Anderson, 2005). This is supported by pyrites with mean δ56Fe values of -1.1 ± 0.2 ‰ in the Gotland Deep. Reactive Fe is derived from oxides and benthic ferrous Fe that is produced by dissimilatory iron reduction and that is suggested to be associated with negative δ56Fe values (Severmann et al., 2006b). Therefore, our data support the suggestion of Lyons and Severmann (2006) that Fe isotopes can be used to fingerprint the Fe enrichment process by shelf to basin shuffling of Fe. If negative Fe isotopic signatures are characteristic for euxinic sediment formation, widespread euxinia in the past might have shifted the Fe isotopic composition of the ocean towards more positive δ56Fe values.

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Methane, sulfide and oxygen fluxes at methane and brine seeps of the Nile Deep Sea Fan (Eastern Mediterranean)

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The Nile deep sea fan (NDSF) of the Eastern Mediterranean hosts a huge number of active seep structures, which have only been discovered very recently. Here we have, for the first time, investigated the in situ benthic oxygen consumption and methane turnover at different seep systems of the eastern and central provinces of the NDSF in water depths of 1000-3000 m. The expedition BIONIL (M70/2) with RV Meteor and ROV QUEST (Marum) contributes to the DFG/BMBF Geotechnologien program MUMM and to the ESF EUROCORES project MEDIFLUX.

For our investigations several in situ instruments were used and combined with on board biogeochemical analyses: a microprofiler system measuring O₂, H₂S, pH and T in micrometer resolution, a benthic chamber to measure oxygen consumption and sulfide export, as well as a newly developed instrument for sulfate reduction rate measurements (INSINC).

The study focused on 3 different types of seep systems – the gas emitting center of the Amon mud volcano, the mud/brine seep at the outer rim of Amon, as well as the large carbonate pavements in the central province of the NDSF characterized by low fluid flow rates.

At cold seeps, the presence of bacterial mats indicates high methane and sulfide fluxes often also linked to high oxygen consumption rates. The three systems investigated here were characterized by very different types of bacterial mats, namely a Beggiatoa type (Amon center), a Thiomargarita type (Amon flank) and an Arcobacter type (carbonate pavements). Here we compare flux rates (methane, sulfide, oxygen) as well as microbial turnover rates of these different mat communities and investigate their link to fluid flow velocity and other environmental parameters.

Geochemical characteristics of Selenium-rich silicalite formation in Ziyang, Southern Qinling, China

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A sediment formation, composed of siliceous rocks, mud stone/shale or callys and carbonate and siltstone, has been identified for enrichment of organic matter and bacterium-alga microbe. We define this specific formation as "silicalite formation". This paper aims to study the geochemical characteristics of selenium-rich silicalite formation in Ziyang.

The study area located in the Southern Qinling of China (lower Cambrian in peripheral margins of the Yangtze Block), is known for selenium-rich in rock, and occurred serious selenium-poisoning symptom in the 1960’s. Concerns on health problem and mineral resource of Se, the selenium-rich silicalite formation in this area has attracted scientific interests.

The selenium-rich siliceous rocks are important component of the Cambrian silicalite formation of Ziyang in the north of Daba region, which is characterized by hydrothermal sedimentation. Cherts are characterized by elevated concentrations of SiO₂, Se, Ba, Cu, Ni, V, As, Sb, U but lower MgO and Al₂O₃. The ratio of U/Th>1 , plots for Al-Fe-Mn and Fe-Mn-(Cu+Co+Ni) triangle diagrams, and correlations for P-Y, Zr-Cr and U-Th, all suggest hydrothermally sedimentary origin. The REE patterns show negative Ce and positive Eu anomalies. The isotopic compositions of silicon and oxygen are both similar with the hydrothermal origin. The temperature of hot water is about 78.6ºC-126.20ºC and suggests deep-water reservoir of siliceous rock sedimentation. The silicon-rich hydrothermal liquid contributed to enrichment of selenium in the study area.

In conclusion, further study of the forming environment and metallogenic characteristics of the selenium-rich silicalite formation is of great significance for both Se-related ore minerals and health interests.

Acknowledgment
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δ¹³C carb and δ¹³C org excursions in the post-glacial Sinian to Early Cambrian interval in Guizhou, South China

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The investigated area is located on the southeast border of the Yangtze platform. Five lithostratic units are recognized in ascending order: the Nantuo (NT), Doushantuo (DST), Dengying (DY), Gezhongwu (GZW) and Niutitang (NTT) formations. The DST Fm overlies conformably on the NT Fm characterized by glaciogenous diamictite. In the basal part of the DST Fm is a -4 m thick dolostone bed (so called cap carbonate). Upon this bed is the main part of the DST Formation dominated by phosphorite intercalated with dolostone and dolomitic pelite. The overlying DY Fm is composed of pure dolostone, followed by another set of phosphorite deposits called the GZW Fm. The GZW Fm is rich in small shelly fossils of Cambrian age, and covered by the NT Fm, a set of black shales with copious sponge fossils.

The values of δ¹³C carb show a wide range from -6.20‰ to 4.00‰, roughly consistent with that illustrated by Jacobsen & Kaufman (1999) for the same interval. The δ¹³C carb curve starts with a moderate positive shift after the glaciogenous diamictite and then goes into a negative shift, which persists up to the boundary between the DST Fm and the DY Fm. The second positive shift of δ¹³C carb occurs within the DY Fm, followed by another negative shift in the GZW and NTT formations. The values of δ¹³C org vary from -21.99‰ to -33.58‰, leading to a maximum oscillatory amplitude of 11.59‰. Being similar to the δ¹³C carb curve in shape, the δ¹³C org curve also demonstrates two positive shifts in the NT Fm and the DY Fm, and two negative shifts in the DST Fm and the interval from the GZW Fm to the NTT Fm.

Some studies have provided paired analyses of δ¹³C carb and δ¹³C org. Holland & Mckenzie (1991) show that the temporal carbon-isotopic curves of calcite and particulate organic carbon in a modern eutrophic lake correlate with each other to some extent, and the carbon-isotopic difference (ΔB = δ¹³C POC-calcite) indicating the effect of photosynthetic isotopic fractionation increases in response to increasing concentration of dissolved carbon dioxide (CO₂(aq)). However, the timing of the peaks or valleys of δ¹³C carb and δ¹³C org curves may not always coincide due to other factors besides photosynthesis, which complicates the use of ΔB for evaluating the relative variations of CO₂(aq) with geologic time (Kump et al., 1999). In our study, the coincidence of δ¹³C carb and δ¹³C org profiles suggests a dominating effect of photosynthesis on carbon-isotopic discrimination. Thus ΔB may be useful to understanding the relative changes of CO₂(aq) that may have occurred in the investigated area during the post-glacial Sinian and the Early Cambrian. This work was supported by NSFC (Grant Nos. 40472014 and 40572017).

Cosmogenic ²¹Ne/³He in olivines and pyroxenes from a Pleistocene basalt flow, western Grand Canyon National Park, Arizona, USA

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The Bar Ten lava flow is a Pleistocene basalt flow located in the western margin of the Unkaret Volcanic Field in Grand Canyon National Park (AZ, USA). It was chosen as a calibration site for the production of cosmogenic ³He and ²¹Ne (³He, and ²¹Ne) because it has more than 600 m of relief and has negligible erosion due to a regional desert climate. Together with other calibration sites of CRONUS-EU, it was selected to evaluate how production rates are affected by changes in altitude and latitude. The lava flow erupted between 60 and 150 ka based on two ⁴⁰Ar/³⁹Ar and one thermoluminescence ages. Low K content, excess Ar, and abundant glass in this basalt flow have made it difficult to obtain more accurate ages. Cosmogenic samples were collected from stable primary surfaces at elevations of 1180 to 1820 m along a vertical transect between 36.2239 and 36.2417° N. He, Ne, and Ar were analyzed by step-heating of olivine and pyroxene separates and ³He, and ²¹Ne components have been determined. We evaluated ²¹Ne/³He values, assuming that eruption age and erosion should have no effect on the ratio, if ³He, and ²¹Ne are produced at constant rates relative to each other. ²¹Ne/³He varies from 0.19-0.20 for pyroxenes and from 0.35-0.39 for olivines. The difference between mineral phases may be due to differences in mineral composition affecting production of ²¹Ne; production of ³He, is less sensitive to variations in mineral composition. Olivines in our study contain 26-27 wt.% Mg, whereas pyroxenes contain 9-11 wt.% Mg. Lower Mg content decreases the production of ²¹Ne, and thus lowers the ²¹Ne/³He value for pyroxenes compared to that of olivines. Production rates based on elemental composition or on published calibrated values were scaled to our specific field site using several scaling methods. These production rates yield cosmogenic ages that are bracketed by the ⁴⁰Ar/³⁹Ar and thermoluminescence ages, but the independent dating techniques are thus far not accurate enough to specify which production rate and which scaling method is best suited for this calibration site.
Comparison of thermodynamic data for aqueous species with focus on hyperalkaline conditions

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Introduction and objective

Presently, geochemical databases lack agreement on thermodynamic properties for a substantial number of aqueous species and minerals. Some discussion of thermodynamic data can be found in the literature for minerals and solid phases (e.g. Arthur et al., 2005), but not much attention has been paid to aqueous species.

The objective of this study is to address the thermodynamic properties of aqueous species with emphasis on major components relevant for hyperalkaline conditions. For this purpose, the most commonly used and accessible thermodynamic databases have been treated in similar fashion. Six databases were included: llnl-EQ3/6, minteq, phreeqc, wateq4f, JAEA and NAPSI.

Method and results

Pertinent temperature dependent thermodynamic data for 66 aqueous species were evaluated. The equilibrium constant for species association (log K at 25 ºC), ΔHR and the temperature dependence of log K (analytical expressions where available) were taken for each species and each database. The data bases were first brought to a common format in terms of basis species. Results for log K up to either 100 ºC or 300 ºC (extrapolated by Van’t Hoff, or given by analytic expressions) were graphically compared relative to the value at 25 ºC, and in absolute terms. Select literature sources and the HKF/SUPCRT model were used in addition to try and resolve some of the discrepancies.

Discussion

The results point at some obvious short comings, limitations and discrepancies, but some of the interpretation is limited by the absence of an absolute reference. Modelling calculations on alkaline systems using different databases and including select solid phases are recommended for a more practical comparison, and this work is currently in progress.

This research project is associated with the Grimsel Test Site (CH) and supported by Nagra (CH), POSIVA (SF) and JAEA (JP).

References


Passivating layer formation during glauconite dissolution: implications for mineral sequestration of CO₂

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The kinetic of glauconite dissolution in the pH range from 2 to 10 (T= 25ºC) has been determined from flow-batch reactor experiments. The textural and microstructural aspects induced by the dissolution process have also been characterized by XRD, HREM and BET. As a result of this analysis it is shown that, in acid conditions, glauconite is slightly more soluble than other silicates ubiquitous in sediments. The dissolution mechanism is incongruent at very acid pH values and tends to be congruent for intermediate and neutral values. Microstructural analysis show that kinetic factors are strongly influenced by structural factors. Dissolution of glauconite takes place in two steps involving, first, the disorder of tetrahedral and octahedral layers and, second, the release of cations to the solution, this process being controlled by the rate of liberation of the interlayer cation (K⁺). As a consequence, an amorphous phase is formed that evolves compositionally to a more silica-rich end-member. The reactive surface is reduced during this process, giving rise to the formation of a passivating layer that has considerable influence on the dissolution rate. These experimental results have been used to analyze, by geochemical modelling, the response of glauconitic sediments during carbonation reactions.

References

The replacement of gypsum by CaCO₃ polymorphs: Reaction steps and formation of pseudomorphs

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On the Earth’s surface, the replacement of evaporitic calcium sulphates (anhydrite and gypsum) by CaCO₃ is a common phenomenon that can lead to the formation of large deposits of diagenetic carbonates. In spite of the geological and industrial implications of this phenomenon, very few experimental studies have been conducted to investigate the microscopic mechanisms involved in this replacement process. Here we present an experimental study of the interaction between gypsum and carbonate-bearing aqueous solutions. This interaction leads to the replacement of gypsum single crystals (~3 mm³) by an aggregate of CaCO₃ crystals. Scanning Electron Microscopy (SEM) and glancing incidence X-ray diffraction (GIXRD) were used to monitor the development of the replacement process. The replacement takes place through a number of solvent-mediated transformations, which involves the dissolution of gypsum and the sequential formation and dissolution of different CaCO₃ polymorphs. Although the actual sequence of reactions depends on the initial concentration of carbonate, amorphous calcium carbonate (ACC) is always the first phase that forms and can be considered a precursor for the formation of more stable crystalline CaCO₃ polymorphs. Moreover, the initial concentration of carbonate also controls the kinetics of the replacement and the degree of faithfulness of the pseudomorphs. The phase formation sequence and the textural characteristics of the replacement are interpreted on the basis of the evolution of physicochemical parameters, like the supersaturation with respect to the different CaCO₃ polymorphs and the [SO₄²⁻]/[CO₃²⁻] ratio in the aqueous solution.

From crystals to clusters: A molecular simulation study of CaCO₃ configurations

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Equilibrium relationships involving solids are based in bulk thermodynamic properties that concern ideal crystals of infinite size. However, real processes towards equilibrium imply development of finite molecular-scale entities. The configuration of these early-stage clusters and the estimation of their excess energies with respect to the ideal crystal is key to understand the macroscopic behaviour of a given system. Here, starting from the ideal atomic positions in calcite, aragonite, or vaterite, the relaxation in vacuum of finite clusters of CaCO₃ has been explored. With the aim of determining the influence of the cluster size on its energy and on its geometrical configuration, a series of CaCO₃ clusters have been simulated and their lattice energies calculated. The cluster geometry has been fully optimized at constant pressure and its energy has been determined using GULP. A wide variety of clusters ranging from 1 to 2000 formulae has been considered for each (calcite, aragonite, or vaterite) starting structure. GULP calculations have been carried out using the pair potentials set derived by Rhol et al (2003). In a number of cases the final configuration has been checked with good agreement using the DFT code SIESTA (Soler et al., 2002). Although these simulations represent not fully realistic scenarios, some results are relevant from the point of view of the polymorphic precipitation of CaCO₃. A fundamental question like the size that must have a cluster to be considered calcite, aragonite, or vaterite is addressed from the diffraction patterns of the relaxed clusters.

Equilibrium relationships involving solids are based in bulk thermodynamic properties that concern ideal crystals of infinite size. However, real processes towards equilibrium imply development of finite molecular-scale entities. The configuration of these early-stage clusters and the estimation of their excess energies with respect to the ideal crystal is key to understand the macroscopic behaviour of a given system. Here, starting from the ideal atomic positions in calcite, aragonite, or vaterite, the relaxation in vacuum of finite clusters of CaCO₃ has been explored. With the aim of determining the influence of the cluster size on its energy and on its geometrical configuration, a series of CaCO₃ clusters have been simulated and their lattice energies calculated. The cluster geometry has been fully optimized at constant pressure and its energy has been determined using GULP. A wide variety of clusters ranging from 1 to 2000 formulae has been considered for each (calcite, aragonite, or vaterite) starting structure. GULP calculations have been carried out using the pair potentials set derived by Rhol et al (2003). In a number of cases the final configuration has been checked with good agreement using the DFT code SIESTA (Soler et al., 2002). Although these simulations represent not fully realistic scenarios, some results are relevant from the point of view of the polymorphic precipitation of CaCO₃. A fundamental question like the size that must have a cluster to be considered calcite, aragonite, or vaterite is addressed from the diffraction patterns of the relaxed clusters.

Figure 1: relaxed aragonite cluster with 250 formulae (a) and calculated diffraction patterns (b).

References
Mapping petrographic variations with gammaspectrometry in granites: The example of the Três Córregos Granitic Complex, SE Brazil
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Two large Neoproterozoic bodies, the Cunhaporanga and Três Córregos Granitic complexes (CGC, TCGC) crop out in Paraná state, SE Brazil, constituted mainly by calc-alkaline granitoids. Both show ellipsoidal outlines, with a NE orientation, the prevailing basement structural trend in SE Brazil. CGC shows poor outcrop pattern and a large faciological diversity, not so TCGC. Aerial gammaspectrometric surveys were used to test variations in K, U, Th abundances for definition of facies domains in both complexes. Colorgraded maps were prepared for TC, the three elements and several calculated factors (including U/Th, U/K, Th/K ratios, F factor, triangular K-U-Th, etc.). In the case of TCGC, the color maps clearly reproduce the petrographic distribution pattern established during ground mapping. Aerial gammaspectrometry showed, for TCGC, the potential for accurately pinpointing petrographic variations.

Melt supply and magmatic evolution at a large central MOR volcano located in the Lucky Strike Segment
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New major and trace element, volatile (H₂O and CO₂) and Sr-Nd-Pb isotopic, data on samples from the Lucky Strike segment (LSS) are presented. All studied samples are E-MORBs, but different degrees of enrichment are identified. LSS basalts have been subdivided into three distinct compositional groups: In Group 1, the basalts have the highest more-to-less incompatible element ratios (e.g. La/Sm, Nb/Zr, Ba/Y) and have the most Sr-Nd-Pb radiogenic values. They are spatially restricted to the central part of the axial volcano, are highly vesicular, and plagioclase phryic. Group 3 basalts have the lowest more-to-less incompatible element ratios and the lowest Sr-Nd-Pb radiogenic values. They were collected throughout the LSS (from 37°12,0' to 37°27,3' in latitude), are almost aphyric and exhibit low vesicularity. Group 2 basalts have chemical characteristics intermediate between those of Groups 1 and 3. This subdivision is readily recognised in the volatiles data. Group 1 glasses have higher dissolved H₂O concentrations (and estimated pre-eruptive CO₂ concentrations), relative to those of Group 3, but have lower H₂O/Ce ratios (108-197 and 251-343 for Groups 1 and 3, respectively) that are well below the average defined for this MAR region (253±33).

Taking into account the sample spatial distribution, the bathymetric (shallow depths at segment centre), and the gravity data (negative “bull’s eyes” RMBA anomalies at segment midpoint), together with the geochemical data interpretation, a genetic volcanic model is generated. The enriched, more fertile, mantle heterogeneities (Group 1), related to Azores mantle plume material, in the LSS sub-oceanic mantle, are delivered to the centre of the segment by highly focused, sub-lithospheric processes. Forming wetter domains, they start to melt first, deeper in the mantle, melting more, but generating lower melt fractions, than the ambient mantle (Group 3). Group 1 vesiculating melts, having their density reduced, will be aggregated in a high-level axial magma chamber (AMC). The limit of neutral buoyancy of these magmas is never reached, thus the magmas are delivered vertically to the segment centre. Further magmas, formed from melting of the ambient mantle, will be aggregated in the AMC. Thus, initial mixing of Group 1 and 3 melts and, lastly, only differentiation of Group 3 melts will produce Group 2 and 3 basalts, respectively. The disruption of pressure equilibrium of the magmatic system as a result of the ridge extensional stress regime, and the subsequent magnitude of internal overpressure in the magma reservoir will control the magma delivery along the LSS.
**C_{32} N-Alkan-1-ol as specific indicator of C4 tropical plants in marine sediments**

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Contents, distribution patterns and molecular stable carbon isotope composition of these compounds have been studied as markers of continental vegetation over the last 320 kyr in a set of samples from the tropical Indian Ocean core MD98-2165 (9°38’96S, 118°20’31E, 2100 m).

The concentration changes of these compounds show a general pattern dominated by the well defined glacial-interglacial oscillation. Eolian inputs were much stronger during the glacial periods. The n-alkanes range between C_{23} and C_{33} and are characterised by high odd-over-even carbon number preference and predominance of the C_{31} n-alkane, whereas the n-alkanols range between C_{20} and C_{32} and are dominated by even-over-odd carbon numbers with maxima at C_{28} or C_{32} n-alkanol. In this respect, warmer and wetter conditions appear to favour deposition and preservation of the C_{30} homologue and colder and drier conditions favour the C_{28} n-alkanol. However, the C_{32} n-alkanol becomes an additional major homologue during the glacial times, suggesting an expansion of C_{4} plants during these arid conditions as reported by Rommerskirchen (2006). The stable carbon isotope weighted mean average of the n-alkanes (n-C_{27} to n-C_{33}) fall in the range between ~30.5 and ~34.5‰, typical of leaf-wax n-alkanes biosynthesised by C_{3} plants. The lower δ^{13}C values are observed during warm and humid interglacial periods, when the estimated C_{4} plants contribution decreased ~15 wt %. This is consistent with the negative relationship existent between δ^{13}C of C_{3} plants and water availability (Liu et al., 2005). The weighted mean average δ^{13}C values of n-alkanols (C_{20}-C_{32}) fall in the range between ~24.4 and ~32.6‰, again with lower δ^{13}C values during interglacial periods. Amazingly, the δ^{13}C of C_{32} n-alkanol reveals a clear C_{4} plant signature during cold and dry conditions. These results demonstrate that n-alkanes and n-alkanols, but most particularly the C_{32} n-alkanol, show a distinct pattern of contributions from C_{4} plants to marine sediments during arid conditions and therefore, they can be used as indirect proxy of continental climate conditions in the tropics.

**Chemical weathering rates inferred from cosmogenic radionuclides and immobile element enrichment: Measurements in the Idaho Batholith**

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Chemical weathering rates inferred from cosmogenic radionuclides and Earth surface processes. It nourishes ecosystems by supplying nutrients to natural waters, promotes physical erosion by weakening bedrock, and buffers Earth’s climate over geologic time by modulating atmospheric carbon dioxide concentrations. Long-term measurements of chemical weathering rates (and of their dependence on external factors such as climate) are thus important for understanding the biogeochemical and geomorphological evolution of the Earth’s surface, and for quantifying the recent impact of humans on the environment. Chemical weathering fluxes can be measured in mountainous terrain using cosmogenic radionuclide measurements of long-term denudation rates, coupled with measurements of the rock-to-soil enrichment of chemically inert tracers (Kirchner et al., 1997; Riebe et al., 2001; Riebe et al., 2003). This technique has two major strengths: (1) it can be applied to a wide range of actively eroding landscapes, whereas other methods typically require non-eroding, datable soils, and (2) it intrinsically averages over the long timescales of soil formation and denudation (typically 1000-100,000 years in soil-mantled hillslopes), and thus sheds light on landscape evolution processes. Here we use this method to measure chemical weathering fluxes along an altitudinal transect on Pilot Peak. This transect spans 1500 meters of altitude in the granitic Idaho Batholith, USA, and thus spans ~10 °C in mean annual temperature. Pilot Peak is unglaciated, exhibits little variability in bedrock mineralogy, and is mantled with well-mixed soil at all elevations. Our preliminary data suggest that rates of chemical weathering, as a function of total denudation rates, are not a strong function of elevation, and hence not a strong function of temperature. These results also imply that chemical weathering fluxes account for less than 20% of the total denudation flux at Pilot Peak, and thus point toward the dominance of physical processes over chemical processes in sculpting this landscape.

**References**


Revealing the importance of endospores in sediments

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Introduction
Endospores are bacterial resting stages being able to remain viable for long periods of time. Consequently, they can be expected to accumulate in sediments during burial and may contribute significantly to total cell counts. This emphasises the need for a new cultivation-independent approach for the quantification of bacterial endospores in sediments.

Application of dipicolinic acid for estimation of endospore numbers
In the present study, dipicolinic acid (DPA), a biomarker for endospores, was used to quantify endospores in sediment samples. Sediment cores of about 6 m length were collected from different sites in the backbarrier tidal flat of the island of Spiekeroog in the southern North Sea and analysed for their DPA content to determine endospore depth profiles. For conversion of sediment DPA contents into spore numbers, purified endospores of tidal flat strains were investigated for their DPA content.

Contribution of endospores to total cell counts
Sediment samples taken from different lithological subunits of the cores showed high variations in DPA contents. Estimated spore numbers were in a range of 10^5 to 10^7 endospores g^-1 sediment and accounted for up to 10% of total cell counts. Huge differences in endospore numbers estimated from DPA contents and determined by viable counts obtained after pasteurization (Köpke et al., 2005) were found. The conversion of sediment DPA contents into spore numbers, purified endospores of tidal flat strains were investigated for their DPA content.

Conclusions
Since quantification of endospores on the basis of DPA content does neither discriminate between viable and non-viable spores nor between different physiological groups, it apparently provides a more realistic estimate of endospores as part of the microbial community than cultivation-dependent approaches. For this reason, we suggest to use DPA for the determination of endospore numbers in addition to total cell counts in order to reveal the importance of endospores in sedimentary microbial communities.

References

New approaches for the analysis of stable and radiogenic strontium isotopes using LA-MC-ICP-MS

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Stable strontium isotopes in various marine carbonates have been determined using an “AXIOM” MC-ICP-MS in combination with a NewWave UP193 laser ablation unit. Using new developed measurement protocols we did achieve an external reproducibility of Sr87/Sr86 ratios in carbonates of about 18 ppm (RSD). For recent and sub-recent marine carbonates a radiogenic strontium isotope ratio Sr87/Sr86 of 0.70917(1) was determined, which agrees well with the accepted value for modern sea water. It was achieved without the use of any additional correction of the data. Only the rubidium correction was performed in its accepted form and the strontium isotope ratios were normalized to a Sr86/Sr88 ratio of 0.1194 using the exponential law for fractionation correction.

A major benefit of the applied method is the direct determination of the stable strontium isotope fractionation. Assuming stable plasma conditions and a reproducible sample ablation this method is advantageous when compared to “conventional” MC-ICP-MS. It avoids additional fractionation of the sample strontium due to the chemical pretreatment (ion chromatography and solution preparation).

In aragonitic sclerosponge samples the stable strontium isotope fractionation was determined via LA-MC-ICP-MS. In these samples, spanning a temperature range of about 11°C, stable strontium isotope fractionation was found to be temperature dependent. The Sr86/Sr88 ratio of 0.1194 using the analytical uncertainty with previous findings for coralline aragonite of 0.033(5) per mill/°C (Fietzke & Eisenhauer, 2006).

References
The evolution of the Ediacaran sulfur cycle: A paired sulfate-pyrite $\delta^{34}$S approach

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An anomalous enrichment in marine sulfate $\delta^{34}$S$_{SO_4}$ is preserved in globally-distributed latest Ediacaran – early Cambrian strata. The proximity of this anomaly to the Ediacaran-Cambrian boundary and the associated evolutionary radiation has invited speculation that the two are causally related. Here we present a high resolution record of paired sulfate ($\delta^{34}$S$_{SO_4}$) and pyrite ($\delta^{34}$S$_{pyr}$) from sediments of the Ara Group, Sultanate of Oman. An enrichment in $\delta^{34}$S$_{pyr}$ coincides with the interval of enriched $\delta^{34}$S$_{SO_4}$, beginning at ca. 550 million years ago (Ma) and continuing through at least ca. 540 Ma. These data are evaluated using a new approach based on paired $\delta^{34}$SSO$_4$$^{--}$$\delta^{34}$Spyr data that enables us to calculate both $\delta^{34}$Sin, the isotopic composition of the sulfur flux entering the ocean, and $f_{pyr}$, the fraction of sulfur buried as pyrite. It appears that basal Ediacaran $\delta^{34}$Sin was significantly enriched beyond bulk Earth composition and became progressively more enriched through at least the earliest Cambrian. The rise in $\delta^{34}$Sin is correlated with the known record of increasing Ediacaran $\delta^{87}$Sr/$\delta^{86}$Sr, indicating a tectonic control on riverine sulfate delivery. The ~30permil decline in $\delta^{34}$SSo$_4$ observed in the Paleozoic is interpreted as representing in part the return of $\delta^{34}$Sin toward bulk Earth values. Against this background of increasing Ediacaran $\delta^{34}$Sin, the Ara $\delta^{34}$S enrichment is caused by an additional increase in $f_{pyr}$, which is most likely driven by enhanced primary production and increased sedimentation rates associated with the assembly of Gondwanaland. The data presented here constrain the changes in biogeochemical cycling that caused the Ara sulfur anomaly and serve as a contextual framework for understanding the E-C boundary, as well as biological and environmental change into the Paleozoic.

Micron-scale resolution of sulfur cycling in a microbial mat

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Microbial mats consist of finely laminated layers of diverse microbial communities. Mat organization is thought to result from strong spatial gradients in light intensity and redox in the uppermost few millimeters. Optical examination reveals microbial laminations on scales between 5mm and 5µm throughout the thickness of the microbial mat. However, such fine laminations at depth have usually been regarded as a ‘relict architecture’ inherited from an older mat surface. To further our understanding of microbial processes within this laminated architecture, we have investigated sulfur cycling (as recorded by sulfide production) within a benthic microbial mat.

We present a high-resolution spatial profile of sulfide abundance and isotopic ($\delta^{34}$S) composition on the micron-scale through a microbial mat community analyzed using a Cameca NanoSIMS 50L ion microprobe. We find a fine-scale (0.1-2mm) banding of sulfide throughout the mats as visible to the naked eye. In addition, there are micron-scale (~4µm) laminations observed using the NanoSIMS both in optical CCD and element scanning mode. We have mapped the sulfide $\delta^{34}$S profile from the mat surface down to a depth of ~1cm at ~100µm resolution with a typical analytical error of ±0.5‰ (1σ). $\delta^{34}$S varies over ~25‰ as a function of depth through the mat. An apparent oscillatory behavior in $\delta^{34}$S exists over ~4mm, which approximates the spacing of the coarsest mat laminations. This result suggests that the deeper mat architecture reflects ongoing microbial activity rather than inherited architecture. At any given depth, there can be up to ~5-10‰ variability in $\delta^{34}$S in immediately adjacent (~10µm apart) locations. High-resolution images (5-20µm squares) of elemental abundance and isotopic composition indicate that the ubiquitous banding in sulfide abundance appears to control the $\delta^{34}$S variability, with the offset between high- and low-sulfide regions up to ~10‰. Control experiments in standard solutions did not reveal any banding or the same scale of isotopic variability as observed in the microbial mat. We therefore believe that the banding and isotopic variability observed in the microbial mat are not an analytical artefact, but rather reflect very-fine-scale lamination in microbial activity preserved at depth within the mat, as is supported by microscopic observations. The environmental conditions that maintain such rigid laminations at depth (~1 cm), far from the sharp redox gradients of the mat surface, remain poorly constrained.; however, our results suggest that the full scope of sulfur cycling with microbial mats remains far from being completely understood or fully appreciated.
Structural incorporation of trivalent f elements into the trioctahedral clay mineral hectorite

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Clay minerals may play an important role in a high-level nuclear waste repository system. Clay-based materials have a high affinity for trivalent actinides, and several distinct molecular level mechanisms of actinide retention can operate: outer- and inner-sphere complexation, cation-exchange (interlayer), and structural incorporation.

Radionuclide immobilization by incorporation into the bulk structure of clay minerals may occur via coprecipitation. However, the size mismatch with the cations which typically occur in the octahedral sites of sheet silicates would result in large lattice strains [1]. Nevertheless, recent TRLFS data for Eu(III)/Cm(III) coprecipitated with hectorite at 90°C [2] suggest that such a substitution mechanism may operate [3,4].

Conventional EXAFS spectra collected on powders of Eu-containing hectorite suggested that Eu(III) was hexacoordinated with oxygens, as in a Mg structural site [5]. Neighbouring structural cations were not detected, maybe due to cancellation effects between EXAFS waves backscattered by (out-of-plane) Si and in-plane (Mg,Al) cations [6]. Polarized-EXAFS (P-EXAFS) experiments on self-supported films of these oriented clay minerals were thus carried out. Spectra were collected for varying europium contents to determine the influence of the degree of substitution on the local crystal structure.

References


Potassium content in the Earth’s core: A high-pressure and high temperature study of the Fe-K system

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The transition metal behavior of potassium at high pressure suggests that a significant amount of potassium could reside in the Earth's core. The radioactive isotope $^{40}$K could indeed contribute to power the Earth's dynamo but a high concentration may prevent inner core formation. We report a diamond anvil cell study of the Fe-K system up to 42 GPa and 3000K. Using in situ X-ray diffraction carried out at the European Synchrotron Radiation Facility, we show that Fe and K can alloy in reducing conditions, provided the change in the chemical bonding character of K from alkaline- to transition-metal is complete (above 20-25 GPa). The incorporation of potassium causes iron lattice to expand with increasing potassium concentration. However, a precise determination of cell parameters of both Fe and K indicates that a maximum amount of 700±300 ppm in weight of K can be accommodated in the ε-Fe lattice. Such pure metal (K,Fe) experiments provide an upper limit to the potassium concentration in the Earth’s core. Our estimate is lower than those proposed in previous studies and corresponds to a power limited to 4.3TW, may be more consistent with models of inner core growth and core-mantle boundary heat flow.
Hydrogeochemistry of alluvial groundwater in agricultural area: A case study in Gumushacikoy Aquifer, Turkey

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Ground and surface water quality can be affected by three different forms of pollution, which are chemical, biological and physical pollution. These polluting factors can influence natural environment and human health. Nitrites in soil and groundwater generally move relatively slow and there is approximately 20 years lag time between the detection of the pollutant the pollution activity and in groundwater. In this study, groundwater pollution originated from agricultural activities and municipal wastewaters were investigated in Gumushacikoy urban area. The water analyses from 49 water wells in the plain, taken over a 2-year period, were used to determine the NO$_3^-$, NO$_2^-$ and NH$_4^+$ contamination in the alluvial groundwater. The concentrations of nitrate (NO$_3^-$) in groundwater of Gumushacikoy Plain range from 0-15.61 mg/l, nitrite (NO$_2^-$) 0-0.007 mg/l and ammonium (NH$_4^+$) 0-0.5 mg/l. Most of the drinking water samples high in nitrite and ammonium concentrations and exceeding the limit of 0 mg/l (TSE 266, Turkish Drinking Water Standard). However other chemical parameters such as pH, EC, TH, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, HCO$_3^-$, Cl$^-$, SO$_4^{2-}$ and F$^-$ were also measured. The pH and EC values of of the well water samples are changing between 6.8 – 9.9 and 439-1276 respectively. Drinking water well of some villages have low pH value according to the Turkish Drinking Water Standard. Total hardness of the groundwater samples are ranging between 2.5-57.75 according to the FH. The pH and EC values range between “very soft” and “very hard”. Water type of the Gumushacikoy groundwater is Ca-HCO$_3$. Carbonate hardness of the all drinking waters have bigger than %50. To the chemical analyse results, most of the well waters which are using for drinking purposes should not be used when considering to the NO$_3^-$, NH$_4^+$, pH, total hardness. The present state of the quality of the Gumushacikoy alluvial groundwater necessitates taking some technical measurements in order to preserve and improve water quality.

References
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The concept of convergence in surface roughness and its relationship to rock and mineral surface reactivity

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In material science, the evolution of surface topography by processes such as abrasion has been traditionally quantified by roughness parameters. These parameters characterize quantitatively analyzed surfaces by a statistical treatment of \{x, y, z\} data. With this approach, we are able to quantify the evolution of surface deviations on a regular relief. However, complications arise because most natural rock surfaces show a multitude of wavelengths in terms of surface relief. To detect and quantify the alteration of rock surface topography, a statistical treatment of surface data must accommodate the occurrence of surface “building blocks” of different length. This is important because various surface building blocks typically show different reaction velocities during dissolution or precipitation.

Our approach makes use of so-called convergent surface roughness parameters, in which surface roughness parameters are calculated for differently-sized “footprints” from vertical scanning interferometry (VSI) data. We show several applications demonstrating the importance of convergent surface roughness parameters. In a study of oxidative weathering of organic matter (OM) in black shales, we can demonstrate that root mean square roughness ($R_q$) is tied to the distribution of OM components having a high reactivity for oxidative weathering. In a second study, convergent $R_q$ data measured at iron oxide incrustations of oxidative-weathered uranium-bearing shale correlate linearly but inversely with the uranium (U) concentration of the incrustation. These surface data show a relationship between the occurrence of macropores (d ~ 500 nm) and the U content of the weathering product. As a third example, we demonstrate the application of surface roughness data to determine corrosion rates of volcanic glass surfaces. All examples underscore the importance of statistical surface parameters in the identification and characterization of the surface components that dominate reactivity.

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Magnetite in bacteria: A FMR study

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Under controlled conditions, most of the known magnetotactic bacteria (MTB) precipitate intercellular magnetite crystals within membrane-bound organelles (magnetosomes). The magnetite crystals have an array of physical properties such as size and shape that fall within a narrow distribution. The magnetic properties of cultivated and wild magnetotactic bacteria have been studied in detail by classical rock magnetic methods. Recently ferromagnetic resonance (FMR) spectroscopy has been introduced as an additional tool to assess size and shape distribution in order to identify MTB. We used a pure culture of *Magnetospirillum gryphiswaldense* to analyse FMR effects of magnetite in MTB between 293 and 77K.

Under the TEM the MTB revealed chains of near-equidimensional magnetite crystals of about 50 nm in size which is characteristic for single-domain nanoparticles. For the FMR measurements the MTB were freeze-dried and fixed with paraffin in a glass tube.

At 293 K, the FMR measurement (ν = 9.5 GHz) revealed an asymmetric spectrum with a line width of 187 mT and a g-value of 1.885 (Figure 1). Considering the magnetite in the MTB as a “chain of spheres” the absorption spectrum is dominated by shape anisotropy. No angular dependence of the spectrum was found, which indicates a random distribution of the magnetite chains in the sample. At 77K a different FMR signal with a line width of 198 mT and g = 2.24 was observed. This temperature is below the Verwey transition (Tv = 120 K) where magnetite undergoes a crystallographic transition from cubic to monoclinic symmetry. Based on literature data, it can be postulated that the FMR spectrum at 77K is dominated by magnetocrystalline anisotropy. Considering the spectral development with temperature, the change from a shape-dominated to a magnetocrystalline-dominated anisotropy in the MTB at T < 110 K can be postulated (Figure 1).

**Figure 1:** FMR spectra at 293, 133, 103, and 77K.

The spectral behavior of magnetite nanoparticles in chains at low temperature can be a diagnostic tool to detect magnetotactic bacteria in sediments and soils or magnetite arrays in geological environments indicative of bacterial origin.

Extreme oligotrophy in subsurface sediments of the South Pacific Gyre: Evidence from low oxygen fluxes

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To study subsurface microbial life at its energy limits, we investigated benthic microbial oxygen consumption as a key parameter for organic matter oxidation during an IODP site survey to the South Pacific Gyre in December 2006. The scientific goal of the expedition with the R/V Roger Revelle was to understand the nature of subseafloor sedimentary life in the most ultra-oligotrophic oceanic region on Earth. Here, primary production, particle fluxes and sedimentation are extraordinarily low. We investigated benthic microbial respiration rates by measuring oxygen concentrations in sediments on different spatial scales ex situ (in piston, gravity and multi-cores), and in situ (using a benthic lander equipped with an incubation chamber, a microelectrode profiler, and an optode profiler). Along a transect from 24° to 46°S and 165° to 117° W, cores at 10 of 11 sites were oxygenated for their entire lengths (as much as 8m below seafloor), at concentrations >150µM O₂. This represents the deepest oxygen penetration ever measured in marine sediments. All profiles showed a similar pattern of a rapid decrease in oxygen concentrations from ~220 µM to ~170µM within the first 50cm, which can be explained by oxidation of sedimented organic matter. In the deeper zones, only a very small gradient of ~6µM m-1 was present, indicating extremely low oxygen fluxes and consequently low respiration rates.

We conclude, that the South Pacific Gyre represents the most oxidized and energy-limited marine benthic habitat on earth, with respiration rates at least 3 orders of magnitude lower than previously analyzed marine sediments.
The kinetics of biologically-mediated mineral oxide reduction and biomineralization using time-resolved X-ray diffraction

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The ways in which microorganisms catalyze or inhibit the breakdown and formation of minerals have broad implications for stable isotope geochemistry, acid mine drainage, climate change investigations, the search for life on other planets, and the evolution of life on this planet. We are investigating the kinetics of microbial-mineral interactions using X-ray diffraction (XRD), an old technique applied in a new way.

With the advent of the high-resolution imaging plate, we can take XRD scans in rapid succession (one every 2-10 minutes) and analyze changes in mineral phases as time progresses. This “time-resolved” XRD technique, combined with Rietveld analysis of the diffraction data, has allowed us to decipher discrete changes in unit cell parameters, phase abundances, and atomic displacements.

Total membrane (TM) fractions of the facultative anaerobe Shewanella oneidensis MR-1 can catalyze reduction of solid-phase metal cations (Ruebush et al., 2006). In our experiments, these TM fractions were placed in a silica glass capillary with the manganese oxide birnessite, HEPES buffer (pH=7.0) and Na-formate, which serves as an electron donor. Using a Rigaku II D/Max X-ray microdiffractometer with a Mo-source, we succeeded in monitoring changes in mineralogy within the reaction cell. Our experiments revealed that the reduction of Mn began within minutes and continued until the birnessite had reacted completely. A secondary phase, rhodochrosite (MnCO3), appeared upon the bioreduction of the birnessite.

We conducted the experiment at TM concentrations of 1.4 mg/ml and 3.5 mg/ml, Na-formate concentrations of 1M and 2M and total birnessite weights of .3 and .6 mg. The rate of reduction and re-mineralization was fastest with low TM and high formate concentration, and slowest with high TM and low formate concentration.

References

Rhodium, gold and other highly siderophile elements in chondrites

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Osmium isotopic data and concentrations of the highly siderophile elements (HSE) Re, Os, Ir, Ru, Pt and Pd, recently obtained on chondrites by isotope dilution and Carius tube digestion in reverse aqua regia indicate systematic differences in the HSE composition of chondrite groups, notably in Re/Os and Pd/Ir. Unfortunately, these studies did not provide data for two other HSE, Rh and Au, because both elements are monoisotopic. Yet, Rh and Au may be critical elements for (1) a comprehensive understanding of the different HSE patterns of the chondrite groups and their origin; (2) distinguishing likely lunar impactor populations during the late heavy bombardment; and (3) for a complete characterization of the HSE pattern of the Earth’s primitive mantle and its origin.

Here, we report abundances of Re, Ir, Ru, Pt, Pd, Rh and Au for a set of carbonaceous, ordinary, enstatite and R-chondrites. The new Rh and Au data, along with previous high-precision HSE concentration data on whole rocks of chondrites, require the presence of several distinct components in order to explain their CI-normalized patterns. (1) Carbonaceous chondrites show nearly flat HSE patterns from Re to Pt with CI-like or lower Re/Ir. Ordinary and enstatite chondrites show systematic fractionations from Re to Ir (decreasing) and from Ir to Pt (increasing) indicative for a complex high temperature history of ordinary and enstatite chondrites and the presence of at least two refractory components. (2) Most chondrites show a sometimes substantial drop in normalized abundance between Pt and Rh, suggesting the removal of a refractory metal phase from solar gas in a narrow temperature range (near 1400 K), and likely before condensation of the major fraction of Ni and Fe occurred (< 1350 K). (3) Chondrites are characterized by variable enrichment or depletion of Pd and Au, suggesting the variable presence of a component depleted in refractory siderophiles and enriched in moderately volatiles.
Search for an $^{60}$Fe supernova-produced isotopic signal in marine sediments

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The recent observation of an $^{60}$Fe peak in a deep-sea FeMn crust has been interpreted as due to the signature left by the ejecta of a supernova (SN) relatively close to the solar system 2.8 ± 0.4 Myr ago [1]. To confirm this interpretation with better time resolution and more direct flux estimate, we have performed Accelerator Mass Spectrometry (AMS) $^{60}$Fe measurements along a dated marine sediment core.

FeMn crusts are authigenic objects. Marine sediments are composed of a larger variety of geochemical phases. Since the iron in the alumino-silicate phase is not equilibrated with the soluble $^{60}$Fe in the ocean, its inclusion would lower the $^{60}$Fe/Fe ratio compared to the authigenic fraction. Therefore, we used a chemical procedure to isolate this fraction [2]. The AMS measurements were carried out at the facility of Garching. In order to verify that our chemistry was dissolving the phase containing the $^{60}$Fe seen in the crust, we tested it on samples from the same crust. We also observed an $^{60}$Fe/Fe peak, consistent with that found by [1].

The $^{60}$Fe signal in the FeMn crust was observed over a depth interval corresponding to 800,000 years [1]. However, we initially assumed that this was due to the inherent time resolution associated with the growth and sampling of the FeMn crust. Assuming a short deposition time e.g. 10,000 years [3], and considering the characteristics of the marine sediment core, we can calculate a $^{60}$Fe/Fe ratio in the authigenic phase of the sediment of 5x10$^{-14}$.

We performed $^{60}$Fe/Fe measurements along the sediment core from 1.7 to 3.2 Myr. The extension of the original time interval (2.4-3.2 Myr [1]) is from taking into account (i) that $^{10}$Be dating has been repeated in the crust, (ii) 1/2$^{10}$Be uncertainty.

We found no evidence for an $^{60}$Fe/Fe peak in the sediment in the time interval 1.7-3.2 Myr, with upper limits at least an order of magnitude lower than the value expected under the above assumptions. We will discuss possible reasons for this result, including the possibility that the deposition time was indeed >>10 kyr.

References

The groundwater beneath Hekla volcano, Iceland; A natural analogue for CO$_2$ sequestration

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The increased concentration of CO$_2$ in the atmosphere has made it necessary to develop methods to store CO$_2$. One of the possibilities for CO$_2$ storage is by reacting it with basalt and thereby precipitating the CO$_2$ as calcite (CaCO$_3$). A pilot project is being performed in Iceland by Reykjavik Energy, University of Iceland, Columbia University and University of Tolouse.

The Hekla volcano is one of Europe’s most active volcanoes (e.g. Flaathen and Gislason, 2007) and its magma chamber degasses even under quiet periods where the main emitted gases are CO$_2$, HF and SO$_2$. These are some of the same gases emitted from geothermal power plants and aluminum smelters in Iceland. This make Hekla volcano a very good natural analogue to CO$_2$ sequestration in basalt.

The lava fields surrounding the volcano host a large ground water body. Water samples from its springs have been collected periodically for 20 years. Analysis and modelling of this water can tell us what may happen when CO$_2$ is being injected into basalt.

The gases emitted from the magma chamber make the ground water acidic. The acidity enhances the dissolution rate of the basalt releasing elements like Ca into the ground water. These reactions consume protons and the increase in concentration of elements in the ground water together with increase in pH leads to the precipitation of secondary minerals like calcite.

Modelling performed by the PHREEQC 2.11 computer code (Parkhurst and Appelo, 1999) shows that calcite goes from being undersaturated to almost saturated with increase in pH.

At the early state of dissolution of the basalt, at low pH, the concentration of toxic metals like Cr and Pb in the ground water might be high. The pH of the groundwaters in the vicinity of Mt. Hekla range from about 7 to 9. The concentration of toxic metals is very low in these waters (nmole/kg) which is also the case for Fe. Modelling shows that Fe-hydroxides are supersaturated in the groundwaters and the precipitation of this phase might scavenge the toxic metals.

References
Investigation of weathering rinds on Earth and Mars by depth selective Mössbauer spectroscopy

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The two Mars Exploration Rovers, “Spirit” and “Opportunity”, each carry a miniaturised Mössbauer spectrometer (MIMOS II) [1]. MIMOS II operates in backscattering geometry and can obtain 14.4 keV gamma ray spectra and 6.4 keV X-ray spectra simultaneously. Comparing 14.4 keV and 6.4 keV spectra yields depth selective information about a sample: 14.4 keV gamma rays have a larger escape depth from a sample than 6.4 keV X-rays because of their higher energy. As a consequence, a 6.4 keV spectrum contains more information about the near-surface part of a sample than a 14.4 keV spectrum. This allows for the detection and characterization of coatings such as weathering rinds without abrading the surface of the sample.

At the landing site of the Spirit rover in Gusev crater, a dark coating was detected on the rock “Mazatzal” [2]. 14.4 keV and 6.4 keV spectra obtained on the brushed surface of Mazatzal show significant differences in the relative intensity of “nanophase oxide”, a “poorly crystalline product of oxidative weathering that contains nanometer-sized particles of Fe3+-bearing material” [3].

To investigate the depth selectivity in Mössbauer spectra experimentally, measurements were done on samples composed of thin sections of one mineral or iron foil, respectively, on another mineral. The influence of coatings of varying thickness and composition on Mössbauer spectra can be studied in a simulation. A Monte Carlo simulation compiled for this work allows the modelling of a sample composed of two homogeneous layers, each containing up to ten different minerals. The thickness of a coating can be determined by comparing measured and the according simulated spectra. In the case of Mazatzal, modelling the coating with a thickness of 10 micrometers leads to best agreement between measured and simulated spectra. [4]

References:


Integrated air quality assessment – Pine needle δ13C, δ15N as proxy for atmospheric CO2 and NOx loads

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In a multidisciplinary approach atmospheric quality in the Greater Cologne Area (GCA) was studied using pine needles as pollutant bioreceptors. Here we discuss the potential of the δ13C and δ15N isotopic composition of pine needle biomass to record the atmospheric loading with CO2 and NOx released from anthropogenic combustion processes. The gaseous pollutant load estimated by isotope proxies is compared and interpreted in concert with persistent organic pollutant as well as major and trace element concentration data.

The GCA comprises a variety of CO2 and NOx emission sources, including lignite fueled power plants, regions of high traffic density, domestic heating, intensive agriculture and large industrial complexes along the Rhine Valley. A substantial part of atmospheric CO2 in large conurbations will derive from fossil fuel combustion. Two reaction modes for increased CO2 in atmosphere are known. A fertilizing effect by which the addition of isotopically light CO2 will lead to a decline in foliage δ13C values. Conversely, high concentration of CO2 will cause stress and trigger closure of stomata, resulting in heavier foliage isotopes. For 5 needle age classes taken separately in summer and winter a systematic trend to δ13C values heavier by about 2.5 permil with age was noted, attributed to declining photosynthetic activity. Differences between locations were larger than within location. Although influenced by a variety of environmental conditions the significantly lighter δ13C of pine needles in urban Cologne reflects traffic emissions. The area affected by lignite combustion revealed no deviation in foliage δ13C due to more intensive air mixing in these regions.

The δ15N values of vegetation have been shown react to NOx in surrounding air via direct stomatal uptake or via precipitation and root uptake. Hereby pollution stress induces heavier δ15N values. Most often foliage and soil δ15N are decoupled emphasizing the importance of atmospheric NOx uptake and remineralization for foliage N-isotopes.

Investigation of 5 needle cohorts shows a systematic trends towards slightly lighter δ15N values with age. Intra-site variability was low but inter-site variation high, allowing for excellent spatial discrimination. The δ15N of pine needles showed a trend to heavier values in farming and forested areas but lighter values in urbanized regions and in areas affected by lignite mining. A trend inversion occurred in inner city areas, where changes from high to low δ15N were noted. Heavier N-isotopes of foliage caused by NOx-stress are in compliance with previous observation but seem to be restricted to areas most affected by traffic emissions.
The weathering engine conveyor belt and corestone size distributions

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In weathering profiles developed at Gettysburg (Pennsylvania, U.S.A.), unweathered diabase bedrock fractures and chemically alters by spheroidal weathering to produce a population of corestones surrounded by rindlets overlain by saprolite. It appears that once corestones reach a limiting size they no longer form new rindlets but weather strictly by a diffusion-limited infiltration mechanism.

We model the gross features of the chemistry and mechanics of rindlet formation and the production of weatherable surface area for a steady erosion rate. The model yields a steady state profile of corestone volume fraction, fC, decreasing upwards to the erosional surface from a value fC ≈ 1 at a depth, H, where chemical weathering is negligible. Populations of corestones in eroding or eroded concentrations in organic acids. An additional reaction front was confirmed by precipitation experiments.

There is a linear increase in solubility constant log Ksp calculated for the reaction:

\[ \text{Pb}_5(\text{PO}_4)_3\text{Cl} \leftrightarrow 5\text{Pb}^2+ + 3\text{PO}_4^{3-} + \text{Cl}^- \]

with increasing As content in the series, from -79.60±0.02 for Pb5(AsO4)3Cl at 25°C to -76.32±0.25 for Pb5(AsO4)3Cl at 25°C. For all phases the solubility product decreased linearly with the inverse temperature indicating a constant enthalpy of dissolution reaction in the experimental range.

References

The Ordovician Galiñeiro peralkaline gneiss complex, Vigo, NW Spain

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The Variscan mountain chain in Brittany (France), NW Spain, Portugal and SW Spain contains numerous orthogneiss complexes of early Paleozoic age, predominantly cropping out in the central zone of the orogen. Most have calcalkaline, alkaline and some peralkaline compositions. The first two are cut by numerous basic dikes.

The Galiñeiro peralkaline complex, situated mainly South of the city of Vigo near the Atlantic coast, is the largest and best investigated of these complexes. Fieldwork and petrographic studies done by the first author in the fifties and sixties of last century were followed in the eighties and nineties by detailed mineralogical and geochemical work by the third and second authors.

The results of both studies are highly complementary and give evidence of rock and mineral behaviour both at the intrusive stage and under Hercynian lowP, intermediate T metamorphic conditions leading to strong recrystallization, including total unmixing of the supposed original hypersolvus feldspar.

The rocks of the complex are enriched in REE and HFSE, present in a wide variety of accessories: bastnäsite, REE silicates (e.g., allanite, thaleneit-yttrialiet), REE niobotantalates (aeschnyite, fergusonite-formannite, samarskite, pyrochlore-betafite), REE phosphates (monazite, xenotime), Th-rich minerals (thorite, P-rich thorite), and zircon.

Magmatic fractionation, most likely from a mantle-derived volatile-rich alkaline basalt parent, led to peralkaline silicic differentiates with residual fluids extremely enriched in fluorine and other ligands, which complexed the REE and HFSE. Decrease in fluorine activity with falling temperature and the crystallization of F-bearing major minerals caused the breakdown of complexes, releasing the rare earths and the remainder of the high-field-strength elements, and formation of HFSE- and REE-rich minerals.

The elevated fluorine, CO₂ and sulfide contents of the Galiñeiro system, together with the energy inputs of the different phases of Hercynian metamorphism, caused episodic remobilisation, reflected by the zircon U–Pb concordant ages at 370 and 310 Ma, and the exotic geochemical features (Zr/Hf remobilisation, reflected by the zircon U–Pb concordant ages)

The functional species of a mineral surface and their interaction with the adjacent water molecules – Determined by nonlinear optics and quantum chemistry

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The functional species of the mineral surfaces, which control the mineral/water interaction, are not definitely known for most crystal faces because it is difficult to obtain chemical in situ information with interface selectivity. Here we apply interface selective vibrational sum frequency spectroscopy to the sapphire (001) surface. Additionally we carry out density functional theory and ab initio calculations on aluminium-oxide clusters as models for the sapphire (001) surface. The results of experiment and theory are well in agreement. This work is part of an ongoing fundamental study of the sorption mechanism of actinides on single crystal faces by various experimental and theoretical techniques. Sapphire serves as a simple model for natural clay minerals.

From the ideal termination of the bulk crystal structure, the (001) surface is expected to exhibit a single type of aluminol species with the OH group in a bridge position. We distinguish four OH species which are all doubly coordinated but exhibit different tilt angles of their OH bonds. Depending on the tilt, different geometries arise for hydrogen bonding with water molecules. At high pH the interaction of the mineral surface with the neighboring water molecules is dominated by electrostatic forces. The net dipole moment of these water molecules points into the direction of the mineral surface which is in agreement with the expected negative surface charge. In the pH range between 1.3 and 6 the interaction of the water molecules with the mineral surface is dominated by hydrogen bonds. Two populations of water molecules exist near the interface which are characterized by specific hydrogen bonding to the different aluminol species. Due to these bonds the net dipole moment of one water population points to the mineral surface, the net dipole of the other population points into the opposite direction. Since the relative concentrations of the different aluminol species depend on the pH, the relative concentrations of the two water populations changes also. In summary, a picture at the molecular level with surprising richness of details is obtained.

Reference
(U-Th)/He apatite constraints on the erosional history of the southwestern Colorado Plateau and implications for Early Tertiary uplift and carving of a “proto-Grand Canyon”

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Resolving the timing and relationships between regional unroofing, canyon incision, and topographic uplift in continental plateaus is a challenging problem. The regional unroofing history of the Colorado Plateau, and its relationship to Grand Canyon incision (up to 1.5 km) and plateau uplift (~1.9 km) since the Late Cretaceous, is controversial. We used (U-Th)/He apatite thermochronometry (36 samples, 230 single-grain analyses) across the southwestern quadrant of the Colorado Plateau to address these issues. Our data document overall southwest to northeast unroofing from plateau margin to plateau interior, during denudation phases in the Late Cretaceous/Early Tertiary (80 to 55 Ma), mid Tertiary (28 to 16 Ma), and Late Tertiary (<6 Ma). Distributions of apatite dates modeled using the radiation damage trapping model [1,2] suggest that eastern Grand Canyon samples from the basement and the Kaibab surface nearby had similar Early to Cretaceous/Early Tertiary (80 to 55 Ma), mid Tertiary (28 to 16 Ma), and Late Tertiary (<6 Ma) distributions of apatite. If these models are correct, they indicate that a significant (~1500 m) paleo-Grand Canyon was carved in post-Paleozoic sediments in this region during Early Tertiary time. Evidence for kilometer-scale topographic relief would require substantial uplift during Sevier/Laramide time, preceding regional unroofing of this portion of the plateau interior. Although the data do not preclude additional post-Laramide uplift, the subsequent regional unroofing phases could be explained by drainage reorganization associated with rift-related lowering of adjacent regions without additional elevation gain of the plateau.

References

A Comparison of the elemental composition of Wild 2 grains with other extraterrestrial materials

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NASA’s Stardust spacecraft passed through the dust coma of Comet 81P/Wild 2 at a speed of ~6 km/s in January 2004, collecting dust particles in low-density silica aerogel and as impact residue in craters in Al-foil. These samples, which were delivered to Earth on January 15, 2006, provided the first opportunity to analyze material from the Kuiper Belt, the presumed source of short-period comets like Wild 2. The elemental compositions of twenty-three particles captured in aerogel and the residue in seven craters in Al-foil were determined during the Stardust Preliminary Examination (Flynn et al., 2006). The results were generally consistent with the more limited elemental composition data obtained on grains from Comet 1P/Halley, an Oort cloud comet, which were analyzed by impact-ionization mass spectrometers on the Giotto and VEGA spacecraft which flew through the Halley coma in 1986.

To first-order, the mean elemental composition of the Wild 2 particles agrees with the composition of the CI carbonaceous meteorites, which are believed to represent the initial composition of the Solar System, for the refractory elements. However the Fe/Si ratio is somewhat lower than CI in the Wild 2 particles. In addition, S is depleted relative to the CI abundance and several moderately-volatile minor elements (Cu, Zn, Ga, and Ge) are enriched in the Wild 2 samples over the CI meteorite abundances.

Both the depletion of Fe and the enrichment of moderately-volatile elements were previously reported in the fine-grained, anhydrous IDPs, some of which have inferred atmospheric entry speeds suggesting a cometary origin (Brownlee et al., 1993). The CI meteorite element abundances are taken to represent the Solar Nebula composition for non-volatile elements because of the good agreement between CI abundances and the composition of the Solar photosphere, measured by spectroscopy. These preliminary results on the Wild 2 material suggest that the outer region of the Solar Nebula, where comets such as Wild 2 are believed to have formed, may have contained higher concentrations of some moderately-volatile elements and lower Fe than the inner region of the Solar Nebula, where the meteorites formed. Alternatively, since the abundances of Cu, Zn, and Ga are not well-determined in the Solar photosphere, it is possible that abundances of these elements in the Wild 2 particles and the anhydrous IDPs may better reflect the composition of the Solar Nebula for these moderately-volatile elements than does the composition of the CI meteorites.

References
**Modeling silicate-rich fluids at high pressures**

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Comprehension of rock-forming processes at depths corresponding to the lower crust and active subduction zones requires an understanding of silicate-rich fluids coexisting with rock-forming minerals. However, existing models for aqueous silicate solutions are difficult to extrapolate to pressures higher than 0.5 – 1.0 GPa. An alternative approach is to treat H$_2$O in terms of a statistical thermodynamic model involving a dynamic equilibrium between "gas-like" disordered and "liquid-like" clustered molecules (Gerya and Perchuk, 1997; Gerya et al., 2004), where $X$(aq) is the mole fraction of the latter. Gerya et al. (2005) successfully tested this approach for SiO$_2$-H$_2$O solutions to 1300°C and 2 GPa. We extend this model to include the ionization of water, combining available and also new experimental solubility data for quartz (SiO$_2$), corundum (Al$_2$O$_3$), wollastonite (CaSiO$_3$), grossular (Ca$_3$Al$_2$Si$_3$O$_12$), zoisite (Ca$_2$Al$_3$Si$_3$O$_12$(OH)), sanidine (K$_0.9$Na$_{0.1}$AlSi$_3$O$_8$) and albite (NaAlSi$_3$O$_8$) in pure H$_2$O, as well as quartz and corundum solubilities in KOH solutions, to develop a simple thermodynamic description for aqueous fluids in the model system KNCASH. $\Delta G_r$ of dissolution reactions is thus expressed in terms of the standard-state molar thermodynamic parameters $\Delta H^o$, $\Delta S^o$, $\Delta C_{p}(T)$, $\Delta V(T,P)$, the molality of the dissolved species, pH and $X$(aq). The model successfully returns the available experimental data. The formalism requires data on speciation to define the influence of $X$(aq) and pH on the reaction and to determine the number of species and reactions involved. However, a simplified "component" approach for oxides can be developed to approximately model KNCASH fluids from 0.2 to 3 GPa. The incorporation of pH into the model reduces the need for "mixing terms" to describe the interaction of dissolved oxides. Calculations suggest the formation of alumina-silica, alkali-silica, alkali-alumina as well as silica-alumina-alkali species. This information can also be directly derived from a comparison of the different experimentally investigated fluid-solid systems. There is no indication at present for the formation of multi-oxide complexes with Ca.

**Cosmogenic $^3$He exposure dating of the Quaternary lavas at Fogo, Cape Verdes: Dating flank collapse and magmatic reorganisation**

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Construction and destruction of young ocean island volcanoes is often episodic and governed by periods of intense volcanism and flank collapse. Conventional dating methods are often insufficient to constrain late Quaternary events; rocks may be too young to be dated precisely by $^{40}$Ar/$^{39}$Ar, or lack datable material (e.g. charcoal) for $^{14}$C. Cosmogenic $^3$He exposure dating of basaltic lavas is a powerful alternative, with potential to date flows beyond a few kyr. We present results from a study to date Quaternary lavas of Fogo, Cape Verdes. The growth of Fogo occurred in two main stages, separated by a large flank collapse removing the summit and eastern flank of the pre-collapse Monte Amarelo volcano. The collapse produced a 9 km wide escarpment with a headwall cliff that is still 1 km high despite the infilling with over 1.5 km of post-collapse lava flows from the Cha das Caldeiras volcano. Dyke swarms in the Monte Amarelo volcano indicate that the collapse was preceded by a structural reconfiguration of an initially radial dyke swarm to a single, dominantly north–south swarm across the summit region. This coincided with an eastward shift in magmatic activity. The recent history of the Cha das Caldeiras volcano has seen similar structural reconfiguration of dyke swarms and eastward shift of volcanism resulting in the extinction of post–collapse volcanic rift zones in the west of the island. Dating these events is vital for understanding the timing of (future) volcano flank collapses of Fogo.

Lava flows erupted immediately prior to, and after the collapse bracket its age and exposure ages from two pre-collapse ankaramite flows yield 24 and 110 ka, while post-collapse flows yield 14 to 9 ka. We infer two possible scenarios; (i) the collapse occurred between 14 and 24 ka or, (ii) the young exposure age of the pre-collapse flow is an artefact of ash cover/erosion and collapse occurred closer to 110 ka. This has profound implications for the interpretation of future flank collapses on Fogo. The post-collapse flows are among the youngest flows on the western side and the early Holocene ages imply that the magmatic reconfiguration and possible onset of renewed instability of the eastern flank has been developing for several thousand years. If the collapse occurred between 14 and 24 ka, flank instability may be in its early stages. If the collapse occurred around 110 ka, the duration of the pre-Monte Amarelo collapse reorganization may be comparable to the duration of the present one, with the prospect of a near-future collapse likely.

**References**


Trace metal dynamics and transport in a polar glacier-dominated watershed: Taylor Valley, Antarctica

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Anthropogenically introduced trace metals travel to even the most remote locations on earth including Greenland and Antarctica. Little is known about metal dynamics in the largest ice-free area in Antarctica, the McMurdo Dry Valleys, which includes Taylor Valley (~78°S). Previous work has examined metal concentrations in Taylor Valley glacier melt streams and lakes (Green et al., 1986). In this work, concentrations of metals (V, Pb, Cd, Cu) in Canada Glacier snow is compared to stream and lake concentrations to determine melt evolution and to ultimately make predictions about stream chemistries.

Samples were collected using ultraclean techniques to minimize contamination. The sequence of median trace metal molar abundance in Canada Glacier snow is Cu>V>Pb>Cd. Canada Glacier’s melt streams have different relative abundances than the snow. The western melt stream, Andersen Creek is V>Cu>Cd>Pb. Whereas the eastern melt stream, Canada Stream, is Cu>V>Cd>Pb. Median Na:Cl ratios increase from snow values (0.4) in both Andersen Creek and Canada Stream (0.9), suggesting in-stream chemical weathering and salt dissolution. The western and eastern lakes fed by these streams, Lake Hoare and Lake Fryxell have similar Na+:Cl surface water values as the streams. In general V, Cu, Cd, and Pb to Cl ratios are all highest in Canada Glacier snow and lowest in its streams. The exception is Cu:Cl, which is highest in lake surface water followed by snow and streams. Total Hg:Cl ratios in the Lake Fryxell Basin indicate substantial removal of Hg relative to Cl as the waters evolve from snow to lake with the largest losses occurring from stream to lake (Lyons et al., 1999). There is no net gain of trace metals relative to Cl through weathering as with Na+. Their concentrations relate more to other processes such as adsorption, biotic uptake and/or removal by suspended material, which are connected to discharge, pH, and biomass abundance.

References

Quaternary records of ocean pH

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Atmospheric CO₂ (pCO₂) is an important greenhouse gas that regulates the Earth’s climate on geological and shorter timescales. Proxy data for the ocean carbonate system in the past have a crucial role to play in the understanding how CO₂ is partitioned between the ocean and the atmosphere on these timescales. Of particular importance in this regard are the suite of proxies based on the isotopic and trace element composition of foraminifera, and in particular, the isotopic composition of boron (δ¹¹B) which a number of studies have shown faithfully records the pH of seawater in which the foraminifera grew.

There are a number of factors complicating the application of the boron isotope pH proxy, some of which arise from the analytical difficulties involving the precise and accurate measurement of its isotopic composition. We have recently developed an approach, using multicollector inductively coupled plasma mass spectrometry, that overcomes these analytical problems. This technique is both rapid and precise (better than 0.3 ‰) allowing the routine determination of δ¹¹B in a small number of foraminifera. We present here the first application of this technique.

In contrast to previous work we find that the measured isotopic composition by MC-ICPMS for a variety of Holocene species (ranging in δ¹¹B from 16 to 21 ‰) from a range of depth habitats and physiology, is very close to that of the dissolved B(OH)₄ species predicted using an isotopic equilibrium constant of 1.0272 [1] and pre-industrial carbonate system parameters. This result greatly simplifies the use of the proxy. In this contribution we determine Quaternary and Late Neogene changes in pH on various timescales in several localities in the equatorial oceans (Carribean, Eastern Atlantic, Western & Eastern Pacific). Using these data to gain a global perspective, we can distinguish local short term changes in pH from changes relating to the global reorganization of the carbonate system that accompanied glacial-interglacial climate change, and use our pH reconstructions to estimate the magnitude of pCO₂ changes beyond the reach of the ice-cores.

Reference
Extraterrestrial $^3$He is delivered to the earth surface by interplanetary dust particles (IDPs) characterized by a very high $^3$He/$^4$He ratio (2.4x10$^{-8}$), several orders of magnitude higher than ratios measured in terrigeneous matter (e.g. review by Farley, 2001, and Schlosser and Winckler, 2002).

Several recent studies in marine sediments (Marcantonio et al., 2001, Higgins 2001) and polar ice (Brook et al 2000, Winckler and Fischer 2002) have opened up the application of extraterrestrial $^3$He as a constant flux proxy, at least over the last 400 ka, with a mean flux around 8 ± 3 x 10$^{-13}$ ccSTP/cm$^2$/ka. In order to measure the present $^3$He$_{ET}$ flux, we started in 2001 to collect dust in the Paris region every two months, corresponding to an area-time product of 0.03 m$^2$.a.

As expected from such small area-time products, the data are scattered due to the small number of IDPs sampled, preventing the observation of any seasonal variability: the observed total $^3$He flux range from 1 to 200 x 10$^{-13}$ ccSTP/cm$^2$/ka, with a mean value of (32 ± 9) x 10$^{-13}$ ccSTP/cm$^2$/ka. However, $^3$He/$^4$He ratios are often below 10$^{-7}$ and the terrestrial $^3$He component has to be estimated. Our measurements can be considered as binary mixings between an IDP and a terrigeneous end-member with a $^3$He/$^4$He ratio of 1x10$^{-6}$, leading to an estimate of the present $^3$He$_{ET}$ flux of (30 ± 9) x 10$^{-13}$ ccSTP/cm$^2$/ka.

This flux is significantly higher than the mean accepted value of 8 ± 3 x 10$^{-13}$ ccSTP/cm$^2$/ka, which is all the more surprising that we would expect statistical underestimation due to the small area-time products sampled, especially compared to marine sediments where values up to 0.2 are frequent (Farley et al., 1997). Different explanations can be considered: (1) There may be temporal variations which are smoothed in the data are scattered due to the small number of IDPs sampled, preventing the observation of any seasonal variability: the observed total $^3$He flux range from 1 to 200 x 10$^{-13}$ ccSTP/cm$^2$/ka, with a mean value of (32 ± 9) x 10$^{-13}$ ccSTP/cm$^2$/ka. However, $^3$He/$^4$He ratios are often below 10$^{-7}$ and the terrestrial $^3$He component has to be estimated. Our measurements can be considered as binary mixings between an IDP and a terrigeneous end-member with a $^3$He/$^4$He ratio of 1x10$^{-6}$, leading to an estimate of the present $^3$He$_{ET}$ flux of (30 ± 9) x 10$^{-13}$ ccSTP/cm$^2$/ka.

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References


Chemical and isotopic constraints on water/rock interactions at the Lost City hydrothermal field, Mid-Atlantic Ridge

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Low temperature vent fluids issuing from the ultramafic-hosted hydrothermal system at Lost City, 30°N Mid-Atlantic Ridge, are enriched in dissolved volatiles (H$_2$, CH$_4$) while attaining elevated pH values, indicative of the serpentinization processes that govern water/rock interactions deep in the oceanic crust. Most importantly, serpentinization described mainly by the exothermic hydrolysis of Fe-bearing olivine has been directly linked to the heat source that drives subseafloor hydrothermal alteration at Lost City. The extent of exothermic heat generation, however, has been shown to be strongly dependent on the availability of fresh peridotite, with theoretical calculations indicating that low fluid/rock mass ratios (<1) are prerequisites for exothermic reactions to be the primary source of heat in this system [1].

Based on the Sr and $^{87}$Sr/$^{86}$Sr composition of vent fluids sampled from Lost City [2], however, estimations of the integrated w/r ratios range between 6 and 8. Furthermore, constraints on the fluid/rock mass ratios together with reported δ$^{18}$O isotopic vent fluid compositions (0.7‰) permit subseafloor reaction temperatures in excess of 250°C to be approximated, following the temperature-dependent oxygen isotope fractionation between serpentine and water. These estimations are in general agreement with previous theoretical studies [1], further supporting, however, extensive conductive heat loss occurring within the upflow zone of the Lost City hydrothermal system. Evidence of such extended conductive cooling stage include the relatively elevated precipitation temperatures (130-220°C) predicted by the negative δ$^{18}$O composition values (~14.2‰) reported for carbonate veins in basement peridotite. In addition, endmember dissolved boron concentrations of the Lost City vent fluids (~30 μmol/kg) [3] are significantly lower than those measured in other MAR hydrothermal systems, while with δ$^{11}$B isotopic composition maintaining values (~30‰) [3] reflective of elevated temperature hydrothermal alteration conditions, an substantial boron uptake into secondary phases along the discharge zone can be suggested; a process consistent with the proposed extensive conductive cooling that appears to greatly affect the chemical evolution of the Lost City hydrothermal vent fluids.

References

Geochemical anomalies in stream sediments of the upper Sava River drainage basin (Croatia, Slovenia), determined by statistical methods

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Introduction

Sava River is a transboundary river of supraregional interest, draining 95,719 km² in Slovenia, Croatia, Bosnia and Herzegovina and Serbia. It is a typical Alpine river, flowing from Julian Alps. It becomes a typically lowland river when entering Croatia. The upper flow of Sava River can be compared with Soča/Isonzo River, which flows from the other side of Julian Alps toward Adriatic Sea.

The aim of the work was to extend the mineralogical and geochemical dataset of stream sediments from Upper Sava River and to study the possible influence of sub-basins of Savinja, Krka and Kupa rivers on main course of Sava River.

Methods

Mineral composition was determined by X-ray diffraction and chemical composition by inductively coupled plasma mass spectroscopy (ICP-MS). Two different procedures to identify anomalous geochemical data were used: the box plot method and the median absolute deviation (MAD).

Results and discussion

Results obtained by the box plot method showed that anomalous concentrations (extreme or outlier) of Zn, Pb, In, Cu, Co, Se, Zr, Cd, As, K, Na, Ti, Ba, B, Mn, Fe are present in sediments of the Celje region, of Cr, Ni, S, In, Cu, Mo, Pb in Moste Dam (pollution traced down to camping Šobec), and of Hg in Litija-Zagorje mining region. The MAD method is more sensitive. It depicts the same polluted areas, but with more anomalous values, which are above threshold values for toxicity. Both statistical methods (box plot and MAD) show two anomalous values for Hg in Sava River near Kranj and Zagorje. The concentrations are much higher than those causing significant toxic effects (>2 ppm). The two locations of Sava River in Croatia show very clean environment with respect to trace elements, although Sava River passed big cities of Zagreb and Sisak. The results clearly indicate self-purification mechanisms of Sava River.

Recommendations and perspectives

Similar future sediment study is recommended on middle and lower Sava drainage basin of interest for Croatia, Bosnia and Herzegovina and Serbia to detect possible pollution centers. In the case of significant pollution, remediation of sediments and watershed management should be applied.

Isotopic and geochemical evidence of gas producing microbial ecosystems in coal seams and gobs in the SW Upper Silesian basin, Czechia

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Gas habitat

Gas samples were collected from coal seams of Namurian A-C age, gobs and overburden reservoirs in the Late Carboniferous Upper Silesian basin (USB), NE Czech Republic. The δ13C values of methane and (C1/(C1+C2) ratios suggest occurrence two genetic types of gases. (Fig. 1).

Discussion of the results

Thermogenic 13C enriched and wet gas is extracted from the unmined seams in the Ostrava Fm. Dry and isotopically light gas is encountered in the gobs as reported also from Polish mines (Kotarba 2001).

Conclusions

Presence of microbial gas in the USB evidences activity of deep biosphere down to depth of 1000 m. Supply of oxygenated compounds and H2 is the limiting factor of microbial activity (Horsfield et al. 2006). The temperature conditions of are favorable for methanogenesis at dept range up to 2 km (70°C).

References

Hydrothermal stability of adenine under controlled fugacities of N\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}

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Demonstrating that organic compounds are stable at high temperatures is important in the context of Archean hydrothermal systems as potential sites for the synthesis of the first organic molecules on Earth. Among such molecules, amino acids have been the subject of numerous studies (e.g. Miller and Bada, 1988; Shock, 1990; Andersson and Holm, 2000). In contrast, nucleic acid bases have received much less attention. Consequently, the present experimental study was undertaken to investigate the stability of adenine at 300°C. The experiments were carried out in sealed autoclaves under fugacities of gaseous CO\textsubscript{2}, N\textsubscript{2} and H\textsubscript{2} representative of those encountered in marine hydrothermal systems. The fluid phase was generated from the decomposition of oxalic acid, sodium nitrite and ammonium chloride, and the oxidation of metallic iron. The results of the experiments seem to indicate that the concentration of adenine stops decreasing after ~ 96 hours (Figure 1). This suggests that an equilibrium state may have been established between adenine and the inorganic constituents of the fluid phase, which is corroborated by independent thermodynamic calculations.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1}
\caption{Evolution of the concentration of adenine as a function of time. The dashed extension represents an extrapolation beyond the duration of the experiments.}
\end{figure}

References

The importance of constant flux proxies in paleoceanography

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For all paleoceanographic reconstructions from marine archives a precise chronology is the most essential prerequisite for reliable estimates of processes in the past and for compatibility between different records. All paleoceanographic studies, in particular those aiming at the reconstruction of fluxes from pelagic sediments (for example those on paleoproductivity or dust fluxes) face two main additional problems which complicate a reliable application. For some components of interest (such as organic carbon or biogenic opal) only a small and even variable fraction may be preserved between signal formation in surface waters and deposition in the sediments. The second problem which can affect all paleoceanographic reconstructions from marine sediments is sediment redistribution by currents or within nepheloid bottom layers. These processes can alter the true signatures to variable extents thereby completely masking the original signatures. This is of course particularly important in dynamic bottom current regimes but sediment redistribution can also be active at any other location.

In order to overcome and, in the optimal case, quantify and correct for these effects, a number of so-called constant flux proxies have been developed and applied. The most frequently used of those is the U-series nuclide \(^{230}\text{Th}\), which is produced at a constant rate in the water column of the Ocean from homogenously distributed uranium, and which is only advected with water masses to a very limited extent due to its high particle reactivity. Other examples are \(^{3}\text{He}\) derived from interplanetary dust particles (IDPs), which are deposited on the surface of the earth at a nearly constant rate or, less frequently used, cosmogenic \(^{10}\text{Be}\).

I will give an overview of these constant flux proxies and discuss recent new findings on their strengths and weaknesses. As in most cases in paleoceanographic and geochemical research, none of these proxies is perfect but in view of the possibly huge misinterpretations occurring without their use, their application is absolutely crucial for any reliable paleoceanographic reconstruction. This is because effects of sediment redistribution cannot be readily identified from sedimentary parameters, they may occur at unexpected locations, and places with potentially focussed sediments are preferentially chosen as coring sites due to the expectable high time-resolution of the records.
High-grade metamorphic ortho- and paragneisses are exposed in the proximity of the 0.9 Ga Proterozoic Rogaland anorthosite massif, SW-Norway. The study area is located 5-20 km northeast of the intrusive contact with the anorthosite. In this area, migmatitic opx-bearing granitic gneisses are the main rock type present, transsected by metabasites as dykes. Minor migmatitic garnet-sillimanite-cordierite gneisses, quartzites, calc-silicate rocks, marbles, and rare sapphirine granulites occur as folded layers or discontinuous lenses in between large Opx-gneiss bodies. They aimed of the present study was to elucidate the composition of the protoliths of the different rock units, to reconstruct their tectono-metamorphic evolution, and to investigate the influence of a possible contact-thermal overprint related to the emplacement of the Rogaland anorthosite massif.

Regarding their geochemical characteristics, the Opx-gneisses can be classified as granites, granodiorites and diorites. They are peraluminous in composition and mainly show I-type to S-type, post-collisional granite signatures. Protoliths of the metabasites are tholeiitic mid ocean ridge basalts, whereas those of the paragneisses mainly comprise arkosen and greywackes.

All rock units experienced high-grade regional metamorphism with associated ductile deformation and partial melting. The peak-metamorphic assemblage of the Opx-gneisses is garnet-orthopyroxene-plagioclase-quartz, whereas that of the metabasites is orthopyroxene-clinoxyroxene-plagioclase-quartz. Retrograde biotite and amphibole define a strong foliation. For the thermobarometric calculations Opx-gneiss and metabasite samples from 5 km up to 20 km distance to the anorthosite contact were chosen. For all samples similar granulite facies peak-metamorphic conditions of 900 ± 100 °C at 6 ± 1 kbar are calculated, providing evidence against a contact-thermal effect related to the emplacement of the Rogaland anorthosite. Following this, contact-metamorphism induced by the anorthosite emplacement, as evidenced by pigeonite-in and osmullite-in isograds, is restricted to a distance of < 5 km to the contact.

Clearly, pure pyrocatechol is usually colorless in aqueous systems without autoxidation but its color changed completely to a dark cyan as a result of Al complexation. In particular, no visible change to the color of this complex was observed in the experiment conducted at pH 3.5, 7.0 and 9.0. In the UV region of the spectrum, the absorption maximum of pyrocatechol occurred at 212 nm and 275 nm when compared to the metal-ligand spectrum, here the absorption maximum occurred at 278 nm and the absorption intensity increased considerably. In the Vis region of the spectrum, ligand bands from the complex appeared with absorption maxima of 597 nm and 650 nm that conformed to the orange and red light regions. After the addition of auxochromes, a rise of the chromophore system occurred, and it was this effect that determined the shape of the UV-Vis spectrum of the Al-pyrocatechol complex. This compound, shown in its solid state, had a very smooth surface with sharp-edged breakages as presented in the SEM photomicrograph. Primarily, organic substances with o-hydroxy groups showed specific effects on Al chemistry in the environment due to their favorable reaction to Al chelation.

Reference
Occurrence of sursassite in the Lienne valley, Stavelot Massif, Belgian Ardennes

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In quartz veinlets crosscutting the red-purple metapelites of the Ottré Formation (Salm Group) in the core of the Lienne syncline, sursassite occurs as orange-red needles associated with manganese oxide masses mostly composed of cryptomelane. Detailed petrographic observation coupled with electron microprobe analytical work reveals sursassite in close association with spessartine, manganooi clinochlore (Schreyer et al., 1986), hematite, and fluorapatite.

The chemical composition of sursassite shows the presence of about 2 wt % MgO, and up to 4 wt % CaO, whereas Fe2O3 does not exceed 1 wt %. These substitutions are interpreted in comparison with pumpellyite-(Mg). Heterogeneities have also been detected in the distribution of V and As. From a chemical point of view, these zones rich in V and As correspond to ardennite s.l., previously identified in Bierleux (Pasero et al., 1994).

Sursassite constitutes a new additional phase among the minerals characteristic of the low-grade metamorphism known in the Lienne valley in the western part of the Stavelot Massif, i.e. about 300°C and 1.5kb (Theye et al., 1996). The formation of sursassite, associated with manganooi clinochlore and spessartine, in relationship with quartz veinlets, shows analogous with the formation of carpholite. Due to the presence of about 0.4 Mn³⁺ per formula unit of sursassite, it seems reasonable to consider that sursassite could play the role of carpholite in the more oxidized horizons of the Ottré Formation in the Lienne Valley.

References

Onset of MORB melting: High-pressure eclogite-facies pegmatites as an example of internal fluid recycling

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Zoisite-bearing high-pressure pegmatites from the Münchberg Massif, Germany, provide an excellent example for the characteristics of the onset of metasatite melting at eclogite-facies conditions. Pegmatites were derived by partial melting of MORB-like eclogite at T ≥ 680°C/2.3 GPa to 750°C/3.1 GPa, which produced small amounts of tonalitic to trondhjemitic melt. The melt concentrated locally in isolated, small melt pockets and crystallized primary zoisite as liquidus phase at P ≥ 2.3 GPa/680°C to 2.1 GPa/750°C. Compositional zoning of pegmatite zoisite records an ensuing multi-stage uplift history with successive, discrete crystallization events at 1.4 ± 0.2 GPa/650 to 700°C and 1.0 ± 0.1 GPa/620 to 650°C. Resorption textures indicate re-heating and thermal perturbation of the whole system prior to each successive crystallization event. Final solidification of zoisite-pegmatites occurred at 0.9 ± 0.1 GPa/620 to 650°C. The data suggest that isolated melt + zoisite crystal mash pockets formed an integral part of the eclogite throughout uplift from melt formation at T ≥ 680°C/2.3 GPa to 750°C/3.1 GPa to final solidification at ~ 0.9 GPa/620 to 630°C; i.e. over 45 to 60 km. The entire pegmatite-forming process was most likely fluid conserving: Any fluid present during high-pressure melt formation was trapped by fully or nearly water-saturated siliceous melts; due to the small melt fractions these melts did not migrate out of the rock but stayed in isolated pockets within the rock unit; finally, any fluid liberated during pegmatite crystallization interacted with neighbouring, dehydrated eclogite-facies assemblages to form amphibolite-facies hydrous minerals.

Based on average compositions of zoisite-pegmatite, as representative for the tonalitic to trondhjemitic high-pressure melt, and host eclogite, we calculated a set of empirical melt/eclogite partition coefficients. $D_{\text{melt/eclogite}}$ values for Ta, Zr, Hf, Tm, Yb, Lu, V, Sc, Cr, Cu, and Ni range from 0.051 to 0.7 and indicate compatibility with respect to eclogite. Rubidium, Ba, Th, K, La, Ce, Sr, Nd, Sm, Eu, Ti, and Tb are moderately incompatible with respect to eclogite and have $D_{\text{melt/eclogite}}$ values between 1.11 and 10.6.

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From microbes to mountains: 
Molecular signatures of life and its environment
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Biomarkers serve as a rich source of information about ancient environments and provide important proxy tools for studies of past climatic change. Interpretations of molecular and isotopic signatures are grounded in studies of the habitat and growth of modern analogs to biologic sources for ancient compounds. Molecular signatures are rarely simple recorders of material or physical properties (like temperature), and can be influenced by variations in lipid and isotopic properties both within and between organisms. This presentation will highlight two examples of molecular proxies and the importance of ecological and physiological influences on their geochemical record.

The first example underscores the role of ecology on the molecular signatures of modern marine Archaea. Recent studies point to crenarchaeota as important agents in ammonium oxidation, consistent with an apparent affinity of these organisms with deeper habitats and upwelling regions. Archaeal lipid signatures in the modern ocean include inputs from both euryoarchaeota and crenarchaeota, and the relative importance of these inputs can vary with nutrients, especially nitrogen. Ancient archaeal lipid signatures will reflect ecological shifts in regions with variable oceanographic conditions, potentially complicating their utility for temperature reconstruction in such settings.

In the second example, we consider how plant lipids record deuterium abundance in waters in their growth habitat. Large isotopic fractionation associated with lipid biosynthesis can be attenuated by evaporative effects which yield leaf waters enriched in D relative to precipitation. Thus the apparent (or net) fraction between plant lipids and environmental waters reflect both physiological and climatic properties. Understanding of such influences empowers better reconstructions of this emerging proxy for paleohydrologic signatures. We apply such insights to a lipid-based method for reconstructing uplift of the Tibetan plateau and explore implications for understanding tectonic and climatic interactions.

Provenance and genesis of the high Ti heavy mineral sand deposits of South Kerala, SW India: Constraints from CCSEM analysis
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Computer Controlled Scanning Electron Microscopy (CCSEM) is a new fully automated method for the chemical and physical characterisation of the heavy mineral fraction in sands (Frei et al., 2005). For example, CCSEM allows to determine the chemical variation of individual mineral groups (e.g. garnet or ilmenite) and their modal abundance. In this contribution we demonstrate the capabilities of CCSEM for investigating the grade, genesis and provenance of Ti heavy mineral sand deposits.

The world-class heavy-mineral deposits occurring in beach sands around the town of Chavara in SW India are characterized by abundant ilmenite with elevated TiO₂ contents, often exceeding 60 wt. %. In order to determine the provenance and genesis of these high-TiO₂ ilmenite deposits, we have collected a large number of beach sediment samples from an approximately 800 km long stretch of coastline from northern Kerala state to well within the Tamil Nadu state. An additional set of river sediment samples was also taken, roughly covering the areas drained inland from the beach samples. The heavy-minerals in all samples were analyzed by CCSEM, providing both chemical analyses of individual grains as well as the modal composition of heavy-minerals in the sediment. The results show that the sediments in the Chavara high-Ti ilmenite deposits are distinct by minor elements in ilmenite and garnet chemistry as well as heavy mineral assemblage: ilmenite has high MgO and low MnO contents, garnets have low grossular components and the heavy-mineral assemblage is dominated by sillimanite-kyanite in addition to ilmenite. These features correlate with basement geology in the hinterland, and with the results for sediments from rivers, draining the basement. Based on these observations we conclude that high-Ti ilmenite from Chavara beaches is derived from the granulite-facies metasedimentary rocks exposed in the khondalite belt. Our study demonstrates that rapid mineral analyses in sediments by CCSEM is an efficient and powerful new tool for the characterization of mineral compositions and assemblages in sediments, the identification of their possible source regions and thus ultimately for refined exploration for industrial mineral resources.

Reference
Trace element and isotopic characterization of Neoarchean - Paleoproterozoic BIFs (Black Hills, South Dakota, USA) straddling the first rise of atmospheric oxygen between 2.4 and 2.0 Ga

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Banded iron formations (BIF) were deposited in the Black Hills, South Dakota, both prior to and after the first main oxygenation of the atmosphere at ~2.4-2.3 Ga. Paleoproterozoic oxide BIFs deposited before this event still indicate prevalence of reducing conditions in the depositional basins, consistent with the occurrence of stratigraphically associated uranium- and pyrite-rich conglomerates. In contrast, mixed silicate-carbonate-oxide BIFs were formed long after this 2.4-2.3 Ga event, with deposition straddling the end of the ~2.3-2.0 Ga positive δ13C anomaly. The older, oxide-facies and detritus-free BIFs were deposited during rifting at ~2.56-2.48 Ga, associated with initial break-up of the Kenorland supercontinent. These BIFs exhibit REE characteristics typical of ambient seawater signatures (positive La, Eu, Y, and negative Ce anomalies in PAAS-normalized REE diagrams); Sm-Nd model ages of 3.78-2.56 Ga; a high-µ(238U/204Pb) tenor, typical of the Wyoming craton; and low 208Pb/204Pb relative to 206Pb/204Pb ratios, implying pronounced fractionation of U relative to Th during source rock weathering processes and (or) during deposition. Deposition of the younger, silicate-carbonate-oxide BIFs appears to have occurred in a rifted continental margin that developed as a consequence of final break-up of Kenorland beginning at ~2.1 Ga, during discrete episodes of rifting precisely dated at 2.02-1.98 and 1.89-1.88 Ga. These horizons of younger BIF both reveal significant detrital input. They also exhibit Sm-Nd model ages of 3.83-2.51 Ga, comparable to the older BIFs. However, the younger BIFs differ by their less-fractionated PAAS-normalized REE patterns, lack of La anomalies, only weakly positive Eu anomalies, and positive Ce anomalies. Positive Ce anomalies may reflect more oxidative scavenging of Ce(IV) onto Fe-oxyhydroxides, generally pointing to a more oxidized seawater environment during their deposition.

Earth’s oldest BIFs (Isua, W Greenland) – Constraints from Ge/Si ratios, REE systematics and Sm-Nd and Pb isotopes for different interacting water masses during their formation

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We report trace element, Sm-Nd and Pb isotopic data for individual micro- and mesobands of the Earth’s oldest Banded Iron Formation (BIF) from the ~3.7-3.8 Ga Isua Greenstone Belt (IGB, West Greenland) in an attempt to contribute to the characterization of the depositional environment and to the understanding of depositional mechanisms of these earliest chemical sediments. REE-Y patterns of the individual mesobands show features of modern seawater with diagnostic Ce/Ce*, Pr/Pr* and Y/Ho anomalies. Uranogenic Pb isotope data define a correlation line with a slope of 3691 ± 41 Ma, indicating that the U-Pb system remained closed after the formation of this BIF. High 207Pb/204Pb relative to 206Pb/204Pb ratios compared to average mantle growth evolution models are a feature shared by BIF, penecontemporaneous basalts and clastic volcanogenic metasediments and are indicative of the ultimate high-µ(238U/204Pb) character of the source region, an essentially mafic Hadean protocrust. Sm-Nd isotopic relations on a layer-by-layer basis point to two REE sources controlling the arc basin depositional environment of the BIF, one being seafloor-ventilated hydrothermal fluids (εNd (3.7 Ga) ~+3.1), the other being ambient surface seawater which reached its composition by erosion of parts of the protocrustal landmass (εNd(3.7 Ga) ~+1.6). Systematic trends in Ge/Si ratios support the above theory and suggest that significant amounts of silica were derived from unexposed and/or destroyed mafic Hadean landmass, unlike iron which probably originated from oceanic crust following hydrothermal alteration by deep percolating seawater.
Long-term turnover of plant derived sugars in soils below natural forest and plantation in Ethiopia

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Background
Carbohydrates are an important pool in the terrestrial carbon cycle. In order to predict future concentrations of CO₂ in the atmosphere, it is crucial to quantify mean residence times (MRT) of carbon species in soils. Furthermore, it is important to investigate which types of land use are suitable for long-term carbon-storage in soils.

Materials and Methods
In our study, we investigated the MRT of plant derived sugars in tropical soils by compound specific isotope analysis (CSIA). Samples were collected in a natural forest dominated by *Podocarpus falcatus* and in an adjacent 40 year old *Eucalyptus saligna* plantation in southern Ethiopia. Contents of Xylose and Arabinose were analyzed via GC-C-IRMS simultaneously with δ¹³C values to one meter depth. [1] The ¹⁴C age of Black Carbon was used for the calculation of MRT in a model, implying advection, diffusion and decay. [2] Calibration of the model was conducted by using a shift in δ¹³C values as a consequence of a change from C₄ to C₃ vegetation in the study area about 600 years ago.

Results and Discussion
MRT of Xylose and Arabinose were the same in the natural forest and the plantation. MRT was exponentially dependent on depth. 70 percent of the sugars had MRT of less than 20 years. Only 1.3 to 2.0 percent of the Xylose and 5.0 to 5.7 percent of Arabinose reached MRT of more than 1500 years. Nonetheless, the *Eucalyptus* plantation contained 33 to 44 percent less sugars down to one meter depth (p<0.01).

Conclusion
The fewer amounts of sugars below *Eucalyptus* should be due to accelerated mineralisation while clear-cutting of the natural forest and reduced litter input after the conversion. Because MRT do not differ between the natural forest and the plantation, the land use with the highest carbon input in the soil should be preferred for carbon-sequestration.

References

New method (HR-SF-ICP-MS) to measure biosilica production and dissolution in ocean surface waters

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A new method is described for a accurate and simultaneous determinations of the rate of production and dissolution of biosilica in marine surface waters, using isotopic dilution technique. This technique consists to label diatoms sampled from the euphotic layer with ⁴⁰Si spike in the form of Si(OH)₄. The samples are then incubated under *in situ* conditions during a given time (usually 24h). The isotopic dilution of the enriched seawater is used to estimate the dissolution of biosilica and the change in the isotopic composition of silica itself is used to estimate its production.

Such sampling method and the calculation model associated are described in Corvaisier et al. [2005][1].

In this study we propose to measure the silicon isotopic abundances by a HR-SF-ICP-MS (Element 2) in wet plasma mode instead of TIMS (Finnigan THQ) [1].

In this purpose we apply first an alkaline digestion on biosilica or a preconcentration/subsequent-dissolution using the adapted MAGIC method for the dissolved silicon.

The sample is introduced through a glass concentric nebulizer (100µl/min) and a glass jacketed trace cyclonic spray chamber. Instrumental mass bias is measured with the standard-sample bracketing technique using standards with the same matrix as the sample to avoid the matrix effects. We correct the blank contribution by subtraction of the average of two blanks bracketing the sample. A complete analyse (including standards and blanks) is performed in only 20 minutes. The repeatability and the internal precision on the silicon isotopic abundances of a 100ppb Si solution of a diluted alkaline digestion and diluted preconcentration are better than 1%, similar to the TIMS [1].

This new method is much faster and easier than when using TIMS [1]. Moreover because HR-SF-ICP-MS are now widespread instruments it will help to expand biosilica production-dissolution data which are currently very scarce (up to 2003, only 56 published profiles). In fine a better constrain of the silicon budget (production vs. dissolution) in the surface ocean will be gained.

Reference
Hydroxyl contents of deep mantle minerals coexisting with CH4-rich fluids: Implications for the focusing of fluids in the upper mantle by redox processes

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The high solubility of hydroxyl in nominally anhydrous minerals such as olivine and wadsleyite at high pressures has been used to argue that they may be important hosts for H2O in the mantle. However, volatiles in the Earth's interior are more accurately described in the system C-O-H where the activity of H2O is a function of the oxygen fugacity. The oxygen fugacities in the lower regions of the upper mantle and in the transition zone and lower mantle are likely to be quite low and at least 4 log units below the FMQ oxygen buffer. Calculations show that at these conditions a C-O-H fluid will be CH4-rich. The lower activity of H2O in the fluid should lower the equilibrium OH- content of coexisting nominally anhydrous minerals such as wadsleyite. Experiments have been performed to study the properties of such reduced fluid phases and examine if they influence the OH- contents of nominally anhydrous mantle minerals at high pressure.

The experiments used a standard double capsule technique with an outer capsule containing a redox buffer (Mo-MoO2 or Co-CoO) plus H2O and an inner Pt capsule containing San Carlos olivine or garnet compositions in a graphite liner. Samples were equilibrated between 10 and 15 GPa in a 5000 tonne multianvil press. Results show that at plausible mantle oxygen fugacities minerals such as wadsleyite have H2O contents over ten times lower than those reported at H2O saturation. CH4-rich fluids do not show evidence of having a significant dissolved silicate component. These reduced, low-density fluids should have a tendency to rise out of the deeper mantle and be oxidised to H2O and CO2 in the shallow upper mantle. This mechanism may tend to concentrate C-O-H volatiles in the upper mantle, leaving the deeper mantle dryer and with a higher viscosity.

Building Lost City: Serpentinization, mass transfer and life in a peridotite-hosted hydrothermal system

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The Lost City Hydrothermal Field (LCHF; Atlantis Massif, Mid-Atlantic Ridge, 30°N) is the product of reactions between seawater and ultramafic rocks that produce high alkaline (pH 10 to 11), 40 to 90°C fluids that form up to 60m tall carbonate-brucite towers. The fluids are enriched in H2, CH4 and other hydrocarbons, produced abiotically through Fischer-Tropsch type reactions, and support dense microbial communities that include anaerobic CH4- and S-cycling thermophiles. We present an overview of multidisciplinary investigations of the LCHF and highlight the complex interplay between deformation, fluid flow, mass transfer and microbial activity that occur within this long-lived, peridotite-hosted hydrothermal system and the chemical and biological impacts of such off-axis systems on the global ridge system.

Textures and bulk rock chemistries of the harzburgitic serpentinites reflect formation and uplift of a heterogeneous lithosphere in a magma-starved spreading environment, with progressive serpentinization, talc- amphibole metasomatism and veining. Seawater-peridotite interaction at 150-250°C and high fluid-rock ratios (>100 and up to 106) produced enrichments in B, U and light REE, systematic changes in Sr- and Nd-isotope ratios toward seawater values, and highly depleted bulk rock O-, H-, and B-isotopic compositions in the basement. B-isotope analyses of the fluids and hydrothermal precipitates indicate that brucite is a significant, temporally variable, reservoir for Mg and B in these systems.

High fluid fluxes have important implications for S- and C-cycles: sulfur geochemistry indicates a loss of primary sulfide, an uptake of seawater sulfate, and local microbial remediated sulfate reduction and sulfate oxidation in the basement. Our studies show that the total carbon stored in the serpentinites is dominated by hydrocarbons and suggest that serpentinites may represent an important, as yet unidentified, reservoir for dissolved organic carbon from seawater. We conclude that high seawater fluxes and the interaction with both variably fresh peridotites and pervasively serpentinized peridotites is crucial to the formation of volatile-rich Lost City-type systems and that transform-related normal faulting and mass wasting in the south of the massif facilitates seawater penetration necessary to sustain hydrothermal activity over tens of thousands of years.
Prevention of asbestos floating from outdated construction materials

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Approaching Crisis

Human beings have used a huge amount of asbestos since the stone age because of its good spinnability in the beginning and then because of good physico-chemical properties in industrialized nations. Asbestos is frequently used in construction materials, and they should start to fly as extremely fine fibers many years after they are used and when the construction materials are worn out. The fiber is believed to cause especially malignant mesothelima and other related diseases.

How to Cope with the Problem

Special reagent (Patent pending) has been invented to prevent asbestos floatation into the air. The reagent has high affinity with all kinds of asbestos and envelopes them when it is sprayed on the asbestos-containing materials. Once it envelopes asbestos and dried up, it is hardly possible to separate the reagent from asbestos. Among the asbestos, crocidolite asbestos is the most tough one and we treated crocidolite with the reagent. Then we leached it by strong sulfuric acid (1.8M) for more than 96 hours. The reagent-treated asbestos are then pulverized under 400 micron. Each fine fiber of crocidolite asbestos is entirely enveloped by the solidified reagent. As long as we observed them under the phase contrast microscope, we can hardly identify crocidolite. Using a highly efficient XRD, the crocidolite can be identified.

Conclusion

We of course prefer to recycle as many kinds of materials as possible. However, we may not be able to recycle asbestos at all. On the contrary, we prefer asbestos-free atmosphere. When houses, buildings, facilities and their equipment are reconstructed or repaired, fine asbestos fibers may start to fly even if the construction materials are not yet worn out. Therefore, somehow floatation of fine asbestos fibers have to be prevented. We are going to show how the reagent works to prevent floatation of fibrous asbestos.

Reference


Mass transfer by fluid and duration of oxygen isotope exchange during contact metamorphism at Hirao-dai, Japan

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A reaction zone between a metamorphosed basic dyke (MB) and marble at Hirao-dai, north Kyushu, Japan, consists of well-organized sequential zones of diopside, garnet and wollastonite; textures are characteristic of diffusion-controlled structures. The reaction zone formed during contact metamorphism associated with intrusion of a Cretaceous granodiorite at about 300 MPa and 700°C (Fukuyama, et al., 2004). The MB consists of diopside, biotite and plagioclase (XAb=0.4-0.8), whereas the marble is almost pure calcite.

Minimum estimate of time-integrated flux forming a reaction zone is 3.46 mol fluid/mol reaction zone: 1.29 mol fluid/mole as reactive fluid and 2.17 mol fluid/mol as non-reactive fluid. 1mol of reaction zone consists of 0.42 mol diopside, 0.11 mol garnet, and 0.48mol wollastonite from overall reaction: 0.07K2.00Mg3.89Fe1.42Al2.48Ti0.16Si5.82O20(OH)4 + 0.02Na0.64Ca0.36Al1.36Si2.64O8 + 0.05CaMg0.77Fe0.23Si2.00O6 + 0.42CaMg0.72Fe0.28Si2.64O8 + 0.05CaMg0.77Fe0.23Si2.00O6 + 1.15CaCO3 + 1.09SiO2 + 0.03FeO 0.02AlO2/3 = 0.42CaMg0.72Fe0.28Si2.64O8 + 0.11Ca3.36Fe0.14Al2.06Si3.00O12 + 0.48CaSiO3 + 0.01TiO2 + 0.01NaO1/2 + 0.14KO1/2 + 0.14H2O + 1.15CO2. This estimate is based on the mineralogical evidence and steady-diffusion modelling (Fukuyama, et al., 2006).

We measured 18O and 13C of calcite along a line segment perpendicular to the reaction zone-marble boundary. 15O composition isn't change, but 18O composition changes in proportion to distance from the reaction zone-marble contact. This shows that 18O is strongly fractionated between CaCO3 or CO2 and H2O because mineral reactions may buffer the CO2-H2O content of fluid.

The duration of oxygen isotope exchange (t) can be calculated from effective diffusive width (W) and diffusive coefficient of oxygen in calcite (D) using the following equation: W2/2D=2Dt

The minimum estimated duration of oxygen isotope exchange is 357 m.y. We interpret this duration is the same as the duration of reaction zone formed, giving the fluid velocity 5.3*10-11 m/s.

References

Thermochemical coupling in deep mantle plumes: A case study of Turkana, N. Kenya

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Subducted oceanic crust forms the likely source for a dense and more fertile layer at the core-mantle boundary. Numerical modeling predicts that entrainment of this dense material by an upwelling thermal plume will result in episodic volcanism occurring at episodic intervals on time scales of several to hundreds of millions of years (Lin & van Keken 2005).

Our study of 40 my of mafic eruptive activity in Turkana, Kenya reveals volcanological and geochemical features that are fully compatible with the numerical models, suggesting that magmatism in this part of the East African Rift System reflects deep entrainment of recycled oceanic crust by a thermally-driven plume. Volcanism at Turkana occurred in three distinct pulses separated by several million years each. No flood basalt province typical of strictly thermal plume head volcanism is associated with any of the pulses. The most voluminous pulse (26-16 Ma) led to rift propagation to both north and south, with fault growth and new rift basin development. Episodic volcanism is also reported from Samburu, Kenya, 200 km to the south (Tatsumi & Kimura 1991) and 100 km to the north in Ethiopia (George et al. 1998) in each case subsequent to peak Turkana episodes. These features contrast with observations in Afar, where plume head volcanism occurred 30 Ma and modern basalts are erupted along extensional features in the rift axis.

Mafic lavas from the major episode in Turkana – including abundant picrites – are geochemically distinctive. They have Sr-Nd-Pb-He isotopic signatures characteristic of high-µ ocean island basalts, and olivine Ca, Ni contents indicative of a pyroxenitic source (Sobolev et al. 2005, Herzberg 2006). We postulate that entrained fertile pyroxenite has been a source of mafic volcanism at Turkana.

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Impact-generated ultrafine particles of olivine and serpentine suggesting a source of aerogels in the air of the early Earth

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Intense impacts of meteorites on to early oceans have been suggested in the period of Late Heavy Bombardment [1, 2]. The mechanism of oceanic impact is different from that of subaerial impact. The oceanic impacts generate Ultrafine Particles (UPs) [3] and have possibility to generate a large amount of UPs of serpentine. However, few experimental investigations of impact-serpentinitization exist. The UPs formation following impact explosion might influence the environment of the early Earth.

We performed shock-recovery experiments using a single-stage propellant gun to simulate simple ocean impact events of meteorites. The samples are powder of olivine with and without water in steel sample container. The products were analyzed with XRD, SEM and TEM.

SEM observation shows the formations of UPs of metal oxides. In addition, TEM observation shows the formation of UPs of olivine with different compositions from the starting one, serpentine and brucite. The grains of such UPs were some hundreds of nanometres in size.

Formation of UPs was unexpected from our impact experiments because the experimental conditions were far below the theoretical vaporization and/or melting conditions of starting materials. Here we propose that the presence of water significantly promoted the conversion of samples into UPs. The UPs formation by oceanic impacts may influence the change of Earth’s environment such as generating aerosol and shielding sunlight.

References
Sulfide oxidation, acidification and deoxygenation by reaction of resuspended sulfidic benthic sediments.

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Black, gel-like, benthic sediments with high acid volatile sulfur (AVS) concentrations (1-6% dry mass) are common in waterways affected by acid sulphate leachate. These sediments are often called monosulfidic black ooze (MBO). Floodwater re-suspension of MBO has been implicated in massive fish kills associated with severe deoxygenation and acidification of coastal lowland rivers. This study examines changes to sediment and water chemistry during laboratory experiments designed to simulate flood-induced sediment re-suspension events. Re-suspension of MBO in water decreased dissolved oxygen from 7.70 mg.L-1 to 0.86 mg.L-1 within 1-2 minutes. The oxidation of the acid volatile sulfur fraction in the MBO resulted in the rapid formation of elemental sulfur. pH remained near-neutral during this oxidation step. It was 4 days until the elemental sulfur began to oxidise, causing acidification (pH <3.5). Metal concentrations within the MBO material were within sediment quality guidelines. However, the oxidation of AVS and acidification of the MBO material mobilised metals to the water column at concentrations greatly exceeding the recommended water quality guidelines. The current sediment quality guidelines for metals can be a poor estimate of the environmental risk, particularly as shown here for sediments that contain elevated acid volatile sulfur contents.

Fe, Co and Ni in Ureilites: Metal-silicate equilibration in the UPB

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Ureilites are coarse-grained olivine- and pigeonite-bearing achondrites with carbon-rich material occurring along grain boundaries [1]. It is suggested that Ureilites represent asteroidal mantle restites [2].

In this study we present Fe, Co and Ni concentration data of olivine from eight Ureilites with different Fe-contents, ranging from 8 to 22% fa. Measurements have been conducted by means of LA-ICP MS at the University of Göttingen.

Starting from a CI1 composition we calculated a model core compositions for each Ureilite. With the equations taken from Seifert et. al [3], we calculated the Co and Ni content of olivine that equilibrated with metal of the model core composition at temperatures ranging from 1000°C to 1500°C. These data are compared to measured Ureilite olivine compositions. Our data give olivine-metal equilibration temperature of about 1185°C. Exceptions are LEW85440 and ALHA77257 which show a higher equilibration temperatures of ~1230°C. EET96331, which is very low in Co and Ni compared to Ureilite olivine with similar Fe-content, gives a significantly lower equilibration temperature of ~800°C.

Ureilite olivines seem to have been equilibrated with a metal with a composition similar to the core of the UPB. Except for EET96331, equilibration temperatures range from 1173 to 1240°C, which is broadly in agreement with olivine-pigeonite thermometer data published by Singletary et al. [4]. The Fe-, Co- and Ni-composition of the Ureilite olivine has been established during metamorphism. This has implications for future Fe-Ni-isotope relative age dating, which is in progress.

Zircon as a magma mixing proxy: 
Textural, chemical and isotopic evidence from a young plutonic system

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Ion microprobe U-Pb zircon analyses of the Miocene Monte Capanne Plutonic System (MCPS, Tuscan Magmatic Province, Italy) reveal a range of ages (ca. 7-10 Ma) pointing out to a protracted magmatic history (2-3 Ma; Daly et al., 2007) where magma mixing is believed to have played a significant role. As a companion study, we have investigated the textural, chemical and Hf isotopic response of zircon to various magmatic processes, with particular emphasis on magma mixing. For this purpose, we are using CL, BSE imaging as well as electron microprobe chemical data on a variety of magma products, including mafic microgranular enclaves, host monzogranites, mafic (Orano) dykes and granite porphyries. Importantly, zircon ages for these components partially overlap, suggesting that zircon was transferred and/or recycled throughout the lifetime of the whole plutonic system. A variety of textures have been encountered (inclusion-rich cores, patchy-zoning, small and large scale oscillatory zoning, pristine cores) as well as an extremely large range of trace to minor elements compositions (e.g., Hf: 7159-21284 ppm, Y: 39-8661 ppm, U: 67-65319 ppm and Th: 0-46225 ppm). While partitioning of Hf is largely temperature-dependent, intra-grain variations (zoning) in other elements (P, Th, U and HREE) are interpreted to reflect changes in melt chemistry due to mixing between mafic and felsic magmas, where growth/resorption of zircon was also associated with reactions between other accessory minerals (particularly apatite and monazite; Dini et al., 2004). The chemical signature of the dominant oscillatory zoning texture suggests growth from melts relatively depleted in trace elements, emphasising the important role of crystal fractionation in the evolution of the MCPS. These interpretations are in perfect agreement with models involving other phases, namely plagioclase (Gagnevin et al., 2004) and K-feldspar (Gagnevin et al., 2005a, b).

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Sr/Ca as a proxy for temperature in the deep-sea coral Desmophyllum dianthus

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We test Sr/Ca as a proxy for temperature in the cosmopolitan deep-sea coral species Desmophyllum dianthus. Several individuals of recent coral from regions of the deep-ocean typified by near constant temperate were selected from existing collections. Sub-samples were removed from the most recent portions of each skeleton and subjected to a full trace-metal cleaning protocol. Skeletal Sr/Ca was determined using isotope-dilution on a Neptune (ThermoFinnigan) multi-collector magnetic-sector ICP-MS. Intra-run reproducibility of a deep-sea coral consistency standard was better than 1‰ (2s), an improvement over most existing ICP-MS and optical spectroscopic methods. Across 8 individuals of D. dianthus spanning a 12°C range of growth temperatures, skeletal Sr/Ca decreases linearly as a function of temperature ($R^2 = 0.82$) with a shallower slope than most surface coral calibrations. Applied to the new archive of deep-sea coral, the Sr/Ca temperature proxy has the potential to generate high-resolution records of past deep-sea temperature.
Oxygen gas-phase formation in iron chemical gardens

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In this work we have employed the chemical gardens reaction as a laboratory device for in situ, follow the mixing of aqueous solutions of iron salts with sodium silicate and to characterize the reaction products by SEM HREM, XRD and XPS.

Chemical gardens are well known tubular structures formed in reaction–precipitation systems given rise to the formation of colorful, plant-like aggregates. Moreover, recent investigations have contributed to a renewed scientific interest in these self-organised structures. Although the reaction in chemical gardens is largely driven by pH gradients between the dissolving iron salt and the Na-silicate, recent works suggest that a strong redox processes can also take place during the formation of iron-silicate membranes.

One intriguing aspect related with silica gardens formation is the presence of small bubbles that are, in some instances, attached to the surface of the silica membranes, thus acting as templates for the formation of hollow tubular structures.

The aim of this research was to experimentally verify the composition and mechanisms of bubbles formation on Fe-Silica garden. From experiments performed in strictly anoxic environments will also be discussed.

In situ determination of iron species by UV-VIS showed the presence of Iron(VI)-ferrate oxyanion. Thus, a model for O2-bubble formation in silica garden is proposed, based on the rapid reduction of Fe(VI) to Fe(III) species through the of the strong pH gradient taken place across the silica membrane. Implications of these results for the formation of Fe-silicate phases in anoxic sedimentary environments will also be discussed.

Reference


The double-spike cookbook

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In recent years there has arisen considerable interest in exploring natural stable isotope fractionation of "non-traditional" elements. Here, the techniques of standard/sample bracketing or addition of a second element in the mass range (e.g. Cu with Zn) can be used on MC-ICP-MS instruments, but not TIMS. But the obvious method of choice in terms of accuracy – as well as simplicity in preseparation chemistry – is to add a double spike (DS) of the same element to the sample. The DS "freezes in" the natural fractionation at the time of its addition, and is thereafter insensitive to any chemical or instrumental fractionation.

The natural fractionation is solved for via mass balance of 3 independent isotope ratios (effectively a 3D isotope space). The DS technique can thus be used for any element with four or more isotopes—or 33 elements in all. Nevertheless, it has been seriously underutilized, in part due to the unease of data reduction, but mostly from uncertainty in the choice of the double spike itself. The task is made all the more difficult from the sheer number of candidate double spikes and isotope spaces to consider. For example, for Fe there are only 4 such spaces, while for Sn, with its 10 isotopes, there are 840 possible isotope spaces. The rigorous "optimization" of any double spike problem, then, presents a formidable challenge.

What is presently hampering the widespread use of double spikes is a lack of a comprehensive solution to the problem. Here, I remedy the situation by tackling all 3868 isotope spaces of the 33 elements (201 isotopes) that can be double spiked. The approach yields (1) an estimate of the "best" mixture (M) to use within a given 3D isotope space (and its corresponding spike, S), along with (2) a "figure of merit" enabling comparison between different isotope spaces of each element. Together, these provide first-order answers to questions of what DS to use, what the optimal mixture is, and what isotope space yields the best error propagation? Exclusion of particular isotopes (e.g. isobaric interferences) becomes an easy task since all isotope spaces have been evaluated. The methodology contrasts with that of previous studies in two ways: first, the "optimal" mixture is explicitly solved for rather than the spike composition, and second, more rigorous criteria are used. Normal compositions (N) were taken from IUPAC. The "optimization" was performed by multi-dimensional numerical minimization using a penalty function approach. Four criteria are built into the function: (1) M should lie far from S and close to N, (2) the angle between the fractionation vector through N and the mixing line should be large, (3) the so-called "intersection angle" should be large, and (4) the absolute magnitudes of the 3 isotope ratios of M should lie close to unity. Once a promising DS has been identified, its performance as a function of spike-to-sample ratio can then be examined.

These calculations should remove a major obstacle to implementing the double-spike technique, and hopefully make its use more routine and in vogue in future stable isotope studies.
Geochemical and Sr-Nd-Hf isotopic variations in Tajikistan loess: In search of source and climatic proxies

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Late Tertiary to Quaternary loess-paleosol sequences provide invaluable record of the changing environment in continental areas during that time interval. Climatic proxies in loess-paleosol sequences have been retrieved by a number of ways, including palynology, grain-size analysis, clay minerals, carbonate or organic matter contents or magnetic susceptibility. Loess source proxys include quartz morphology, heavy minerals assemblages, major and trace elements and Sr-Nd isotopic compositions. Some proxies are useful both as dust source proxy and as climatic proxy. We have been studying various loess-paleosol sequences in the Chinese Loess Plateau (Gallet et al. 1996, Jahn et al. 2001). On these sections we tested and proved the usefulness of geochemical and isotopic tools in loess research. Recently we extended our area of investigation to Central Asia, and the Chashmanigar (Tajikistan) loess section was chosen because some detailed stratigraphic and magnetic susceptibility data have been published by Ding et al. (2002). This section is about 200 m thick and consists of an alternation of loess and paleosol layers. A combination of geochemical and isotopic data is used to trace back the source(s) of these eolian deposits and their weathering history. Isotopic data (Sr-Nd-Hf) for whole-rock samples and for chemically separated fractions allow to document the change in protolith composition in response to climatic and tectonic events in the area. Major-elements, organic matter and carbonate content were measured on whole-rocks samples. Preliminary results show that our previous understanding of loess-paleosol geochemistry, first established on the Loess Plateau of China, is still valid here. Pedogenesis is clearly distinguished by the depletion or relative enrichment of a number of chemically mobile elements. There is a direct relationship between magnetic susceptibility increase in paleosol and depletion/enrichment of some chemical elements. We are currently working to translate this relationship into more quantitative laws.

References


The effect of variable source of terrestrial organic carbon on geochemical records of atmospheric level of CO\(_2\)

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Carbon isotope analyses of fossil plants (\(\delta^{13}C\)\(_{\text{plant}}\)) have been widely used as chemostratigraphic and palaeoenvironmental tools. It has even been suggested that \(\delta^{13}C\)\(_{\text{plant}}\) can be used as a proxy of \(\delta^{13}C\) of palaeo-atmospheric CO\(_2\) [1-2]. This parameter is an important variable for calculating p\(_{\text{CO2}}\) from the \(\delta^{13}C\) of soil carbonate [3], the current largest database on records of atmospheric level of CO\(_2\). However, the \(\delta^{13}C\) of modern plants varies between species and palaeo-studies have attempted to go around this issue by focussing on monospecific dataset through time [4].

Here, we present evidences that in addition to species, the provenance of the woody debris will also introduce a significant variability in \(\delta^{13}C\)\(_{\text{plant}}\). The transfer of particulate organic carbon (POC) has been studied in suspended material carried by small rivers draining active mountain belts (Southern Alps, New Zealand and Taiwan). In this active mountain belt, sediment discharge is dominated by landslide-derived material. The altitudinal spread of these landslides means that the POC samples vegetation dominated by C3-type plants and therefore having a variable \(\delta^{13}C\)\(_{\text{plant}}\) [5]. Our sampling of pine trees along an altitudinal transect in Taiwan shows a range of in \(\delta^{13}C\)\(_{\text{plant}}\) of 2‰, in line with previous findings [5]. The \(\delta^{13}C\) of the POC in a single river sampled throughout the rainy season in Taiwan ranges from -21.5 to -25‰, while the range is >5‰ in Western Southern Alps. Of course not all of these variations can be attributed to a variable isotopic composition of the vegetation and the fossil component can be as large as 90%. But in some Taiwanese rivers this fossil component corresponds to the recycling of Miocene woody debris. Based on these observations, we would argue that the use of \(\delta^{13}C\)\(_{\text{plant}}\) for calculating p\(_{\text{CO2}}\) is of very little help and also that it can be misleading in chemostratigraphy.

References

Diel iron cycling in acidic rivers of southwestern Spain

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Background
In June 2006, diel sampling was conducted on the Tinto, Odiel, and Agrio Rivers of Huelva Province, Spain. These rivers are highly acidic due to acid rock drainage from massive sulfide deposits of the Iberian Pyrite Belt (Cánovas et al., 2007). Variables quantified included streamflow, temperature, pH, Eh, photo-synthetically active radiation, and concentrations of dissolved and total metals, anions, Fe(II)/Fe(III), and As(III)/As(V).

Results
Average 24-h pH values were 2.36, 2.30, and 3.04 at the Tinto, Agrio, and Odiel Rivers, respectively. Both pH and streamflow were essentially constant with time in each river. The only solute that showed a robust diel concentration cycle in all three rivers was dissolved Fe(II). Concentrations of Fe(II) at mid-day were 1.8 to 28 times higher than concentrations in the early morning (pre-dawn). The daytime mFe(II) increases were most likely caused by photoreduction of dissolved or solid-phase Fe(III). The night-time mFe(II) decreases were attributed to biologically catalyzed re-oxidation of Fe(II) to Fe(III). First-order rate constants of (2 to 7) x 10^-5 sec^-1 for the bacterial oxidation of Fe(II) were estimated from the observed decreases in mFe(II) during the night. Maximum rates of bacterial Fe(II) oxidation (estimated to be > 3 µmol/L/h) occurred at mid-day. This amount of Fe(II) oxidation can support a growth rate of over 10^6 cells/L/h for At. ferrooxidans, the dominant procaryote in the Tinto River (López-Archilla et al., 2001).

Conclusions
Photoreduction plays a key role in biogeochemical cycling of Fe in the Tinto and neighboring rivers, and it has not been reported in previous geochemical and ecological studies of this extremely acidic and Fe-rich environment (e.g., Amils et al., 2007). Further work is needed to quantify the relative rates of Fe(II) production by photoreduction and by heterotrophic Fe(III)-reducing bacteria. The results of this study have implications for the primitive life that may have existed in acidic aqueous environments on early Earth or other planetary bodies such as Mars.

References

Interaction of the magma with the sedimentary wall rock and magnetite ore genesis in the Panzhihua mafic layered intrusion, SW China

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The Panzhihua intrusion is a gabbroic Fe-Ti-V oxide ore-bearing sill associated with the Emeishan flood basalts in SW China (Zhou et al. 2005). It is overlain by a syenitic body and it concordantly intrudes late-Proterozoic dolomitic limestones, remnants of which can be found as metamorphosed xenoliths in the gabbroic body. Compositions of metasediments from the contact aureole show evidence for a pronounced transfer of certain major and trace elements between magma and sediments, perhaps linked to hydrothermal circulation driven by magma emplacement.

Numerical modeling with PELE (Boudreau, 1999) shows that when magma with the average chemical composition of Emeishan basalt fractionally crystallizes under oxidising conditions (oxygen buffer > FMQ) and/or with high water contents, magnetite appears early in the crystallization sequence. This is a condition for an efficient segregation of magnetite and for the formation of the ore deposit.

Mineralogical and chemical studies of the contact aureole demonstrate that footwall dolomites were degassed during intrusion of the gabbro. We propose that CO2-rich fluids released by this degassing increased the oxygen fugacity of the magma and caused early and massive crystallization of magnetite.

Because magnetite crystallized when the intrusion was largely molten, it migrated to the base of the gabbroic body. The increase of the viscosity in the magma and the decrease of its density during the late stages of crystallization promoted the segregation of evolved felsic liquids that solidified as syenite intrusions. The association of gabbroic and syenitic bodies in Panzhihua region results from fractional crystallization of common parental magmas.

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Stability of hydrous ringwoodite in the Martian mantle

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Introduction
Branching networks of valleys and huge outflow channels on Mars provide evidence for the previous existence of water on its planetary surface. The water was probably once stored in the Martian interior and was then liberated to the surface. To understand this process, knowledge of Martian mantle structure and stability of hydrous phases is required.

Experiments
In order to identify possible hydrous high-pressure minerals in the Martian mantle and to determine their stability fields, we have conducted a series of multi-anvil experiments at the Bayerisches Geoinstitut, University of Bayreuth. First experiments were performed at pressures of 15 to 18 GPa and at variable temperatures between 750°C and 1150°C using a mixture of 2 Mg(OH)2 + Fe2SiO4 + SiO2 as starting material. Experimental run products were examined by transmission electron microscopy, microprobe, IR and RAMAN spectroscopy.

Results and discussion
At 15 GPa and temperatures between 750° and 1150°C cubic ringwoodite exists as single phase. Microprobe analyses yield the expected ringwoodite composition nominally equivalent to Fa48. At 18 GPa and 950 °C we observe a change to the three-phase assemblage ringwoodite + wüstite + stishovite, while the specimen compressed to the same pressure was melted at 1150°C. In comparison to the dry, Mg-rich system [1], the enhanced iron and water contents lower thus the transformation pressure by 3 GPa (from 21 GPa to 18 GPa) as well as the liquidus temperatures by at least 500°C. IR spectroscopy attests to an uptake of about 2800 ppm H2O. To understand the incorporation mechanism of water we have also used Fe L3/2 electron energy loss spectroscopy, revealing that the iron is purely ferrous. Thus, the water is probably accommodated by the replacement of Mg2+ by 2H+.

Reference

Application of the field seismic data in the security assessment of coal mining in Marbi Area

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Introduction
The Marbi area is located in Shanxi Province in north China, where plenty of coal resources are mined. In the past decades, a large amount of seismic exploration work with the aim at coal recourses has been done in the area successively. Based on the foundation of seismic exploration data, this study focuses on the structure of sedimentary basin and the security assessment of coal mining in the Marbi area.

Experiment and Results
Our data processing, combined with the existed local geological information, can be summarized concisely into the following steps (Claerbout, 1985; Ecker et al., 1996; Li et al., 2006): (1) carefully checked the positions of field shot-receiver pairs to obtain accurate localities; (2) calculated the static corrections in details; (3) eliminated bad shots, bad courses and abnormal amplitudes; (4) selected appropriate deconvolution parameters; (5) made accurate velocity analysis and got residual static corrections through stacking; (6) carried out the post stack processing and precise migration.

The result shows that there is a large syncline structure in the center of the region, suggesting long-term tectonic compression influenced Marbi area since Triassic. This crustal deformation was accompanied with dense rock cracking in both coal sills and their wall rocks, which could lead to the security difficulty and potential danger to the deep exploitation for coal mines.

Acknowledgment
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References
Recycling deep cratonic lithosphere and generation of intraplate magmatism

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Recycling continental lithosphere via foundering is suggested to be an important geodynamic process but is difficult to document (Sobolev et al., 2005). Here we show that Early Cretaceous alkaline picrites and high-magnesium basalts from the North China craton provide evidence for such recycling. These mantle-derived lavas contain both xenocrystic and magmatic olivines. The former have high Fo92-93 and low CaO (<0.10%) and suggest derivation from the Archean mantle lithosphere. More importantly, these lavas contain unusual reversely zoned clinopyroxenes. Compositions of their low Mg cores and high Mg mantles are consistent with crystallization from eclogite- and peridotite-derived melts, respectively. The cores are high in Na2O (up to 2.4%) and frequently contain ilmenite exsolution lamellae, whereas the mantles are low in Na2O (<0.92%) and lamellae-free. These lines of evidence suggest that the cores formed at a significantly greater depth (≥2.5 GPa) than the surrounding mantles (≥1.5 GPa). The whole-rock compositions of the basalts also contain chemical evidence (high Ni/Cr, Fe/Mn, Sr/Y LaN/YbN, and Th/U ratios and low Lu/HF ratio) for their derivation from an olivine-free source and incorporation of melts derived from foundered eclogitic continental crust. Together with our previous studies of the late Jurassic high-Mg intermediate to felsic lavas from western Liaoning in the northeastern North China craton (Gao et al., 2004), these findings indicate that thinning of the North China craton was caused by recycling of the lower lithosphere (mantle and lower crust), and demonstrate that continental lithosphere recycling is a viable means of producing mantle heterogeneity.

The building-up exercise of a thermodynamic data set on ISA-actinide system

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Isosaccharinic acid (ISA) is one of the most important degradation products of cellulose expected in the hyperalkaline conditions defined by cementitious environments. Despite the high affinity shown by this ligand toward actinides complexation, the number and reliability of available experimental studies is still limited (Hummel et al., 2005). Due to the potential effect of these complexes in the performance assessment exercises, this work aims at providing a comprehensive and coherent thermodynamic data set on the ISA-actinide system. For this purpose, the thermodynamic data available in the literature have been complemented with further modelling exercises and estimations based on ionic radii correlations among actinides.

Under slightly reducing conditions and absence of carbonate and calcium, M(OH)ISA ternary complexes (M=Th, U(IV), Np(IV), Pu(IV)) are expected to dominate aqueous speciation. The available publications show a moderate agreement among the stability constants of these complexes, although their structure is still ill-defined and some authors propose complexation reactions where the alcohol groups of ISA are partly deprotonated. Under hyperalkaline conditions and the presence of calcium, the species CaM(OH)4ISA2(aq) has been described for Th and may dominate aqueous speciation of further tetravalent actinides.

The limited number of experimental studies assessing the complexation of An(V) and An(VI) with ISA indicates the possible formation of An(V)O2(OH)x(ISA)y-like complexes. This work has allowed to obtain a complete set of stability constants for complexes of ISA with tetravalent actinides under alkaline to hyperalkaline conditions. Similarly, stoichiometries and stability constants for An(V)-ISA and An(VI)-ISA complexes have been proposed, although further experimental efforts would be advisable to gain confidence on these complexes.

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Experimental determination of C_i/C_o of Rb, Sr and Ba and comparison with C_i/C_o of a migmatite

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Introduction

As a way to settle the difficulties regarding the origin and evolution of granitic rocks, we studied the C_i/C_o values of Rb, Sr and Ba from melts of the Ollo de Sapo Gneiss (modal comp.: Qtz: 42; Pl (An19): 20; Kfs: 8; Bt (Mg 40): 10; Ms: 20) at 6 and 10 kbar, 750, 800, 850 and 900 ºC, and 10% wt water. Experiments were run in a piston-cylinder apparatus at the High Pressure Laboratory of the University of Huelva, and analysis were made using an ICP-MS of the Central Services of the University of Huelva.

A diamond trap has been used to separate melt from residual minerals, so a pressure gradient between powder and trap (which can be a source of disequilibrium) exists, but disappears or is minimised if melt soaks the trap and residual minerals. Thus, melting process begins as a fractional melting followed by a batch melting if melt quantity exceeds a critical amount.

Discussion

At 6 kbar, C_i/C_o values for Rb are lower than 1 (0.67-0.98) with a minimum at 800 ºC due to the high productivity of melt by the breakdown of feldspars; for Sr, C_i/C_o is upper than 1 (1.01-1.24), with a maximum at 800 ºC. Comparing these values with calculated for High Himalayan leucogranites, assuming a greywacke source in presence of water, a clear resemblance for Rb and a difference for Sr and Ba can be seen.

Conclusion

The election of the K_0 values has a decisive influence in C_i/C_o values, although this discrepancy can also be due to a disequilibrium melting because of the diamond trap.

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Radium isotopes as tracers of submarine groundwater and nitrogen discharge in a karstic area

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Introduction

A mass balance for ^223Ra (T_{1/2}=11.4 d) and ^224Ra (T_{1/2}=3.66 d) is applied to a karstic area (Badum, Spain) to evaluate the submarine groundwater discharge (SGD) through coastal springs. The strategy is based on the enrichment of Ra in groundwater compared to surficial waters.

Ra isotopes were measured from coastal, brackish springs and seawater samples by using a Radium Delayed Coincidence Counter (Moore and Arnold, 1996).

Results and discussion

All coastal samples are enriched in radium activities compared to the open sea, the highest activities being found in the springs. ^223Ra and ^224Ra concentrations are highly correlated and Ra vs. salinity plots suggest a mixing process between the springs and the coastal sea endmembers (Fig. 1).

A Ra mass balance allows obtaining a groundwater fraction of 38%. By considering this fraction, the water residence time (0.5 d) also derived from the short-lived Ra isotopes and the sampled water column, a SGD flux is calculated to be 5·10^6 m^3 yr^-1. This flow accounts for a nitrate input of 3 mmol m^-2 d^-1, which is comparable with literature values of SGD-derived nitrogen inputs to coastal areas (Charette and Buesseler, 2004).

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Figure 1. ^223Ra and ^224Ra activities in all water samples indicate the two endmembers.
Short-term geochemical variation within a single eruption event: Mount Edgecumbe volcano, Bay of Plenty, New Zealand

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A re-evaluation of the petrogenetic links between the andesites and rhyolites from the Taupo Volcanic Zone of New Zealand’s North Island by Price et al. (2005) led to the proposal of an evolutionary pattern from andesite-dominated to rhyolite-dominated magmatic systems with time.

In order to understand the processes involved in this long-term shift towards catastrophic rhyolite eruptions, we must first ensure that we fully comprehend the factors controlling short-term variations. However, detailed, stratigraphically controlled sampling of well-documented single eruptive episodes and eruptive sequences has revealed considerable internal complexities at several arc-type volcanoes.

Here we present analyses of multiple samples from an accurately dated, (3115±35 yrs BP, Carroll et al. 1997) andesitic block- and ash-flow deposit on Mount Edgecumbe at the active volcanic front of the TVZ. Our results are based on whole-rock analyses for major element oxides, trace and rare earth elements in addition to Sr and Nd isotope ratios resolving the extent of geochemical variability within a strict time-frame.

References

Cooling rates contraints on the accretion of the plutonic crust at fast-spreading mid-ocean ridges

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We report the results of a thermo-mechanical model of crustal flow beneath fast spreading mid-ocean ridges considering the effect of deep, near off-axis hydrothermal cooling and variable igneous accretion modes. The accretion mode determines the flow lines along which gabbro crystallize and the lateral advection of heat and mass. Near, off-axis hydrothermal cooling determines the shape of the magma chamber and viscosity, which influence the stream function and the shape of flow lines along with plutonic gabbro crystallize. The cooling rate of the plutonic crust along a flow line depends on the velocity and geothermal gradient along it, which are in turn imposed by: (i) the accretion mode, (ii) the extent of off-axis hydrothermal cooling, and (iii) conductive thermal rebound far from the ridge axis. The conventional wisdom that the igneous and metamorphic cooling rates of exposed sections of lower oceanic crust are similar and both reflect the on-axis thermal cooling of the oceanic crust is too simplistic. The cooling history is inherently related to the method used to retrieve it; particularly to the temperature interval recorded by the method. The cooling history may integrate cooling at different depths at distances from the ridge axis, which are not necessarily those of their final depth of emplacement. While igneous cooling rates record the thermal structure of the magma chambers, metamorphic cooling rates may record different extent of the off-axis thermal structure depending on the effective temperature of diffusion initiation and closure temperature. Igneous and metamorphic cooling rate variations with depth are markedly different for a given accretion mode and, if available, both might be used to discriminate among different scenarios proposed for the accretion of the oceanic crust a fast-spreading mid-ocean ridges.
Thermodynamic modelling the sorption of heavy metals and actinides onto clay minerals by Gibbs energy minimization approach

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One of the major aims in the development of sorption models was to set up the simplest chemically reasonable model with the least number of variable parameters capable of describing and predicting sorption over a wide range of conditions. In this study we have investigated the sorption of heavy metals and actinides onto montmorillonite, illite and kaolinite in aqueous solutions by applying the Gibbs energy minimization computer code “HCh” (Yu.V. Shvarov, Moscow State University) via a non-electrostatic model. The emphasis is made on the named clay minerals because of their importance in terrestrial weathering processes and designed industrial applications. The thermodynamic model combines cation exchange at a permanent negatively charged sites and pH-dependent surface complexation at the amphoteric edge-type sites. Site types, their individual capacitance and the acidity constants associated with them, were considered to be non-adjustable parameters and were fixed in all of the calculations: the cation exchange capacity (CEC) is 0.9, 0.25 nd 0.05 equiv/kg and equal to concentration of exchangeable acidity constants associated with them, were considered to be pH-dependent surface complexation at the amphoteric edge-type sites. Site types, their individual capacitance and the acidity constants associated with them, were considered to be non-adjustable parameters and were fixed in all of the calculations: the cation exchange capacity (CEC) is 0.9, 0.25 and 0.05 mol/kg. The equilibrium constants for the adsorption and ion exchange reactions could be found due to correlations with the aqueous hydrolysis constants.

The calculated sorption models showed good approximation of experimental distribution coefficients of majority sorbates onto named three clay minerals. We note that the model parameters discussed here are closely dependent on the decisive variables, namely the surface site capacities. Indeed, the value of the CEC and the density of edge sites directly control the metal uptake by considered clay minerals. It allows to show that: a) the influence of ionic strength and pH of solutions on the metal sorption is differentiated depending on the crystallochemical type of clay mineral. The more sorption capacity of a phase, the influence of concentration of electrolyte is more strongly revealed. As a result, kaolinite could be successfully used in the solutions with I > 0.1 and pH > 5 instead of montmorillonite, which exhibits the highest exchange capacity; b) the sorption show a higher difference in selectivity of the cations in the pH range 4-8, where it is greatly affected by the element chemical properties (affinity to the hydrolysis in solutions and the surface-binding complexation); c) on the contrary, at weakly acidic pH of diluted solutions (low ionic strength), selectivity coefficients Kc could be accepted the same for analogous type of cations, if was not determined exactly. Usually, Kc values for bivalent-monovalent exchange are ~3 to 4 and for bivalent-bivalent exchange around unity.

The Bicaz lake (Romania): Hydrodynamics and trace element behaviour

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The dammed lake of Bicaz (East Carpathians, Romania), presents the following physical characteristics: 31.1 km length, 2 km wide, water volume of 1.150·109 m3. The Bistriţa river is the main tributary with a mean water contribution of 1.721·109 m3/year and a mean suspended matter flow of 291,000 tons/year. This river drains a catchment rich in formerly mined mineralizations of polymetallic sulfides.

Three locations, an upper, a middle, and a down site as well as the main tributary river were sampled for one hydrological year.

The electric conductivity and the concentration of major ions allow to evidence a water layer whose position varies along the lake and according to season (water temperature and lake depth). This current which originates from the Bistriţa river is intensified by the sluice drawing off. The distribution of Fe between dissolved and particulate forms, along the lake and for each season, and the distribution of Mn, excepted in some cases, show the lake is mainly oxidizing. In the dissolved phase, the concentration of Fe and Mn is smaller than in the river. Some trace elements such as Cr and V occur mainly in the particulate form, and are enriched in the dissolved phase compared to the Bistriţa. On the contrary, Ni, As and U are found mainly in the dissolved phase: Ni is enriched compared to the river whereas As and U are similar.

The distribution of Co between particulate matter and solution is variable and does not follow Mn. The concentration of Co in the dissolved phase is smaller than in the river. Thus, stratification of the water column within the lake is disturbed by the river current and by the sluice. The weak relationship between Fe and Mn and analyzed trace elements may be linked to hydrodynamics of the lake.
**A radium and radon investigation of the submarine estuary under Venice**

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Submarine groundwater discharge (SGD) is now recognised as a major pathway for nutrients and contaminants. Mass balance models based on excesses of natural radioactive isotopes in coastal environments (estuary, lagoon) can provide integrated estimates of SGD. In this work, we measured \(^{226}\)Ra and \(^{222}\)Rn activities in the southern part of the Venice lagoon, a most emblematic case of highly vulnerable coastal flatland heavily impacted by anthropogenic activities.

\(^{226}\)Ra activities measurements were performed by isotope dilution and thermal ionization mass spectrometry on small samples (0.5L). Very small variations in \(^{226}\)Ra can be resolved by this technique, thanks to the high precision that is attainable (1 to 5% on 20 to 200 fg samples). \(^{222}\)Rn activities were measured by in-situ continuous-monitoring \(\alpha\)-counting technique with a precision of 10%.

\(^{226}\)Ra and \(^{222}\)Rn activities are significantly higher in the lagoon samples (2.3-5.3 and 26-82 Bq/m\(^3\)) respectively than in the open Adriatic Sea (2.2 and 10 Bq/m\(^3\)) respectively. Mass balance models taking into account riverine inputs, diffusion from sediments, loss, production and decay of the isotopes, do not explain the lagoon excesses and suggest the existence of another source of \(^{226}\)Ra and \(^{222}\)Rn in the lagoon.

Groundwater from the semi-confined aquifer (0-30 m) connected with lagoon waters presents significant enrichment in \(^{226}\)Ra and \(^{222}\)Rn (c.a. 35 Bq/m\(^3\) and 1300 Bq/m\(^3\)), and may be considered as an additional source to generate the required excess. Using these activities, the input of groundwater necessary to explain the observed excess in the lagoon is 5.2x10\(^5\) and 5.5x10\(^5\) m\(^3\)d\(^{-1}\), based on \(^{226}\)Ra and \(^{222}\)Rn mass balance respectively. Furthermore, Rn monitoring during tidal cycles shows that the excess activity is produced during the falling tide, when aquifers significant discharge interstitial waters through the sediments.

**References**


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**Cryptic zoning in garnets from the Nufenen Pass area**

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Garnets from graphite rich black shales of the Mesozoic cover of the Gotthard Massif in the Swiss Alps display textural sector zoning with birefringent lamellae emanating from sector boundaries. Central sections of garnets cut along [110] display 6 sectors, which are in places crowned by a graphite rich cap. The birefringent lamellae are oriented normal to the sector end face. Individual lamellae have a length of up to 300 microns and a thickness of typically 10 microns. The lamellae have an elliptical cross section of a few tens of microns for their long axis on sections parallel to the sector end face. A cross hatched pattern is created with lamellae orientations parallel to the edges of the sector walls. Lamellae are absent in the graphite inclusion rich rim. EPMA analysis of the birefringent lamellae show that they are Ca richer than the adjacent isotropic lamellae which are Fe richer. The composition difference in calcium and iron between the two type of lamellae can be up to 0.2 cation per formula unit. The lamellae are zoned along their length, following the overall garnet zoning pattern. Composition ranges for the two lamellae overlap for a single garnet.

The coexistence of two garnet composition and structure could be explained by a miscibility gap in the solid solution or by crystallisation of one or two metastable precursors. The composition difference between the two type of lamellae is too small to reflect a miscibility gap and lamellae composition overlap. Hence they are not exsolutions. Other type of zoning have been explained by the replacement of heterogeneities in the matrix or concentric zoning due to rythmically changing conditions (Yardley et al., 1996). The crystallographic orientation of the lamellae indicates that they do not represent replacement of matrix heterogeneities. The orientation of the lamellae demonstrates, that at any time, both types of lamellae were crystallizing.

We propose an alternate mechanism for this case. Two garnets with a slightly different composition and structure nucleate topotactically on the surface of a growing garnet with a similar probability. It is enough that continued nucleation of a new garnet layer slightly prefers the same structure to assure a fiber-like growth of both compositions side by side.

**Reference**

**Water solubility in clinopyroxene**

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Clinopyroxenes, in particular omphacites, have the highest water contents among the minerals from mantle xenoliths. In subducting slabs, water in omphacite may contribute significantly to the recycling of water into the mantle. We have therefore measured the solubility of water in both pure CaMgSi$_2$O$_6$ diopside and in diopside containing variable amounts of aluminum as Ca-Tschermak CaAl$_2$SiO$_6$ component. Single crystals of the pyroxenes were grown in piston-cylinder and multi-anvil experiments using oxide/hydroxide mixtures with excess water as starting materials. Water contents were quantified from polarized infrared spectra of clear single crystals.

Water solubility in pure diopside is rather low, in the order of a few hundred ppm at 1.5 – 3 GPa and 800 – 1100 °C. The type of infrared spectra observed varies with the bulk composition of the sample. Diopside crystals synthesized with excess silica show several bands at low frequency between 3280 and 3480 cm$^{-1}$. These bands are attributed to protons on Ca or Mg vacancies. Diopside crystals synthesized with excess MgO or a deficiency of SiO$_2$, which coexist with olivine, show only one sharp band at 3650 cm$^{-1}$. This band is therefore probably due to protons associated with silica vacancies.

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Water solubility in clinopyroxene strongly increases with alumina content and reaches up to 3000 ppm already at 1.5 GPa (Fig. 1). Aluminous diopside samples only show one infrared band at 3650 cm$^{-1}$, corresponding to the substitution of Al$^{3+} + H^+$ for Si$^{4+}$. Our data therefore confirm that Al in pyroxenes largely controls water storage in the uppermost mantle.

Figure 1. Water solubility in aluminous diopside as function of the content of Ca-Tschermak component (in mol %)

**Cosmogenic $^3$He production rate in pyroxenes and olivines at low latitude**

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In the past decade cosmogenic $^3$He has become a widely used chronometer of surface exposure. The low cost of noble gas measurements and the relatively high production rate in mafic minerals have, in particular, been exploited for dating exposure of basaltic rocks. Cosmogenic $^3$He production rate in olivine is well documented, however, only few studies have been dedicated to the determination of the production rate in pyroxene (i.e. [1-2], 39-46°N and 47°S latitude). The study presented here is designed to measure long-term cosmogenic $^3$He production rate in pyroxenes and co-existing olivines at low latitudes, and to document the variation of cosmogenic $^3$He production rate with chemical composition.

Four olivine- and pyroxene-rich basalt flows between 132 and 482 m altitude were sampled from Ascension Island (7.5°S) where the arid climate preserves ropey-flow tops. In pyroxenes, cosmogenic $^3$He concentrations were calculated using (i) the magmatic $^3$He/$^4$He released by in vacuo crushing and melting, and (ii) the $^4$He concentrations measured by melting. The magmatic $^3$He/$^4$He is remarkably constant (6.8±0.4 $R_a$) while the $^3$He/$^4$He of melt extractions range from 100 to 500 $R_a$, suggesting that the correction for non-cosmogenic He is minimal. Cosmogenic $^3$He concentrations in multiple pyroxene samples from each flow range from 1.41 x 10$^7$ to 2.69 x 10$^7$ atoms/g, corresponding to approximately 220 to 350 kyr exposure. Error-weighted mean values have total uncertainties of 5% implying that the flow tops have not been significantly covered or eroded. Measurements of cosmogenic $^3$He concentrations in olivines from the same samples will be conducted and compared to the pyroxenes to constrain the cosmogenic $^3$He production rate in pyroxenes and to explore the production rate variation with chemical composition.

References
Actinide geochemistry: From the molecular level to the real system

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Geochemical processes leading to either mobilization or retention of radionuclides in an aquifer are significantly influenced by their interaction with rock, sediment and colloid surfaces. Therefore, performance assessment of nuclear waste disposal requires the elucidation and quantification of those processes. State-of-the-art analytical techniques as e.g. laser - and X-ray spectroscopy are increasingly applied to study solid-liquid interface reactions and to obtain molecular level speciation insight.

We have studied the sorption of trivalent lanthanides and actinides (M(III)) onto aluminium oxides, hydroxides and purified clay minerals by the time-resolved laser fluorescence spectroscopy and X-Ray-Fluorescence spectroscopy [1, 2]. Chemical nature and structure of surface bound actinides are proposed based on spectroscopic information. Similarities of spectroscopic data obtained for M(III) sorbed onto γ-alumina, gibbsite and clay minerals suggest the formation of very comparable inner-sphere surface complexes like =S-O-\text{An(III)}(OH)_{4-(2-x)}(H_2O)_{5-x} at pH > 5. Those speciation data are found consistent with those predicted by surface complexation modelling. The applicability of data obtained for pure mineral phases to actinide sorption onto heterogeneously composed natural clay rock is investigated by experiments and by geochemical modelling.

The assessment of clay colloid borne actinide migration observed in the frame of in-situ experiments at the Grimsel underground laboratory [3] also calls for detailed information on actinide speciation. Combined spectroscopy and wet chemistry experiments provide a fairly consistent picture of the actinide speciation under given groundwater conditions and impart insight into the dynamics of actinide-colloid interaction. Notably for tetravalent actinides we observe significant impact of ageing on the rate of actinide desorption from clay colloids. Studies are ongoing to elucidate underlying mechanisms.

Above mentioned studies demonstrate the appropriateness of combining spectroscopy and wet chemistry as an appropriate strategy to validate geochemical model assumptions and to reduce uncertainties.

References

Microbial reduction of arsenate with sulfide as electron donor at neutral pH

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Arsenic is a common trace element found in most natural waters, as well as a documented human carcinogen. In the environment, arsenic occurs in the valence states As(V) and As(III). The bioavailability of arsenic is in general controlled by the presence of iron, by sorption of arsenate (As(V)) to iron minerals, and sulfide, resulting in the precipitation of arsenite (As(III)) as arsenic sulfides.

It is well known that arsenate may be microbiologically reduced under anaerobic conditions, and recently microbial reduction of arsenate coupled to the use of sulfide as electron donor was described [1, 2]. This process occurred in soda lakes, with pH 10 and high salt concentration, conditions under which sulfide is less toxic due to the virtual absence of H_2S. Chemical reduction of arsenate with sulfide has been shown to take place at acidic to neutral pH.

We investigated the possibility of biological reduction of arsenate with sulfide as electron donor at neutral pH. Batch incubations were set-up using anaerobic sediment amended with arsenate and sulfide. Arsenate was removed from solution in 5-9 days. In control experiments with autoclaved sediment, part of the arsenate in solution was removed, which may indicate relatively slow sorption of arsenate on soil particles or chemical reduction of arsenate.

Incubations in which arsenate conversion occurred were transferred to fresh culture medium several times and yielded stable enrichment cultures. In these enrichment cultures two dominant bacterial species were present. Application of molecular biological techniques showed that the two species were related to the genus Sulfospirillum and to sulfate reducing bacteria belonging to the delta-proteobacteria. We aim to isolate these two organisms in pure culture and study their physiology and ability to reduce arsenate with sulfide in more detail.

References
Hg accumulation in reducing sediments of the Mediterranean Sea: Trace metal and Hg isotope evidence

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Mercury (Hg) has a complex biogeochemical cycle involving multiple oxidation states with gaseous, dissolved, and particle-associated species. We investigated the effects of different redox conditions on Hg partitioning in the marine environment. We analyzed Hg concentration and isotopic composition, as well as concentrations of a suite of trace metals that are widely used as indicators of productivity and redox conditions, in sediments from a mid-Pleistocene sapropel sequence in the Tyrrhenian Basin of the Mediterranean Sea. During episodes of sapropel formation, high productivity and reducing conditions produce organic-rich sediments, with characteristic trace metal patterns. Concentrations of Hg and other metals covary with total organic carbon (TOC) content, with a Hg enrichment factor of 3.9 in high TOC sapropels versus low TOC non-sapropels. Enrichment factors determined for other elements are 1.3-2.1 for Cr, Cu and Zn; 3.0-4.9 for V, Co, Ni and U; 5.0-8.0 for Mo and Cd; and 13 for Re. Hg concentrations in these sediments are highly correlated with trace elements normally associated with organic matter delivery (Co, Ni, Cu, Zn and Cd) as well as with elements associated with enrichment in reducing sediments by mineral precipitation and adsorption occurring below the sediment-water interface (V, Cr, Mo, Re and U) (Tribovillard et al., 2006). The strong correlation between Hg and both suites of trace metals suggests that particulate scavenging and/or in situ precipitation contributes to Hg accumulation in marine sediments. If we specifically look at the variation in metal concentrations in only those samples with low TOC content deposited under oxic conditions (non-sapropel layers), we find that Hg does not covary with V, Cr, Ni, Mo, Cd, Re or U, but does covary with Co, Cu, and Zn. These patterns may be related to variations in terrigenous sediment sources or preservation of these metals in sediments.

We also explored whether Hg isotope values could provide insight into changes in Hg deposition between sapropel and non-sapropel layers. Preliminary isotopic analyses show that sapropels have lower δ²⁰⁶Hg values (Blum and Bergquist, 2007) than non-sapropel layers (-1.1‰ vs -0.7‰). This likely reflects either a change in Hg sources or isotopic fractionation during redox transformations.

References:

Mobilisation and speciation of depleted uranium in water and soils

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Depleted uranium (DU) from penetrating ammunition was exposed to several environmental conditions in order to determine the binding forms of uranium as well as its dissolved and solid forms.

In a first series fresh disks of DU were treated with a calcium phosphate solution. The results from time-resolved laser-induced fluorescence spectroscopy clearly show that metaautunite Ca(UO₂)₂(PO₄)₂ x 2-6(H₂O) has formed during alteration [1].

In a second experiment the corrosion and leaching of used DU was investigated for three years in a column with a soil core. The columns were irrigated with synthetic rainwater.

The luminescence spectrum of a yellow material, which was crystallized at the soil surface was assigned clearly to be the mineral sabugalite AlH(UO₂)(PO₄)₄ x 16(H₂O).

In contrast to the luminescence spectra of the solid material the spectra of the uranium species in the dissolved samples could only obtained at temperatures below 220 K. From the shape of the spectrum and the emission maxima of the luminescence of seepage water samples it could be clearly concluded that the solution species are mostly uranyl carbonate species UO₂(CO₃)³⁻ [2].

References:
NWA 2999, an angrite with unusual bulk chemistry or a new type of achondrite?

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Introduction

NWA 2999 is classified as an angrite based on mineralogy and oxygen isotopes [1]. Chemical data indicate differences in bulk chemistry to other angrites, making this a unique meteorite.

Chemistry

Major elements were determined by XRF, trace elements on a different sample by INAA. For analytical procedures see [2,3]. Compared to average angrite, the Mg content is significantly higher, Si and the refractory elements Ca, Al and Ti as well as P are much lower. Unlike other angrites, NWA 2999 has abundant FeNi-metal, and corresponding levels of Ir, Au, Ni and Co.

Interpretation

Mixing calculations with average angrite composition were performed: Delivering the excess siderophiles is possible by contributing 8% of the mass by an iron meteorite. But this is unlikely, because it cannot explain the high Mg and the low Ca, Al and Ti contents.

Adding more than 60% of a primitive meteoritic component would have diluted the refractory elements to the measured values and led to the high Mg, Cr and siderophile element contents. The added component could have lost its P by metal-silicate equilibration before the metal was incorporated in NWA 2999. However the assumption of more than 60% of external matter is difficult to reconcile with the angritic oxygen isotopic data and the low contents of volatiles.

An alternative view is to take both components from the same parent body. A differentiated lithology with elevated Ti, Ca, Al and REE, but with low Mg, Cr and almost no Ni and Ir is mixed with a core-mantle component, high in Mg, Cr, Fe, Ni, Au and Ir of the same parent body. Mixing could be the result of a large impact on the APB.

Another yet possibility is an origin from a different, until now unknown parent body, which is similar to angrites with respect to mineralogy and oxygen isotopes.

References


Physicochemical Speciation of Iron in the Baltic Sea

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Size fractionated classes of Fe in surface water at two stations, one in central Baltic Sea (the Landsort Deep) and one in Bothnian Sea, were measured from spring until autumn to evaluate temporal variations in the physicochemical speciation. Membrane filtration, cross-flow ultrafiltration and DGT (diffusive gradients in thin films) were among the applied techniques. Average concentrations for total, <0.22 and <1kDa Fe were 32, 7.0 and 5.9nM respectively at the Landsort Deep. For the Bothnian Sea, these figures were 96, 21 and 6.2nM. DGT-labile concentrations of Fe were significantly lower than <1kDa at both stations. This probably indicates that a large portion of the DGT-labile Fe was organic bound, which would slow down the diffusion rate. The DGT-labile Fe concentration was on average 0.6 nM at Landsort Deep, and 1.0 nM in the Bothnian Sea. If assuming that all DGT-labile Fe was bound to fulvic acids the concentrations becomes about 5 times higher, but still lower than <1kDa. No clear trends were observed for the DGT measured concentrations. In both areas the concentration of Fe in all but the DGT-labile fraction decreased 60-80% towards end of the sampling period. Average ratios between total Fe and <0.22µm were about 4-5 at both stations, but in the Bothnian Sea also a clear difference between <0.22µm and <1kDa was observed, indicating a significant colloidal fraction. At the Landsort Deep, a peak of <1kDa Fe was evident in end of July, despite stable total concentrations during the summer. A small peak of <1kDa Fe was also observed in the Bothnian Sea, but not as clear as in Landsort. These peaks coincide with drops in biomass, indicating that this is a mineralization event. We hypothesize that the difference in concentration between DGT-labile and <1kDa is caused by organically bound species that are influenced by the presence of phytoplankton.
Imperfect accretion during the giant impact stage of terrestrial planet formation

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In the standard scenario of planet formation, terrestrial planets are formed in two stages: the formation of several tens of Mars-sized protoplanets through accretion of planetesimals, and collisions among these protoplanets (called giant impacts). Although the nature of giant impacts determines the final masses, spin parameters, and orbital elements of the terrestrial planets, all the previous N-body simulation of terrestrial planet formation (e.g., Chambers 2001, Raymond et al. 2004, Kokubo et al. 2004) have been based on the assumption of the perfect accretion, that is, colliding two protoplanets always merge without mass loss. Agnor and Asphaug (2004) performed 48 SPH simulations for mutual collision of 1 Mars-mass protoplanets. They showed that the two protoplanets bounce and escape to infinity for collision with relatively faster impact velocity (e.g., > 1.4 × escape velocity for 30 deg of the impact angle), and they estimated that more than roughly half of giant impact events are not coalescence events.

In order to incorporate the effect of imperfect accretion into N-body simulations, we need to know the accretion condition for various types of giant impacts. Using the specialized computers for gravitational N-body problems (GRAPE), we performed more than 1000 runs of impact SPH simulations for various mass ratios (γ), impact angles (ξ), and impact velocities (vinp). From the results of more than 1000 runs, we formulated the boundary of vinp between coalition and rebound as parameters of γ and ξ. We also formulated the mass(es) and orbit(s) of post-impact planet(s).

We applied the above formulation to the impact events obtained by Kokubo et al. (2006), and found that 261 out of 635 giant impacts, that is 41%, are not coalescence events. We will also report the effects of imperfect accretion on the final states of the terrestrial planets such as the largest mass and rotation velocity.

References

Isotopic evidence for Silicon within the Earth’s core

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We present the first isotopic evidence for Si within the Earth’s Core. It has long been proposed that the Earth’s core must contain significant quantities of light elements, such as H, C, Si, S and K [1]. The high Mg/Si of the terrestrial mantle has been used to argue that Si in particular is an important component in the core [e.g 2]. Recent estimates indicate that it contains as much as 5–7 wt% [e.g 3], and the partitioning of Si into the metallic core should yield isotopic effects because of differences in bonding of Si between metals and silicates.

We analysed the Si isotope compositions for different bulk silicate reservoirs of the solar system as sampled by chondrites, basaltic achondrites thought to come from Vesta and Mars, and basaltic rocks from the Moon and the Earth’s mantle. The mean values of these reservoirs obtained for this study are in excellent accord with previous estimates, however, the spread in the data is an order of magnitude lower. A significant difference is found between the bulk silicate Earth (BSE) and Moon on the one hand and meteorites on the other.

It appears unlikely that this observed Si isotope shift can be produced by volatilisation processes during the early accretion history of the Earth. Rather, the observed Si isotope shift was probably produced during Si partitioning into the Earth’s core. We modelled the potential Si isotope fractionation during silicate-metal partitioning and can show that both the direction and magnitude of such fractionations are consistent with the observed isotopic differences between BSE/Moon and meteorites.

References
Resolving the evolution of a subduction zone: Eastern Srednogorie, SE Europe

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Eastern Srednogorie zone is the easternmost part of the mineralized ABTS (Apuseni-Banat-Timok-Srednogorie) belt in SE Europe. This belt is a former Late Cretaceous island arc that was formed during the process of northward subduction of the Tethyan ocean beneath the European platform. Compared to the other parts of the belt, magmatic products exhibit the most variable composition. However, the zone is the least studied, and here we present new geochronological, isotope and geochronological data with the aim to understand the genesis of the magmatism. We try to isolate the most primitive initial magmas that fractionated and assimilated parts of the crust to produce the abundant Late Cretaceous magmatism, and to trace the across-and along-arc change in the age and composition of the magmatism.

Magmatic products in the Eastern Srednogorie show the entire spectrum of rocks typical for island-arc environments. Based on their chemical composition three main regions are subdivided from south to north; (1) tholeiitic to calc-alkaline, basic to acid intrusives in the southern; (2) predominantly potassic to ultrapotassic mafic-intermediate volcanics in the central (3) calc-alkaline basic-intermediate volcanics in the northern part. Trace and REE distribution patterns argue for subduction related magmatism for all rock varieties.

TIMS and LA-ICPMS dating of single zircon grains shows that magmatic activity started at about 86 Ma with few intrusions but the climax of the magmatism was in the Campanian (81-78 Ma). Whole-rock Pb and Sr isotopes of most mafic magmas show the least radiogenic compositions (87Sr/86Sr of 0.7040, 206Pb/204Pb 18.38, 207Pb/204Pb 15.57 and 208Pb/204Pb, 38.27). These values are less radiogenic compared to Late Cretaceous magmatic rocks of the adjacent Central Srednogorie zone. In addition, the majority of the analysed rocks contain Cretaceous zircons with positive εHf at 80 Ma (from 0 to +12), suggesting a mantle-dominated origin. However, these rocks contain variable amounts of inherited zircons with negative, crustal-like εHf at 80 Ma This fact clearly show that the rocks suffer some contamination by crustal-derived lithologies. The amount of crustal contamination increases with time. Potential candidates for the contaminants are the Carboniferous and Permian basement rocks, as revealed by the U-Pb single zircon ages of the inherited crystals. The DM model Hf ages of inherited zircons and zircons from the basement rocks cluster around 900 Ma.

Chronological history of UHP rocks from the Chinese Continental Scientific Drilling: A multi-methodical approach

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Ultrahigh pressure (UHP) rocks from the Chinese Continental Scientific Drilling (CCSD) program were chosen to study the Sm-Nd and Lu-Hf isotope systems in combination with U-Pb LA-ICP-MS and SHRIMP dating of distinct zircon domains. Comprehensive studies of the different lithologies on various sections of the drill hole should provide a better understanding of the metamorphic evolution of the Sulu terrane. Additionally, our multi-methodical approach provides the opportunity to compare the different chronometers and test their robustness and limitations (e.g. mineral inclusions, incomplete equilibration, resetting). Multistage zircon growth can be observed in most Sulu-Dabie UHP rocks. Inherited and metamorphic zircons were distinguished on the basis of transmitted light microscopy, cathodoluminescence (CL) imaging, trace element contents, Hf isotope composition and mineral inclusions. Inherited zircon of middle Neoproterozoic age have variable trace element pattern that are considerably different from that of metamorphic zircon domains. Based on CL, mineral inclusion and U-Pb ages up to three phases of Triassic zircon growth or re-crystallisation can be identified in a single sample. The ages are interpreted to date the time of (1) prograde and (2) UHP metamorphism during subduction, and (3) later retrograde metamorphism during exhumation.

Metamorphic domains from a single sample have commonly a uniform Hf isotope composition indicating isotope equilibration in the decimetre-scale during the Triassic UHP event. This composition varies between different samples and is generally significantly more radiogenic than that of the inherited cores and thus the bulk rock. Its respective value is controlled by the percentage of dissolved or re-crystallized inherited zircon, with low Lu/Hf and relatively unradiogenic 176Hf/177Hf, and the bulk rock composition.

Analyses of the Lu-Hf and Sm-Nd system of mineral separates (garnet, clinopyroxene ...) are currently in progress. According to SHRIMP and LA-ICP-MS U-Pb ages of metamorphic zircon from the same and various other UHP rocks ([1-3] and references therein) lasted the metamorphic evolution of the Sulu-Dabie terrane around 30 Myr, with about 20 Myr of HP or UHP metamorphism.

References
Dynamics and longevity of the magmatic system of Furnas volcano, São Miguel, Azores

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Furnas is the easternmost of the three active trachytic central volcanoes on the island of São Miguel, Azores. It is regarded as one of the most active and dangerous volcanoes in the Azores archipelago owing to a population of several thousand people living within the caldera and in the immediate vicinity of the volcanic complex. Throughout its history, volcanic activity at Furnas has been essentially explosive but eruptive styles have varied from mild effusive activity to at least two caldera-forming eruptions ~30,000 and 12,000-10,000 years BP [1].

During the past 5,000 years, ten explosive eruptions occurred at Furnas, which produced a total of ~0.9 km$^3$ (DRE) of fairly homogeneous trachytic magma. The deposits of these eruptions are collectively referred to as Furnas A-J members of the Upper Furnas Group [1,2]. The latest eruption (Furnas J) occurred after the settlement of the Azores archipelago in 1630 AD. Eruptions of the Upper Furnas Group were mainly characterised by alternating episodes of magmatic and phreatomagmatic activity producing deposits of interbedded ash and lapilli that overlie the widespread Fogo A deposit from adjacent Fogo volcano [3]. At least three of these eruptions, namely Furnas E, Furnas I and the 1630 AD event (Furnas J), were accompanied by trachyte dome extrusion in the final phases of the eruption [3].

To develop a fuller understanding of the underlying dynamics of the magma system of Furnas, we have investigated the whole-rock major and trace element geochemistry of the products of the Upper Furnas Group and the older caldera-forming events. These data are discussed together with U-Th-Ra isotopic disequilibria obtained on trachyte pumice clasts and lavas to place constraints on the dynamics and longevity of the magma system of Furnas.

References

Designing a dissimilatory iron reducer. Reconstitution of the Fe(III)-reducing electron transport chain of Shewanella oneidensis MR-1 in Escherichia coli

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Shewanella oneidensis uses several electron acceptors to support anaerobic respiration including soluble species and remarkably insoluble species such as iron(III) and manganese(IV) oxides. The pathway of electron flow from the cytoplasmic membrane to the outer membrane remains elusive after years of research with different Shewanella species. We are pursuing a novel approach to identify the essential components of the electron transport chain by reconstituting the pathway for iron(III) reduction by S. oneidensis in Escherichia coli. We generated a suitable E. coli strain as a platform for this work and integrated the central electron transfer protein, CymA into the genome. CymA allows for electron transfer from the cytoplasmic membrane to the periplasmic space in Shewanella species. We showed (i) that the expressed CymA activity is growth supporting for E. coli, (ii) that CymA couples directly to the soluble fumarate reductase of S. oneidensis, and (iii) that CymA in vitro facilitates reduction of ferric citrate and the soluble quinone analog AQDS. Our generated E. coli strain is a dissimilatory iron reducer in that it can use ferric-NTA as a terminal electron acceptor during growth with glycerol as the sole carbon and electron source. We could furthermore show through in vitro assays that a direct interaction between CymA and the periplasmic decaheme cytochrome MtrA from S. oneidensis is possible.
Magma mixing and mingling textures and geochemistry of microgranular enclaves in granitoids of SE Semnan, N Iran

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Discussion

Many granitoid intrusions display textural and geochemical evidence for the intrusion of mafic and silicic magmas during their genesis [1]. The post-middle Eocene granitoids from SE Semnan, N Iran have many fine grained mafic microgranular enclaves, with diameters between 1 to 15 cm. Their composition varies from monzonite, quartzmonzodiorite – monzodiorite and monzogabbro – and exhibits evidence for magma mixing and mingling both at outcrop and at thin sections. These textures are antarapakivi feldspars, acicular and prismatic apatites, inclusion of mafic zones in feldspars, spongy cellular plagioclase, reverse zoning in plagioclases and etc.. In host granitoid rocks there are also two types of biotites in composition (that one types have high TiO2, Al2O3, MgO and low SiO2, are similar to contents of these elements in mafic microgranular enclaves and second types are depleted in TiO2, MgO and enriched in Al2O3 and SiO2) and reverse plagioclases zoned. The magmatic origin of enclaves is suggested by their typical igneous textures, such as with abundant acicular apatite, elongate zircon, the euhedral form of the mafic phases, porphyritic texture and plagioclase zoned [2]. These observations suggest that the mafic microgranular enclaves are derived from a hybrid magma formed as a result of the intrusion of mafic magma into the base of a felsic magma chamber.

Conclusions

The mafic microgranular enclaves have igneous mineralogy and textures. The petrographic, chemistry of minerals and whole-rock geochemical relations, in the mafic microgranular enclaves and their host rocks, indicate that magma mixing and mingling played a important role during their evolution.

References

Carbonate clumped isotope thermometry of molluscs and its applications to Pleistocene gastropod fossils from South Dakota

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Ghosh et al., (2006) [1] present a carbonate clumped isotope palaeo-thermometer. Otolith aragonite from fishes collected over a range of known temperatures [2] validates the original calibration of this thermometer for inorganic calcite precipitate (ICP) and coralline aragonite [1]. Here we present a calibration for molluscs, including gastropods collected from nature and inferred to have grown at widely different temperatures (2-25°C). The growth temperatures for these samples were estimated based on mean annual temperature (MAT) at the site of collection. We speculate that these growth temperature estimates could be biased by unknown and possibly variable amounts to due seasonality of growth and/or other factors. Despite these uncertainties, the mean trend in the relationship between inferred growth temperature and 47 is the enrichment, in per mil, of 13C-18O-16O in CO2 relative to 12C-16O-16O. 

The proportionality for molluscs can be described between 18O of rainfall from the same area. Our results suggest that the statistically indistinguishable and more precisely known trend for ICP should be used for molluscs.

We apply the carbonate clumped isotope thermometer to gastropods (Physella) deposited concurrently with mammoth skeletons in a sinkhole deposit in South Dakota, USA. The age of deposition of the analyzed samples was 26,075 ± 880 years BP, based on 14C dates for bone apatite collected from the same strata [5]. We analyzed aragonite powder from 15 Physella shells collected from various depths across a 255 cm vertical section from this location. Our results provide an estimate of 31.2 ± 3.34°C for the average temperature of water at the time of deposition. The average δ18O value of sinkhole water was (calculated assuming an equilibrium fractionation of 18O between carbonate and water [6]) -0.0496, where 47 = the enrichment, in per mil, of 13C-18O-16O in CO2 relative to the amount expected for a stochastic (random) distribution of isotopes among all CO2 isotopologues [3,4], and T is the temperature in Kelvin. However, due to scatter in these new data, we suggest that the statistically indistinguishable and more precisely known trend for ICP should be used for molluscs.

References
Isotopic composition of methane and $\Sigma$CO$_2$ from Arsenic affected area of West Bengal, India

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Ground water is a potential source of methane (CH$_4$) in Arsenic affected area of Bengal Basin. Harvey et al. (2002) observed high CH$_4$ concentration in the water with high As abundances at depth and predicted increase in CH$_4$ concentration during dry seasons. We present our study on tube well water samples collected during dry season (middle of February 2007) from two different localities in West Bengal, belonging to two different palaeodrainage systems i.e. Bhagirathi Ganges delta (BL) and Damodar river fan delta (BG) (tributary of river Bhagirathi) (Acharyya and Shah, 2007). Many of these wells were previously studied for As concentration (Acharyya and Shah, 2007).

CH$_4$ and $\Sigma$CO$_2$ present in the water samples were analyzed for carbon isotopic ratios to trace the sources of carbon to the ground water. Most of the samples analyzed for $\Sigma$CO$_2$ in this study have $\delta^{13}$C in the range -10.8‰ to -13.5‰, suggesting that the CO$_2$ in these samples originate from silicate weathering with CO$_2$ from vegetation ($C_3$ type). Barring one sample, we saw two distinct clusters of $\delta^{13}$C values in CH$_4$: -74.9 ‰ to -87.5 ‰ for BL water compared to a range of -30.5 to -40.2 ‰ in BG water. Isotopic signatures suggest a predominance of the carbonate reduction pathway in BL sites and high activity of CH$_4$ oxidation or substrata depletion in BG sites. Our preliminary results suggest that the process of release of arsenic from hydrated iron oxide is triggered by the activities of anaerobic bacteria in a reducing environment with consequent production of CH$_4$ with distinctly depleted isotopic character.

We also observed an anomalous enrichment of $\delta^{13}$C value (+55 per mil) in one of the samples with low CH$_4$ concentration from BL locality.

References
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Nanoscale size effects on reduction of hematite nanoparticles and surface reactions of Uranium(VI)

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The high surface area to mass ratios of hematite nanoparticles can increase the extents of surface reactions that affects the environmental biogeochemistry of pristine and contaminated environments. Surface reactions of interest include adsorption and surface-mediated reduction. Microbial iron reduction can produce Fe(II), which, when adsorbed to Fe(III) oxides, is an effective reductant of contaminants including uranium(VI). In order to understand nanoscale effects on the rate of microbial iron reduction and surface-mediated uranium(VI) reduction, hematite nanoparticles with diameters of 8, 50, and 200 nm were synthesized using gas phase methods that provide control of their composition and sizes.

The microbially-mediated rate of hematite reduction by the iron-reducing bacteria Geobacter sulfurreducens has been studied in anaerobic batch experiments. Abiotic reductive dissolution rates using ascorbic acid and the reduced form of the electron shuttle AQDS have also been studied. The dissolution rates increase with decreasing particle size; however, when normalized to surface area, the dissolution rates are similar for all but a few conditions.

Uranium(VI) adsorption to the three sizes of hematite particles was evaluated over the range of pH (3-11) and total uranium concentration ($10^{-6}$ to $10^{-4}$ M) to elucidate the size dependence of U(VI) adsorption to hematite. All experiments were conducted in a CO$_2$-suppressed glovebox to prevent the formation of dissolved U(VI)-carbonate complexes, which can affect U(VI) adsorption. Surface complexation modeling was used to provide a quantitative reaction-based framework for evaluating the effects of particle size on adsorption. A model was developed that can predict U(VI) adsorption over a range of pH values and total U(VI) loadings.

Rates of U(VI) reduction by adsorbed Fe(II) were investigated in batch experiments. Reduction is interpreted as a pseudo-first-order reaction with respect to the activity of the adsorbed U(VI) with an excess of Fe(II) relative to U(VI). At each sampling time, a portion of the suspension was filtered and analyzed for dissolved iron and uranium using ICP-MS. Additional portions of the suspension were chemically treated for the extraction of total U(VI) and Fe(II). Selective extraction of U(VI) uses 0.1 M NaHCO$_3$ while that of Fe(II) uses 0.5 M HCl. The concentration of Fe(II) was subsequently measured using the ferrozine method.
Tracking CO₂ leakage with noble gases

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The geological storage of greenhouse gases such as CO₂ in saline aquifers is an active research topic. By this way, effects of these gases on the environment may be significantly reduced. One limiting parameter of this type of storage is actually the hypothetical CO₂ leakage through the caprocks. Some studies of natural CO₂ gas fields have shown that noble gases are able to trace CO₂ origins and physical processes which have occurred in the subsurface (Gilfillan, 2006). Unfortunately, the migration of noble gases through low permeability media is still poorly constrained.

Here, we describe experimental results concerning the diffusion of gases through different porous clayey media. The experimental setup is a diffusion reactor composed of two gas reservoirs separated by a water saturated clay membrane. Initially, one side is filled with CO₂ mixed with trace amounts of noble gases (He, Ne, Ar, Kr and Xe), the other side is filled with pure oxygen to equilibrate pressures on both sides of the membrane.

Unexpectedly, diffusion of CO₂ is faster than those of He and any of the other noble gases. This result points to the effect of the solubility in the migration process, allowing CO₂ to migrate faster as it is highly soluble in water. In addition, in clay rocks, the “bound water” plays a role in this migration because solubility and diffusion factors contrast with those associated with “free water”. We used a 2D diffusion model at the pore scale (Kara, 2004) to determine diffusion and partition coefficients of noble gases between free and bound water as a function of petrographical parameters (mineralogy, porosity, tortuosity). The behavior of noble gases during a diffusion process will be presented in order to highlight the main parameters likely to control their migration.

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A δ¹³C depth gradient from a mid-Cryogenian platform margin: Evidence for Neoproterozoic ocean stratification

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A δ¹³C depth gradient of at least 8‰ between shallow and deep water is evident in Neoproterozoic carbonates from the Umberatana Group in the northern Adelaide Fold Belt, South Australia. The progradation of an extensive mid-Cryogenian platform margin allows direct isotopic comparison between shallow-water reef carbonates and synchronous deep-water slope and basinal sediments. With over 1 km of relief this platform margin allows an estimation of seawater δ¹³C in the upper 1000-1400 m of the water column.

We suggest that the observed δ¹³C gradient is the result of poor ocean circulation brought about by salinity stratification that persisted at least for the progradational history of the Oodnaminta platform margin. Such conditions enhanced the effect of the ‘biological pump’ by drawing ¹²C out of the surface ocean and accumulating it in the deep ocean. After prolonged stratification, the vertical δ¹³C gradient increased to the observed magnitude.

Furthermore, we propose that stratification was persistent throughout Neoproterozoic time, and can explain many of the unusual features that characterise this era – large-scale δ¹³C variation, extreme climatic fluctuations, and the presence of cap carbonates. Stratification creates an unstable climate system in which gradual accumulation of CO₂ in deep waters eventually leads to global glaciation due to the lack of deep ocean ventilation. Subtle changes in ocean circulation ventilate the deep ocean and rapidly transfer large amounts of CO₂ to the surface ocean and atmospheric reservoirs, leading to greenhouse temperatures, and facilitating rapid global deglaciation and cap carbonate deposition. Additionally, oxygen accumulated in the surface ocean and atmosphere during prolonged periods of stratification may have triggered the evolution of the Ediacaran fauna during the terminal Neoproterozoic.

The results also imply that the use of carbon isotope chemostratigraphy as a high-resolution chronostratigraphic correlation technique for the Neoproterozoic may be invalided by evidence for strong facies-dependant δ¹³C variation.
Metal sulfates in PM emissions from a coal-fired power plant

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Coal combustion facilities represent a major source of fine particulate matter (PM) in the atmosphere. The particle-capture efficiency of air pollution control devices is size-dependent, and is considerably lower for particles with diameters <2.5 micrometers (PM2.5) than for larger ones. These particles are thus emitted preferentially and, moreover, exhibit relatively long atmospheric residence times. To assess the environmental and health impacts of such PM, it is necessary to obtain information about its mineralogical composition.

We report results from SEM, TEM and XRD investigations on PM emitted from a stoker boiler. The samples, collected on filters placed in the smokestack above all air pollution control devices, represent PM that would have escaped into the atmosphere. Our study demonstrates that these fugitive particles in the PM2.5 fraction consist of amorphous material (Al-Si-glass, soot, native Se) and a variety of crystalline phases, including lime, mullite, and various euhedral metal sulfates. Electron diffraction patterns and chemical compositions obtained by quantitative analytical TEM revealed the presence in the PM of the following sulfates (Gieré et al. 2006): anglesite (PbSO₄) as main host of Pb; anhydrite (CaSO₄); gymnite (ZnSO₄·H₂O); and yavapaite (KFe(SO₄)₂), a mineral that is exceedingly rare in the geosphere. In the larger size fraction, we have identified the following additional phases: voltaiite and zincovoltaiite - Kₓ(Fe²⁺,Zn)ₓ(Fe³⁺,Al)ₓ(SO₄)ₓ·18H₂O, millosevichite - Alₓ(SO₄)₂, meta-aluminite - Alₓ(SO₄)(OH)ₓ·5H₂O, and tamarugite - NaAl(SO₄)ₓ·6H₂O.

It is concluded that most of these metal sulfates were precipitated from the flue gas, that large quantities of these phases may be emitted globally into the atmosphere through combustion processes, and that they have, through hydration and dissolution, a major environmental and health impact.

Reference


Comparative apatite fission track study of conventionally versus selFrag Lab fragmented samples

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Geochronological dating methods like apatite fission track analysis require an efficient liberation of single mineral grains for analysis. The selFrag Lab machine (produced by Amman AG, Langenthal, Switzerland) disaggregates geological materials by releasing short pulsed high-voltage discharges to an in water immersed sample. The produced, fast-expanding plasma channel induces shockwaves, similar to an explosion, that propagate through the sample. Refraction at discontinuities like grain boundaries, crystal internal surfaces or fluid inclusion trails results in selective break-up of the aggregate, yielding natural shaped homogeneous grains (Gnos et al., 2006 and references therein). However the HV-discharge may also produce local temperature peaks of up to 10'000°C of very short duration within the narrow plasma channel. Does this heat production affects fission tracks in apatite? Test were conducted to control whether this very localized heat production leads to partial fission track annealing starting at approximately 60°C. Prolonged exposure to temperatures exceeding 110°C would result in a complete reset of the apatite fission track record. Hence, any temperature impact on the apatite during processing could change the resulting fission track data.

Therefore a comparative study using two different samples, prepared by conventional and selFrag Lab processing, has been performed in order to investigate a possible influence of the selFrag Lab disaggregation method on apatite fission tracks.

Both investigated samples, a granitoid gneiss from Madagascar, and the Fish Canyon Tuff, a frequently used age standard in geochronology, yield statistically identical track length distributions when comparing conventional and selFrag Lab separation methods. This study yields a first confirmation that selFrag Lab processing does not cause annealing under the applied machine settings and seems to provide an alternative method for rock disaggregation for apatite fission track analysis.

Reference

Surface and electronic structure effects on interfacial charge transfer at iron oxide nanoparticle surfaces

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Transition metal oxides and oxyhydroxides form important reactive nanomaterials in certain terrestrial environments. There is considerable interest in defining and understanding nanoparticle reactivity with respect to (bio)geochemical processes, but the task is challenging due to the complex interplay of structural and chemical properties in nanoscale solids. Iron oxide and oxyhydroxide nanoparticles are of particular importance, participating in redox cycles driven by (bio)geochemical processes including inorganic precipitation, (photo)reduction and microbial metabolism. The reductive dissolution of such nanoparticles is an important link between biological and mineral geochemistry. For example, dissimilatory iron reducing bacteria use fine grain iron oxyhydroxide nanoparticles as terminal electron acceptors during anaerobic carbon respiration. Interfacial electron transfer is a key step in such reductive transformations, and is highly sensitive to the interaction between the electron donor and the surface and electronic structure of the substrate.

Soft x-ray spectroscopy can reveal the electronic structure of semiconductor minerals [1] and nanoparticles [2] and is anticipated to be a versatile method for predicting the thermodynamic basis of charge transfer at nanoparticle surfaces. Nanoscale iron oxide and oxyhydroxide nanoparticles exhibit modified electronic structure [2] that would alter the ability of surface adsorbed electron donors to drive reductive dissolution. However, aqueous chemistry studies that attempt to validate these predictions are difficult to interpret on the basis of the x-ray spectroscopy data alone.

We discuss ways to distinguish (i) the thermodynamic and kinetic controls on iron oxide nanoparticle reduction and (ii) the electronic and structural causes of modified reactivity. Optical and infrared spectroscopy do not detect differences in the binding of bidentate organic ligands to iron oxide bulk and nanoparticle surfaces, suggesting a minor effect of modified surface structure. However, deviations from the anticipated the pH-dependence of photoreactivity [3] suggests there may be considerable heterogeneity in nanoparticle redox behavior.

References

Phosphoric acid fractionation factors for aragonite between 25 and 72°C with implications on aragonite-calcite oxygen isotope fractionation

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We determined the intramolecular kinetic oxygen isotope fractionation between CO2 and CO32- during reaction of phosphoric acid with aragonite and calcite between 25 and 72°C. We analyzed clear single aragonite crystals from Bilina (Czech Republic), Leogang (Austria), and Agrigento (Italy), a fine-grained coralliform aggregate from the Styrian Erzberg (Austria), and for comparison calcite NBS-19. The aragonites show a wide range of total oxygen isotope values from 17.5 to 39.5‰ (VSMOW). Our result for NBS-19 (28.76‰ VSMOW) is within 0.12‰ of the recommended value.

The oxygen isotope fractionation between acid-activated CO2 and aragonite at 25°C expressed as a 1000ln value is consistent for our samples with 11.14 ±0.20‰ (n=4). Our new value is significantly larger than the commonly applied values of 10.34 or 10.20 (Sharma and Clayton, 1965) and our new value for calcite NBS-19 (10.08‰), but is similar to those of synthesized aragonite reported by Kim and O’Neil (1997). At temperatures between 25 and 72°C, the phosphoric acid fractionation (PAF) of aragonite can be expressed as:

\[ 1000\text{ln} \alpha_{\text{PAF}} = 5.32*(1000/T[K]) + 5.07 \]

Our results imply that the published equilibrium 18O/16O fractionation factors between aragonite and water (e.g. Kim et al. 2006) need to be revised. Considering our new acid fractionation factors, oxygen isotope fractionation between aragonite and calcite is very small (~0.2‰) as suggested by recent theoretical calculations (Schäuble et al. 2006).

References
Geothermometry of oxidized Zn-Pb ores: Oxygen isotope systematics and a new femtosecond laser technique on monophase fluid inclusions

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We studied the 18O/16O systematics of carbonate minerals from supergene oxidized Zn-Pb deposits and from submarine alteration of ancient slags to constrain oxygen isotope fractionation factors for smithsonite, cerussite, and phosgenite. The temperature dependence of oxygen isotope fractionation between Pb and Zn carbonate minerals and water below 100°C can be expressed as

\[
1000 \ln \alpha_{\text{cerussite-water}} = 2.29 \left(10^6 / T[K]^2\right) - 3.56
\]

\[
1000 \ln \alpha_{\text{smithsonite-water}} = 3.10 \left(10^6 / T[K]^2\right) - 3.50
\]

\[
1000 \ln \alpha_{\text{phosgenite-water}} = 2.55 \left(10^6 / T[K]^2\right) - 3.50
\]

Average formation temperatures of the studied supergene deposits (SW Sardinia, E Belgium, Broken Hill district, Australia, and others) are calculated to be 20 ± 5°C using the estimated isotope compositions of local paleometeoric waters.

We also applied a new technique using a femtosecond laser to nucleate the vapor bubble in monophase fluid inclusions. Homogenization temperatures of inclusions in cerussite and hemimorphite from the same deposits range from +6.1 to +25.5°C and confirm our stable isotope results.

New fluid inclusion and oxygen isotope data from willemite-bearing oxidized Pb-Zn ores from E Belgium and S Portugal, however, suggest that certain mineralization stages in these districts were formed by distinct low-temperature (<50°C) hydrothermal systems involving saline fluids.

Thus, oxygen isotope and fluid inclusion data for base metal carbonate minerals can be used to distinguish ores produced by weathering from very-low-temperature hydrothermal ores. They may also provide valuable paleoclimatic information.

Organic geochemical assessment of the onset of an Oceanic Anoxic Event

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A geochemical study was conducted on cored Posidonia Shale sections and underlying sediments derived from two wells located in the southern North Sea offshore the Netherlands. Samples were subjected to a variety of analytical techniques including CS analysis, Rock Eval pyrolysis, GC-MS and carbon and sulphur isotope analysis. It is well established that the Posidonia Shale (Early Toarcian) is marked by the deposition of organic-rich shales throughout Europe as a result of an Oceanic Anoxic Event (OAE). Our data provides evidence that establishment of these anoxic conditions is a gradual process from sediment anoxic conditions into true anoxia within the Posidonia Shale. This is indicated by the depth profile of most of the measured parameters. The values of sulphur content, TOC, hydrogen index, Ts/Tm ratio and pristane/phytane ratio gradually increase in the underlying sediments with decreasing depth towards the Posidonia Shale. Within the Posidonia Shale the values of those parameters remain constant.

The carbon isotope data show a negative excursion within the Posidonia, in agreement with earlier reports. This indicates that OAE might have been a global event. Our research focuses, among others, on the question whether this proto OAE development can be recognised throughout the basin.

![Figure 1: Illustration of the carbon isotope excursion (approximately 7 ‰) in the Posidonia Shale (shaded region)](image-url)
Oceanic hornfels: Records of heat transport near axial magma chamber roofs

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The transfer of heat from the lower to upper ocean crust is the most fundamental process shaping the morphology of mid-ocean ridges and determining the mechanism of accretion of the lower crust. At fast-spreading mid-ocean ridges, the heat that drives high temperature hydrothermal systems is focused at the top of axial magma chambers (AMCs) that reside 1–2 km beneath the seafloor. Theoretical models predict that heat is exchanged across thin (<100 m), hot (>650°C), impermeable conductive boundary layers (CBLs) sandwiched between AMCs and permeable upper crust. The thickness of the CBL is predicted to vary with time, in response to magmatic activity and would have a finite life that is dependent upon the longevity of an AMC. Thus, CBLs are not static features, but rather should vary in thickness and position, depending on the magma supply and frequency of diking. While conceptually robust, there is sparse evidence in support of these predictions, perhaps because CBLs are transient and short-lived, thus preventing their preservation.

The expected characteristics for CBLs were recognized within hornfelsic dikes found within a contact aureole at the base of the sheeted dike complex in the Troodos ophiolite (Gillis and Roberts, 1999), and dikes intruding the uppermost gabbros in the Oman ophiolite and two regionally extensive tectonic escarpments of young fast-spreading East Pacific Rise crust exposed at Pito and Hess Deeps. These very fine-grained, granoblastic hornfels occur either as in situ dikes or xenoliths in the gabbro sequence. Where in situ, they form massive, indurated outcrops that lack the common ladder-like fracture patterns of sheeted dikes. Hydrothermally altered dikes are partially to completely recrystallized to pyroxene and/or hornblende hornfels, recording episodes of re-heating at 750–1050°C. Field relationships and temperature constraints indicate that the heat flux across the CBLs is 12–33 Wm−2, similar to the latent heat of crystallization released to build a vertical thickness of 6 km crust. These are also similar to normalized values for hydrothermal plumes (20–40 MW/km), indicating that the heat that drives hydrothermal convection is transferred across a conductive boundary layer.

Collectively, widespread distribution of hornfelsic dikes at or just below the sheeted dike – gabbro transition indicate that thermally metamorphosed rocks are common feature in ocean crust. I will argue that these thermally metamorphosed rocks are remnants of preserved CBLs that record the migration of magma–hydrothermal boundaries, thus providing tangible evidence for AMC dynamics.

Assimilation of the plutonic roots of the Andean arc: Evidence from CO2-rich fluid inclusions in olivines

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Assimilation of young plutonic rocks by magmas of similar compositions is not easily seen in isotopic signatures because of their low isotopic contrast with the magmas. However, variability of trace element ratios in Tatara-San Pedro basalts (SVZ of the Andes) suggests assimilation (Dungan et al., 2001). Mineral inclusions and healed microfractures (HMF, Dungan and Davidson, 2004) show the xenocrystic nature of their crystals.

We compare olivine xenocrysts from a basaltic unit with amphibole- and phlogopite-bearing gabbroic xenoliths from a Holocene dacite (Costa et al., 2002) and analyse the contents of their HMFs using SEM, electron microprobe, Raman spectroscopy, microthermometry and LA-ICP-MS.

The better preserved fluid inclusions and textures in xenoliths reflect interactions between CO2-rich, saline H2O-bearing fluids and gabbroic intrusions. This subsolidus history then influences the partial melting and assimilation of the gabbros at the contact of the dacite host. The presence of hydrous minerals, especially micas, favours melting even at moderate magmatic temperatures.

In olivine xenocrysts from the basaltic units, most of the healed microfractures have been reopened upon ascent or eruption, thereby partly destroying the subsolidus signal. Diffusion modeling on iron-rich zones along the HMFs give a very short residence times (a few hours) suggesting syn- or post-eruptive healing. This is easily explained by the higher temperature of the basaltic host compared to the dacite. However some fluid inclusions are preserved and their similarity with those found in the xenoliths suggests similar origins for the xenocrysts.

Distinct mineralogical assemblages between xenocrysts-bearing basalts (olivine + plagioclase + clinopyroxene) and the gabbroic xenoliths (lacking clinopyroxene) show the diversity of the plutonic crust that was sampled by these magmas. Variable amounts of micas and amphiboles in the original gabbro will influence the chemical effect of assimilation on the bulk rock chemistry of the host magma.

References
**Proton and lead adsorption onto roots of the grass species**

*Festuca rubra*

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Metal adsorption onto biological surfaces can significantly affect metal speciation and mobility in near-surface environments. Cell wall adsorption, whether involving bacterial or root cells, is likely the first step in nutrient acquisition, but can affect the distribution of heavy metals and radionuclides as well. Many previous studies have focused on bacterial cell wall adsorption. However, plant roots can adsorb a range of metals as well. Quantifying metal adsorption onto plant root surfaces will assist in understanding the speciation of metals in complex soil systems, and can provide insights into how plants compete with soil bacteria for metal nutrients.

In this study, we measured proton and Pb binding onto roots of *Festuca rubra*, a species of grass commonly referred to as red fescue. Potentiometric titrations were performed on washed root material, using 0.1 M NaClO₄ to buffer ionic strength. Like bacteria, the roots exhibited continuous buffering behavior from pH 3 to 9. We use a discrete-site non-electrostatic surface complexation model (SCM) to constrain acidity constants and concentrations for root cell wall functional groups from the titration data. The Pb adsorption experiments were conducted at fixed Pb and root concentrations, with fixed ionic strength, as a function of pH. The roots displayed a typical adsorption edge, with the extent of adsorption increasing with increasing pH, and we use the Pb adsorption data to constrain the values of the thermodynamic stability constants for the important Pb-root surface complexes.

Our results indicate that the cell wall material associated with *F. rubra* roots has a different functional group chemistry than the cell wall material associated with bacteria. Nevertheless, plants and bacteria show a similar overall ability to uptake metals. We use the modeling results from this study to estimate Pb distributions in realistic soil systems containing root material, bacterial cells, and mineral surfaces, and we demonstrate that each reservoir can be important in determining the distribution of Pb in soil settings.

**Direct evidence of the feedback between climate and weathering**

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The major long term climate moderating process on the surface of the Earth is the link between climate and chemical weathering through the greenhouse effect; the higher the temperature, the faster the weathering rate and CO₂ sequestration. Weathering releases divalent cations to the ocean via riverine transport, either in dissolved and suspended form, where they promote the drawdown of CO₂ from the atmosphere by carbonate mineral precipitation (e.g. Walker et al. 1981; Gislason et al. 2006). To test this widely held hypothesis, we performed a field study determining the weathering rates of 8 Icelandic watersheds over the past 40 years. The annual average temperature of individual watersheds increased by 0.4 to 1.4 °C. Precipitation increased or decreased depending on the catchment. Riverine transport of weathering products from each watershed has continuously increased. The increase in dissolved riverine inorganic carbon and calcium transport range from less than one percent to 70 percent for the period 1960 to 2000. The riverine suspended inorganic particulate matter in the same catchments for the same period has increased by 2 – 600 percent. These results clearly indicate 1) the strong feedback between climate and Earth surface weathering, and 2) that the climate moderating effect of weathering, and therefore atmospheric CO₂ sequestration, may be far faster than previously thought.

**References**

The sedimentation rate controls microfossil preservation

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One of the greatest challenges to finding definitive evidence for life on early Earth is the discovery of well preserved fossils. The microscopic, soft bodied organisms that are expected to dominate early or extreme environments do not preserve well. Several laboratory studies have recreated microbial “fossils” \cite{1, 2}, but the conditions under which microfossils are formed in natural environments are still poorly understood. Knowing these conditions and being able to predict where they occur are key factors to discovering preserved microorganisms. Exposure to iron in particular appears to control the formation of microfossils in many terrestrial and marine environments \cite{3}.

We present new data from oolitic ironstones at the Callovian-Oxfordian boundary in the eastern Jura mountains of northern Switzerland linking the preservation of fossil microorganisms to the depositional environment and to the concentration of iron. The lowest Oxfordian deposits contain lithic- and bioclasts, which are indicative of a highly condensed sequence with reworking and a sedimentation hiatus. In this sequence, filamentous, tubular structures of 1-2 μm are found in ferriferous encrustations and goethitic ooids. The filaments appear identical to those formed by a recently characterized modern analog, the NO\textsubscript{3}- reducing, iron-oxidizing bacteria. Depositional sequences from the upper Callovian stage exhibiting a higher sedimentation rate do not contain the same structures. We hypothesize that 1) the activities of iron-oxidizing and -reducing bacteria contributed to the form of iron that was accumulated and 2) a hiatus in sedimentation during development of the sequence enabled the microbial structures to be preserved. In contrast, when the sedimentation rate was increased, the burial of the microorganisms facilitated the breakdown of their associated structures. We suggest that this environment provides a model system for establishing the relationship between sedimentation and the preservation of soft bodied, microscopic organisms.

References

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Single crystal X-ray refinement and thermodynamic properties of stoichiometric jarosite, KFe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}

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Jarosite and related minerals are invariably found in natural environments acidified either through the action of acid rain or by acidic mine drainage. In spite of their importance and common occurrence, the data which could describe the solubility, precipitation, and distribution of elements between jarosite and aqueous solutions are fragmented or questionable.

The first goal of this study is to prepare stoichiometric jarosite samples for further thermodynamic investigation. We have synthesized only jarosite samples which have been prepared according to the published procedures \cite{1} by oxidizing metallic iron in acidic K\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2-}-containing solutions under hydrothermal conditions. Iron was added in the form of an iron wire. Synthesis was carried out in a Teflon cylinder placed into a conventional oven at 200°C. The yellow product was readily identified by X-ray diffraction (XRD) as jarosite and no other crystalline phases were detected. The yield of the synthesis was 230 mg. The single-crystal XRD refinement for the sample with \(R_i=0.0316\) for the unique observed reflections \((|F_o| > 4\sigma_F)\) and \(wR_i=0.0423\) for all data gave the unit-cell parameters \(a = 7.288(1)\) and \(c = 17.203(4)\) Å. The Fe site occupancy in this sample is 97(1) %, significantly higher than the ~85 % reported from a conventional synthesis routes.

The second goal of this study is to determine thermodynamic properties of the jarosite sample. The thermodynamic measurement will be carried out using acid-solution calorimetry to obtain the enthalpy of formation. Heat capacity and entropy at standard temperature and pressure will be measured by adiabatic calorimetry. The measured enthalpy and entropy will be combined to a Gibbs free energy of formation. Then we will proceed to refine the existing values by comparing them to phase equilibrium data, either in nature or laboratory.

The data which will be presented can be used to calculate phase diagrams for this group of phases at conditions relevant to low-temperature geochemical processes (25 °C, 1 bar), metallurgical treatment (75 – 110 °C), and stability of phases on the surface of planets.

Reference

**In situ redox chemistry of hydrothermal fluids at the Loihi Seamount Microbial Observatory**

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Loihi Seamount is a submarine, active volcano located on the southeast flanks of the Big Island of Hawaii. It is considered to be the youngest volcano in the Hawaiian chain, sharing the hot spot magma chamber with Mauna Loa and Kilauea. Sites of both vigorous and diffuse hydrothermal venting can be found surrounding the pit crater summit (~1000m) and on the flanks of the seamount, down to its base (~5000m). Vent fluids at Loihi are chemically distinct from other well-studied marine hydrothermal systems and have been shown to be enriched in carbon dioxide, iron(II), and manganese(II), and deplete in sulfur species. The Loihi summit is located within a zone of low oxygen, further enabling elevated iron(II) concentrations and support for a dominant community of iron-oxidizing bacteria.

We deployed a combination of a sensor wand consisting of up to four voltammetric working electrodes and the ROV Jason temperature probe, and/or a submersible micromanipulator with voltammetric electrodes to provide real time in situ redox characterizations of hydrothermal fluids and geochemical gradients associated with iron-oxidizing microbial mats and flocs. Our in situ electrochemical analyses provided an efficient and valuable means for directed discrete sampling of hydrothermal fluids and microbial flocs, as well as previously unattainable high spatial resolution geochemical profiles through the mats.

**Automated fission track dating of apatite and monazite by image analysis and ICP-MS**

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The microscopic identification and counting of fission-tracks in accessory minerals by a manual observer has been a significant limitation to the widespread adoption of fission track dating (FTD). Manual counting methods require a high level of observer skill and calibration, and provides a practical limit to the number of tracks counted and hence on the precision achieved. It has long been hoped that automated methods for track recognition and counting could enhance the objectivity of fission-track analysis, and improve both precision and overall productivity. We have recently developed a new image analysis method, called 'Coincidence Mapping', that for the first time shows great promise in achieving these aims.

Another limitation in traditional FTD arises from the use of thermal neutron irradiation to induce more fission-tracks as a proxy for uranium abundance in the same area counted for fossil fission-tracks. While providing an elegant analytical solution at the ppm level with high spatial resolution (typically <100µm), this approach involves sample turnaround times of mostly several months. Laser-ablation ICP-MS techniques are now able to provide rapid uranium analyses with similar spatial resolution to the older method (Hasebe et al., 2004). This approach greatly improves sample throughput, but has the disadvantage that the target grain and its fossil fission-tracks are destroyed. A combination of automated fission-track counting and laser ablation ICP-MS analysis, however, should prove particularly advantageous.

Implementation of our automated fission-track counting system requires a microscope with both transmitted and reflected light optics, a motorised stage and digital microscope camera, all under computer control. The software system consists of an image acquisition module that automatically acquires a series of reflected and transmitted light images at each area selected for counting. These are archived and a separate automated counting and review module is then used offline to analyse the data. The archived images constitute a digital replica of the mineral grains which are then analysed by laser ablation ICP-MS using the stage coordinates to control positioning. The system has so far been applied successfully to fission track dating of accessory apatite and monazite.

**Reference**

Water column structure of the Eocene Arctic Ocean from Nd-Sr isotope proxies in fossil fish debris

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Nd-Sr isotopic compositions of Eocene fish debris (teeth, bones, scales) and reduced organic coatings reveal details of Arctic Ocean Basin water column structure at Lomonosov Ridge. Nd in marine fossil fish debris is acquired post-mortem at the sediment-water interface, recording bottom water composition; Sr is metabolized by fish (in this case a variety of smelt) living in equilibrium with their surroundings, recording the 87Sr/86Sr of the photic zone. Samples from IODP Expedition 302 all record isotopic values consistent with a brackish-to-fresh water surface environment (87Sr/86Sr = ~0.7079-0.7087) that was poorly mixed with Eocene global seawater (~0.7077-0.7078). Leaching experiments show reduced organic coatings to be consistently more radiogenic (~0.7090-0.7094) than cleaned ichthyolith phosphate. Ichthyolith Sr isotopic variations likely reflect changes in localized river input as a function of shifts in the Arctic hydrologic cycle. We suggest that 87Sr/86Sr might be used as a proxy for salinity of surface waters. Model mixing calculations indicate salinities of ~5 to ~20 per mil, close to but lower than estimates based on O isotopes. Significant salinity drops (i.e., 55 Ma PETM and 48.5 Ma Azolla event) do not show large excursions in 87Sr/86Sr. Epsilon Nd in cleaned ichthyoliths (-5.7 to -7.8) overlaps Neogene Arctic Intermediate Water (B. Haley, pers. comm.), distinct from modern AFW (-10.5) and North Atlantic Deep Water. Eocene ichthyolith Nd may record some deep-water exchange with Pacific/Tethyan water masses, but inputs from local sources are also permissible. The Sr-Nd isotopic record is consistent with highly restricted basin-wide circulation in the Eocene, indicative of a poorly mixed ocean and highly stratified water column with anoxic bottom waters. A stable, “fresh” water upper layer was likely a pervasive feature of the Eocene Arctic Ocean, recording enhanced continental runoff during an unprecedented warm interval lasting from the 55 Ma PETM to the first appearance of ice rafted debris at ~45 Ma.

Trace element zonation of plagioclase from the Kunene Intrusive Complex (NW Namibia)

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The Mesoproterozoic Kunene Intrusive Complex (NW Namibia) consists of two main anorthosite bodies. A pale coloured so-called white anorthosite is intruded by the dark anorthosite which comprises leucogabbroanorrites, anorthosites and leucotroctolites. Anhedral cumulus plagioclase of the white anorthosite is often turbid due to post-emplacement alteration. The An contents range from 40 to 50 mol.%. Individual grains either display a constant composition or minor An variations (±5 mol.%) which in some grains appear oscillatory with wavelengths of up to 1000 µm.

Anhedral to subhedral tabular coarse cumulus plagioclase of the dark anorthosite is optically clear and contains dust like Fe-Ti oxide inclusions. The An contents range between 43-75 mol.%. Some plagioclase phenocrysts display oscillatory zoning with wavelengths of up to 1500 µm and differences in the An-content of up to 8 mol.%, whereas others are characterized by a homogeneous composition.

Oscillatory zoning patterns of plagioclase from both anorthosite units are interpreted to be ingneous in origin, reflecting movements of the crystals in the magma reservoir. Plagioclase phenocrysts that display a nearly constant composition, on the other hand, are suggested to be affected by a post-magmatic reequilibration.

Since plagioclase is the main mineral present in anorthosites, major and trace element zoning patterns can provide important information about processes like cumulate formation, ascent of magma, and possibly also post-emplacement alteration. LA-ICP-MS analyses on profiles across plagioclase phenocrysts are in progress to examine the behaviour of the trace elements during the different stages of anorthosite formation.
Exhumation histories of high-pressure rocks: New insights from Rb-Sr geochronology

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High-pressure (HP) rocks can be considered as 'flight recorders', potentially recording their individual P-T-time-deformation path through evolving orogens. Reading the flight recorder requires both deciphering of the geochronological information, and correlating it with data on pressure, temperature and tectonometamorphic processes. Isotopic signatures of minerals, like the Rb-Sr system of white mica, has long been considered as particularly sensitive to temperature. This often prompted direct translation of sets of mineral ages into cooling histories, with inference of exhumation paths from thermal histories. However, this approach is problematic because microscale spatial correlations of isotopic ages with mineral growth zonation and recrystallization fronts (Vance et al. 2003) indicate that factors like availability of fluids, mineral recrystallization, and the modal rock composition similarly play vital roles in determining whether an isotopic system remains closed.

As an alternative approach, assemblages which remained closed for intermineral isotope exchange can be used to generate Rb-Sr 'event ages' for specific metamorphic processes. It is shown that the Rb-Sr system of white mica in eclogite may persist unchanged even through very high temperatures (>650°C). Key requirements for this high thermal stability are a) absence of free aqueous fluids after crystallization, evidenced from absence of fluid-mediated retrogression reactions, and b) modally controlled closed system behaviour, i.e., presence of white mica in an assemblage solely of phases like garnet and omphacite which do not allow for significant diffusional Sr isotope exchange even at the highest temperatures reached. A valid Rb-Sr multimineral isochron comprising all phases of an eclogite assemblage can be interpreted as dating eclogitization (cf. Glodny et al. 2005), and directly linked to PT data from the same sample to constrain eclogitization conditions.

The same concept applies to assemblages formed later in a HP rocks’ history. Veins, precipitated from fluids during exhumation, may be used to determine age and PT conditions of amphibolite- or greenschist facies overprints. Different event ages combine to an exhumation history, established beyond the pitfalls of closure temperature theory. Using examples from the Tauern Window (Austria) and the Bergen Arcs (Norway), the potential of this approach to precisely constrain contrasting exhumation histories is demonstrated.

References
Inferences for the style of subduction in the Carpathian-Pannonian region based on boron signatures

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Miocene calc-alkaline (CA) volcanic suites – more or less parallel with the Carpathian Mt. range – suggest a southwest-westward subduction process. Indeed, composition of the CA volcanic rocks shows typical subduction-related features, such as elevated LILE and relatively depleted HFSE. Boron, a fluid-mobile, incompatible trace element can be effectively used to monitor the subduction influence along the arc. In general, the boron concentration of the CA volcanic rocks of the region is typical of subduction-related magmas; however, it shows both significant spatial and temporal variations.

In the western segment of the arc, we cannot see a clear variation in the B content, nor in the B/Nb ratio towards the back-arc region, such as was found in other arcs (e.g., Japan and Kurile, Kamchatka). However, a gradual temporal decrease of these values can be observed. These features can be explained by the strong connection of the CA volcanism in this segment to the lithospheric extension of the Pannonian Basin, more than to the southward dipping subduction.

In the eastern segment of the region, the volcanic arc is narrower. Here, volcanism is getting to be younger towards the southeast. The boron content is increasing to the south along the arc; however, a sharp decrease can be observed at South Harghita. This is consistent with the change in the overall composition of the volcanic rocks and the position of the Trotus fault, which divides two main lithospheric domains.

In the northeastern part of the arc, a kind of transition is observed. At first sight, no correlation can be recognized between the B content and the spatial and temporal distribution of the volcanics. But separately, in the more basic and in the more silica rich rocks, we observe a B content decrease towards SSE. The present volcanological information is too incomplete to understand this. It may indicate the influence of the subduction-related fluids originating from a previously existing subducting slab under the Tokaj region.

Electrodynamic disaggregation of geologic material

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A series of tests were run on a selfFrag Lab electrodynamic disaggregation machine produced by selfFrag AG, Langenthal, Switzerland. The operation principle is an electrical discharge passing trough a non-conductive material (e.g., rock) immersed in a dielectric liquid. The electrical pulses are of very short duration (<500 ns). In this case, the solid material becomes the better conductor, and hence the electrical “discharge channel” will pass through the solid material. High amounts of energy are deposited along this discharge channel leading to local temperature of up to 10000 °K and pressures of up to 1010 Pa (Rudashevsky et al., 1995; Andres and Timoshkin, 1997), thus conditions reached by using conventional explosives.

The tests using different geologic material immersed in deionised water showed that electrical discharges as low as 80 kV and a few hundred pulses at a frequency of 1-5 Hz are commonly sufficient to disintegrate rocks or other mineral aggregates. Accessory minerals separated at voltages of 80 – 100 kV retain their original shape (e.g. zircon, apatite, magnetite); the minerals may break under increased energy input. Sieves replacing the reactor vessel bottom allow small enough material to be removed during operation, and hence to prevent further grain size reduction. Major rock constituents generally disaggregate mainly along internal impurities or fissures, leading to a grain size reduction. However, the minerals contain fewer inclusions. Rare artefacts of the method are formation of melt films, and contamination by very small particles derived from the electrode material. The amount of contamination from the electrode material is much lower than by using conventional crushing methods. A closed disposable microcontainer allows to disaggregate sub-gram samples for microanalysis minimizing loss. Preliminary result did not show negative effects on isotopic systems.

Major advantages in comparison with conventional methods (jaw crusher, vibration disk mill, ball mill) lie in the reduction of fines, the omission of dust, the production of inclusion-free and/or isometrically shaped products, and the reduction of cross contamination.

References
From phosphors to ceramic magnets
stability, crystal chemistry and
applications of hexa-aluminitates
and -ferrites

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The groups of hexa-aluminates and -ferrites exhibit a wide
range of applications. From lamp phosphors in the case of Ba-
aluminates (Eu & Mn doped – green, Eu doped – blue
luminescence) to ceramic magnets such as Sr-ferrites doped
with Co and La a wide range of daily applications can be
presented.

In the group of hexa-phases compounds exhibiting
magnetoplumbite- and beta-alumina structures are stable. A
wide crystal chemical variety gives rise to numerous
properties with large potential for chemical fine tuning.

Phase relations and crystal chemical aspects like solid
solution series in the multicomponent systems
CaO/SrO/BaO/EuO/La2O3 – Al2O3/Fe2O3 – MgO/CoO are
presented and discussed. The crystal structures present can be
explained as mixed layer structures. Starting from the spinel
structural type modifications consisting of rock salt-units and
perovskite-units build up the different hexa-phases.

Furthermore shaping aspects like ceramic foams
consisting of Ca-aluminates aiming towards catalytic
applications will be presented.

Indications for pedogenic formation
of perylene in terrestrial soil:
First results from stable carbon
isotope ratios

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Concentrations and isotope compositions of polycyclic
aromatic hydrocarbons (PAHs) were determined in natural
soils of Southern Germany. Surprisingly, perylene
concentrations increased with soil depth when compared to the
other PAH compounds present, but only in specific profiles.
Its low solubility made vertical transport by seepage water
unlikely. We therefore stipulate atmospheric deposition of
combustion-derived perylene in the top-soil and in-situ
generation in the sub-soil of these selected profiles. This could
have been caused by microbial activities or other catalytic
processes yet unknown. In order to distinguish between
pyrogenic and natural generation we compared compound-
specific \[^{13}C/^{12}C\] ratios (\(\delta^{13}C\)) between perylene and other
PAHs in samples from the top-soil and from the sub-soil.
Despite high amounts of co-extracted non-target compounds
and low perylene concentrations relative to other PAHs
(benzo(e)pyrene and benzo(a)pyrene) successful clean-up of
the extracts led to determination of a unique \(\delta^{13}C\) value for
perylene in the upper horizon. The \(\delta^{13}C\) value of perylene in
the sub-soil was 3.4 permille more negative than for top-soil
perylene, and 5.2 permille more negative than other equal-
mass PAHs (with m/z of 252) in the top-soil. Future work will
include isotopic characterization of atmospheric input and in
situ synthesis of PAHs.
Modelling continental weathering: from the lab to the field

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CO₂ consumption through continental silicate weathering at the watershed scale has been generally described as a parametric function of mean annual continental runoff and temperature, based on river chemistry. These mathematical expressions have been successfully used in numerical modelling of the evolution of the past geochemical cycles and climate. They have the advantage of integrating numerous processes (hydrologic, biogeochemical, and kinetic) and to rely directly upon field constraints, but they leave us without any access to the intimate processes of chemical weathering, and do not allow a hierarchization of its controlling factors. Here we present sensitivity tests performed with the WITCH numerical model which describes weathering in soil profiles through vertical multiple box modelling based on a rigorous description of mineral-water interactions. This model is coupled to a vegetation productivity model, and we explore the response of continental vegetation on weathering. We also test the impact of using laboratory-based kinetic weathering rates to estimate the main cation fluxes exported from the soil profile. We show that such method does not lead to any large overestimation of the CO₂ consumption, if the chemical affinity of reactions, and secondary minerals precipitation rates in soils are accurately accounted for. Sensitivity of the kinetic model WITCH to drainage and annual mean temperature is compared to the sensitivity expected from field parametric laws. Particularly, we show that parametric laws underestimate by one to two order of magnitude the weathering rates at low runoff (below 100 mm/yr), while the agreement is good at higher runoff. Although the specific contribution of the low runoff areas to the CO₂ consumption is low, they are typical of the weathering regime of 44 % of the total continental surface.

Interaction of calcite with Cr(III) and evidence for direct inorganic formation of vaterite

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The interaction of freshly cleaved \{10 \bar{1} 4\} calcite surfaces with 100 mg/L (~2 mmol/L) Cr(III) solutions was investigated at room temperature under atmospheric conditions using in-situ AFM for a time-period of up to 20 min. It was observed that the initial typical nanoscale dissolution features (rhombohedral etch pits) are successively filled with matter up until the final overgrowth of spheroidal-like particle aggregates. Ex-situ experiments with variable time exposures (1 min, 20 min and 1 month) were also carried out in order to study the surface of the interacted calcite crystals using a combination of techniques. A detailed SEM-EDS, XRD and FTIR study of the experimental products revealed that the surface precipitates consist of amorphous Cr(III) hydroxide/oxyhydroxide phases. EPMA (WDS) elemental maps on polished-thin sections of teeth-like material removed from the solid interface after long-term interaction (1 month) indicated the formation of a peculiar carbonate phase containing both Ca and Cr in variable concentrations. It should be noted that distinct Ca carbonate (or even hydroxycarbonate) solid phases containing Cr(III) are rather unknown in nature, except maybe the case of a meteorite. Preliminary computational investigations showed a difficulty of Cr³⁺ ions to be hosted in the calcite surface structure.

On the other hand, detailed XPS and Laser µ-Raman studies of \{10 \bar{1} 4\} calcite surfaces interacted for 20 min with Cr(III) solutions indicated the presence of vaterite. In this case, the thickness of the Cr(III)-modified carbonate surface was investigated using accelerator-based techniques, namely ¹²C-RBS. The formation of vaterite on the surface of calcite, and in general the direct inorganic formation of vaterite in the presence of Cr(III)₉⁺, was also confirmed by means of macroscopic experiments aiming at crystal growth of CaCO₃ into appropriate glass tubes filled with Cr(III)-doped hydrogel.
Extreme Hf isotope signals from basement weathering and its influence on the seawater Hf-Nd isotope array

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Differential weathering of Lu and Hf host minerals in rocks leads to Hf isotope composition of river water with a more radiogenic composition than the bulk rock that they drain [1]. In contrast, the Nd isotope composition of river water is very similar to that of bulk rock due to congruent weathering of Sm and Nd from their shared mineral hosts. We measured Hf and Nd isotope ratios in seawater and from the Hudson River in NY. The Hf isotopic composition of the upper Hudson draining Grenville-aged metamorphic rocks is extreme, with εHf values of +24 to +128. Associated marble and amphibolite bedrock have normal crustal εHf values (0 to –11), whereas apatite and garnet from these rocks have εHf values as high as +2250 and +103 [2,3]. In contrast, Nd compositions of the upper Hudson are similar to bulk rocks (εNd = –8). After the Mohawk River, which drains Orдовician-Devonian limestone and shale, joins the main stem of the Hudson, river water εHf and εNd decrease to +6 and -10. On the New Jersey Bight, εHf and εNd are +3 and -8.

The Hf and Nd isotope composition of filtered seawater in the Atlantic overlap data for ferromanganese nodule crusts. Vertical profiles exhibit almost negligible εHf gradients suggesting rapid vertical, but little lateral, transport. Surface water εHf is less radiogenic close to the Saharan dust plume suggesting an eolian source of Hf with a signal that is not fractionated through weathering processes.

We suggest that the radiogenic Hf character of the seawater Hf-Nd array is due to the preferential weathering of high Lu/Hf phases in basement rocks such as apatite. When this source rock is old evolved crust, dissolution of these high Lu/Hf phases contributes a very radiogenic Hf isotope composition, as evidenced by the upper Hudson river water samples. This differential chemical weathering will be prominent at times when there are no glaciers, and particularly prominent when glacial action has exposed fresh surfaces containing less resistant minerals to weathering [4].

References
Cosmogenic nuclide intercalibration and erosion rate study on fault scarps of the Bishop Tuff, CA, USA

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The Bishop Tuff in eastern California is a welded ignimbrite deposit that erupted 760 ± 2 ka ago from the Long Valley Caldera, as dated with 40Ar/39Ar on sanidines [1]. Surface samples from the Bishop Tuff were collected for comparing the production rates of cosmogenic nuclides (3He, 21Ne, 10Be, 26Al) in various minerals available in the sampled ignimbrite unit, like quartz, pyroxene, magnetite and sanidine. Although the Bishop Tuff has experienced erosion and absolute calibration is thus not possible, still production rate ratios can be assessed. So far, 20 samples have been analyzed for the 21Ne concentration in quartz. For one of those samples, 3He and 21Ne have been determined in coexisting clino- and orthopyroxene. The concentrations of cosmogenic 3He are difficult to assess due to possible contributions of both magmatic and nucleogenic 3He. However, the ratios of cosmogenic 21Ne(ox)/21Ne(qz) and 21Ne(ox)/21Ne(qz) are ~1.23 and ~1.45 respectively. In comparison, using the elemental production rates of Kober et al. [2005] [2], would imply ratios of 21Ne(ox)/21Ne(qz) 1.38 (cpx) and 1.50 (opx) for the chemical composition of these analyzed pyroxenes. In the near future we would also like to determine the production rate ratios 21Ne/10Be and 21Ne/26Al in the same quartz samples.

In addition to the production rate nuclide intercalibration, we performed an erosion rate study at the Bishop Tuff. We sampled the footwalls of 3 normal fault scarps, extending from the fault center to the tapering end, that run N-S through the SW of the Bishop Tuff due to tectonic extension of the area. 18 preliminary exposure ages – calculated from 21Ne concentration in quartz – range from 260 to 505 ka, i.e. ~35 – 70 percent lower than the eruption age of the Bishop Tuff. The discrepancy shows that about 1.0 to 1.8 m of material has been removed since the eruption. The 21Ne ages vary rather systematically with the oldest ages mostly at the tapering ends of the scarps and the youngest ages at the fault centers where the vertical displacement is maximal. As the faults are active and they propagate [3] our data indicates that the process of erosion is more pronounced on the fault centers compared to the lower fault tips. In general, ages from bedrock samples (n = 14) show more variation than desert pavement samples (n = 4).

References

Crystal orientation selection during growth of brachiopod shell calcite

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The progresses in the technique of electron backscatter diffraction (EBSD) in combination with SEM provides an ideal set of imaging and diffraction methods to reveal the architecture of calcitic brachiopod shells. Usually calcitic brachiopods show a two-layered shell with a hard nanocrystalline primary layer and a fibrous secondary layer where the fibers are single crystals with the morphological fiber axis perpendicular to the crystallographic c-axis.

The investigated species, *Kakanuiella chathamensis* and *Liothyrella neozelanica* differ from this assembly: the former one is built entirely of hard nano- to microcrystalline calcite whereas the latter one shows a usual primary layer, but a secondary layer which is prismatic and a fibrous tertiary layer. Our observations on the interface between the primary and the secondary layer in *L. neozelanica* suggest a mechanism how the unusual crystallographic texture may arise.

Even though *Kakanuiella chathamensis* consists only of primary layer material we observe some textural features and a pattern in the distribution of hardness within the shell.

Figure 1: EBSD-Map of the three layered shell of *L. neozelanica* (black bar down left: 500 µm).

References
Earth’s core formation aided by flow channelling induced by Rayleigh-Taylor instabilities

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The core formation mechanism remains poorly known. Geochemical constraints by Hf/W systematics indicate a fast process which was largely completed within 33 Ma for the Earth. An unstable gravitational configuration of a dense molten metallic layer overlying a cold chondritic protocore is predicted by most studies, which leads to the formation of a Rayleigh-Taylor instability. We propose the application of Stevenson’s (1989) stress-induced melt channelling mechanism in the region surrounding an incipient iron diapir. We therefore perform numerical experiments solving the two-phase, two composition flow equations within a 2D rectangular box with symmetrical boundary conditions. We apply the Compaction Boussinesq Approximation (CBA) and include a depth-dependent gravity. For simplicity we use a constant viscosity for the solid phase and melt-fraction dependent rheology for the partially molten region around the diapir. A systematic investigation of the physical conditions under which the melt channels can form in comparison with the time scale of core formation and whether they are applicable to the early Earth is in progress. As a result, for sufficiently small melt retention numbers iron-melt focussing channels develop within a region of approximately twice the diapir’s size. This could lead to effective draining of the surrounding region and might initiate cascading daughter diapirs or the formation of dykes. The mechanism could effectively enhance melt accumulation in the protocore and accelerate the process of core formation.

Tracing oceanic sulphate with phosphorite geochemistry

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Sedimentary phosphorites contain francolite (carbonate fluorapatite) as the major mineral phase. Francolite is thought to incorporate $SO_4^{2-}$ in proportion to its concentration in ambient pore fluids (Jarvis et al., 1994) and thus could be a potential indicator of past seawater sulphate concentrations. This is attempted by relating $SO_4/P_2O_5$ ratios of recent and ancient phosphorite rocks to ocean sulphate levels.

Phosphorite can form under diverse redox conditions, which can lead to variations in incorporated $SO_4^{2-}$. By comparing francolite-bound sulphate $\delta^{34}S$ and $\delta^{18}O$ and carbonate $\delta^{13}C$, the impact of sulphate reduction and sulphide reoxidation on sulphate concentrations can be better constrained. Weathering is also considered to lead to the loss of $SO_4^{2-}$ in francolite, and this can be partially evaluated by CO$_2$ concentrations in francolite. However, our study suggests that sulphate is only lost from associated organics and pyrite during weathering.

The sulphate concentration and $\delta^{34}S$ of phosphorites do not correlate with Ce-anomaly, which is a redox-dependent parameter. The decoupling of REE from $SO_4^{2-}$ and $\delta^{34}S$ may result from the different timings and mechanisms of incorporation of REE and sulphate into the francolite lattice. Therefore, REE do not provide reliable constraints on the degree of preservation of francolite sulphur systematics.

Francolite $SO_4^{2-}$ is found to be lower than previously reported in Miocene phosphorites. This could relate to the removal of all non-francolite S during sample preparation in our study. $SO_4^{2-}$ levels in Neoproterozoic and Cambrian francolites are also low. Uppermost $SO_4^{2-}/P_2O_5$ ratios from the best preserved samples (from the Miocene, Cambrian and Ediacaran) in our study can be used to constrain minimum $SO_4^{2-}$ concentrations in the ocean.

Reference
Bistability of atmospheric oxygen and the Great Oxidation

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Earth history has been characterized by a series of major transitions separated by long periods of relative stability. The largest chemical transition was the ‘Great Oxidation’, approximately 2.4 billion years ago, when atmospheric oxygen concentrations rose from less than $10^{-5}$ of the present atmospheric level (PAL) to more than 0.01 PAL, and possibly to more than 0.1 PAL. This transition took place long after oxygenic photosynthesis is thought to have evolved, but the causes of this delay and of the Great Oxidation itself have been unclear. We show that the origin of oxygenic photosynthesis gave rise to two simultaneously stable steady states for atmospheric oxygen. The existence of a low oxygen (less than $10^{-5}$ PAL) steady state explains how a reducing atmosphere could persist for at least 300 million years after the onset of oxygenic photosynthesis. The Great Oxidation can be understood as a switch to the high-oxygen (more than $5 \times 10^{-3}$ PAL) steady state. The bistability arises because ultraviolet shielding of the troposphere by ozone becomes effective once oxygen levels exceed $10^{-5}$ PAL, causing a nonlinear increase in the lifetime of atmospheric oxygen (Goldblatt et al. 2006). The long term redox forcing of the surface system was probably a decrease in reductant input due to a progressive oxidation of the crust (Claire et al. 2006). Once the system was in a bistable regime, the Great Oxidation could have been triggered by a perturbation to the carbon cycle too small to leave a carbon isotope signal. Our results indicate that the existence of oxygenic photosynthesis is not a sufficient condition for either an oxygen-rich atmosphere or the presence of an ozone layer, which has implications for detecting life on other planets by remote sensing and for the evolution of multicellular life.

References


A coordinated continental and regional soil geochemical survey of North America


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The U.S. Geological Survey and collaborating partners in Canada and Mexico, have initiated a project that will produce a soil geochemical survey of North America. Pilot phase sampling and analyses have been completed along two continental transects, one of which extends from the west to east coasts of the United States along the 38th parallel. The data for a number of elements in this east-west transect reveal geochemical patterns that correlate with bedrock and glacial deposit composition.

One example of soil-bedrock correlation is elevated Cr concentrations in some California soils, which contain 2000-8000 ppm Cr compared to a median of 27 ppm for all samples across the east-west transect. The origin of this Cr anomaly is revealed by a more detailed regional-scale pilot study north of the San Francisco Bay extending from the Pacific Ocean to the California-Nevada border. This regional study incorporates geochemical data from nearly 2000 soil samples. Cr and Ni in these samples display patterns reflecting the underlying geology.

Elevated concentrations of soil Cr (2000-8000 ppm) and Ni (1000-5000 ppm) overlie serpentinite rocks in the foothills of the Sierra Nevada Mountains and in the Coast Ranges west of the Sacramento Valley. Chromium in these serpentinite-derived soil samples is predominantly in a refractory form, as chromite (FeCr$_2$O$_4$). Soils with Tertiary volcanic and granitic parent material located at higher elevation in the Sierra Nevada Mountains, as well as alluvial soil in the eastern Sacramento Valley, have much lower Cr and Ni concentrations relative to serpentinite soil (less than 100 and 50 ppm, respectively). Surprisingly, soil with elevated Cr and Ni content (150-400 ppm and 60-300, respectively) occurs in Sacramento Valley soil west of the Sacramento River. Chromium in this western valley geographic setting is in a less refractory form than that in soil overlying serpentinite, is more easily mobilized from soil into groundwater, and spatially correlates with the elevated groundwater Cr levels.

The geochemical studies at national and regional scales complement each other. The former targets areas of interest and the latter provides more detailed process insights.
Tracking microbial life in the marine subsurface

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Evidence has grown that deeply buried marine sediments are habitats to living communities of microorganisms, even under scarcity of nutrients and terminal electron acceptors and apparently hostile environmental conditions. The contribution of such communities to element cycling remains elusive, but direct microbiological assays are difficult to conduct due to extreme in situ conditions. We suggest to make use of anorganic, cell-independent proxies to bypass this hassle and propose the application of oxygen stable isotopes of dissolved inorganic phosphate (DIP) in marine pore waters.

The \(^{18}\text{O}/^{16}\text{O}\) ratio of pore water DIP is significantly affected by active microbial phosphate (PO\(_4\)) metabolism. The exchange of oxygen atoms between water and phosphate is enhanced by extra- and intrazellular hydrolase enzymes in living cell PO\(_4\) uptake and processing, and can be distinguished from abiotic fractionations during sediment diagenesis (Blake et al. 2005). Therefore we consider the \(^{18}\text{O}\) of pore water DIP a fairly robust and feasible parameter for the identification and profiling of microbial activity in deep sediment cores.

We here present a modified microextraction technique for marine pore water PO\(_4\). DIP is concentrated by magnesium induced coprecipitation, separated from interferring anions by a preparative ion chromatography using anion exchange resin, and subsequently precipitated as silver phosphate (Ag\(_3\)PO\(_4\), Colman 2002). Ag\(_3\)PO\(_4\) is finally combusted in an elemental analyzer, and transferred online via continuous flow to an isotope ratio mass spectrometer. The amount of DIP required for the precipitation of crystal Ag\(_3\)PO\(_4\) can thereby be reduced to less than 1mg, making an analysis of pore water samples which are limited in sample volume and DIP content possible.

On research cruise MSM04-4a with German vessel Maria S. Merian we recovered four sediment cores up to 42m below sea floor offshore Morocco using a remotely operated seafloor drill rig, and took pore water samples with an average depth resolution of 0.5m for the application of the novel technique described above.

References
Chemical weathering of Taranaki volcanics, North Island, New Zealand

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New Zealand’s North Island watersheds in the Taranaki and Manawatu-Wanganui regions have been subject to volcanism since the Miocene. We sampled water and sediments from watersheds that contain both volcanic and sedimentary rocks. Water and sediment samples were collected and analyzed for major, minor and trace elements, in order to quantify the weathering intensities in the watersheds and to establish the relationship between physical and chemical weathering yields in volcanic lithologies.

Results reveal distinct chemical signatures, with waters draining the Taranaki region volcanics significantly enriched in K+ and depleted in Sr2+ compared to those draining the Manawatu-Wanganui region volcanics, which also traverse expanses of sedimentary siltstones and mudstones. These depletions may reflect the relative absence of CaCO3 in the Taranaki region watersheds. In addition, sediment samples from the Taranaki Region show significant enrichment in Ti, Al, Ca, Fe, Mg, Mn, Mg, Ca, and P and depletion in Si and Rb compared to those of the Manawatu-Wanganui region.

Mineral stability diagrams for streamwater samples show that primary feldspar minerals present would weather to kaolinite while clay minerals would likely be present as kaolinite, illite, or Mg-montmorillonite. Normalized sediment values for the Taranaki region exhibited a best fit pattern to average Mt. Egmont andesite values with relative soluble alkali and alkaline earth elements Na, K, Rb, Sr, and Ba and insoluble elements Ti, Al, and Fe, while normalized values for the Manawatu-Wanganui region exhibited a best fit pattern to near shore mud.

From total dissolved solids concentrations and annual volumetric water discharge, chemical weathering yields of 60–238 tons km⁻² a⁻¹ are obtained. These weathering yields fall within the middle to upper range of those previously reported for New Zealand’s Southern Alps (93–480 tons km⁻² a⁻¹) and East Cape (62–400 tons km⁻² a⁻¹). Calculated silicate weathering yields of 12–33.6 tons km⁻² a⁻¹ and CO2 consumption of 852–2390×10⁶ moles km⁻² a⁻¹ for the rivers draining the Taranaki volcanic region are higher than those previously reported for watersheds hosted in sedimentary and metamorphosed rock terrains on HSIs. CO2 consumption is found to be within the range which others have reported for the basaltic terrains of the Deccan Traps (580–2450×10⁶ moles km⁻² a⁻¹) and Réunion Island (1300–4400×10⁶ moles km⁻² a⁻¹). Calculated chemical weathering yields demonstrate the importance of taking into account weathering on high-standing oceanic islands, particularly those with volcanic terrains, when considering global geochemical fluxes.

The nature of the mantle source of Archean ferropicrites

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Although ferropicrites have been recognized as an unusually Fe-rich mafic igneous rock for some time, the nature of their mantle source remains unclear. Ferropicrites are most common in Archean terranes and four occurrences from the Superior craton form the basis of this study: the Taconic, Lusby Lake, Grassy Portage Bay, and Dayohessarah Lake greenstone belts. Ferropicrites from the first three belts occur as ash to lapilli tuffs, while those from the latter belt occur as coarse-grained intrusive rocks cutting basalts and komatite flows. These ferropicrites are mafic to ultramafic rocks (15-23 wt% MgO) characterized by low Al₂O₃ (<8 wt%), high FeO* (15-21 wt%), and relatively high TiO₂ contents (1-2 wt%). They have fractionated REE profiles (La/Yb = 8-20; Gd/Yb = 3-4.5) and relatively high contents of HFSE (Nb = 10-18 ppm; Nb/La = 0.8-3.0). In contrast, coexisting komatitites from Dayohessarah have higher Al₂O₃ (9-11wt%) and lower contents of FeO* (~11 wt%), TiO₂ (~0.5 wt%), HFSE, and LREE, despite having similar MgO contents; they also exhibit flat REE profiles (La/Yb = 1-2).

These geochemical differences require that the two magma types have different mantle sources. Peridotite-basalt mixtures that have been proposed as possible ferropicrite mantle sources fail to reproduce ferropicrite Fe contents. A garnet pyroxenite mantle source does not have sufficient Mg to produce liquids with up to 20 wt% MgO, and an olivine-dominated source seems to be required. Melting experiments on model mantle compositions (KLB-1, Mg # = 89.6) suggest that komatiitic liquids like those at Dayohessarah can be produced at 45 kbar, but do not reproduce the Fe contents of ferropicritic liquids under any conditions. Experimental melts of a model Martian mantle composition (Mg # ~80) at 15 kbar have nearly identical Fe contents to our ferropicrites, and melts produced at 50 kbar have Fe contents significantly higher than our ferropicrites. Interpolation of these data shows that the mantle source of our ferropicrites would have a Mg # of ~80 at 15 kbar, which would require large degrees of partial melting, or a Mg # of ~85 at 50 kbar. In the latter scenario, these ferropicritic liquids would be the result of smaller degrees of partial melting, consistent with their fractionated trace element profiles and lower Al contents relative to komatitites, if garnet were not completely consumed during ferropicrite petrogenesis.
Hf isotopes as the key for distinguishing slab melting in arcs: 
The case of the Mexican Volcanic Belt

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Convergent margins are important as the global setting 
where crust is recycled into the mantle and new continent is 
made. Despite major advances in delineating the processes 
that control arc magma generation, the problem persists of 
distinguishing slab, mantle wedge, and crustal contributions, 
along with the question of whether there is significant melting of 
subducted ocean crust. Especially in thick crust regions, the 
importance of crustal versus mantle contributions to lavas 
represents a long-standing fundamental issue in arc magma 
geochemistry. We show, based on evidence from Hf isotopes, 
that frontal arc magmas from the Central Mexican Volcanic 
Belt (CMVB), including the large andesitic stratovolcanoes 
Popocatepetl and Nevado de Toluca, display negligible crustal 
contamination, and contain a component derived from melting 
of regional subducted oceanic crust plus sediments.

Despite thick continental crust, the CMVB erupts near 
primitive lavas including “high-Nb” alkaline basalts that show 
negligible trace element “subduction signatures”. The “high 
 Nb” basalts define the regional mantle wedge composition in 
isotope-trace element space, and show well-defined Hf-Nd-
Pb-Sr isotope “arrays”. In “normal” CMVB lavas with 
“subduction signatures”, a key feature is that they form trends 
from the “high-Nb” lavas toward even higher Hf isotope 
ratios, thus their sources are more “depleted mantle-like” than 
the regional mantle wedge. Of prime importance here is that 
higher Hf isotopes in these “normal” lavas correlate with low 
Lu/Hf and Pb isotope ratios.

These negative correlations can be simply modeled as 
mixtures of the regional mantle wedge, represented by “high-
 Nb” basalts, with a low degree composite melt of the 
subducted slab represented by altered Pacific ocean crust plus 
DSDPSite 487 sediment, located near the trench. Neither 
altered Pacific crust nor sediment by themselves explain the 
“normal” CMVB data, but the ocean crust component 
predominates. Thus, the integrated data allow us to clearly 
distinguish between mantle and crustal sources and point to 
substantial subducted slab melt contributions to these lavas.

It is fitting for a symposium that asks what have we 
learned from Hf isotopes that we don’t know already from Nd, 
that Lu-Hf provides key evidence identifying mantle 
signatures in a thick crust arc, and for distinguishing the slab 
melt contribution from other possibilities. These observations 
are also significant in the context of global arc data.

Relationships between magnetic properties and heavy metals in 
*Nerium oleander* leaves and soils 
(Viseu, Central Portugal)

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Magnetic parameters (χ, ARM, IRM) and selected 
heavy metals concentration (Cu, Fe, Mn, Zn, Pb, and Cr) of 
*Nerium oleander* leaves and topsoils were determined for 24 
samples sites in the urban area of Viseu (Central Portugal). 
The purpose of this study is to relate magnetic properties to 
heavy metals concentrations and to assess the urban pollution 
levels. The table bellow presents some statistical information 
on the results obtained.

<table>
<thead>
<tr>
<th>Variables (units)</th>
<th>Topsoils</th>
<th>Leaves</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n/Min-Max/ Mean</td>
<td>n/Min-Max/ Mean</td>
</tr>
<tr>
<td>χ (10^-3 kg^-1)</td>
<td>23 44.9-141.9 78.4</td>
<td>27 2.3-193.2 51.6</td>
</tr>
<tr>
<td>IRM (Am kg^-1)</td>
<td>23 155.5-878.8 391.9</td>
<td>27 4.7-120.9 31.3</td>
</tr>
<tr>
<td>ARM (Am kg^-1)</td>
<td>23 4.5-39.8 12.3</td>
<td></td>
</tr>
<tr>
<td>Fe (mg/kg)</td>
<td>23 17.800-61 400 37239.1</td>
<td>27 207.1-1396.5 766.0</td>
</tr>
<tr>
<td>Mn (mg/kg)</td>
<td>23 258.0-833.6 455.5</td>
<td>26 37.7-231.6 108.7</td>
</tr>
<tr>
<td>Cr (mg/kg)</td>
<td>26 0.3-6.8 3.3</td>
<td></td>
</tr>
<tr>
<td>Zn (mg/kg)</td>
<td>23 18.7-499.9 184.4</td>
<td>27 34.2-126.5 67.7</td>
</tr>
<tr>
<td>Cu (mg/kg)</td>
<td>23 19.7-164.8 66.3</td>
<td>27 9.4-44.1 23.4</td>
</tr>
<tr>
<td>Pb (mg/kg)</td>
<td>23 16.2-149.0 62.7</td>
<td>24 0.2-2.5 1.2</td>
</tr>
</tbody>
</table>

Significant correlations were found between most 
chemical elements and magnetic parameters determined in 
leaves. This is confirmed by a factor analysis, where the 
dominant factor (60% of the total variance) shows only 
positive contributions including both physical and chemical 
parameters (Cu, Fe, Mn, Pb, Zn, magnetic susceptibility, and 
IRM). The second factor (18% of the total variance) shows 
positive contributions of Fe and Cr and negative of IRM and 
magnetic susceptibility. Communalities are higher than 0.82, 
with the exception of Mn (0.44) and Pb (0.65). The same 
pattern was observed for topsoils. Again, chemical and 
magnetic parameters are related with significant correlations 
and a factor analysis shows positive contributions of all of 
them to the most important factor (49% of the total variance). 
The second factor (25% of the total variance) shows positive 
contributions of ARM and Fe and negative contributions of Pb 
and Zn. Communalities are all higher than 0.55 and most 
are exceed 0.75.

These results indicate that factor 1 in both cases is clearly 
related to contamination induced by anthropogenic activities 
and that magnetic parameters of leaves and soils can be used 
as an indicator of the degree of chemical contamination and 
pollution levels. Factor 2 is probably related to natural 
variations of the composition of leaves and topsoils.
Remediation of azo dyes by natural manganese oxides

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In the present work, the degradation of azo dyes (60 mg/L) and aromatic amines (60 mg/L) in the presence of natural Mn oxides was investigated in batch experiments. A 1/10 (w/v) solid/solution ratio was used.

Discussion

Dyes Acid Orange 7 and Acid Yellow 36 were decolourised by the manganese oxide (natural pH of 8-9), indicating that they were either being degraded or adsorbed onto the mineral surface[1]. As no sterilised Mn oxide samples were used, the possibility of the reactions being solely biologically mediated cannot be discounted. Experiments performed in the absence and presence of nutrients also gave different results.

The biological activity of these systems was assessed by using molecular biological techniques such as DNA extraction followed by Polymerase Chain Reaction (PCR) [2]. Results indicate the presence of microorganisms in all samples analysed.

Conclusions

The ability of natural ‘waste’ Mn oxide compounds to undergo oxidation and reduction reactions makes them suitable to be used as redox mediators (electron shuttles) in the degradation of azo dyes and aromatic amines in natural environments. It is not clear from these experiments whether this process is either a chemically and/or a biologically mediated processes.

References


Biogeochemical and mineralogical characteristics of the acid mine drainage system in Aljustrel and S. Domingos mines, Iberian Pyrite Belt

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Aljustrel and S. Domingos are important mines of the Iberian Pyrite Belt, the former currently active and the latter closed since the sixties. Both systems were sampled and analysed. Samples included old and recent mine taillings, stream sediments, surface waters, and biological material (algae). Acid drainage is very similar in both areas but acid waters in Aljustrel have 7 to 8 times higher metal concentrations than in S. Domingos. However, in S. Domingos the system is much more contained.

Aljustrel: Água Forte stream drains the major taillings. This stream receives domestic waste-waters 2 Km away, which act as a neutralizing agent to the acid waters (pH 2). Waste-waters pH is ≈8, and drops to values near 4 upon mixing with the acid waters. In Summer, acid drainage stops but waters down-stream maintain their pH close to 4. The ubiquitous presence of gypsum and jarosite in sediments and crusts provide a source for acidity due to their dissolution. Sediments down-stream have iron-rich surface layers and dark coloured material in the deeper layers (sulphides?). Modelling results show that such pH values may be attained only if precipitation of iron oxides and sulphides occur during mixing of waters. Water samples from sites with abundant iron-oxide sediments present the association Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans, Acidithiobacillus albertensis, and Leptospirillum ferriphilum.

S. Domingos: Has a much more complex secondary mineral assemblage: gypsum, jarosite, schulenbergite, natrojarosite, szomolnokite, and coquimbite. Along the major flow path from the dams and pits, both water chemistry and parameters do not change appreciably.

Algae from both mining areas were centrifuged to extract part of their water content, and their tissues were dissolved. Concentrations of Cu and Zn in the organic material were 3 to 4 times lower than in the liquid extracts, whose concentrations were about half the corresponding concentrations in the flowing waters. Pb, Co, and Cd have only trace concentrations.

Contribution of project METALTRAVEL - POCI/CTE-GEX/61700/2004, funded by FCT
H-O isotopes and water content in nominally anhydrous minerals from UHP eclogite in the Dabie orogen

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Fluid activity during subduction-zone metamorphism is an important issue with respect to chemical geodynamics of continental collision. In particular, it has been intriguing where retrograde fluid comes from during exhumation of deeply subducted continental crust. Mineral water concentration and stable isotope analyses are a powerful means to decipher the origin and nature of aqueous fluid in UHP metamorphic minerals. Using a stepwise heating procedure, a number of FTIR analyses demonstrate that only molecule H_2O is removed from garnet from eclogite, without significant loss of structural OH. A TC/EA-MS online method, together with the stepwise heating procedure, is used to determine both H isotope ratios and concentrations of total water and structural hydroxyl in nominally anhydrous minerals from UHP eclogite at Bixiling in the Dabie orogen, China. The results show total H_2O concentrations of 1791 to 2997 ppm in omphacite and 522 to 981 ppm in garnet, and hydroxyl concentrations of 1242 to 2808 ppm H_2O in omphacite and 279 to 747 ppm in garnet. Except for quartz which has a higher concentration of molecule H_2O (189 ppm) than structural hydroxyl (117 ppm), all of the other minerals have much higher concentrations of structural hydroxyl than molecule H_2O. The eclogite has total water δD values of −112 to −92‰ for omphacite and −98 to −94‰ for garnet; structural hydroxyl δD values of −91 to −85‰ for omphacite and −87 to −72‰ for garnet. It appears that the total H_2O is depleted in D relative the structural OH in the nominally anhydrous minerals. The nominally anhydrous minerals have similar δD values to each other, but are lower than δD values of −59 to −58‰ for muscovite. On the other hand, hydroxyl δD values for the nominally anhydrous minerals are close to hydroxyl δD values for hydrous minerals. Laser fluorination analysis obtained that the eclogite has an δ^{18}O value of 2.5‰ for zircon, 2.7 to 3.7‰ for garnet and 3.3 to 4.5‰ for omphacite. They are lower than normal mantle zircon δ^{18}O values. Both O and H isotope equilibrium and disequilibrium occur between coexisting omphacite and garnet, but retrograde metamorphism occurred with internal buffering of stable isotope compositions. Thus both O and H isotope signatures of minerals from the eclogite indicate incorporation of meteoric water into eclogite protolith by high-T hydrothermal alteration and subsequent magmatism. The meteoric signature was preserved in the UHP minerals during the subduction of continental slab, with only limited activity of fluid within the slab. Nevertheless, fluid became available during exhumation due to a decrease in water solubility with pressure decrease. Therefore, exsolution of structural hydroxyl and molecular water from the minerals is the most plausible source for the retrograde fluid.

A fractal concentration-mass method for geochemical anomaly separation in Shizhuyuan tungsten deposit area

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Anomaly separation plays an important role in mineral exploration. A fractal concentration-mass (C-M) method was presented for separating geochemical anomalies from background. The method is derived from Mandelbrot's coastline length-ruler model by replacing the length with mass and ruler with concentration. In log-log plot, the concentration-mass pattern follows the fractal distribution with uni-scale or multi-scale, which was used to discriminate geochemical processes and to separate geochemical anomaly from background.

The C-M method was tested on stream sediment geochemical data in Shizhuyuan tungsten deposit area, Hunan province in China. The stream sediments were sampled using grid method by 31 multiply 31 kilometers with one sample per square kilometer (n=961). Six elements, W, Sn, Pb, Ag, Ni and Ba, were selected to test the C-M method in this area, in which W, Sn, Pb, Ag with mineralization and Ni, Ba without. The results indicated that multi-scale fractal or mixing-dominant geochemical processes was occurred in this area and the anomaly can be separated from background efficiently. Compared with the typical method (anomaly determined by average plus double standard deviation), the anomaly area of W, Sn, Pb, Ag determined by C-M method is evidently smaller (with larger anomaly value) and more coincident with known deposit sites, and the anomaly area of Ni, Ba is distinctly larger (with smaller anomaly value) and more consistent with the Devonian and pre-Cambrian strata area respectively. Therefore, the C-M fractal method is efficiently in separating geochemical anomaly from background with good qualities in aiming at deposit target promptly or in avoiding losing weak anomaly information.
Geochemical features of the basic-ultrabasic rocks of the Udokan-Chiney region (Siberia, Russia)

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The problem and the main goal of the study

Mantle magma’s intrusions inside the Southern framework of the Siberian platform reflect the main destruction episodes on the Earth. They are the Paleopangea falling to pieces in the Early proterozoic époque and the tectonic activity in Kz. To understand the magmatic evolution and the associated ore-forming processes in the Udokan-Chiney region it is necessary to study geochemical features of the basic-ultrabasic rocks from numerous massifs located inside this area.

Results

The composition of the rocks (main and trace elements) from different Paleoproterozoic massifs – Chiney, Luktur, Mylove, and Neoproterozoic massifs – Doros, Udokan Great Dyke, so as the Mz and Kz basalts have been studied by XRF and ICP-MS. In this range (from ancient to modern rocks) there is an evolution of its compositions: close to N-MORB – E-MORB – OIB. La/Yb and Th/Ta ratios of the studied massifs change significantly (fig.1) and demonstrate the role of the different sources in their magma generation.

Figure 1: La/Yb vs. Th/Ta diagram for the studied complexes from Udokan-Chiney region.

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Nothing paradoxical about Helium concentrations in OIBs

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We show that the He concentration paradox, as well as the full range of noble gas concentrations observed in mid-ocean ridge basalt (MORB) and ocean island basalt (OIB) glasses, can self-consistently be explained by disequilibrium, open-system degassing of the erupting magma. We demonstrate that a higher CO₂ and H₂O content of OIBs, compared to MORBs, leads to more extensive degassing of He in OIB lavas.

Outgassing during melt production at mid-ocean ridges has led to a volatile depleted upper-mantle MORB source with low ³He/⁴He ratios. Consequently, ³He/⁴He ratios in OIBs, often a factor of 4-6 higher than in MORBs, are conventionally viewed as evidence for an undegassed, primitive mantle source. However, this conventional model provides no viable explanation for why noble gas abundances in OIBs are an order of magnitude lower than in MORBs. This has been called the “He concentration paradox”, which has contributed to a long-standing controversy about the structure and dynamics of Earth’s mantle.

If, during magma eruption there is insufficient time for all volatiles to diffuse from the melt into gaseous bubbles, the abundance of dissolved volatile species is controlled by both solubility and diffusivity. Because of its relatively high diffusivity, He degassing of OIB and MORB magmas is not significantly limited by diffusion and is predominantly controlled by solubility. On-average higher CO₂ content of OIBs relative to MORBs dilutes He in the exsolved gas phase, thereby lowering partial pressures and decreasing absolute He solubility. This explains why OIB lavas have lower He abundances than MORBs, even though the OIB parental magma is more He rich. On the other hand, degassing of Ne and Ar is limited by diffusion during eruption of both MORB and OIB magmas. When combined with higher He loss in OIBs, this explains the low He/Ne and He/Ar ratios of OIBs relative to MORBs.

The observed noble gas content in OIBs is entirely consistent with degassing of a parental magma derived from a mantle source with a primordial component and total ³He, ²²Ne, and ³⁶Ar abundances of approximately 4×10⁻⁹, 1×10⁻⁹, and 3×10⁻⁹ cm³ STP g⁻¹, respectively. The percentage of primitive mantle component in the OIB source is on average less than 20%, but our present calculations do not constrain the size nor the location of the primitive reservoir. Regardless of whole mantle convection, it appears that part of the Earth’s mantle has remained relatively undegassed and primordial in volatile content over Earth’s history.
Mud-breccia clasts and sediments as nucleation sites for hydrocarbon-derived ferromanganese nodules in carbonate-mud mounds from the Gulf of Cadiz

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During the Anastasya-01 cruise (TASYO project), extensive nodule fields were discovered and sampled for the first time at water depths ranging from 850 to 1000 m, associated with hydrocarbon-derived carbonate chimneys and crusts in the Guadalquivir Diapiric Ridge area (eastern Central Atlantic) [1]. Nodules show a wide range of sizes and predominantly tabular shapes. They are formed of multiple millimetre-thick layers of Fe and Mn oxides surrounding the nucleus composed of Early-Middle Miocene plastic marls and mud-breccia sediment, which were derived from underlying units by fluid venting. Fe-Mn layers and carbonated cores display the same microtextural features, composed by zoned rhombohedral crystals (authigenic Fe-Mn oxides in layers, and siderite to rhodochrosite in the nuclei) surrounded by detrital grains (silicates) and frambooidal associations (fresh pyrite or totally pseudomorphised by goethite). The center of the rhombohedral crystals are enriched in manganese and their exterior edges are iron enriched for both, Fe-Mn oxides and Fe-Mn carbonates. Nodules show a high mean abundance of Fe (38.6%) moderate Mn (6.0%), and low contents of trace metals and REEs compared to the average content of deep-seabed polymetallic nodules [2]. The studied nodules hold in their oxide layers and cores hydrocarbons (n-alkanes), with a first concentration maximum at n–C18, derived from marine bacterial activity, also with presence of aromatic hydrocarbons such as phenanthrene, characteristic of mature petroleum. Bacteria-mediated oxidation of hydrocarbons through Mn4+ and Fe3+ reduction, could be related to the precipitation of Fe-Mn carbonates and sulphides, forming siderite-rhodochrosite concretions bellow the redox boundary within the sediment, that later were transformed into ferromanganese-oxide nodules by exhumation and exposition to the sea bottom oxidising waters.

References
Slab-mantle interaction and petrogenesis of interplate basalts

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Interplate basalts have been produced from mantle reservoirs which content of protholiths of former oceanic crust. The peculiarity melting of these sources were studied experimentally at temperature range 1250-1400°C and pressure 1.5-4.0 GPa by using the peridotite ampoule method. In peridotite-basalt-volatile (H₂O or H₂O+CO₂) systems (PBV) as the model such reservoirs high magnesian melts (14-18 % MgO) in equilibrium with Opx+Cpx formed by react slab-derived liquids with mantle peridotite (“reaction” melts). Their volume depend on volume basalt of slab. In the some experiments during partial melting of peridotite formed 3-5 % "filmy" andesitic or more high siliceous (up to 60 % SiO₂) liquids.

Figure 1: Photo of experimental sample in the backscattered electrons. T=1250 C, P=2.5 GPa, 5% H₂O+CO₂

Make allowance of volume slab basalts my proposed, that the slab-mantle sources would be produced more bigger volumes of magnesian basalts at comparatively lover temperatures to compare with normal partial melting of peridotite. All these observations, based on experimental study PBV systems, probably may extent to petrogenesis of interplate basalts.

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Bacterial nanowires: Extracellular electron transfer and mineral transformation

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Dissimilatory metal reducing bacteria use solid phase iron and manganese oxides as electron acceptors and couple this enzymatic reduction to growth. This mode of anaerobic respiration profoundly influences mineralogical transformation in diverse natural environments. But the use of metal oxides as electron acceptors presents challenges to bacteria that must coordinate transfer of electrons from bacteria to the mineral surfaces. Recent results demonstrate that metal reducing bacteria, such as Geobacter and Shewanella spp., produce electrically conductive appendages called bacterial nanowires under conditions that limit availability of electron acceptor (Reguera et al., 2005; Gorby et al., 2006). A combination of scanning electron microscopy (SEM) and scanning tunneling microscopy (STM) confirmed that wild type S. oneidensis MR-1 produced electrically conductive nanowires that connected cells together into an electrically integrated cellular network. Conductivity of Shewanella nanowires requires the presence of cytochromes, which were previously shown to enzymatically reduce solid phase Fe(III) and Mn(IV) minerals (e.g. Beliaev et al., 2001). Mutants lacking these electron transport proteins produced appendages resembling nanowires that were not conductive. These mutants did not reduce Fe(III) (hydr)oxides, produce electricity in microbial fuel cells, or form thick biofilms (Gorby et al., 2006).

Nanowires are not exclusive to dissimilatory metal reducing bacteria. Organisms ranging from oxygenic cyanobacteria to thermophilic syntrophic bacteria produce electrically conductive nanowires (Gorby et al., 2006). Structure ressembling nanowires are commonly observed in iron oxidizing environments. This presentation will provide our current understanding of the diversity, distribution, and implication of bacterial nanowires in a variety of microorganisms.

References
Melting and mixing processes in mantle wedges

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Partial melting of mantle and subducting slab material is one of the crucial mechanisms of mass transfer in subduction zones. To study the dynamics of this phenomenon we used 2-D coupled petrological-thermomechanical model with different tectonic setups (i.e. intra-oceanic subduction and active continental margin). To simulate water propagation and magmatic processes we implemented slab dehydration, partial melting and hydration of mantle wedge. We studied mantle wedge processes in various resolutions (form 0.5 million to 10 billion markers) to resolve complexity of theses processes.

Hydrated and partially molten material (plumes) rise through the mantle wedge along trajectories determined by the balance between buoyancy force and mantle flow. Their geometries differ depending on physical properties of mantle and diapir as well the dynamics of the system. Variations in plume development have influence on surface processes like slab retreat and speed of back-arc opening or rotation of fore-arc.

Slab plumes material can be homogenous (only mantle material) or heterogeneous (mantle and slab material). In case of heterogeneous plume during its growth materials mix chaotically resulting in attenuation and duplication of the original layering on scales of 1–1000 m. This process may verify marble cake theory and explain existence of complex peridotitic structures exhumed to the surface.

The use of overbank sediments data for geochemical mapping and contamination assessment: Results from selected floodplains of Serbia

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Introduction

Profiles made from the data of the overbank sediments from the flood plains of Serbia contain the geochemical inscription of the depositional milieu of the preindustrial era. Taking into consideration that they represent wider drainage areas together with the stream sediments, they were used to create regional geochemical map. Contents of the certain chemical elements from the overbank and stream sediments along with anthropogenic influence on the certain localities were represented on the map.

Discussion and results

Geochemical prospecting and mapping were done in accordance with the criteria of the West European Geochemical Surveys (WEGS). The area of the East Serbia drained by the river Timok with its tributaries was selected for investigations. Differences in Pb, Zn, Cu, Au, Sb, As, Cd, Cr, Ni, Co, V and other elements were noted in overbank and stream sediments of the main flow and its tributaries. The contents of certain elements are presented in the table below:

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Au</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Timok</td>
<td>12</td>
<td>62</td>
<td>28</td>
<td>0.02</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Borska</td>
<td>34</td>
<td>60</td>
<td>300</td>
<td>0.04</td>
<td>15</td>
</tr>
<tr>
<td>River</td>
<td>80</td>
<td>75</td>
<td>6222</td>
<td>5.54</td>
<td>5</td>
</tr>
<tr>
<td>Crni</td>
<td>41</td>
<td>59</td>
<td>84</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>Timok</td>
<td>50</td>
<td>348</td>
<td>139</td>
<td>0.05</td>
<td>20</td>
</tr>
<tr>
<td>Values (ppm)</td>
<td>As</td>
<td>Cd</td>
<td>Cr</td>
<td>V</td>
<td></td>
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<tr>
<td>River</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td></td>
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<tr>
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<td>10</td>
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<tr>
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<td></td>
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<tr>
<td>Timok</td>
<td>40</td>
<td>1.5</td>
<td>50</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

OB= overbank sediments; STR = stream sediments

Conclusion

Obtained results are presented on the geochemical maps of the Eastern Serbia, on the diagrams, tables and geological cross sections. Obvious differences in concentrations of certain elements from overbank and stream sediments reflect anthropogenic influence on the environment.

References

Lifetime of the active solar nebula
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The duration of formation of the very early solar system objects, such as the Ca-Al-rich Inclusions (CAIs) and chondrules, that are considered to be products of high temperature nebular processes, effectively defines the lifetime of the active solar nebula. Most of the CAIs host radiogenic isotopic anomalies from in-situ decay of short-lived now extinct nuclides, while a subset of CAIs are devoid of such anomalies but host large magnitude stable isotope anomalies. The latter group appears to have formed in the solar nebula within the first $10^5$ years, prior to the injection of freshly synthesized short-lived nuclide into it [1]. The formation of the CAIs hosting radiogenic isotope anomalies spread over a time scale of a few times $10^5$ years [2], although recent data suggest that this could be as short as $5\times10^4$ years [see, e.g., 3]. There is a general consensus at present that formation of chondrules started about a million years after the formation of the CAIs, and the inferred duration of chondrule formation, based on study of $^{26}$Al records, varies from less than a million years to three million years [3]. A detail study of chondrules from unequilibrated ordinary chondrites (UOCs) belonging to the L group and representing various petrologic types, show that the major episode of chondrule formation started $\sim1.5$ Ma after CAI formation and lasted $\sim1$ Ma [4]. The longer duration of formation for UOC chondrules, inferred in earlier studies, appears to be an artifact caused by thermal metamorphism affecting some of the chondrules belonging to low petrologic type. In contrast, data for chondrules from carbonaceous chondrites, obtained by us [5] and others, suggest that chondrule formation in the outer region of the inner solar system persisted for a much longer duration of $\sim3$ Ma. Plausible scenarios that may accommodate these observations relevant to the lifetime of an active solar nebula will be presented.

References

Sulfur K-edge X-ray absorption spectroscopy as a tool to investigate microbial triggered sulfate reduction
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Investigation on the chemical states of sulfur is essential to characterize reaction products from microbial catalyzed neutralization of acidic mine waters and from laboratory experiments carried out with the iron and sulfate containing mineral jarosite (KFe$_4$(SO$_4$)$_2$(OH)$_6$) exposed to sulfate reducing bacteria as a model system. With an element specific technique like the x-ray absorption spectroscopy (XAS), and therein from the near edge structure (XANES) information on the chemical binding form of sulfur can be obtained. XANES spectra at the sulfur K edge (around 2.48 keV) have been recorded at the XAS beamline of the synchrotron radiation source ANKA at the Forschungszentrum Karlsruhe.

Due to the oxidation of metal sulfides (e.g. FeS$_2$) in coal mining sites metal ions and sulfuric acid are released in the adjacent waters. Thus, the acidic pit lakes that form in abandoned mining sites are an environmental hazard. A stimulation of sulfate reducing bacteria (SRBs) at the sediment water interface might act as a starting point to neutralize such lakes by transforming dissolved iron, metal and sulfate ions as well as the iron sulfate minerals of the lake sediment (e.g. jarosite) back into iron sulfides. Analysis of the sulfur K edge XANES shows in near surface samples of the sediment that was locally covered with calcium carbonate and organic carbon to increase bacterial activity reduced sulfur species (monosulfide). To understand the processes at the sediment water interface synthetic jarosite has been exposed to SRBs in the laboratory. Resonances in the spectra were assigned to monosulfide and disulfide sulfur besides the sulfate of the remaining reactant jarosite. Re-oxidation experiments indicate a similar behavior as for the lake sediments: the decrease of monosulfides to sulfur and to sulfate (Göttlicher and Mangold, 2005).

Reference
A synchrotron radiation laboratory for environmental studies

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Samples required to solve Earth and environmental questions are often complex (e.g., weathered minerals and rocks, contaminated soils, lake and dump sediments). They consist of mixtures of mineral phases (often with micrometer particle sizes), microbes, and in some cases living tissues or are only available in scarce amounts of tiny particles (exhaust particles, precipitations in extreme environments). Elemental distribution, spatially resolved chemical speciation and mineral phase identification are helpful to uncover relationships between mineral phases, main and trace elements and finally to comprehensively understand natural and anthropogenic affected systems. Such problems can be addressed by a combination of microfocused synchrotron X-ray techniques as they have been setup with the Synchrotron Radiation Laboratory for Environmental Studies at ANKA. The lab consists of a microfocus X-ray beamline (SUL-X) that enable elemental mapping using X-ray fluorescence analysis (XRF), chemical speciation with X-ray absorption spectroscopy (XAS) and mineral phase determination by X-ray diffraction (XRD), successively at the same sample position. Moreover, the laboratory is supplemented with an infrared microscope (SUL-IR) at an edge radiation IR beamline.

First measurements during the commissioning period of SUL-X comprise localization and speciation of arsenic in natural iron minerals for water treatment and in weathering rims of sulfides in tailing impoundments by microfocused XRF analysis and X-ray absorption near edge structure (µ-XANES) spectroscopy. Selected area XRD has been used to identify mineral formations in sea water ice. µ-XRD and µ-XANES spectroscopy is applied to characterize lead in human bone junctions.

To meet the demand of speciation of low Z elements like Al, Si, P, S for environmental questions, it is planned to offer XAS at energies down to the Al K edge (1.5keV).

Microstrain and structural defects in the magnesian calcite skeleton of the Crown of Thorns starfish

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Sea stars have a magnesium calcite (Ca_{1-x}Mg_{x}CO_3) skeleton made up of small ossicles which form an open meshwork supporting the body. In spite of their spongy morphology, the skeletal parts are single crystals as in other echinoderms (sea urchins, sea lilies, sea cucumbers and brittle stars). The skeletons are metastable formations as their composition often lies within the miscibility gap between calcite and dolomite. The Crown of Thorns starfish (CoT) was chosen for this x-ray diffraction study for its extraordinary high magnesium content of x = 0.17. The name is for the large number of long spikes. The high Mg content indicates an average water temperature of the habitat of about 29°C.

The x-ray powder reflections of CoT are slightly broadened with respect to those of quartz which was used as internal standard. A Williamson Hall plot indicates that the broadening is almost entirely due to microscopic strain caused by lattice imperfections rather than to small crystallite size. Annealing experiments suggest that the microstrain can only partly be explained by the different sizes of Mg^{2+} and Ca^{2+} cations incorporated in the calcite lattice. A single crystal structure refinement revealed the presence of vacancies on cation sites and misoriented CO_3 groups.

After annealing at 300°C, the appearance of few weak extra reflections indicate the beginning of the exsolution of high-magnesium calcite to low-magnesium calcite and calcian dolomite.

Annealing at lower temperatures (100 - 200°C) causes some changes of the microstructure which show up in the diffraction patterns. The lattice parameters expand slightly on increasing temperature of the heat treatment [1]. Simultaneously, the broadening of the x-ray powder reflections is reduced indicating less microstrain. Single crystal structure refinements show a reduction of vacancies and smaller atomic displacement parameters suggesting some healing of structural defects.

Annealing at about 250°C, however, causes an increase of the reflection broadening indicating larger microstrain introduced by newly formed lattice imperfections. Additional weak diffuse intensity was found close to the strongest reflections which can be ascribed to Huang scattering caused by the occupation of interstitial lattice sites. The formation of interstitials seems to be an intermediate step before at higher temperatures unmixing of the solid solution begins.

Reference
Mobile fission and activation products in nuclear waste disposal

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When disposing nuclear waste in clay formations it is expected that the most radiotoxic elements like Pu, Np or Am do move only few centimetres to meters before they decay. Only a few radionuclides are able to reach biosphere and contribute to their long-term exposure risks, mainly $^{129}$I, $^{36}$Cl, $^{79}$Se and in some cases $^{14}$C and $^{99}$Tc, whatever the scenario considered. The recent OECD/NEA cosponsored international MOFAP workshop focussed on transport and chemical behaviour of these less toxic radionuclides. New research themes have been addressed, such as how to translate molecular level information to large migration distances. Diffusion studies need to face mineralogical heterogeneities over tens to hundreds of meters. The large volume of traversed rock will provide so many retention sites that despite weak retention, even these “mobile” nuclides may show significant retardation. The question however has been posed how to measure reliably very low retenion parameters. Additionally, the radioactivity of some of the nuclides in the waste is so low that sophisticated techniques must be employed to measure them. An important issue is whether redox states or organic/inorganic speciation change from its initial state at the moment of release from the waste during long term contact with surfaces, hydrogen saturated environments etc.

Changes in soil reactive aluminium fractions following logging in podzols of British Columbia, Canada

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The potential for aluminium stress in ecosystems

Al is the 3rd most abundant crustal element, and in soluble forms is toxic to most organisms. The potential for acidic soils to be Al toxic is considerable. Ecosystems stressed by human interventions such as forest harvesting are particularly at risk. This study investigates the effects of clear-cut logging on soil reactive Al fractions, including exchangeable Al ($\text{Al}_{\text{exch}}$), organically bound Al ($\text{Al}_{\text{org}}$), and Al associated with poorly crystalline minerals. The study soils are humo-ferric podzols located in the coastal mountains of southern British Columbia, Canada. These soils are strongly acidic and are at risk for Al stress. We collected soil samples from undisturbed plots (control), and compared them to samples from neighbouring plots that were clear-cut 1 to 15 years prior to sampling.

Results and discussion

$\text{Al}_{\text{exch}}$ and $\text{Al}_{\text{org}}$ are influenced similarly by logging. These Al pools are unaffected in plots logged 1 - 2 years ago, show an increase in plots logged 3 - 10 years ago, then decrease to control levels or below at 12 - 15 years after logging. This pattern matches closely the observed variation in the organic matter content. Organic matter provides exchange sites as well as sites for specific Al adsorption.

The increase in $\text{Al}_{\text{exch}}$ is mitigated by a concomitant increase in exchangeable calcium. The Ca/Al ratio, a valuable ecological indicator used for the identification of the risk of adverse effects due to Al stress, was remarkably constant in control and logged plots.

Poorly crystalline mineral fractions consist mainly in imogolite-type material (ITM). Control soils average 23g/kg ITM in the B and C horizons. Logged soils exhibit highly variable ITM content, indicating a possible disruption of the podzolization process. With an Al/Si ratio around 2, ITM stores a significant fraction of the reactive Al in these soils.

Conclusion

All reactive Al pools in these soils are affected by logging. The impacts of these changes on the ecosystem are under investigation.

Selected Reference

Modelling of denitrification plumes induced by organic matter injection in aquifers

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Injection of organic matter can be an effective method for the remediation of nitrate-polluted aquifers. Microbial activity mediates the reduction of nitrate to N₂ by organic matter what can be exemplified by the following reaction:

\[ 5CH_4O + 4NO_3^- \rightarrow N_2 + HCO_3^- + H^+ + H_2O \]

Nitrate pollution is of special concern in many areas of Catalonia (NE Spain). Although the accepted limit for drinking waters is 50 mg·L⁻¹, many aquifers in the region contain \([NO_3^-]>75 \text{ mg·L}^-1\], reaching in some cases up to 400 mg·L⁻¹. The Catalan Water Agency is presently designing an in situ experiment of organic matter-doped water injection in a selected aquifer with high nitrate concentration (~75 mg·L⁻¹ NO₃⁻). The extent and intensity of an aquifer denitrification plume is controlled by geochemical and hydrological parameters and variables (initial injected organic matter concentration, aquifer redox conditions, hydraulic conductivity, dispersivity and porosity).

The denitrifying capacity of the selected aquifer under study was tested in batch experiments in laboratory. From these experiments, a rate law of denitrification was determined and implemented in a series of 3-D reactive transport simulations aimed at selecting the optimal injection conditions, namely the injection rate of the reactive solution, organic matter concentration and injection pulse frequency.

Main parameters controlling the rate law were initial nitrate content, organic matter concentration and temperature.

In the numerical simulations, the total mass of organic matter to be injected (1.74 Kg CH₂O·day⁻¹) and total injection time (23 days) were kept constant while different organic matter concentrations and water injection rates were considered. The results show that solutions with organic matter concentration higher than 80 mg·L⁻¹ at injection rates from 5000 to 20,000 L·day⁻¹ generate a durable denitrification plume (>50 days under the maximum limit of nitrate concentration). Injection of water with lower CH₂O concentrations and higher injection rates leads to larger plumes but with lower denitrification intensity. The in situ test will also characterise aquifer properties such as depth-related redox conditions and the aquifer parameters given that the injection rate and the extent of the denitrification plume does not only depend on the geochemical variables but also on the ground water velocity.

U-series isotopes in suspended sediments of the Himalayan rivers

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Geochemical analysis of river sediments allows to study and quantify the parameters which control erosion and weathering processes at the scale of the watershed. In particular, \(^{238}\text{U}-^{234}\text{U}-^{230}\text{Th}-^{226}\text{Ra}\) disequilibria are useful in supplying constraints on the time-scales of erosion and weathering processes (Granet et al., subm.; Chabaux et al., 2003).

Previous studies were carried out on different kind of sediments: bedloads and river bank sediments (i.e. Granet et al., subm.), and suspended materials (i.e. Dosseto et al., 2006). These works highlight quite different U-Th-Ra values for coarse sediments and suspended materials, which still need to be explained in order to propose robust time-scales of erosion and weathering processes.

Here we analysed U-Th-Ra disequilibria for all the solid phases carried by the Ganges river and its tributaries to understand the relationships among the different kind of sediments: river coarse sediments (Granet et al., subm.) and suspended materials sampled at different depths in the water column.

U-Th-Ra analyses of samples collected at the same location highlight a wide range of values from the coarse sediments to the surface suspended materials. The chemical heterogeneity is explained by the fact that the U-Th-Ra composition of the suspended materials is the result of a mixing between coarse sediments and fine materials collected at the same sampling location but which have different origins at the scale of the Ganges basin. The data allow to conclude that the fine materials originate from the Ganges alluvial plain where they have been trapped before to be reworked and carried by the rivers.

The chemical differences observed between suspended materials and river coarse sediments are due to their different origin and history. This certainly accounts for the different time-scales of transfer proposed for these solid phases: long times of about 100’s ka for the coarse sediments (Granet et al., subm.), and, in agreement with the mixing scenario, short times for the suspended materials.

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Time-space migration of melting within the E-Atlantic plume and magmatism in Portugal: U-Pb ages and Pb-Sr-Hf isotopes

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To examine time-space relations between gabbroic to granitic anorogenic magmatism in Portugal and seamount formation in the central east Atlantic region we have undertaken (1) U-Pb dating on zircon and titanite, (2) U-Pb and Rb-Sr isotope analyses on grain-by-grain selected feldspars and (3) Hf isotope analyses of the dated zircons. Ages are 68.9 ± 0.3 (2σ) and 70.0 ± 1.0 Ma for the Monchique complex, and 77.1 ± 0.4 and 75.8 ± 0.2 Ma for the Sines massif. For the Sintra magmatic complex four ages of 82.1 ± 0.2, 83.4 ± 0.7, 80.2 ± 0.6, and 81.7 ± 0.4 Ma are obtained. An older age of 88.2 ± 0.5 Ma is defined for the Ribamar complex. These ages define a period of at least 19 million years for alkalic magmatism showing a systematic increase in ages from south to north. For intrusional-subvolcanic rocks exposes more than 100 km to the north, much older ages of 146.5 ± 1.6, 142.3 ± 1.0, and 145.3 ± 1.4 Ma were determined.

Corrected for in-situ decay of U and Rb (isotope dilution) Pb, in the Cretaceous rocks lies at 18.522-19.299 for 206Pb/204Pb; at 15.555-16.007 for 207Pb/204Pb, and at 38.482-39.350 for 208Pb/204Pb, and Sr are 0.70274 to 0.70481. For Hf isotopes, εHf range from +4.3 to +9.6. Most sources are less radiogenic in 206Pb than the Cretaceous seamounts but they partly overlap with data from younger seamounts and the Madeira Archipelago. Examined in the Pb vs. εHf correlation diagrams all data plot in or adjacent to the field of worldwide OIB sources, being significantly different from any Atlantic MORB source. Cretaceous anorogenic alkaline magmatism in Portugal therefore requires melting of OIB-like mantle sources possibly followed by melting of the Iberian subcontinental mantle, as well as small contributions from old crust. The large spectra of lithologies seems to reflect differences in degrees of melting in possibly both, the plume and the subcontinental mantle. Emplacement of the 88 to 69 Ma alkaline complexes including the 77 Ma old Ormonde seamount is younger than Cretaceous seamount formation along the continent-ocean transition in the central east Atlantic. On the other hand, it is much older than Oligo-Miocene and Quaternary seamount emplacement. This pattern allows to establish that melting within the plume migrated in time from West (104-81 Ma) to East (88-69 Ma) and South (< 69 Ma).

Lithium incorporation in olivine

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The relative concentrations of the two stable isotopes of lithium are increasingly being used to investigate chemical homogeneity and evolution of the upper mantle. The principal host for lithium in the mantle is olivine, but how univalent species, such as Li and Na, are incorporated into the crystal structure remains poorly understood. Here, we describe the results of isobaric crystal-melt partitioning experiments which, together with thermodynamic modelling, provide insight into the mechanisms of incorporation of Li in forsterite and natural olivine of mantle composition.

The results of partitioning experiments conducted on end-member forsterite doped with varying concentrations of lithium and trivalent cations show that the dominant substitution mechanism depends strongly on the concentrations of dopant elements. At relatively high concentrations (>20 ppm Li in the crystal), lithium is principally incorporated into near end member forsterite via coupled substitution with trivalent cations such as Al and Fe³⁺. At <20 ppm Li in the crystal, however, there is no correlation between Li partitioning and trivalent element concentration and results indicate charge-balance via vacancy or interstitial defect formation.

The lithium contents of natural olivine from the spinel stability field were measured using LA-ICPMS. The amount of Li in olivine is low (<5 ppm) and, unlike Na, does not correlate with the concentration of any trivalent cation species. We therefore conducted a series of additional experiments in order to investigate Li incorporation in natural, Fe-bearing olivine. In these experiments, crystals were grown at 1 atm from a natural basanite melt, at a range of oxygen fugacities. The results demonstrate that the partitioning of lithium between iron-bearing olivine (approximately Fo89) and melt is strongly dependent on oxygen fugacity (fO₂). The concentrations of lithium in mineral-melt pairs from our experiments show that DLi olivine-melt decreases from 0.3 at IW to 0.15 at NNO. This negative dependence on fO₂ suggests that lithium is incorporated into Fe-bearing olivine either through formation of oxygen vacancies or coupled to tetrahedral Fe²⁺. The consequences are that partitioning and diffusion of Li in natural materials is strongly dependent on the activities of major components in the medium.
A chondritic and nonchondritic Earth: What would the dynamists say?

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The question of the origin of water on Earth is as pure as SMOW: it can be reduced to endogenic or an exogenic sources, however the reduction problem is anything but simple. This complex question must be probed via theoretical, physical, isotopic, and geochemical arguments, each of which require highly specialized skills. Many of the physical arguments can be numerically probed via n-body simulations that build terrestrial planets from smaller bodies in the inner solar system during its formation period, while many of the isotopic and geochemical arguments can be explored via sample collections and remote measurements of terrestrial and extraterrestrial materials. To properly address the question of the origin of water on Earth requires that each of these approaches use the other approach as a constraint.

For example, upon building their planets, the dynamists will negate or affirm the simulated planets with constraints including (D/H) ratios, water abundances, noble gas isotopic ratios and abundances, and nitrogen, oxygen, and HSE isotopic compositions. And, upon collecting their samples, the geochemists will negate or affirm the samples’ origins using physical models of solar nebula gas temperatures, time for core formation, dates of chondrules and zircons and mixes of solar elements to construct a body with plausible elemental compositions. However, their tasks are not finished, until a synthesis of the two approaches is attempted.

In this work I will present the second approach from the geochemical angle with a first synthesis between the two approaches. While a chondritic Earth is often assumed by geochemists, the implications for a nonchondritic Earth are: 1) the heat-4He paradox [1]. Which type of Earth better meets the dynamical constraints?

References


2.7-2.6 Ga Archaean ecology determined by microbial activities: A view from C and S isotopes

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The well-preserved Belingwe Greenstone Belt (2.7-2.6Ga) in Southern Zimbabwe was deposited in a sub-continental basin upon a basement gneiss. The isotopic study from drill-cores was based on clastic sedimentary units of two formations: Manjeri Fm. (2.7Ga) and Cheshire Fm. (2.6Ga). The most interesting sections of the Manjeri Fm. are two carbon- and sulphur-rich black shale layers, Shavi and Jimmy Members, with reduced carbon contents up to 20wt%. The very wide δ13C range of 40‰ obtained on pyrite separates (from −23.7 to +16.7‰) and the similarly wide δ34S range of nearly 32‰ (from −38.4 to −7.0‰) indicate primary bacterial matter. Such variations are in favour of biological fractionation that indicate various co-existing metabolic pathways: an oxygenic photosynthesis signature and anoxicogenic processes. There is also strong evidence for sulphate-reducing activity and even for S-oxidizers in various sections of the core. Some results associated with δ13C measured in carbonate clumps suggest the existence of a methane seep environment, emphasizing that complex microbial communities existed at 2.7Ga, based on well represented C and S biological cycles.

The Jimmy Member has been sampled from three different cores. The isotopic results suggest variations in the biological activities between the three localities. There is evidence of changing processes in the microbial mats, which allows an overview of the ecology of the Belingwe basin at this specific period. In fact, these changes are caused by changing biotopes in the environment, most likely due to the subsidence of the basin shifting sedimentation for shallow water to a deeper setting.

In the Cheshire black shales, δ13C values with between −44 and −32‰ suggest that methanogenic and even methanotrophic processes were present in the basin too. In addition to this study, δ13C for carbonate and reduced carbon have been measured on different stromatolitic sequences (Abell et al., 1985) from the two formations. The isotopic fractionations obtained are in favour of the Rubisco I signature indicating cyanobacterial activity.

All these information allow the re-constitution of the ecosystems that were present between 2.7 and 2.6Ga in the Belingwe basin. Multiple biological activities and various ecologies were needed to colonize the entire planet and to allow the evolution of the Archaean life.

References

Natural pigments as enamel opacifiers on ancient glass: Raman study of lazurite colour decoration on 1st to 2nd century glass vessels from Lubieszewo (Lübsow), Poland

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Glass vessels decorated with colourful designs either by application of pigments or a low melting coloured glass flux were highly estimated by the Germanic population along the Northern and Eastern borders of the Roman Empire in the 1st and 2nd century AD. Despite the fact that a number of splendid examples with depictions of birds, fishes and plants has survived in high ranking tombs of the barbaric elite, investigations either of the glass composition or the decoration technique employed are still quite limited.

In the case of the Lübsow glasses the basic pattern is scratched on the glass body before the coloured glass flux layers carrying the pigments are applied. The presence of lazurite grains as colouring and opacifying agent was confirmed by Raman micro-spectroscopy of a pale grey ornament with a more vivid blue colour visible from the back side of the sherd.

The use of Lapis Lazuli as decorative inlay or as pigment for wall paintings in Mesopotamia, Egypt, Greece and the Roman Empire is a well known fact (see e.g. Derakhshani 1999). The as yet earliest evidence for its application in a high temperature process seems to fall into the 13th century with a high pressure phase Mg5Al5Si6O21(OH)7 named MgMgAl-pumpellyite in analogy to the phase MgAl-pumpellyite (Schiffman & Liou 1980) that was identified in experiments in the system MgO-Al2O3-SiO2-H2O for the first time (Schreyer et al. 1986). Due to its close chemical similarity to pyrope and the high-pressure, low-temperature stability delineated by Fockenberg (1998) up to 10 GPa, this phase was proposed to be an important water reservoir in cold subducting slabs (e.g. Schreyer et al. 1991; Fockenberg 1998). Gottschalk et al. (2000) found strong evidence that Mg5Al5Si6O21(OH)7 is isostructural to natural sursassite, Mn2Al5Si6O22(OH)6. Therefore, they suggested calling this high-pressure phase Mg-sursassite.

Calorimetric and P-V-T data for Mg-sursassite have been obtained by Grevel et al. (2001). The enthalpy of drop-solution was measured by high-temperature oxide melt calorimetry using lead borate as solvent. The resulting values were used to calculate the enthalpy of formation from different thermodynamic data sets; they range from -13892.2 kJ mol⁻¹ to -13927.9 kJ mol⁻¹ (formation from the elements). The heat capacity of the phase has been measured at T = 50 °C to T = 500 °C by differential scanning calorimetry. A Berman & Brown (1985) type four-term equation represents the heat capacity over the entire temperature range to within the experimental uncertainty: $C_p(T) = (1571.104 - 10560.89 \times T^{-3} + 26217890.0 \times T - 1798861000.0) \times 10^{-5} \times T^4 (J K^{-1} mol^{-1})$ (T in K).

The P-V-T behaviour of Mg-sursassite has been determined under high pressures and high temperatures up to 8 GPa and 800 °C using a MAX 80 cubic anvil high-pressure apparatus. By fitting a Birch-Murnaghan EOS to the data, the bulk modulus was determined as $116.0 \pm 1.3 \text{ GPa}$, K = 4, $V_{TO} = 446.49 \text{ Å}^3 \exp\left\{[(0.33 \pm 0.05) \times 10^{-4} + (0.65 \pm 0.85) \times 10^{-8} T dT]/(cK_f/\partial T)_{T=50} = -0.014 \pm 0.002 \text{ GPa K}^{-1}\right\}$. The thermodynamic data obtained are consistent with the phase equilibrium data (Fockenberg 1998) and included into the internally consistent dataset of Grevel (2004); the best agreement was obtained with $\Delta_f H_{298} = -13907.33 \text{ kJ mol}^{-1}$, and $S_f^{298} = 608.39 \text{ JK}^{-1} \text{ mol}^{-1}$.

References

The “Mg-sursassite” story

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The high-pressure phase Mg5Al5Si6O21(OH)7 named MgMgAl-pumpellyite in analogy to the phase MgAl-pumpellyite (Schiffman & Liou 1980) was identified in experiments in the system MgO-Al2O3-SiO2-H2O for the first time (Schreyer et al. 1986). Due to its close chemical similarity to pyrope and the high-pressure, low-temperature stability delineated by Fockenberg (1998) up to 10 GPa, this phase was proposed to be an important water reservoir in cold subducting slabs (e.g. Schreyer et al. 1991; Fockenberg 1998). Gottschalk et al. (2000) found strong evidence that Mg5Al5Si6O21(OH)7 is isostructural to natural sursassite, Mn2Al5Si6O22(OH)6. Therefore, they suggested calling this high-pressure phase Mg-sursassite.

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References
Significance of Biomarkers for P/T and F/F Mass Extinctions

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The most significant pulses of evolution throughout Earth’s history have coincided with abrupt extinction events (e.g. Benton & Twitchett 2003). The most pronounced extinction of the Phanerozoic occurred near to the Permian-Triassic (P/Tr) boundary. Many trigger mechanisms have been proposed for the P/Tr event and include bolide impact, Siberian flood basalt volcanism, ocean anoxia, H2S emissions and catastrophic release of methane from the collapse of gas hydrates, all leading to the loss of many marine organisms and land plants. Biomarkers derived from pigments of photosynthetic green sulfur bacteria have been reported in sections from W. Australia and S. China, indicating the presence of toxic H2S in the zone of light penetration (PZE) of the Tethys Ocean during the P/Tr extinction (Grice et al., 2005). Similar observations were made in a section from W. Canada (Hays et al., 2007) suggesting that the Panthalassic Ocean was also prone to periodic euxinia. Any H2S reaching the atmosphere would have been both toxic and persistent (Kump et al., 2005). The significance and value of biogeochemical markers for identifying changes at the P/Tr and F/F will be presented. In particular, the pervasiveness of PZE conditions and the origin and importance of the biomarker crocetane, generally associated with the anaerobic oxidation of methane, will also be presented.

References

Amorphous components in the shell material of the brachiopod *Megerlia truncata*

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Brachiopods have existed throughout the phanerozoic and they developed shell materials employing the two principal mineral groups of hard biologic tissue: calcium carbonate and calcium phosphate, each with distinct hierarchical architecture [1, 2, 3]. We have observed a large domain filled with amorphous calcium carbonate in the shell of the modern brachiopod *Megerlia Truncata* by transmission electron microscopy. The domain has the typical outer shape and size of calcite crystals composing the fibrous secondary layer shell. It is adjacent to a large solid inclusion incorporated into the shell, suggesting that the amorphous material is related to a repair mechanism. The fibres of the secondary shell layer are surrounded by an an organic sheath. Along the innermost segment of the secondary layer, in addition to the organic sheaths, thick organic membranes are present. The amorphous domain is located between two thick organic membranes. In the outer nanocrystalline (primary) layer we do not observe any organic material between the crystallites. Under TEM imaging conditions the amorphous carbonate crystallized in situ to vaterite. Our observations indicate that brachiopod shell formation may occur via an amorphous calcium carbonate precursor that is produced in an initial stage prior to the crystallization of calcite.

References
Non-monotonic scenarios for the Earth’s thermal history
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Expected variations of heat loss out of the Earth’s mantle with the cycle of aggregation and separation of supercontinents and the consequent variations of the wavelength of mantle flow are important, of the order of 20 TW on a timescale of a few hundreds million years [Grigné et al. 2005]. Monotonic models of planetary thermal evolution do not account for those variations and thus, may not be relevant for the Earth. The observed variations obtained in numerical models of mantle convection including continents are presented.

On a longer timescale, an event that may influence the heat loss of a terrestrial planet in a more dramatic way is the possible cessation of plate tectonics [e.g. Lenardic et al., 2004, Sleep 2000]. This possibility is studied here using models of thermal convection including a temperature-dependent viscosity and plastic yielding, which leads to either a stagnant lid or a plate-like regime, depending on the chosen parameters for plastic yielding, on the vigour of convection, on the thermal state of the mantle and on the geometry of the flow. We discuss the consequences of switching between the two regimes on the thermal state of the mantle, particularly on the temperature and heat flux at the core-mantle boundary, and on the thermal evolution of terrestrial planets.

References:

The non-existence of the SEP noble gas component – Implications for geo- and cosmochemistry from Genesis samples
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Dust grains from the lunar regolith appear to contain a solar noble gas component isotopically heavier than the solar wind that is trapped at larger depths. This component was attributed to solar particles implanted at considerably higher energies than the solar wind and dubbed "SEP" for Solar Energetic Particles. Though it has been impossible to reconcile the high apparent abundance of the “SEP” component in lunar samples with the very low flux of solar energetic particles measured in-situ in space, the “SEP” component also found wide acceptance for the interpretation of N and O data in cosmo- and geochemistry.

Ne and Ar data from a metallic glass exposed on the Genesis mission now have clarified this conundrum. The isotopic and elemental depth profiles in the glass are very similar to those predicted for a solar wind uniform in composition implanted with the velocity distribution as measured by Genesis instruments. Thus, the gases at larger depths do not represent an isotopically distinct component but are solar wind particles that got fractionated with implantation depth as a function of their mass (Grimberg et al., 2006).

In this contribution we will discuss some implications of this finding for noble gas geo- and cosmochemistry. The interpretation of solar Ne in the Earth’s mantle being due to accretion of grains irradiated by an early solar corpuscular radiation (Trieloff et al., 2000) may be maintained, except that the observed Ne composition in this case would not be a result of large contributions of “SEP”-Ne but rather has to be implantation-fractionated SW-Ne. Similarly, the inferred isotopic composition of solar O in lunar dust reported by Hashizume and Chaussidon (2005) with a $\Delta^{17}O$ value less than -20% needs not to be revised, though the O measured by these authors has now to be viewed as fractionated SW-O rather than as “SEP”-O. On the other hand, the proposed inverse trend between the isotopic composition of Ne and N from SW to “SEP” (Mathew et al., 1998) needs to be reinterpreted in the light of our results.

References
Modelling of radium-barium sulphate co-precipitation in the near field of a HLNW repository

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The solubility limit of radium is one of the main uncertainties remaining in the safety assessment of high-level nuclear waste repositories. Previous evaluations have commonly considered RaSO₄ as the solubility limiting phase, although observations in Nature indicate that this phase never occurs. Since the pioneering laboratory work of Germann (1921) and Doerner and Hoskins (1925), which showed a readily incorporation of radium into the barium sulphate (barite) lattice, most studies have concluded that the fate of radium in waters is intimately linked to barite precipitation. Both radium and barium are present in spent nuclear fuel. Most of the barium will be created during fuel irradiation, but some will also be generated shortly after the fuel is discharged from the reactor through decay of the short-lived isotopes of caesium, namely ¹³⁴Cs and ¹³⁷Cs. About 5 kg of Ba are estimated for each waste canister (SKB, 2006). On the other hand, radium is progressively generated by U-Th isotope decay chain, and maximum Ra inventory is going to be produced from the spent fuel after 100,000 years. The coexistence of both, Ba and Ra, in the fuel makes feasible the formation of (Ba,Ra)SO₄ solid solution, and, therefore, there is a great potential for reducing the calculated releases of ²²⁶Ra if co-precipitation effects are considered. These solid solution would occur at the interface between canister and clay-based barrier when, as a consequence of failure of canister integrity, a sulphate-rich water from the barrier leaches Ba and Ra from the spent fuel. In this conceptual model, the supply of sulphate is a key parameter to ensure (Ba,Ra)SO₄ formation. Calcium sulphate is a common accessory mineral in many bentonite rocks used in the barriers, although it can be easily leached by inflowing groundwaters, especially in ice-melting water intrusion.

In this study, we have calculated the effect of solid solution formation on the radium solubility limit in wide ranges of radium, barium and sulphate concentrations. The results obtained show that radium solubility limit can be reduced up to 4-5 orders of magnitude, mainly in those cases in which initial barium concentration is higher.

References

Single particle sampling and analysis

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The ability to sample and analyse individual particles is paramount for the determination of their sources, their distribution and to understand their interaction with the environment. Electromagnetic and thermophoretic sampler have been designed for collecting the ultrafine fraction (< 0.5PM) directly onto TEM grids. The results from numerical modelling of the deposition patterns and the sampling efficiency compared well with the experimentally determined performance of the samplers. Particle counts and chemical analysis (SEM, TEM) of individual particles sampled on a TEM grid can, therefore, easily be translated into quantitative information about the sampled aerosol.

Different sources of ultrafine particles have been studied using the new collectors. Particle emission from railway traffic and welding workplaces have been investigated by conventional EDS-based single particle analysis. Synchrotron based scanning transmission X-ray microscopy (STXM) and carbon(1s) near edge xray adsorption fine structure (NEXAFS) spectroscopy have been used to analyse soot particles produced by diesel engines and wood fires. First results show clear differences in the chemical structure of the particles from the two sources. NEXAFS may, therefore, be used as tool for the source apportionment of soot particles, but also to follow their evolution with time.
An improved single-step distillation of chromium-reducible sulfur

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The determination of elemental sulfur by chromium distillation is a controversial subject. Since elemental sulfur is an important intermediate in sulfur transformations in natural environments, a reliable method for quantitative recovery is required. Especially in the assessment of risks from acid sulfate soils a quantitative determination of all reduced inorganic sulfur compounds (RIS) is essential. In this field the chromium distillation has already been shown to be superior to other methods (e.g. Sullivan et al., 1999).

In the analysis of elemental sulfur Canfield et al. (1986) found a recovery of 92 % but did not specify any further the form of elemental sulfur deployed. Wieder et al. (1985) observed 94.4 % recovery by using powdered elemental sulfur but only in minor amounts. Fossing and Jørgensen (1989) and Kallmeyer et al. (2004) proved that the recovery of elemental sulfur is clearly limited. In their experiments only in dissolved state a quantitative recovery could be obtained. Neither granular nor colloidal sulfur showed recoveries >50%. Our experiments carried out with the procedure according to Canfield et al. (1986) yielded recoveries of less than 50% in the analysis of powdered elemental sulfur.

Our modified method provides recoveries >90% (mean value: 94 %) for powdered, colloidal and dissolved elemental sulfur up to at least 16 mg S (approx. 3.2% of a 0.5 g sample). Nevertheless all other reduced inorganic sulfur species are quantitatively recovered. The modified method is selective towards RIS. It does not affect organosulfur compounds or sulfates. The selectivity was verified with methionine, cystine, cysteine, taurine, gypsum and barite.

The obvious advantage of this method is the ensured quantitative recovery of elemental sulfur. Furthermore no additional toxic solvents, e.g. dimethylformamide (DMF) (Kallmeyer et al., 2004), are required. Besides that the selectivity of procedures involving DMF has not been tested with organosulfur compounds.

References
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Determining mineral solubilities at high pressures: A new method combining weight-loss and in situ approaches

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Although a fairly extensive dataset is now available on the solubility of minerals in aqueous fluids at high pressure and temperature, almost all of the data above 0.5 GPa have been obtained by ex situ quench methods in piston-cylinder apparatus. A few comparative studies between such indirect weight-loss techniques and direct disappearance-of-phase, in situ methods are available, but only for trace elements (e.g. Ayers and Watson, 1993; Audetat and Keppler, 2006; Tropper and Manning, 2005). The results show huge differences, which are not yet satisfactorily explained. Here we introduce a new approach for determining solubilities of dissolved components using a hydrothermal diamond anvil cell (HDAC). We propose to exploit the tendency of crystals to approach an idiomorphic habit during HDAC runs, as observed by Wang et al. (2004), and also in our own HDAC studies. By defining the habit of a crystal before the run, its changing geometry can be modeled at various stages of the experiment. Knowing its original volume and mass, absolute solubilities can be determined. By comparing masses at various PT conditions, relative changes in solubility can be calculated. Our specially designed HDAC (Burchard et al., 2003) allows fluid pressures up to 4.0 GPa to be reached. The results should allow a more fundamental and objective comparison between in situ and ex situ experiments. The initial focus is on quartz solubility in pure water, in order to assess the voluminous published data at hand, most of which has been obtained by ex situ methods. However, important rock-forming minerals such as feldspar and mica appear viable targets for this approach.

References
Processes controlling the relationship between volcanic fronts and the subducting slab revisited

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Thus far a thorough understanding of the controls on the position of the arc volcanoes above the subducted slab has remained elusive. Recent work by England et al. (2004, GJI, 156, 377) and Syracuse and Abers (2006, G3, 7, 5) explores global variations in depth to the slab below the volcanic front. England et al. find a systematic variation in depth to the slab, which they attribute to the product of the convergence rate of the slab and the angle of descent (Vsinδ). They conclude the downdip velocity (Vsinδ) likely controls the temperature structure in the wedge because as the downdip velocity increases, the rate at which hotter mantle is sucked into the nose of the mantle wedge increases. This observation, when combined with new experimental results on the H2O-saturated melting of peridotite (Grove et al., 2006, EPSL 249, 74), provides a model to explain the location of arcs above the subducted slab. Grove et al. found the vapor-saturated melting curve for peridotite has a negative slope. Therefore as pressure decreases, temperature increases and the minimum depth of melting is limited by the maximum temperature in the shallowest - hottest part of the wedge nose. Thus, the negative slope of the H2O-saturated peridotite solidus controls the minimum depth where melting can occur. Following this model, as the downdip velocity decreases: 1) the depth to the hottest point on the wedge nose is increased, 2) the volcanic arc is shifted away from the trench and 3) the depth to the slab is increased. The H2O-saturated phase relations also predict that there should be a maximum cut-off depth for hydrous flux melting at ~135 - 150 km depth because the hydrous phases (chlorite and serpentine) present in the mantle wedge above the slab and within the slab have dehydrated by this depth. Arc volcanoes >150 km above the slab are therefore likely the product of adiabatic decompression melting, not hydrous flux melting.

DuneXpress, in situ analysis of interstellar dust

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Interstellar grains are messengers through space and time from the remote sites in which they formed and traversed in their journeys. Born as stardust with the elemental and isotopic compositions characteristic of the cool atmospheres of giant stars or of novae and supernovae explosions, they are subsequently modified in the interstellar medium. Interplanetary dust represents more processed material from comets and asteroids at different stages of Solar System evolution. DuneXpress will provide the capability to intercompare between epochs of our cosmological history and our planetary history, via the study of the compositional variation and differences between interplanetary and interstellar dust particles.

The key to this treasure is dust astronomy. Dust astronomy requires a dust telescope in space to detect particles while accurately distinguishing their origins via their interstellar and interplanetary trajectories. Trajectory sensors utilize the electric charge signals induced when charged dust grains fly through the detector. These sensors, in combination with state-of-the-art in-situ dust impact detectors, are capable of determining mass, speed, physical properties and the chemical composition of individual dust grains in space.

The detailed objectives of DuneXpress are: 1. Mapping the seasonal interstellar and interplanetary dust flow. 2. Identification of the chemical and isotopic classes of cosmic dust grains. 3. Determination of the size distribution of interstellar dust. 4. To study the differences between interplanetary dust of cometary and asteroidal origin.

The DuneXpress spacecraft will be placed in a halo orbit at the L2 libration point of the Sun-Earth system, outside the Earth’s debris belts. The spacecraft is three-axes stabilized and provides pointing of the dust telescope to better than one degree. The payload consists of dust telescopes, dust cameras and a plasma monitor. The total sensitive area of the dust instruments will be 1 m². The newly developed dust telescope consists of a Dust Trajectory Sensor (DTS) and a Large-Area Mass Analyzer (LAMA). LAMA consists of an impact target of 0.1 m² sensitive area. It performs time-of-flight measurements of ions generated by hypervelocity dust impacts onto the target. The device employs a reflectron in order to reach a mass resolution M/ΔM ≥ 150.

The mission costs less than 100 M€ and could be launched as early as 2013.
Potential remobilization of phosphorus from acid mining lake sediments

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Introduction and methods

Natural maturation or artificial neutralization measures will lead to an accumulation of organic carbon (C\textsubscript{org}) and phosphorus (P) in acid mining lakes. Concurrently, a reduction of Fe-imports into these lakes is foreseeable (Kleeberg and Grüneberg 2005). Consequently, due to low redox potential and the neutral pH conditions in the sediment, reductive dissolution of Fe-hydroxides and the formation of sulfides might lead to P-remobilization and higher trophy.

This hypothesis was tested by studying the response of undisturbed sediment cores from the mining lake 117 (pelagic pH 3, age 35 a, z\textsubscript{max} 14.4 m, Plessa mining area, Lusatia, Germany) to C\textsubscript{org}- and P-additions. Glucose and dried Chlorella algae where added at rates between 0.2 and 3.5 g C m\textsuperscript{-2} d\textsuperscript{-1}.

Results

Only the columns with high sulfur (S) and relatively low Fe content (Fe:S ratio molar 1.4 – 2.0) showed P release with a flux between 0.15 and 0.46 mg m\textsuperscript{-2} d\textsuperscript{-1}, which is in a range comparable to oligotrophic lakes. The resulting concentration of soluble reactive P (SRP) in the pore water was approximately calculated in adsorption equilibrium with the fraction of Fe which is not immobilized as FeS using PHREEQC (Parkhurst and Appelo 1999). Vivianite formation is probably inhibited as high SRP-concentrations in the pore water up to 0.63 mg l\textsuperscript{-1} can not be explained in equilibrium with Vivianite.

Column experiments proved that P-sorption capacity becomes very low (< 1 mg P m\textsuperscript{-2} d\textsuperscript{-1}) under the influence of FeS\textsubscript{x}-formation in the sediment and without constant supply of Fe(OH)\textsubscript{3}, and that a mobilization of sediment P is possible despite high Fe content. The future P-sorption capacity might be approximated from the ratio of Fe- and S-input into the lake, provided that the supply of C\textsubscript{org} is adequate for intensive sulfate reduction.

References


Estimation of ferromanganese concretions growth rates using \textsuperscript{210}Pb

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The present investigations are devoted to dating of ferromanganese concretions from Gulf of Finland using \textsuperscript{210}Pb. About 90\% of \textsuperscript{210}Pb detected in the concretions are generated directly inside concretions as a result of \textsuperscript{222}Rn decay formed from \textsuperscript{226}Ra. The content of \textsuperscript{228}Ra in the concretions are 10-50 times higher than in all types of bottom sediments irrespective of the morphology of the concretions (Grigoriev et al., 2004).

For the study of \textsuperscript{210}Pb concentrations one spheroidal concretion (20 mm in diameter) sampled in the eastern Gulf of Finland was selected. Four probes for \textsuperscript{210}Pb determination were sampled: 1 – from the centre of the concretion (distance from the centre 0-2.5 mm); 2 – 2.5-5 mm; 3 – 5-8 mm; 4 – 8-9 mm. Analysis of \textsuperscript{210}Pb concentrations was fulfilled in the Center of Isotopic Research of VSEGEI. The radioactive decay spectra of \textsuperscript{210}Pb and its daughter elements were detected with liquid-scintillation spectrometer Quantulus 1220.

The first model does not take into account \textsuperscript{222}Rn emanation. Composing equations set and solving it we got the minimal value of concretion age 670±50 yr. Accordingly the rate of concretions radial growth is within the range 0.013 – 0.042 mm/yr.

For the second model we tried to take into account \textsuperscript{222}Rn emanation. For this purpose we applied parameter \(\phi\), which defines emanation process. After solution of the equations set we obtained the age of studied spheroidal concretion is within the range 260 – 490 yr or its radial growth rate is within the range 0.018-0.034 mm/yr.

References

Remobilisation experiment of sulphides from massive Sulphide ore at 350°C and a differential stress without exotic fluid

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The sample for the experiment is massive sulphide ore free of intense deformation textures, and is composed mainly of pyrite (32%), pyrrhotite (8%), chalcopyrite (9%), sphalerite (7%), quartz (25%) and silicates (14%). Fluid inclusions in quartz have salinities in the range of 15.96~22.98 wt% NaCl equiv.

A sample cylinder 17 mm in diameter and 40 mm in length was dried in an oven at 100°C for 24 hours before being mounted in a 3-axes rock stress machine with piston-cylinder equipment. After the experiment for 13 hours at temperature of 350°C, confining pressure of 414 MPa and axial pressure of 1276 MPa, the sample was cooled at room temperatures for 24 hours.

In the experimental product, pyrite has been intensely cataclastically deformed, resulting in numerous cracks and angular fragments. By contrast, pyrrhotite, chalcopyrite, and sphalerite are dominated by plastic deformation. Remobilised chalcopyrite and pyrrhotite occur as veinlets cutting pyrite porphyroclasts or as cementing materials of pyrite fragments, whereas remobilised sphalerite is only seen in minor amount in a few veinlets. The sulphides in the veinlets and breccia matrix are not connected to the same minerals outside the pyrite porphyroclast, indicating that remobilisation was not in solid state due to mineral plasticity, but driven by fluid. Under transmitted light, no dehydration textures of hydrous minerals have been observed, indicating that, the fluid for sulphide remobilisation in this experiment was derived mainly by breakdown of fluid inclusions.

The results of this experiment have lead to the following conclusions: 1) Deformation without exotic fluid can induce remobilisation of ore components. 2) Apart from metamorphic dewatering of hydrous minerals, breakdown of fluid inclusions due to deformation is capable to provide sufficient fluid for metal remobilisation. 3) Deformed pyrite is the best substrate for the precipitation of remobilised sulphides. 4) Sphalerite shows less strong tendency to remobilise than chalcopyrite under condition of the present experiment.

Petrography and Geochemistry Features of the Yoncayolu Metamorphics in Erzincan, NE Turkey

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The study area is located of between transitional zone Pontide and Anatolide tectonic units, on the eastern of Erzincan (NE, Turkey). The aim of this study to explain mineralogy, petrography and geochemical characteristics of Yoncayolu Metamorphics. Permo-Triassic aged these metamorphics extend almost parallel to North Anatolian Fault and have lenses of phyllite, schist, calc-schist, quartzite, orthogneiss and metabasics of very-low grade, low-grade and often medium grade metamorphic rocks. These metamorphics are overlaid by Lias-Dogger aged Cayderesi Limestones. The Refahiye Ophiolite Melange cover both of these units tectonically [1].

In the study area, sericite+chlorite+quartz+muscovite-mineral assemblaged schists, amphibole+albite+K-feldspar+quartz+chlorite-mineral assemblaged gneisses, and quartz+sericite+calkite+chlorite-mineral assemblaged calc-schist are determined. Metabasics are characterized with light schistosity rather than formation of new minerals. Metamorphics are cut often by quartz veins and dense epidotization is observed at their contacts.

Metamorphics have a composition of 50-77% SiO₂, 9-21% Al₂O₃, 2-12% Fe₂O₃, 1-7% MgO, 2-5% Na₂O, 0-1,2,2% K₂O. Comparing to SiO₂ with major element values, a negative correlation between SiO₂- Al₂O₃, SiO₂- Fe₂O₃, SiO₂- MgO, SiO₂-CaO are seen whereas, there is a positive correlation between SiO₂-Na₂O. Similarly a negative correlation exist between SiO₂-Ga, SiO₂-Sr, SiO₂-Ni and a positive correlation between SiO₂-Nb, SiO₂-Zr, SiO₂-Y. Phyllite, schist and calc-silicate rocks fall in the within the calc-alkaline field on an AFM plot but metabasic rocks fall within the tholeiitic field. On the Ni-Zr/TiO₂ diagram all of the samples values point a igneous origin [2]. On the diagrams a positive correlation of K₂O versus Th, Ba, Rb are exists that are related to clay minerals within metamorphics.

Metamorphics exhibit an increase from very low grade to medium grade metamorphism along south to north.

References

Phosphates from the Martian meteorites: A cathodoluminescence spectroscopical overview

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Introduction
The purpose of this study is to identify and microcharacterize the phosphates in Martian meteorites.

Samples and Experimental Procedures
Standard polished geological thin sections were prepared from the Nakhla, ALH84001 and Y-000593 nakhlites for WDS analysis and CL spectral investigation. Details on the CL equipments, methods, sample preparation and samples can be found in [1-3].

Discussion of results
Various phosphates such as β-Ca-phosphate (ALH84001), chloroapatite (Nakhla) and apatite (Y-000593-nakhlite) have been identified in these samples (Fig. 1), indicating the mineralogical information on the fluid-rock-atmospheric interactions in the Martian environment.

Table 1: CL properties of three Martian meteorites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CL spectra (nm)</th>
<th>Phosphate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALH84001 (#3734,373 83739 fragm.)</td>
<td>350: Ce, La 478: Ce, La 578: Dy 600: Sm 648: Sm 780: Nd</td>
<td>β-Ca-phosphate</td>
<td>[1]</td>
</tr>
<tr>
<td>Nakhla</td>
<td>514: Al, REE</td>
<td>Chloroapatite</td>
<td>[2]</td>
</tr>
<tr>
<td>Y-000593 (nakhlite)</td>
<td>578: Dy 598: Sm 650: Sm</td>
<td>Apatite</td>
<td>[3]</td>
</tr>
</tbody>
</table>

Table 1: CL properties of three Martian meteorites.

References

Micro-Raman spectroscopy and optical reflectance studies of coals with different rank

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Powerfull techniques for studying changes in the structure of organic matter during coalification and graphitisation processes include micro-Raman spectroscopy and optical reflectance.

Since coal is a heterogeneous rock with different maceral composition, the coalification studies should include the properties of each individualized component and not the average samples. Therefore, micro-Raman spectroscopy and optical reflectance analysis were performed on collotelinite and fusinite macerals from a set of coals with increasing rank.

The Raman analysis indicates the presence of bands at 1580 cm⁻¹ (G), 1470 cm⁻¹, 1350 cm⁻¹ (D₁) and 1170 cm⁻¹ on the first-order Raman spectrum on both macerals from the different coal samples. From table 1 several differences between both macerals can be observed, lower values of FWHMₕ and higher values of reflectance, vₕ and D₁/G were obtained on fusinite in all samples with the exception of sample 3153 (anthracite). With increasing reflectance a narrowing of the G band and its shift toward higher wavenumbers occur on both macerals. However the D₁/G intensity area show a slight decrease on collotelinite (except for sample 3153) and a rather constant values on fusinite. The results show that within the same coal sample the Raman parameters and reflectance in collotelinite and fusinite are different and their evolution with increasing of coal rank is also different.

Table 1: Raman parameters and reflectance of collotelinite and fusinite macerals from a set of coals of increasing rank.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ro</th>
<th>vₕ</th>
<th>FWHMₕ</th>
<th>D₁/G</th>
<th>Ro</th>
<th>vₕ</th>
<th>FWHMₕ</th>
<th>D₁/G</th>
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<td>1557</td>
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<td>59</td>
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<td>5.15</td>
<td>1591</td>
<td>54</td>
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<tr>
<td>1558</td>
<td>0.63</td>
<td>1591</td>
<td>67</td>
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<td>57</td>
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<td>1591</td>
<td>56</td>
<td>3.5</td>
</tr>
<tr>
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<td>1591</td>
<td>59</td>
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<td>1592</td>
<td>48</td>
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</tr>
<tr>
<td>1556</td>
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<td>54</td>
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<td>1594</td>
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<td>5.05</td>
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<tr>
<td>1553</td>
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<td>1596</td>
<td>34</td>
<td>2.5</td>
<td>6.11</td>
<td>1594</td>
<td>42</td>
<td>3.3</td>
</tr>
</tbody>
</table>

ν₋: G band wavenumber; FWHM₋: full width at half maximum of G band; D₁/G: intensity area ratio, all are mean values; Ro: mean random reflectance.

Acknowledgements
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Stable isotope fingerprinting of iron metabolism in higher plants

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The fractionation of stable iron isotopes by biological processes is currently a matter of intense debate. Our study is the first to show that higher plants fractionate stable iron isotopes during Fe acquisition and translocation in a significant and plant-specific manner [1].

To maintain an optimal iron supply plants have adopted two different strategies to acquire iron from the soil [2]. Strategy I plants reduce Fe(III) in the rhizosphere, as only Fe(II) can be transported across the plasma membrane of root cells. Strategy II plants acquire Fe(III) by complexation with phytosiderophores. In which form iron is translocated from roots to shoots is so far unclear [3].

Stable iron isotope compositions reflect these two uptake strategies when soils are Fe sufficient [1]. Reduction of Fe(III) in soils by strategy I plants results in the uptake of light iron compared to the available Fe in soils; complexation with siderophores by strategy II plants results in only minor fractionation. Furthermore, younger parts of strategy I plants get increasingly depleted in heavy isotopes from the first to the fourth leaf, while strategy II plants incorporate Fe of virtually uniform isotope composition throughout [1].

Here we report new results of changes in Fe isotopic compositions of strategy I (tomato, bean) and strategy II plants (oat) during growth in a nutrient solution environment under Fe-sufficient conditions. Older leaves of strategy I plants get increasingly enriched in heavy Fe isotopes whereas younger leaves become lighter while the plant grows (δ56Fe = up to -3 ± 0.05 (2SD) ‰). In strategy II plants all parts of the plant incorporate similar isotope compositions during growth. These results now show that indeed younger leaves of strategy I plants receive a substantial proportion of their Fe from older leaves. Apparently differences in iron translocation mechanisms between strategy I and II plants exist. Inside the plant Fe is scavenged by complexing agents, e.g. nicotianamine in the cells or citrate in the xylem. Nicotianamine has the ability to bind ferrous and ferric iron. The current hypothesis is that strategy I plants change the Fe redox state during translocation. In contrast, Fe in strategy II plants remains in the ferric state but changes its ligands.

Under Fe deficiency plants mobilize Fe from phytoferritin in older leaves, which includes a reduction step. The challenge is now to assign Fe isotope labels to these redox changes during re-/translocation.

References

Further evidence for a two stage magmatic underplating event in the Ivrea-Verbano Zone, Italy

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Magmatites of the continental crust are essentially formed by two tectono-magmatic processes: In the course of subduction and by the way of “magmatic underplating”. While subduction processes can be studied at many different places world-wide, the process of “magmatic underplating” can only be studied directly in the Ivrea-Verbano Zone (IVZ) of the Southern Alps (Italy). So our understanding of this not less important mechanism of crustal growth is still unsatisfactory inasmuch as reliable age data providing tight time constraints on the duration of the underplating processes are still missing. One of the major open questions still is, for instance, whether magma formation and emplacement is a discrete or a continuous event. The IVZ is interpreted as being a slice of the South-Alpine lower crust intruded by mantle magmas. Rocks of this zone have been grouped in two major units, the voluminous composite Mafic Complex (=Mafic Formation) and the high-grade paragneiss Kinzigite Formation. For the main intrusive body of the Mafic Complex in the Val Sesia and Val Sessera sections an intrusion age of 288 ± 4 Ma is postulated [1]. This speaks in favour of a short, discrete main underplating event in the Lower Permian. In addition, the age data indicate that a significant thermal event affected the country rock of the Mafic Complex around 310 Ma, the significance of which is not yet clear. “Strati-graphically” this thermal event seems to be most prominent in the lower most parts of the crust. We have investigated the Campello Monti and Monte Capio area (Val Strona). Here the Mafic Complex forms a composite intrusion which only in parts can be paralleled with the main intrusive body in the Val Sesia. Especially an amphibole-garnet-bearing gabbro strongly resembles the amphibole-gabbro of the lower mafic complex in the Val Sessera [1]. From the former a zircon LA-MC-ICP-MS U-Pb intrusion age of 331.5 ± 3.8 Ma could be determined. This new age is the first unequivocal evidence that an older magmatic event occurred in the lower part of the IVZ crust in the Middle Carboniferous. This substantiates that the underplating event in the IVZ indeed was a long lasting process with a duration of ca. 50 Ma but comprising a number of discrete intrusive phases of only a few million years duration. The geodynamic implications of this new aspect in the evolution of the IVZ in the framework of the Variscan orogeny, mainly the onset of crustal thinning already in the Carboniferous, remain to be investigated.

Reference
Silica polymerization. Rate constants at 23° to 80°C as a function of pH

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When monomeric silica concentration exceeds the solubility of amorphous silica, monomeric silica reacts to form polymeric silica. It is generally agreed that the polymerization proceeds until the concentration of monomeric silica is equal to the solubility of amorphous silica. Much work has been done over the years to determine the rate of silica polymerization but to date there is no general agreement on rate laws. Rate orders of 1 to 8 and rate maximum between pH 6 to 9 have been reported. Part of the discrepancies is probably due to failures to recognize things like induction periods and failure to account for higher amorphous silica solubility at high pH values.

After the initial stages of silica polymerization, where silica is forming nuclei of critical size, the polymers have a tendency to maximize the number of siloxane bonds (Si-O-Si) and minimize the number uncondensed SiOH groups and they become spherical units. These polymers grow with addition of monomeric silica on their surfaces. At this stage of silica polymerization there is equilibrium between the silica polymers and monomeric silica in solution. As polymerization continues the polymers increase in size and the area, to which the monomers are added, is continuously changing affecting the polymerization rate. Silica polymerization stops when the polymers are so big that surface energy does not contribute much to the total energy of the polymers. Polymers of that size have similar solubility as amorphous silica.

In this contribution are presented the results of silica polymerization experiments in the pH range 5.66-9.18 at 23°, 2.48-8.50 at 58° and 2.18-8.75 at 80°C. Ionic strength was 0.11±0.02M in all cases. Rate of silica polymerization was monitored by analyzing concentration of molybdate active silica. Results indicate that the rate of silica polymerization is greatly affected by the pH value of the solution and there is no maximum in polymerization rates over the pH range of this study. The calculated rate constants increase with rising pH value over the whole pH range of the experiments at all experimental temperatures.

The sulphur isotopic evolution of late Neoarchean and early Paleoproterozoic seawater

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Despite its well accepted importance for reconstructing the redox evolution of Earth’s ocean-atmosphere system, our knowledge of the abundance and isotopic composition of seawater sulphate decreases substantially with increasing time. This is most apparent for the Precambrian. In particular, the proposed rise in atmospheric oxygen abundance (Great Oxidation Event) around 2.3 Ga ago and an assumed parallel increase in the abundance of dissolved oceanic sulphate is not documented at all.

Here, we report abundances for sulphate sulphur as well as sulphur and oxygen isotopic compositions for the Neoarchean-Paleoproterozoic succession deposited on the Kaapvaal Craton between 2.65 and 1.92 Ga, i.e. the Transvaal Supergroup of eastern Transvaal and correlative units in the Griqualand West Subbasin.

Trace sulphate extracted from 16 carbonates of the Koegas, Duitschland, Mooidraai, Silverton and Lucknow formations gradually increase from less than 0.1 to 23.5nmol/kg. The respective sulphate sulphur isotopic composition varies between +4.6 and +34.6‰ with a distinct stratigraphic trend being discernible. The oxygen isotope values for the trace sulphate displays a range between +6.1 to +21.1‰.

Individual stratigraphic units are well constrained in their isotopic composition. Yet, the truly global significance of the isotope record needs to be verified with additional analyses. So far, respective host carbonates have provided a carbonate carbon isotopic composition that includes pertinent features considered characteristic for this time interval, such as the globally recorded 13C maximum (the Lomagundi-Jatulian event).

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**Trace element and Ca isotope ratios in calcareous dinoflagellate cysts of** *Thoracosphaera heimii*

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Dinoflagellates are important marine primary producers, which significantly contribute to the global carbon cycle. They can form cysts, composed of organic-material, silicate or calcium carbonate, which are used as stratigraphic and paleoenvironmental indicators.

The export flux of calcareous dinoflagellate cysts is of particular importance in temperate to tropical waters and is dominated by the species *Thoracosphaera heimii*. Providing a significant calcium sink, their Ca isotope fractionation is an important factor for the Ca isotope ratios of the locally deposited carbonate oozes, but might also be important for defining the isotopic Ca budget of the ocean. In addition, *T. heimii* cysts provide the potential to record long-term changes in the ocean chemistry, because their first occurrence dates at the K/T boundary [1].

The CaCO₃ cysts of *T. heimii* might be particularly useful as proxy archive recording ocean surface conditions (e.g. temperature, pH) due to their formation at the deep chlorophyll maximum depth in the water column and the ease in which a monospecific assemblage can be isolated from sediments [2]. Furthermore, they are comparatively insensitive to dissolution.

The dominant calcareous dinoflagellate *T. heimii* was grown in lab cultures at varying temperatures ranging from 12 to 30 °C as described earlier [3]. Trace element to Ca and Ca isotope ratios were analysed on the CaCO₃ cysts, previously cleaned from organic components.

The Ca isotope fractionation for *T. heimii* cysts resembles previous calibrations of other marine calcifiers, including coccolithophores [4], foraminifers and corals [5], in respect to absolute fractionation and temperature sensitivity. In contrast, trace element to Ca ratios and their temperature dependence differ from trends observed for coccolithophores and planktonic foraminifera. These results will be discussed in terms of bimineralisation of *T. heimii* and potential use for paleoceanographic applications.

**References**


**Mechanisms of iron(III) binding to organic matter and its competitive effect on trace metals**

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Organic complexation of iron(III) is important for the binding of trace metals in natural environments because of competition effects. We have investigated the binding mode of iron(III) in the presence of O horizon soil material and isolated fulvic acid by means of EXAFS spectroscopy. The spectra for the O horizon samples showed Fe-O/N interactions at 2.02(2) Å, second-shell Fe-C interactions at 3.00(4) Å, and a mean Fe-Fe distance at 3.37(3) Å (Gustafsson et al., 2007). This showed that the major part of the organically complexed iron(III) was hydrolyzed, and comparisons with literature data revealed that iron(III) had formed a mixture of di- and trimeric complexes with soil organic matter. The results were used to constrain a model for organic complexation, the Stockholm Humic Model. Observed competition effects on Cd ²⁺, Cu ²⁺, Ni ²⁺ and VO ³⁻ were well described with a single dimeric iron(III) complex in the model. In another set of experiments iron(III) was equilibrated with isolated fulvic acid at different initial pH:s, and the mixtures were analyzed with EXAFS spectroscopy after different time periods. These spectra lacked the Fe–Fe distance at 3.37 Å, instead Fe formed a monomeric iron(III) complex with FA or was reduced to Fe(II) after prolonged equilibration times. Our results indicate that the iron(III) binding modes to organic matter need not be identical in soils and aquatic environments. In soil suspensions any added iron(III) is quickly polymerized, whereas in solutions significant amounts of iron(III) complexes may remain as monomeric organic complexes. This shows that much remains to be done before the aquatic geochemistry of iron(III) is fully understood.

**Reference**

Identifying processes and rates of incipient chemical weathering using Pb and U isotopes

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This study focused on the role of incipient chemical weathering on combined U and Pb isotope systematics. Understanding the effect of incipient weathering is particularly relevant for interpreting the marine Pb isotope record during glacial-interglacial transitions. Here, we investigate whether the preferential release of radiogenic Pb, displaced through alpha recoil, could explain Pb isotope variations during the recent deglaciation. Soil samples from a granite chronosequence at the forefield of the Damma glacier were sampled for an experimental study of chemical weathering. A sequential leaching technique was employed on the <1mm grain size fraction (0.05M, 0.1M HBr; 0.05M, 0.6M HCl; leaching each fraction for 24 hours in a shaker) and the residue dissolved by pressure digestion. In order to distinguish the effects of preferential dissolution of U- and Th-rich minerals (Harlavan et al., 1998) and release of alpha-recoiled Pb, we measured both the Pb isotope compositions and $\delta^{234}$U (expressed as the per mil $234U/238U$ variation from secular equilibrium). Most strikingly, even the moraine samples with a maximum of hundreds of years, as opposed to much longer timescales suggested in earlier studies.

Dissolution of magnetite in hydrothermal solutions: Kinetics and speciation by in situ X-ray absorption spectroscopy

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In the research program on mineral sequestration of CO$_2$, time-resolved studies dedicated to fluid-rock interactions are essential. Magnetite (Fe$^{III}$)O$_4$ is an accessory host solid phase (the most reactive host candidates are basic and ultra-basic rocks), but is likely to release critical amounts of dissolved iron in the fluid, iron which is a reactant for the carbonation of carbon dioxide. Furthermore, magnetite may play a major role in the redox control of the system. For those reasons, we studied the dissolution of magnetite in hydrothermal conditions, as a function of pH, temperature and the nature of ligands in presence (the roles of sulfate and chloride ligands were quantitatively compared).

Our methodology is based on in situ x-ray absorption spectroscopy (XAS) on synchrotron sources. For that purpose, we use an high-pressure/high-temperature cell (Testemale et al.) that allows, in the same run, the determination of iron speciation and the measurement of X-ray absorption spectra at the iron K-edge (see Figure 1). The latter is a strong point of this method: the speciation and oxidation state of dissolved iron can be inferred from these x-ray absorption spectra.

We will present a kinetics model for the dissolution of magnetite, in the conditions investigated (300 bar, [30-300°C]), to be compared with literature data. In particular, the role of iron speciation and the stoechiometric nature of the dissolution will be discussed.

Figure 1: Total iron molality (Fe$^{II}$ and Fe$^{III}$), as a function of time, in a 2.5M sulfuric acid solution. For each point, we acquired a XAS spectrum from which the speciation is determined.

Reference
Apatite- and K feldspar-hosted primary carbonatite melt inclusions from mantle xenoliths, Hungary

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Samples

We studied metasomatic mantle xenoliths, consisting of clinopyroxene, apatite, K feldspar and phlogopite, were found in lamprophyre dikes in central Hungary. A large number of multiphase primary carbonatite melt inclusions (CMI) were observed in apatite and K feldspar, but clinopyroxene and phlogopite are barren. Average PM normalized REE distribution of apatite and K feldspar hosted CMI (n=60 and n=20, respectively) are shown on Fig. 1. Both CMI in apatite (Ap) and K feldspar (Kfs) are extremely enriched in LREEs relative to HREEs analyzed by LA-ICP-MS.

Discussion

It is a characteristic geochemical feature that CMI in Kfs contain small amount of P and that in Ap do small amount of K. The REE distribution of CMI in both host minerals show similar pattern (Fig. 1), suggesting common origin of their melts. It is also supported by some unique CMI hosted in Ap having trace element composition and pattern similar to CMI of K feldspar. All of these indicate that there was a liquid-liquid separation between a P-bearing carbonatite melt and a carbonate-bearing silicate melt before crystallization of the host minerals. It seems that the liquid-liquid separation was caused by dramatic compositional change in the continuously migrating “initial” carbonatite melt. This change was linked with an open-system metasomatic interaction between the “initial” melt and the peridotite mantle.

Conclusion

The studied xenoliths were formed by metasomatic interaction between the peridotite mantle and the P-bearing, Mg-calcitic “initial” carbonatite melt.

Fluid composition, density and viscosity changes along terrestrial Pressure-Temperature paths associated with particular tectonic processes

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Physical properties determine how buoyant fluids rise (density) and how fast they flow (viscosity). Such physical properties will also depend on fluid composition, especially where mineral solubility is high. We have modeled the thermal and chemical behavior of dehydration fluids with dissolved constituents generated in and above subduction zones, and also along burial and exhumation paths in the crust. Silica solubility has been used as an example (e.g., Gerya et al. 2005). SiO2–H2O fluid viscosities at quartz-saturation have been modeled following Audétat & Keppler (2004). Silicate-bearing fluid densities have not yet been measured, so in the interim, we have modeled SiO2–H2O fluid densities at quartz-saturation. We assumed an ideal mixture and combined solubility data with properties of the end-member liquids. The results show that fluid-rock interactions are likely to follow distinct patterns along different PT paths. For example, buoyant fluid flow into the overlying hot mantle wedge is up T (while down P) and follows a dissolution path, whereby fluids may create permeability, facilitating higher fluxes. Fluids flowing along the slab-mantle interface move to lower T and P and precipitate dissolved matter, which acts to decrease porosity and probably permeability and reduce flow rates in that direction. Our analysis reveals that subtle differences in fluid PT ascent paths, strongly influence both solubility and fluid density-viscosity evolution along paths and thus also the efficiency and rate of mass transport. Low-viscosity and low-density fluids have the greatest chance of moving at higher velocities. With increases in density, solute concentration increases, buoyancy decreases and viscosity increases. Increased solubility of mineral in fluid thus decreases ease of ascent, but tends to work in the opposite PT direction. So fluids related to rock burial become increasingly dense and more viscose, and thus less mobile. In contrast, rising fluids tend increase their buoyancy and decrease their viscosity but because solute concentrations also decrease, fluid ascent can become restricted by precipitation.

References

Genesis and rates of fluid flow at the Mercator mud volcano, Gulf of Cadiz

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Mud volcanism is a widespread phenomenon in the Gulf of Cadiz (GoC) and provides a window into deep structural and diagenetic processes [1]. Sediment pore fluids from the Mercator mud volcano (MMV), located in the El Arraiche mud volcano field offshore Morocco, are extremely enriched in chloride reaching up to 5.3 M (thus, exceeding normal seawater values by a factor of 9). Na/Cl ratios are close to 1 suggesting halite dissolution by the ascending fluid. This is corroborated by 3D seismic data that shows an active anticline below the eastern flank of the MMV, which can only be explained by a rising salt diapir. Additionally, the fluids are highly enriched in Li and B indicating a deep fluid source from mineral dewatering reactions at elevated temperatures (>100 °C). A deep fluid source is also supported by a radiogenic 87Sr/86Sr porewater signal of 0.7106 as well as the morphology of quartz and gypsum crystals transported within the ascending mud matrix. These crystals are probably of Triassic origin. Hence, the geochemical and the 3D seismic data suggest that the Triassic salt province 500 km further south on the Moroccan Margin might extend further north than previously known and that halokinesis has to be considered as a driving force for mud volcanism in the GoC.

Finally, a 1-D transport-reaction model has been applied to constrain the fluid advection rates. The numerical simulations of conservative porewater compounds Cl, Li, and B reveal upward fluid flow rates of ~6 cm/a at the top of the MMV, gradually decreasing to 0.3 cm/a towards the rim. In addition, a CTD mounted onto a video sled system provided bottom water salinity and temperature information (about 2 m above the seafloor) from tracks crossing the MMV. In combination with the numerical porewater analysis, this unique spatial data set allows to constrain the overall budgets for the release of water, methane, and other porewater constituents as well as the heat flow of the MMV.

References

Arsenic mineralogy in high-As wastes at historic gold mine sites, New Zealand

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The studied mine processing sites are part of the Phoenix Mine and the Blackwater Mine, which are historic gold mines hosted within the Otago schist and Greenland Group schist, respectively. The processing of arsenopyrite ore produced very arsenic rich residues (up to 40 wt% As) and no rehabilitation was undertaken after mine closure at either mine. Thus, the studied sites possess suitable conditions for the study of the physical and chemical characteristics of secondary arsenic minerals, especially with respect to time. At the Blackwater Mines all arsenic was originally present as arsenolite (arsenic trioxide polymorph, AsO3), which is a by-product of arsenopyrite roasting. At the Phoenix Battery, where roasting did not take place, arsenopyrite was the original arsenic phase. High dissolved arsenic concentrations derived from the processing residues are temporarily immobilized by the formation of hydrated iron arsenates in the downstream environment. At the Blackwater Mine the hydrated iron arsenate is in the form of scorodite (FeAsO4·2H2O), whereas at the Phoenix Battery it is in the form of kankite (FeAsO 4·3.5 H 2O). In the past the precipitation of hydrated iron arsenates, especially scorodite, has been mainly associated with acidic environments. The studied mine sites are, however, excellent examples for iron arsenate precipitation in a geological setting with high neutralizing capacity and predominant circum-neutral pH. The stability of the hydrated arsenates depends on dissolved arsenic concentrations and is, therefore, controlled by the solubility and availability of the original As phase. In addition, the stability of As is further enhanced by the inherent morphology of the hydrated iron arsenates which precipitates as an interstitial cement, thereby creating an impermeable surface crust and preventing further dissolution of underlying arsenic minerals.
Application of in situ cosmogenic nuclide analysis to landform evolution in (palaeo)-periglacial south-west Britain

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Located beyond the southern limit of glaciation in Britain, the upland granitic terrain of Dartmoor, south-west England, has been exposed to long intervals of intense periglacial activity during the Pleistocene. This region has been significant in debates about appropriate models of long-term landscape change, most notably two-phase versus single-phase models of landform evolution, and the development of tors (Linton, 1955; Palmer & Nielsen, 1962). However, given the previous lack of quantitative techniques capable of constraining denudation and specific process rates, and thereby testing developmental models, for these features there remains much uncertainty in the interpretation of the classic landforms of the region. Here we present the results of research utilising in-situ cosmogenic nuclides to evaluate geomorphological processes and report on three key aspects of landform development: (1) the formation of tors and models of outcrop emergence in non-glaciated regions; (2) the development of regolith and boulderfields under periglacial conditions; and (3) catchment-averaged denudation rates derived from alluvial sediments. This variety of landforms and scale of investigation facilitates an integrated approach to the understanding of catchment-scale erosional dynamics. In addition, the complex nature of landform development that is evident in the area provides challenges to the application of in-situ cosmogenic nuclides and highlights both the potential and limitations of the technique.

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Origin of tungsten mineralization in the quartzdioritic unit of the Boroujerd Granitoid Complex (Western Iran) using geochemical evidences

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Boroujerd Granitoid Complex of the Sanandaj-Sirjan Zone consists of three main units: granodiorite, quartzdiorite and monzogranite. In Nezamabad area (SE of this complex), quartzdioritic unit has been cut by various quartz-tourmaline veins having NW-SE trending. Tungsten mineralization (scheelite) accompanying by arsenopyrite, pyrite, pyrrhotite, chalcopyrite, sphalerite, malachite, azurite and quartz and tourmaline as gangue are generally associated with the veins.

The geochemical signature of this unit is compared with the well known W-bearing and W-barren granites (Lemann et al., 1994; Srivastava and Sinha, 1997; Singh and Singh, 2001) in order to investigate their relationship with tungsten mineralization in the area.

The host quartzdioritic unit of the quartz-tourmaline veins is mostly depleted in silica (52-63%), total alkalis (4.6%), Rb (94 ppm), Nb (10 ppm), W (6 ppm) and Sn (3 ppm) with low DI and enriched in CaO (6.11%), MgO (4.19%), MnO (0.14%), Sr (285 ppm) and Ba (359 ppm). Compared with the W-barren granites, the K/Rb (211) and Ba/Rb (4) ratios of this granitoid are also higher than its Rb/Sr ratio (0.34). All these geochemical evidences as well as I-type characteristics of the quartzdiorite unit (Ahmadi-Khalaji et al., 2007) indicate that the unit behaves as a barren granite.

On the other hand, geochemical investigation on the metamorphosed sedimentary rocks (hornfels and spottedschist) existing in contact with the quartzdioritic unit demonstrates that the W-bearing fluid originated from the dehydration of the metamorphosed sedimentary rocks and it mixing with granitic fluids.

The quartzdioritic unit is a W-barren granite of a low differentiated magma and has no significant role in tungsten mineralization. In contrary, metamorphic rocks fluids can be considered as the main source for tungsten mineralization rather than granitic fluids.

References
**Reaction textures of allanite in metagranitoids: A sub-micrometer insight in REE-mobility**

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Various reaction textures of accessory allanite in an orthogneiss from the Tauern Window (Austria), which experienced metamorphism (max. 500-550°C, 1.0 GPa; Selverstone 1993), and extensive metasomatism have been investigated by high-resolution BSE images (JEOL Hyperprobe JXA-8500 F, field-emission cathode).

Euhedral to anhedral (Ø 150 - 500 µm), partly zoned allanite crystals have corona-type textures with polycrystalline (REE+Y)-poor epidote/clinozoisite rims (type 1). Variable deformation stages resulted in regularly to sigmoid or irregularly shaped rims of 20 - 200 µm thickness. Anhedral titanite crystals (15 µm) mark the core-rim boundary along the epidote/clinozoisite site of the paragenesis. Micropores within allanite (type 2), partly filled with Th- or REE-silicates, are part of the core-rim zonation (relatively REE+Y+Th-rich to – poor) or scattered over allanite. Th-silicates on grain boundaries of newly formed (REE+Y)-poor epidote/clinozoisite (polycrystalline epidote/ clinozoisite rim of allanite) indicate decomposition and reprecipitation of that phase. Patchy aggregates of allanite and REE-poor epidote with intermediate compositions, changing in an irregular pattern on the µm and sub-µm scale, are the dominant feature in the intensely deformed orthogneiss (type 3). In addition to these well-known textures up to 1 µm wide mineral-filled channels within elongate textures (max. 80 µm) in an allanite of type (3) were found (type 4). The zoned channels pass perpendicular through the internal textures, which are orientated parallel and perpendicular to the long axis of the allanite and connect (REE+Y+Th)-poor with relatively (REE+Y+Th)-enriched parts of the unzoned crystals.

In a preliminary interpretation texture (1) was formed in late- to postmagmatic stage in the protolith, textures (2, 3, 4) indicate a simultaneous fluid-assisted decomposition of allanite and growth of (REE+Y)-poor epidote/clinozoisite in an open system during metamorphism. The Th-silicate on grain boundaries within the epidote/clinozoisite rims of allanite and sub-micrometer wide channels within allanite possibly indicate multistage grain boundary diffusion and a gradually changing composition of the fluid phase during the breakdown process.

**References**


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**The bulk chemical composition of the upper Martian crust**

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There is strong evidence that the Martian surface has been extensively chemically homogenized over time due to broad-scale impact gardening, an apparent lack of plate tectonic fractionation and evolution, long-term global eolian processes, and periodic fluvial transport. Despite wide geographic separation, soil chemistry from landing site analyses (MER, Pathfinder, and Viking) are remarkably similar with most variation attributed to the addition of some local rock components - strongly implying that the unconsolidated fraction of the Martian surface has been reasonably well-homogenized. Gamma-Ray Spectrometer (GRS) elemental abundance maps agree well with surface analyses and, with some notable exceptions, global GRS elemental abundance maps reveal less broad-scale chemical variation compared to the terrestrial or lunar surfaces.

Therefore, it has been suggested that the chemical composition of averaged Martian soil analyses reflect the bulk chemical composition of the Martian surface from which they are derived – much in the same way terrestrial sedimentary chemistry can be used as a proxy for the bulk terrestrial upper crust. Weathering, sedimentary transport, and deposition naturally sample a wide array of source rocks with the resultant chemistry being an efficient mixture of source terrains.

With carefully screened MER APXS data, we develop an estimate of major and trace element crustal chemistry based upon MER soil averages. GRS global chemical averages for certain elements are used to corroborate compositions calculated from the soil data and in some cases GRS global averages for a particular element are assumed to represent the bulk upper crust. Where applicable, SNC chemistry and canonical cosmochemical relationships are also incorporated into the bulk determination.
Petrogenesis of meta-peridotites in the Takab area, NW Iran

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The Takab meta-ultramafic rocks of north western Iran crop out in association with a variety of metamorphic rocks including mafic granulites, amphibolites, calc-silicates, granitic gneisses and pelitic schists. The protoliths of the Takab meta-peridotites were mainly harzburgite and dunite with subordinate lherzolite. All peridotite varieties contain primary Cr,Al-spinel. The peridotites were modified by metasomatism under low-grade conditions and later amphibolite-facies metamorphism, the thermal peak of which occurred at temperature of 410-530ºC, corresponding to an orogenic setting.

Chemical compositions of the porphyroclastic olivine, pyroxene and spinel in the investigated meta-peridotites give temperature of 1000-1200ºC; clinopyroxene barometry yields a pressure of 24±2.7kbar, corresponding to a depth of ca. 72km.

The results are consistent with oceanic lithospheric upper mantle origin (i.e. in an ophiolitic setting) of the meta-ultramafic rocks in the Takab area. Similarities in the stratigraphy, lithology and age data (relative and isotopic ages) of the protoliths of the Takab complex and equivalent units from the Central Iran Zone suggest that the Takab complex has a Neooproterozoic-Early Cambrian age and experienced the Pan-African orogeny. The strips of the ultramafic rock in the study area are remnants of the Proto-Tethyan oceanic lithosphere.

Li isotope fractionation in the subducted slab – A case study from the Raspas complex, Ecuador

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Lithium isotopes are a potentially powerful geochemical tracer of subducted material due to significant isotopic fractionation on the Earth’s surface and the fluid-mobile behaviour of Li. To improve our ability to track recycled Li in the mantle, and to understand the transfer of Li from the slab through the mantle wedge to the volcanic arc, it is important to constrain the Li isotopic composition of subducted material and the isotopic changes that may occur during the subduction process.

Here, we report results from a detailed geochemical and Li isotope study on the now exhumed part of a subducted slab from the Raspas complex (Ecuador), which comprises serpentinites, eclogites, blueschists and high-pressure metapelites. Eclogites show MORB-like trace element signatures and are LREE-depleted. They are characterized by a light Li isotopic composition with δ7Li ranging from 0 to -13. These values are considerably lower than those of fresh and altered MORB (δ7Li = +3 to +14; Chan et al., 1992), but they overlap with those of Alpine eclogites (Zack et al., 2003). In contrast, blueschists and metapelites, as well as the serpentinites that are interpreted to represent the mantle portion of the subducted slab, have Li isotopic compositions in between the eclogites and MORB. A negative correlation between δ7Li and Li/Dy for the eclogites suggests that influx of Li from an external source may have been responsible for decrease in δ7Li in the eclogites. Moreover, the elevated Li concentrations in some of the eclogites (up to 94 ppm) are difficult to reconcile with Li loss during dehydration alone. Although none of the associated lithologies is particularly rich in Li, eclogite-facies fluids that may contain up to 438 ppm Li (Svensen et al., 2001) could provide a suitable source of Li. These results suggest that fluid-assisted kinetic isotope fractionation (Teng et al., 2006) may have played a role in causing the light Li isotope composition of the eclogites, as also suggested by Marschall et al. (2007).

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The Pb isotope evolution of Arctic Ocean intermediate water over the past 16 million years

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We present the first record of the dissolved Pb isotope composition of Arctic intermediate water of the past 16 Myr. The data were obtained from leaches of sediments of IODP Leg 302 (“ACEX”) drill-cores and from a piston-core (PS2185), both located near the North Pole on the Lomonosov Ridge (~1200m water depth). Both the leaches and bulk dissolutions of the same sediments show similar Pb isotope compositions in the “Neogene” (>1 Ma) and in the “Pleistocene” (<1 Ma) sediments, although the median values differ slightly between the two sections (e.g. 206Pb/204Pb ~18.5 in the “Neogene” versus ~18.6 in the “Pleistocene”). These central Arctic isotope signatures are much less radiogenic compared with N. Atlantic records, and, although similar trends between these two basins are observable for the Pleistocene, they differed significantly during the Neogene.

From these observations and comparisons in Pb-Pb isotope space, we argue that the source of dissolved Pb in Arctic intermediate waters has primarily been derived locally from exchange with sinking ice transported sediment particles. These sediments originated from the Eurasian shelves and have continuously been carried to the North Pole region via the Transpolar Drift for the past 16 Ma.

On short millenial time scales of the Quaternary our Arctic records reflect isotopic changes in the Siberian continental sources of Pb. The most likely process driving these changes was incongruent weathering and soil formation during interglacial periods. These soils originated in the marine environment: corals (porites lutea and acropora), Cretaceous limestone (Judea Mt.); Cretaceous evaporitic aragonite (Dead Sea) yielded uniform δ86Sr value (-0.28±0.07 ‰) within the 1σ error of Red Sea and Atlantic seawater (-0.35±0.04 ‰). On the other hand, secondary materials (products of chemical weathering) from the terrestrial environment of the Judea Mt. such as speleothem calcite and terra rossa soil (airborne dust particles residual rock material) both yielded significantly higher δ86Sr value (0.17±0.03 ‰).

All rocks that originated in the marine environment: corals, Cretaceous limestone, and Pliocene epigenetic dolomite (Dead Sea rift margins); as well as lacustrine evaporitic aragonite (Dead Sea) yielded uniform δ86Sr value (~0.28±0.07 ‰). On the other hand, secondary materials (products of chemical weathering) from the terrestrial environment of the Judea Mt. such as speleothem calcite and terra rossa soil (airborne dust particles residual rock material) both yielded significantly higher δ86Sr value (0.17±0.03 ‰). It should be noted that both groups are distinctly different from the SRM987 standard that has by definition a value of 0 ‰. It appears that strontium isotopes are fractionated within the terrestrial environment by geochemical processes such as chemical weathering and genesis of soils and hence δ86Sr/88Sr ratio may be developed as a tracer for these processes.
Growth of the Earth’s core

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Hafnium-tungsten chronometry provides evidence that some magmatic iron meteorite parent bodies formed relatively small cores within a million years of the start of the solar system. Similar timescales can be inferred from martian meteorites and ureilites. There is some evidence that the degree of siderophile element depletion, possibly reflecting relative core size, increased over the first 10⁷ years on Mars and the angrite parent body. How the Earth’s core started is less clear and some assume more efficient core growth under reducing conditions. The Si isotopic compositions of mantle-derived silicate rocks from the Earth and Moon are heavy relative to those from Mars and Vesta which in turn are identical to those of chondrites. A likely explanation for this is Si isotopic fractionation during high pressure and high temperature metal segregation. On this basis Si is one of the light elements in the Earth’s core. There is a hint of an analogous effect for oxygen. However, the heterogeneity within the circumstellar disk renders this interpretation less certain. Similarly, slightly heavy Fe in the bulk silicate Earth may reflect high pressure core formation in the presence of perovskite. The Moon does not have a high pressure core yet lunar basalts display O, Si and Fe isotopic compositions similar to those found on Earth. This can be reconciled with giant impact simulations provided there was efficient mixing between the silicate Earth and the protolunar disk as recently proposed (Pahlevan and Stevenson 2005). This being the case the Moon represents an important new archive for the composition of the early silicate Earth and demonstrates that Si and possibly O were already light elements in the core before the Giant Impact.

Reference


Molecular and isotopic study of acidic metabolites in the deep biosphere employing petroleum reservoirs as natural bioreactors

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Being systems that support a biologically active environment, petroleum reservoirs can be used as naturally occurring analogues to bioreactors in view of studying the anaerobic catabolic and metabolism of an extremophile deep-subsurface biosphere. Although living cells have been identified in deep sub-seafloor sediments (Schippers et al., 2004), cell organic matter is not preserved well in the aqueous environment. The hydrophobic oil matrix of petroleum reservoirs, in contrast, can act as an accumulator of in-situ produced metabolites and cell-wall lipids.

This presentation will examine the molecular distribution and stable carbon isotopic variation between carboxylic acids and their non-carboxylated hydrocarbon counterparts in oils that were biologically degraded to various extents and recovered from different non-communicating compartments of a reservoir. Oils were fractionated into compound classes and further analysed by gas chromatography (GC) and mass spectrometry (MS), as well as isotopic ratio monitoring (irm)GC-MS.

The lack of microbial petroleum degradation in reservoirs that were ever heated >80°C suggests that microbes have been present in the sediments since their deposition and possibly survive by the release of volatile organic acids from dispersed sedimentary organic matter (Wellsbury et al., 1997). Significant migration and recolonization of microbes in the subsurface does not appear to take place. The escape into the deep could be an ancestral evolutionary survival strategy that allows microbes to maintain their viability for extremely long periods, to the expense of pushing the physicochemical limits of life. Understanding the evolution of earth’s early biosphere is therefore closely related to understanding the biochemical adaptation of life to extreme environments, which can only be studied in present-day analogues, one of which are deep anaerobic petroleum reservoirs. This study focusses on the structural and isotopic analysis of carboxylic acids as indicators of deep biosphere processes.

References

Li diffusion and isotopic fractionation in olivines crystals
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In order to constrain the behavior of lithium isotopes in crystals during magma cooling, the study of a fresh pillow lava with large olivine crystals has been undertaken. An ion microprobe was used to measure lithium abundances and isotopic compositions both in olivine phenocrysts and in the pillow rim glass. Profiles in δ7Li conducted through olivines show very different patterns correlated with their cooling history. Olivines embedded in the pillow rim glass display no variation in Li abundance ([Li] = 1.2 μg.g⁻¹) and isotopic composition (δ7Li = +6 ‰). However, large Li isotopic zoning is found from crystal cores (δ7Li = +6 ‰, [Li] = 1.1 μg.g⁻¹) to rims (δ7Li = -11 ‰, [Li] = 1.4 μg.g⁻¹) for olivines set in microcrystalline groundmass. The cores of large olivine phenocrysts are equilibrated with the pillow rim glass (δ7Li = +6 ‰, [Li] = 3.4 μg.g⁻¹).

Recently, detailed investigation of the Li isotopic composition of large phenocrysts in various magmatic environments demonstrated that microscale δ7Li variations were due to fractionation of lithium isotopes during late stage chemical diffusion (Barrat et al., 2005; Beck et al., 2006; Jeffcoate et al., 2006). In our case, the diffusion-induced Li isotopes fractionation is the only process able to explain such diverse zoning in olivines from one single pillow lava. Our study brings new constraints on the Li fractionation during the diffusion process and suggests that the pristine δ7Li values can be completely erased in small phenocrysts, even in the case of rapidly cooled volcanics. The use of Li isotopes in crystals for tracking mantle heterogeneities should be taken with extreme caution.

References

δ7Li systematics of mantle xenoliths from Kilbourne Hole: Unraveling metasomatic & diffusional processes
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We present a detailed Li isotopic study of spinel-peridotites from Kilbourne Hole, New Mexico, including whole rock and hand picked mineral separate δ7Li data (measured by MC-ICP-MS) and in-situ δ7Li data measured by ion microprobe. From this detailed approach the effects of mantle metasomatism and diffusion can be unravelled.

The xenolith suite can be divided into those which are in textural equilibrium, and those which have interacted with the host lava. Whole rock values for the sample suite range from +4.5 ‰ to -2.9 ‰. Of the samples which are in textural equilibrium, mineral separates reveal that olivine, orthopyroxene, and clinopyroxene are all in isotopic equilibrium, and grains analysed by ion microprobe are homogeneous in both Li and δ7Li across grains, with the exception of the outer 50 μm in some clinopyroxene grains. The two lightest δ7Li are found in equilibrated LREE enriched harzburgites, which is consistent with these samples having completely equilibrated with a melt with a slightly negative δ7Li (-3 ‰), possibly from a garnet pyroxenite/eclogite source (although partial equilibration with a heavy δ7Li melt can also explain these data).

Kilbourne Hole peridotite xenoliths have rapid transit times (~0.2 days), which is long enough to produce the Li isotope perturbation observed in the clinopyroxene grains by more rapid diffusion of δ7Li compared to δ6Li from the host lava.

The extent of clinopyroxene reaction correlates with a decrease in whole rock δ7Li, which can be explained by reaction driven diffusion with the host lava. Li diffusion in clinopyroxene is at least ten times faster than in olivine [1], and so interactions between peridotite and melt produce clinopyroxene with lighter δ7Li than co-existing mineral phases. Clinopyroxene data that have very light δ7Li values (e.g. [2]) have been used to argue a very light δ7Li component in the mantle. However, without evidence of Li isotopic equilibrium, the existence of such a component must be treated with caution.

References
Diagnosis of pollution state of the coasts in the vicinity of an oil terminal: Bioremediation effect

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Coastal marine environments near the oil harbour installations can be the object of a chronic oil pollution coming from purging water of the storage tanks of oil, as well as water coming from ballast operations of tankers. In the oil terminal of the south of Tunisia, this water is collected in tanks before their discharge in a natural lagoon which communicates with the Mediterranean Sea. This lagoon is periodically flooded by sea water (tide phenomena). The objective of this work is the diagnosis of the pollution state of the lagoon. This study is based on the analysis of the COT and the technics of liquid and gas chromatography.

Analysis of TOC and TH (total hydrocarbon) in surface sediments of the lagoon permit to note that:
- TH varies between 200 and 4020 ppm.
- A positive correlation calculated between the TOC and TH, attest of the homogeneity of the organic matter contained in the sediments.
- % of saturated hydrocarbons vary between 6 and 12% and are classic of an organic matter inherited from original biomass;
- The organic matter presents a mixed origin terrestrial and marine. N-alkane distribution is bimodal: first mode characterized by n-alkanes from C21 to C33 with a CPI of 2,1 characterising organic matter from waxes plants, the second mode is centred on n-alkanes from C17 to C20 without odd to even prevalence and characterizes a marine organic matter. Presence of UCM with a hump developed under all the range of n-alkanes attest of an important microbial activity in sediments.
- Surface sediments of the lagoon seems not to be contaminated by water coming from the systems of water treatment of oil residues. These results show the role of these lagunar systems to manage and eliminate pollution: bioremediation effect.

References

Weathering processes in karst river, southwest China: Implication from riverine sulphur and strontium isotope

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Geochemistry of river waters draining karst terrain in SW China has been studied in order to characterize the hydrogeochemistry of the rivers, to determine natural chemical and physical weathering rates in typical areas and anthropogenic contaminants. The studied area is impacted by serious sulphuric acid rain because of coal-mining and combustion and coal-formation strata in Guizhou Province. Another aim of the work is to study the effect of sulphuric acid on the carbonate weathering.

Results and Discussions
Water samples of karst river water from the Guizhou province (Wujiang River and Yuanjiang River) in karst-dominated regions were analyzed for dissolved major element concentrations (HCO3-, NO3-, SO42-, Cl-, Ca2+, Mg2+, K+, Na+), Sr2+ and 87Sr/86Sr and δ34S of dissolved sulfate (δ34SSO4) in summer. The waters of the Wujiang River have high Sr2+ concentrations and lower 87Sr/86Sr ratios (0.7074-0.7115), while those of Qingshuijiang River, one of two major tributaries of the Yuanjiang River system, show higher Sr isotopic ratios (0.7088-0.7155) and low Sr concentrations. Weathering rates of silicates and carbonates were determined from major element mass balance with Sr isotope.

The sulfur isotopic compositions (δ34S) in Wujiang River catchments range from -7.70‰ to 13.06‰ and have higher SO42- concentrations, which are inferred to be mainly derived from anthropogenic emissions and/or the oxidation of sulfide minerals in the coal-containing strata in the studied area. Samples from Yuanjiang River, which is dominated by clastic rocks, have relative enrich δ34S (-4.81‰ to 4.13‰) and lower SO42- concentrations, which appears to result from solution of gypsum and rainwater SO42-. The carbonate weathering of sulfuric acid may become an important CO2 source to atmosphere and can counteract the CO2 consumption by silicate weathering, so the presence of sulfuric acid should be seriously considered to calculated CO2 budget in this kind of area.

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Source origin of the ultrapotassic lavas from the Leucite Hills, Wyoming: Hf isotope constraints

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The Leucite Hills of SW Wyoming consist of 22 volcanic outcrops that occur over an area of ~ 2,500 km². The lavas consist of 3 types of lamproite, basic to ultramafic madupite (M), and more silicic wyomingite and orendite (W/O), characterized by phlogopite phenocrysts in a groundmass of leucite, diopside, apatite, ±sanidine, ±glass. Volcanism spanned 3.0-0.89 Ma. 84% of the <0.7 km³ of magma was leucite, diopside, apatite, ±sanidine, ±glass. Volcanism characterized by phlogopite phenocrysts in a groundmass of

late-stage lavas formed by small degrees of melting can be used as high-resolution tracers of source components and heterogeneities in the Hawaiian mantle plume. This study presents high-precision isotopic ratios (Sr, Nd, Hf, Pb) and trace element concentrations of late- and post-shield lavas from four Hawaiian volcanoes: Mauna Kea and Kohala on the Kea-trend and their counterparts Hualalai and Mahukona on the Loa-trend. Mauna Kea and Hualalai demonstrate a systematic shift to distinctly less radiogenic Pb and Sr isotopic compositions as they evolve from the shield to post-shield stage. Post-shield lavas from both volcanoes deviate from the mixing trends (Sr-Pb, Nd-Pb, Hf-Pb) defined by Hawaiian shield-stage lavas, reflecting involvement of a more depleted source component similar to that sampled by rejuvenated lavas from other Hawaiian volcanoes. Interaction with oceanic crust and lithosphere (low 87Sr/86Sr, high 206Pb/204Pb) beneath Hawaii cannot explain the observed compositions of Hualalai post-shield lavas, which have some of the least radiogenic Pb isotopic compositions (206Pb/204Pb = 17.888-18.011) of recent Hawaiian volcanoes. In contrast, Kohala and Mahukona become more radiogenic with respect to Pb during the waning stages of volcanism. Post-shield lavas from these volcanoes remain within the Loa-Kea mixing hyperbola, but are shifted to more depleted Sr, Nd, and Hf isotopic compositions.

Despite their contrasting Pb isotope systematics, post-shield lavas from all four volcanoes preserve the striking Loa-Kea Pb bilateral asymmetry inferred for the Hawaiian plume over the past ~1.5 Myr [1]. However, post-shield lavas and tholeiites from Kohala form a Pb-Pb linear array that crosses the Loa-trend. The coupled isotopic systematics of both volcanic pairs indicates the successive sampling of isotopically distinct material intrinsic to the Hawaiian plume. The enriched trace element signatures of the post-shield lavas ([La/Yb]n = 6.0-16.3) further suggests that this material is not related to MORB. The isotopic similarities between the post-shield and rejuvenated lavas imply continuity of these heterogeneities on a million year timescale and have implications for models of Hawaiian plume structure.

References

Geochemistry of post-shield lavas from paired Loa- and Kea-trend Hawaiian volcanoes

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Late-stage lavas formed by small degrees of melting can be used as high-resolution tracers of source components and heterogeneities in the Hawaiian mantle plume. This study presents high-precision isotopic ratios (Sr, Nd, Hf, Pb) and trace element concentrations of late- and post-shield lavas from four Hawaiian volcanoes: Mauna Kea and Kohala on the Kea-trend and their counterparts Hualalai and Mahukona on the Loa-trend.

Mauna Kea and Hualalai demonstrate a systematic shift to distinctly less radiogenic Pb and Sr isotopic compositions as they evolve from the shield to post-shield stage. Post-shield lavas from both volcanoes deviate from the mixing trends (Sr-Pb, Nd-Pb, Hf-Pb) defined by Hawaiian shield-stage lavas, reflecting involvement of a more depleted source component similar to that sampled by rejuvenated lavas from other Hawaiian volcanoes. Interaction with oceanic crust and lithosphere (low 87Sr/86Sr, high 206Pb/204Pb) beneath Hawaii cannot explain the observed compositions of Hualalai post-shield lavas, which have some of the least radiogenic Pb isotopic compositions (206Pb/204Pb = 17.888-18.011) of recent Hawaiian volcanoes. In contrast, Kohala and Mahukona become more radiogenic with respect to Pb during the waning stages of volcanism. Post-shield lavas from these volcanoes remain within the Loa-Kea mixing hyperbola, but are shifted to more depleted Sr, Nd, and Hf isotopic compositions.

Despite their contrasting Pb isotope systematics, post-shield lavas from all four volcanoes preserve the striking Loa-Kea Pb bilateral asymmetry inferred for the Hawaiian plume over the past ~1.5 Myr [1]. However, post-shield lavas and tholeiites from Kohala form a Pb-Pb linear array that crosses the Loa-Kea isotopic division. The sampling of Loa-type heterogeneities has been observed at other Kea-trend volcanoes [e.g. 2] and may be related to structure within the plume conduit. The coupled isotopic systematics of both volcanic pairs indicates the successive sampling of isotopically distinct material intrinsic to the Hawaiian plume. The enriched trace element signatures of the post-shield lavas ([La/Yb]n = 6.0-16.3) further suggests that this material is not related to MORB. The isotopic similarities between the post-shield and rejuvenated lavas imply continuity of these heterogeneities on a million year timescale and have implications for models of Hawaiian plume structure.

References
Time scales of intracratonic orogeny

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Intracratonic orogeny represents an intriguing endmember of the tectonic spectrum in that deformation is temporarily focused into regions of lithosphere that more generally exhibit plate-like behaviour. There is a general consensus that intracratonic orogeny is driven by stresses generated at plate boundaries. If this assertion is true, there should be a strong correspondence between the evolution of plate margin systems and events within mechanically coupled continental interiors. The intracratonic Petermann and Alice Springs orogens in central Australia form components of a shifting pattern of intraplate deformation whose duration spans the early stages of Gondwanan assembly (c. 600 Ma) to the establishment of a (c. 450-300 Ma) convergent margin along east Gondwana. These orogens have two important similarities. Firstly is the development of comparatively narrow deep foreland basins, which may be coupled with large-scale footwall depression beneath crustal-scale thrust sheets. These observations point to the involvement of weak lithosphere in the intraplate orogenesis. Secondly both record apparently long (> 70 Ma) durations of deformation. The 450-300 Ma Alice Springs Orogen terminated riftting and associated basaltic magmatism, providing an obvious thermal link for localizing the deformation. However an intriguing aspect of the Alice Springs Orogeny is the existence of a long-lived high-T thermal regime marked by the emplacement of crustally derived melts throughout the entire c. 100 Ma orogenic history. Simple calculations suggest that it would be difficult for the lower crust to remain above the solidus for c.100 Ma without significant inputs of heat from the mantle. The Alice Springs Orogeny coincided with the development of a long-lived convergent margin along eastern Gondwana. The development of the margin was characterised by upper plate extension punctuated by transient collision/accretion linked to the incorporation of buoyant colliders. A challenge in understanding the geodynamic evolution of the continental margin-interior system is to decipher event timing within the overall long-lived record of intracratonic deformation in comparison with events on the margin. Within the Alice Springs Orogen, phases of contractional deformation generally coincide with collisional events on the adjacent margin with the locus of most intense deformation coinciding with the footprint of pre-orogenic rifting and mantle-derived magmatism. This suggests that the mantle-driven thermal regime initially associated with rifting, played a central and on-going role in controlling the intracratonic response during the development of the adjacent east Gondwana plate margin.

Processes and timescales of magma genesis and differentiation at Lopevi Volcano, Vanuatu, SW Pacific

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Recently erupted basaltic and andesitic lavas of Lopevi Volcano, one of the most active in Vanuatu, were analysed for whole rock major and trace element abundances, Sr and Nd isotopic ratios and U, Th and Ra isotopic compositions; forming the first detailed U-series study of an individual volcanic centre within the Vanuatu (New Hebrides) arc. The data are used to constrain the processes and timescales of magma genesis and evolution beneath the volcano, leading towards a better understanding of the relationship between magma supply and eruption, which is invaluable for volcanic hazard assessment.

MgO contents of lavas erupted throughout 2000-2003 cluster at around 4-5 wt%, whereas those from earlier eruptions (during the 1930’s and 1960’s) exhibit a wider range, extending to more primitive MgO contents (up to 8.5 wt%). Fractional crystalisation is an important mechanism of differentiation at Lopevi, exerting strong control on major and trace element variations. Increases in SiO2, Na2O, Al2O3, TiO2 (and to a lesser extent K2O and P2O5) and decreases of CaO cannot be an important fractionating mineral during magmatic differentiation at mid-lower crustal depths beneath the volcano.

Enrichment of LREE relative to HFSE and HREE, high Ba/La ratios relative to MORB, uniform HFSE/HFSE ratios (e.g. Ta/Nb) along with 238U excesses (1.250-1.400) in Lopevi lavas identify the contribution of a fluid component to a relatively homogeneous, slightly depleted mantle source. Furthermore, the sub horizontal array displayed by the data on a U-Th equiline diagram indicates this addition occurred significantly recently. 228Ra excesses in the lavas suggest that crustal residence times of magmas at Lopevi are <8000 years. 87Sr/86Sr ratios lie between 0.703992 and 0.704078 and are characteristic of volcanoes similarly located in the central Vanuatu arc, above where the D’Entrecasteaux Ridge is being subducted and accreted (cf. northern and southern sections of the Vanuatu arc).
Functionally diverse chemosynthetic bacteria in hydrothermal sediment, Santorini, Greece: Geochemical implications

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A chemosynthetic microbial community displaying diverse respiratory processes was identified within iron- and arsenic-rich shallow marine sediment (20-40°C, pH 6.0-6.3) from an area of active hydrothermalism in Santorini, Greece. Marine hydrothermal sediments are host to abundant microbial life that exploits the steep geochemical gradients generated by the confluence of reduced metal-rich fluids and oxidised seawater. However, there is relatively little information on the functional range of prokaryotes in these settings, and their impact on geochemical cycling. Microbial functional diversity in the Santorini sediment was determined by enrichment culturing (from the suboxic to anoxic transition zone, Eh 0 to -138 mV), coupled with phylogenetic molecular techniques. Enrichment cultures were successfully obtained for: (1) Fe(III), NO3-, SO42-, and As(V) reducers (with acetate and lactate); (2) anaerobic and microaerophilic Fe(II) oxidisers; and (3) Na2S and As(III) oxidisers. Most-probable number (MPN) counts for these functional groups ranged from 7.50 x 107 to 2.30 x 105 cells ml-1, with relative abundances decreasing as follows: NO3-, As(V) and Fe(III) reducers; Na2S and FeS oxidisers; SO42- reducers; and As(III) and anaerobic Fe(II) oxidisers. 16S rRNA and specific functional gene analyses, utilising the clone library method, revealed a phylogenetically diverse range of enriched bacteria, including a number of novel organisms, and also sequences with close affinity for bacteria known to occur in deep-sea hydrothermal vent sediments (e.g. Shewanella sp., Thiomicrospira sp., Desulfovibrio spp., and Marinobacter spp.). Phylogenetic bacterial and archaeal sediment communities were dominated by δ-Proteobacteria, Chloroflexi, Bacteroidetes, Chlorobi, and Crenarchaeota. Dominant bacteria displayed closest affinities to known iron and sulphur respirers. In particular, community analyses of the oxidised orange surface sediment (Eh 0) were found to be dominated by an enriched anaerobic, nitrate-dependent Fe(II) oxidiser. Overall, results demonstrate the potential for bacteria to respire inorganic substrates important within the Santorini sediment, namely forms of iron, arsenic, sulphur and nitrogen. Moreover, solid-phase and pore water geochemical data allow correlation between the microbial community structure and the sequence of down-core biogeochemical (redox) zonation.

Behaviour of PGEs in sills from the Jurassic Ferrar Large Igneous Province, Antarctica

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The Jurassic Ferrar Large Igneous Province, exposed in a > 3000 km long belt along the margin of the East Antarctic craton, comprises numerous sills, dikes and lava flows as well as the layered mafic Dufek intrusion. Uniform crust-like trace element and isotope data indicate a single magma source within the subcontinental lithospheric mantle characterised by crustal enrichment due to Palaeozoic subduction along the Panthalassa margin of Gondwana. However, the thermal source for the voluminous melt generation is still under debate as the crust-like isotope signatures obscure the detection of a possible mantle plume involvement.

In addition to mineral and bulk-rock chemical data for basaltic andesites and andesites from sills in northern Victoria Land, a subset of 23 samples has so far been analysed for platinum-group elements (PGE) to further describe the genesis of the Ferrar magmatic rocks. The abundances of Ir, Ru, Rh, Pt and Pd were determined by ICP-MS using isotope dilution (except Rh) after sample preparation by NiS-fire assay at the University of Karlsruhe, Germany.

The studied rocks exhibit the common phase assemblage of tholeiitic differentiation sequences composed of varying amounts of pyroxenes, plagioclase, oxides and mesostasis. Most of the wide compositional variations (2-13 wt% MgO) are attributed to low-pressure differentiation after magma intrusion at upper-crustal levels. Compositional differences between rocks that are not affected by in-situ differentiation are ascribed to distinct conditions during pre-emplacement differentiation assuming an identical primary magma.

The PGE totals range from ~ 4 to 40 ppb. The single element abundances exhibit good correlations with the MgO contents of the distinctly evolved samples and are thus interpreted to result mainly from in-situ differentiation as well. While the IPGE (Ir, Ru) are highly compatible during differentiation of the Ferrar magmas, the PPGE (Rh, Pt, Pd) show bimodal variations. They decrease in cumulates, but either increase or decrease in differentiates. The distinct PGE fractionation behaviour results in strongly fractionated primitive mantle-normalised patterns for all analysed samples with considerable enrichment of the PPGE over the IPGE.

Compared to tholeiitic rocks from other magmatic provinces, only the Ferrar rocks exhibit coupled enrichment of Pd, Pt and Cu even in most evolved samples. The decrease of Pt and Pd in some of the more evolved samples does not necessarily signify sulphide fractionation, but may indicate the formation of other PGE-compounds. The inferred sulphur-undersaturated conditions during pre- and post-emplacement differentiation processes are in agreement with the elevated melting degrees as well as the refractory nature of the proposed subcontinental lithospheric mantle source.
Synthetic melt inclusion and quartz-trap methods for determining Pt solubility in a mafic mineral – Halide melt system at 750°C, 400 bar

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The solubility of platinum in a hydrous salt melt (S-free; ~75 wt% CaCl_2+MgCl_2, 25 wt% H_2O) was investigated at conditions consistent with the post-cumulus metamorphism of layered intrusions that host platinum-group element deposits. The salt melts were reacted with metallic Pt or Pt-PtAs_2 (sperrylite) in Pt capsules using conventional Rene 41 cold seal vessels which buffer jO_2 at FMQ-1. The activities of relevant metal-complexing species (e.g., HCl) were buffered by the assemblage tremolite-diopside-enstatite-quartz. Salt melts were trapped (simultaneously) in the matrix of a quartz trap (granulated natural quartz partially isolated in a smaller gold capsule) and in synthetic melt inclusions trapped in pre-fractured quartz. After quenching, the melt inclusions and quartz trap material were analyzed by laser ablation ICP-MS.

Platinum solubility is in the low ppm range. Analysis of different portions of the quartz trap using a 90 μm pit size yielded relatively consistent platinum concentrations of 14.4 ± 6.7 ppm (2σ, n=6; Pt metal source), and 4.6 ppm ± 1.9 ppm (2σ, n=6; Pt-PtAs_2). Based on the consistency of the metal concentrations from different parts of the trap, it is considered that these concentrations are most representative of metal solubility at run conditions and that the laser sampling size sufficiently overcomes local heterogeneity in the distribution of Pt quench products. By contrast, Pt concentrations in hydrosaline melt inclusions from different areas of a 3 mm x 10 mm quartz cylinder range from below detection limits (~0.1 ppm) to 14.4 ppm (n=28; Pt) and to 6.6 ppm (n=31; Pt-PtAs_2). The range in observed metal concentrations in this trapping medium increases with the number of inclusions analyzed, and varies between different areas in the quartz cylinder. This confirms observations that saline inclusions trapped in pre-fractured quartz heal quickly (as early as several hours) at elevated temperatures, and may trap disequilibrium metal concentrations in mineral- or melt-buffered systems (Hanley et al., 2005); thus, they are suitable only for qualitative evaluation of trace metal solubility.

The data demonstrates that Pt is highly soluble at conditions consistent with post-cumulus metamorphic activity in layered intrusions, and that salt melts may significantly modify primary metal concentrations in layered intrusions and redistribute these metals. Additionally, Pt solubility in the hydrosaline melt was reduced by a factor of ~3 in the presence of a platinum arsenide phase.

References

~560 Ma and ~300 Ma Re-Os ages constrain Neoproterozoic Varanger glaciation and record Variscan hydrocarbon migration on extension of Oslo rift

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The Moelv tillite, exposed in the Lower Allochthon of the Scandinavian Caledonides represents the Neoproterozoic Varanger glaciation, which is generally correlated with the ~580 Ma Gaskiers glaciation in Laurentia. To refine a 620 ± 14 Ma maximum age for the Moelv tillite based on detrital zircons [1], Re-Os data were collected from a C-rich shale horizon in the Biri Formation underlying the tillite.

East of the town of Biri, the weakly deformed Biri shale contains a significant silt component, minor but ubiquitous fine-grained pyrite, and an average TOC of 0.7%. Exposures in a steep bedrock stream channel (Djupdalsbekken) show little bleaching or oxidation. Here, where the Biri shale is separated from the Moelv tillite by the Ring conglomerate, two localities were sampled. Seven analyses of four samples taken about 50 m below the Biri-Ring contact yield a statistically tight Re-Os age of ~560 Ma, with an initial 187Os/188Os (Os_i) near 1. Four additional samples, taken ~48 m below the contact, scatter slightly, but all samples regressed together still yield an age within uncertainty of 560 Ma. Re-Os data from samples taken ~3 m below the Biri-Ring contact scatter about a reference line of 600 Ma with Os_i = 1.0. Scatter may result from minor Re and lesser Os loss during recent oxidative weathering. Thus, there is some true geologic variation in the data, but the results clearly support an age close to that of the ~580 Ma Gaskiers glaciation.

A second Biri locality near Øvre Rendal lies on the northern extension of the ~300 Ma Oslo rift. Here, the shale shows strong cleavage, has an average TOC of 2.7%, contains lenses of pyritic sandstone, is unusually thick, and directly underlies the Moelv tillite. Road-cut exposures are locally rusty, but fresh, black samples were obtainable. Ten analyses from six samples taken in a 1-m stratigraphic interval scatter about a reference line of 300 Ma with Os_i = 1.1. Greenschist-facies, dynamic metamorphism does not disturb the Re-Os system in shales [2,3]. We therefore propose that heat from the ~300 Ma rifing event induced hydrocarbon maturation and migration, and that the organic material analyzed was isotopically homogenized (or introduced) during this event.

References
Li as a barometer for biminarlic eclogites

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Seitz et al. (2003) suggested that the partitioning of Li between garnet and clinopyroxene is pressure dependent and may serve as a barometer for eclogites. This suggestion was based on the analysis of natural rocks, the fact that Li is a faithful follower of Mg into octahedral site positions and that only garnets with a majoritic component have MgVI. We can assume a coupled substitution with P and carried out high pressure experiments in CMAS + Li₃PO₄. The experiments were carried out from 6 - 12 GPa, 1200 -1500° using starting materials with varying Li contents to check for compliance with Henry’s law. The run products were analyzed by EPMA and SIMS. The results are shown in Figure 1.

Conclusion

Henry’s Law is fulfilled for Li partitioning between garnet and cpx in the concentration range of 1 - 0.01 wt% Li. The partitioning of Li is dependant mostly on pressure and less so on T (see above figure). Further experiments are needed to reach a better constraint on the pressure, T dependance of the Li-partitioning and achieve a functioning barometer.

References


Removal of uranium, arsenic and phosphorus from aqueous solutions using steel slag

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The European iron and steel industry produces annually ca. 45 million tons of metallurgical slag, of which 37% and 41% are utilized in cement production and road construction, respectively. Over the past ten years, much research has been devoted to potential environmental applications of slags due to their favorable adsorptive properties. We have investigated the uptake of U, As and P by steel slag from aqueous solutions using samples obtained from the Rautaruukki Co., Raabe, Finland. Mineralogically, the solid material is mainly made up of compounds of CaO, FeO and SiO₂. The behavior of the above-mentioned elements was investigated in 24-hour laboratory batch experiments with the initial concentrations of 2–250 mg/L for U, 0.5–60 mg/L for As and 20–500 mg/L for P. Long-term column experiments are also currently in progress in order to study the maximum phosphorus sorption capacity of steel slag. Phosphorus in equilibrated solutions was determined spectrophotometrically and U and As were analysed using ICP-MS.

Uranium showed practically a complete partitioning into the solid phase; for example, with a maximum starting U concentration of 250 mg/L and a liquid/solid (L/S) ratio of 100, only 0.05–0.06 mg/L was left in solution, corresponding to a solid/liquid distribution coefficient in the range of 4–5 x 10⁵. In the batch experiments with initial phosphorus contents of 60–100 mg/L and L/S ratios of 450–500, the sorption capacity of steel slag was mostly in the range of 25–33 g/kg and the sorption percentage 70–96%. In the column experiments on relatively coarse-grained slag (1–4 mm), the sorption efficiency declined to 80% when the slag had achieved a P concentration of 5.1–7.3 g/kg, while in the experimental columns containing fine-grained slag (<1 mm), which are still running, the phosphorus sorption has remained perfect (>99%) after retention of up to 12.4 g/kg of P. In common with U and P, arsenic had a pronounced sorption affinity to steel slag. In all batch experiments conducted so far with a L/S ratio of 1000 or less, the sorption percentage was higher than 92%.

Due to leaching of Ca from steel slag, the mechanism of P and As removal is mainly by precipitation of hydrous calcium phosphates and calcium arsenates, respectively, as confirmed with SEM. The mechanism of U sorption is not yet established but it seems that calcium also plays an important role in this case. In summary, our experimental study shows that steel slag can serve as an excellent sorbent for U, As and P from aqueous solutions.
Colloidal green rust behaviour: Adhesion, transformation and mobility

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One of the more poorly understood processes in nature is the transport mechanisms of solutes and particles. In order to predict the behavior of unwanted compounds in nature, we need to establish these processes. Colloidal transport is believed to be one of the major pathways for distributing contaminants. These contaminants might come from general pollution or from leaking radioactive waste repositories. One very interesting compound that forms colloids and which is believed to exist in such environments is green rust.

Green rust is a layered double hydroxide (LDH) of high reactivity. It consists of ordered layers of Fe(II) and Fe(III), alternating with hydroxide layers and intercalating anions, cations (see poster by Christansen et al.) and water. It can form from partial oxidation of ferrous iron in the groundwater or directly from corrosion of metallic iron, which we use in reactive barriers and for reinforcement of underground radioactive waste repositories. Green rust reacts readily with redox sensitive contaminants due to the Fe in the layered structure and allows for a high degree of adsorption due to a large external and internal surface area.

Im mobilisation of contaminants in or on a solid is desirable, but if the solid is transported as a colloid, the contaminant is mobilised anyway. Therefore, we investigated the attachment ability of green rust using atomic force microscopy (AFM). To survey general colloid behaviour, we examined adhesion on 11 substrates chosen to represent common natural solids. Green rust colloids adhered well to all these substrates regardless of their surface charge.

The mobility of the particles formed from aerial oxidation of green rust was also examined. Upon oxidation, the green rust crystals showed dissolution along the edges. On hydrophilic substrates, elongated goethite crystals typically formed on and near original green rust particles. The stickiness of green rust suggests that it also serves as a substrate for other colloids which might have contaminants adsorbed.

From our experiments we interpret that the presence of green rust will generally limit contaminant transport in the groundwater system.

Mantle magma chambers beneath Gran Canaria

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A suite of basanite-hosted mantle xenoliths from the Quaternary Bandama volcanic center, Gran Canaria, comprises spinel harzburgites, spinel dunites and wehrlites, where Mg# of olivine range from 81 to 91, and clinopyroxenes encompass both igneous (Ti-augite to aegirine-augite) and upper mantle (Cr-diopside) types. They contain abundant silicate melt and CO2-dominated fluid inclusions. Clinopyroxene rim-melt thermobarometry of the host basanites indicates significant crystallization at pressures between 0.9 and 1.2 GPa. Barometry of primary magmatic CO2-inclusions in basanite olivines similarly yields minimum formation pressures between 0.7 and 1.0 GPa indicating cotectic olivine-clinopyroxene-Ti-magnetite crystallization at such pressures.

In the xenoliths, texturally late fluid inclusions coexist with melt inclusions thus indicating higher formation temperatures than the early fluid inclusions, which do not coexist with melt inclusions. The observed density differences of fluid inclusions is interpreted as in situ isobaric heating of the xenoliths in the upper mantle at 0.75 ±0.1 GPa (26 ±3 km depth), from about 750°C to near host-magma temperatures. This depth coincides with a change in the upper mantle P-wave velocity structure from anomalously low velocities of 7.5 -7.8 kms⁻¹ between the Moho and 26 km depth, to normal values of 8.3 kms⁻¹ below [1]. This low-velocity zone is interpreted as a clinopyroxene-enriched underplating zone in upper mantle, i.e. a region containing a complex mixture of harzburgite, wehrlite, and partly crystallized melt pockets. The xenoliths represent fragments of wall-rocks from a magma chamber within this region. A genetic link between magma chamber formation in the uppermost mantle, metasomatic overprinting and magmatic underplating is proposed for Gran Canaria, where a localized underplating zone has developed possibly from the late Pliocene to the Holocene through repeated metasomatic interaction between mantle rocks and ascending magmas.

References
Metasomatically induced alteration and re-equilibration of orthophosphate and silicate minerals: Textures, fluids, and mass transfer

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In nature, total re-equilibration of minerals and mineral assemblages under prevailing P-T-X conditions is greatly enhanced when suitably reactive fluids are involved. Often, however, re-equilibration is only partial and limited to those areas of the grain in immediate contact with the fluid. This can be due to a variety of factors including limited amounts of fluid, a limited reactivity between the fluid and the mineral and/or sufficiently low P-T conditions thus guaranteeing very low reaction rates. In general re-equilibration, whether localized or total, occurs as a result of dissolution-reprecipitation processes, which can also allow for the nucleation and growth of mineral inclusions of one phase within minerals of another phase.

Here a series of different orthophosphate and silicate mineral textures with or without mineral inclusions will be described and interpreted. Each of these textures is the direct result of fluid-induced dissolution-reprecipitation processes and represents the re-equilibration of the orthophosphate mineral on a localized scale. Such re-equilibration textures can have profound implications with regard to dating metasomatic events as well as allowing for P-T-X conditions to be estimated.

From a broader perspective, these fluids have not only interacted with the orthophosphate and silicate minerals but also potentially with the rock as a whole. As a consequence, the documentation and interpretation of metasomatically induced alteration in orthophosphate and silicate minerals has broader implications with respect to obtaining deeper insights into the nature and role of fluids in the crust and upper mantle.

LIBS: A new paradigm for real-time and in-field geochemical analysis

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Laser Induced Breakdown Spectroscopy (LIBS) is a simple atomic emission spectroscopy technique capable of essentially non-destructive determination of the elemental composition of any substance in real time. In LIBS, a focused and pulsed laser beam is directed at a sample surface, where laser energy absorption and resulting material ablation produces a high-temperature microplasma at the sample surface. Small amounts (nanograms) of material are dissociated and ionized, with both continuum and atomic/ionic emission generated by the plasma during cooling. A broadband spectrometer equipped with a CCD array detector can be used to spectrally and temporally resolve the light from the plasma to record emission lines of the full suite of elements present in the sample.

Important attributes of a LIBS sensor system for geochemical analysis include (i) real-time response, (ii) in-situ analysis with no sample preparation required, (iii) a high sensitivity to low atomic weight elements which are often difficult to determine by other techniques, and (iv) standoff detection. LIBS technology is now sufficiently mature, inherently rugged, and affordable to offer a capability for both laboratory and field-deployable analysis. Successful laboratory benchtop and 30-m standoff feasibility studies have been conducted that highlight the potential of LIBS for variety of geochemical, mineralogical, and environmental applications that require either real-time or in-field chemical analysis.
Magmatic processes recorded by garnets from the AD 79 eruption of Vesuvius

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Introduction

Evolved K-phonolitic tephra of Mt. Somma-Vesuvius volcano (Campania, Italy) contains Ti-rich garnets of the andradite-grossular solid solution series (‘melanite’) which are interpreted to be of magmatic origin in the Mercato (~8.1 ka) and Avellino (~3.7 ka) eruptive products (Scheibner et al., 2007).

Here we present data on REE distribution patterns obtained by laser ablation ICP-MS profiles in garnets of similar composition from tephra of the AD 79 eruption of Vesuvius in order to potentially distinguish metasomatic and magmatic garnets. The studied garnets have melanitic compositions and show core/rim structures with higher Fe$$^{2+}$$/Al ratios in the rims and resorption features at the interfaces.

Samples and Analytical Methods

Garnet phenocrysts (~0.3-0.8 mm) were separated from crushed pumice samples taken from the basis of the chemicaly most evolved white tephra and from basis and top of the less evolved grey tephra at Pompeii (‘Necropolis’, Cioni et al., 1995).

Continuous profiles through sectioned garnet crystals were obtained by ICP-MS coupled to a 193 nm ArF excimer laser. Profile width/spot size was 30 µm and resulting profile depth was ~60 µm. Detection limits ranged between 1 to 7 ppm for REE. Major element quantification was accomplished by wavelength dispersive EPMA.

Results and Discussion

LREE concentrations peak at Nd and show almost no variations through cores and rims, in contrast HREE are strongly depleted in the cores by a factor of up to 30 (2 to 10 for individual crystals) relative to the rims. Very high partition coefficients for HREE in melanitic garnets (Scheibner et al., 2007) suggest crystallisation of the cores from a highly fractionated magma unlike any of the eruption products of AD 79. These findings imply a significant contribution of a fractionated magma unlike any of the eruption products of AD 2007).

We have analyzed Pb isotopic ratios of natural fluid and melt inclusions by LA-MC-ICPMS and demonstrate the ability to use Pb ratios normalized to both 204Pb and 206Pb in tracing ore mineralization. The case study follows extensive feasibility tests (Pettke et al., in prep) using synthetic Pb fluid inclusions, in which we attained within run precisions (± 2SE) of as good as 200 ppm (normalized to 206Pb) and 400 ppm (normalized to 204Pb) and shot to shot reproducibilities (± 2SD) of 800 ppm and 7000 ppm, respectively.

Fluid inclusions in this study are from quartz veins in two different Cu-Au porphyry systems in the Apuseni Mountains, Romania. The Apuseni Mountains represent the richest concentration of metal deposits in Europe, and have been mined since pre-Roman times. Mineralization is hosted by sub-volcanic Miocene magmas intruded in a transtensional geodynamic environment. The magmatic rocks are mostly andesitic in composition, several of which contain high Sr and Pb concentrations, LILE enrichment and MORB-like Sr and Nd isotopic compositions characteristic of adakite-like magmas. Stocks hosting the porphyry deposits have adakite-like chemical signatures. Whole rock major, trace, and Pb-Sr-Nd isotopic analyses on the magmatic rocks represent the maximum range in age and composition, including endmembers of hybrid magmas recognized in the field from mingling textures. Pb isotopic ratios of whole rock solutions were measured with MC-ICPMS using TI normalization. Fluid inclusions were measured by LA-MC-ICPMS while admixing desolvated 997-TI standard solution. In high temperature stockwork veins, fluid inclusion ratios are indistinguishable from high temperature sulfides but less radiogenic than galena from the same deposit. Pb ratios of fluids and sulfides overlap ratios from the magmatic host rocks. Feldspar cores and several melt inclusions hosted in the feldspar cores, however, exhibit Pb isotopes more radiogenic than the magmatic rocks and fluids, consistent with observed inverse feldspar zoning. Results will be explored in consideration of the idea that ore deposition is linked to a pulse of more primitive magma into the system (e.g., Kamenov et al., 2005).

References


Using Pb isotopic analyses of fluid and melt inclusions to trace sources of Cu-Au porphyry deposits

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References


Evidence for water on Hadean Earth

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The criteria thought necessary for life are: an energy source, organic molecules, and liquid water. Since the necessary energy sources and molecular building blocks for life were surely available during the formative stages of planetary evolution, the question of when life could first have emerged on Earth reduces to: When did liquid water first appear at the Earth’s surface? While exposure of >3.83 Ga marine sediments indicates the presence of oceans by that time, strategies to assess an earlier hydrosphere are limited by the fact that there is no known Hadean (4.5-4.0 Ga) rock record. However, detrital zircons as old as nearly 4.4 Ga from the Jack Hills, Western Australia, present four kinds of evidence that suggest the presence of liquid water at or near the Earth’s surface during the Hadean. Oxygen isotopes analyses of zircon provides a means to assess the isotopic composition of the protolith. High δ^{18}O values of some Hadean zircons, indicative of a clay-rich protolith, are interpreted as indicating crust-hydrosphere interactions prior to 4 Ga. Inclusion assemblages in Hadean zircons characteristic of hydrated, peraluminous parent magmas are suggestive of the melt protolith having originated at the Earth’s surface and further suggest early development of sedimentary cycling in the presence of a hydrosphere. While specific circumstances could be convolved to create a high δ^{18}O signal along with peraluminous inclusions outside a surficial environment, they represent exceptional occurrences. Crystallization temperatures of >4 Ga granitoid zircons cluster strongly at 680±25°C from which we infer a regulated mechanism producing wet, minimum-melting conditions throughout the Hadean. This distribution is indisputably different from that produced by cooling of mafic and intermediate magmas and we conclude that the vast majority of Hadean zircons could not plausibly be derived from such sources. Instead, the simplest explanation for the dominant low temperature Hadean peak is that it reflects prograde melting under shallow conditions at or near water saturation. In effect, as soon as the source reached anatectic conditions, the majority of melt fertility was lost in the presence of excess water. Comparisons of U-Pb and U-Xe ages in Hadean zircons show varying degrees of Xe loss, but in some cases are concordant within uncertainty. Variable plutonium/uranium ratios in these zircons suggest that Pu and U could be mobile with respect to each other during the Hadean. As Pu and U can be strongly fractionated in aqueous systems, this may indicate, at least locally, the presence oxidized aqueous fluids in the Hadean crust. Although circumstantial, the four lines of evidence discussed above provide a cogent case for the presence of liquid water at or near the Earth’s surface during much of the Hadean.

Rutile 207Pb-206Pb ages in the Jack Hills quartzite, Western Australia

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The Narryer Gneiss Complex of Western Australia is comprised of 3.73–3.30 Ga orthogneisses and ~3 Ga supracrustal rocks that experienced regional metamorphism and local granite emplacement at ~2.5 Ga. In the western Jack Hills, upper greenschist grade quartzites contain detrital zircons approaching 4.4 Ga and thus efforts have been made to date other detrital phases (e.g., monazite, chromite) but as yet the age distribution of rutile has not been assessed. The significance of discovering >4 Ga rutile grains is heightened by possible application of the recently calibrated Zr-in-rutile thermometer which permits a test the Hadean minimum-melting hypothesis of Watson & Harrison (2005). However, the lower bound of estimates of Tc for Pb in rutile, which range from 400-600°C, overlaps with the estimated peak metamorphic temperature in which case the potential for rutile to retain its primary crystallization age would be greatly reduced.

388 207Pb/206Pb SIMS multi-collector analyses of 369 rutile grains from Jack Hills quartzite sample JH0113 yield an distinct age peak at ca. 2.5 Ga and an average age of 2.3±0.2 Ga. Age uncertainty for a 1 min analysis is typically ±2%. A traverse across one large grain revealed significant 207Pb/206Pb age variability. 33 of the dated grains were also analyzed for Zr by EMPA, counting with four spectrometers simultaneously. [Zr] was converted into crystallization temperature using the Watson et al. (2006) thermometer yielding a broadly normal distribution at 665±18°C. The highest recorded temperature (718°C) was obtained near the rim of a ~200 µm rutile grain with the core of the grain closer to the average value.

Given that crystallization temperatures are substantially higher than that attained during greenschist metamorphism, one interpretation is that the Zr-in-rutile thermometer has not been reset but that essentially complete Pb isotope exchange occurred at ca. 2.5 Ga. Alternatively, the very high Ti contents in cracks in detrital zircons from the Jack Hills suggests high Ti mobility during regional metamorphism due to dissolution/reprecipitation of Ti-bearing detrital grains. Evidence supporting this view comes from 2.5 Ga EMPA chemical Pb ages of monazites included in rutile which further suggest fluid-mediated dissolution/reprecipitation reactions at that time. This would explain the substantial disturbance to the 142/144Nd systems in Hadean zircons (Caro et al., 2006) if monazite inclusions are the principal host of LREE’s. This interpretation, however, does not explain the level and uniformity of the Zr-in-rutile temperatures and could suggest non-equilibrium Zr abundances in rutile.
Intra-test variation in the trace element composition of planktonic foraminifera: Implications for biomineralization processes

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The trace element chemistry of the calcite shells (tests) of planktonic foraminifera is a prime source of palaeoenvironmental information. Trace element partition coefficients are usually determined empirically, yet it is clear that calcification is biologically controlled. Better interpretation of the chemistry of foraminiferal calcite thus requires an understanding of the fundamental processes of mineralization and their influence on the resulting mineral chemistry.

To this end we have analysed the intra-test variation of a number of trace elements in the planktonic foraminifera species Gr. inflata, Gr. scitula and O. universa. Samples were recovered from a deep sediment trap (3km water depth) in the N. Atlantic (48.6N, 16.3W). The chemical and physical characteristics of the water column at this site are monitored, so the conditions under which calcification took place can be assessed. Measurements were made by laser ablation (LA) inductively-coupled plasma mass spectrometry (ICP-MS). A 193nm ArF Excimer laser was used to ablate through the test walls and time resolved signals from the quadrapole ICP-MS provide depth profiles of trace elements. Internal standardisation was performed using Ca and signals were calibrated using a calcite powder pellet and NIST 612 glass.

All three species display a 100-200% increase in Mg/Ca through the test wall which is far greater than expected as a result of vertical migration of the foraminifera and associated changes in water temperature. Other light trace elements (Li/Ca and B/Ca) show similar behaviour, but Sr/Ca ratios show no variation greater than the analytical uncertainty (~10% RSD). The change in Mg/Ca, Li/Ca and B/Ca through the test wall is most likely due to biomineralization processes. The implications of these data for foraminifera calcification models will be discussed.

Hydrogeochemical Properties of Ladik Hot Water Spring (Samsun, Turkey)

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In this investigation Ladik (Samsun) hot water spring has been studied from the point of geology, hydrogeochemistry and discharge. The study area is located around middle-north of Turkey. The geology of the study area and its vicinity consist of Permian aged recristallized limestone, Jurassic-Cretaceous limestone, Eocene-Neogene aged sandstone and claystone and Quaternary aged alluvium. The North Anatolian Fault (NAF) is situated near the hot water spring. Ladik hot water is come out to the surface where cross cut the NS and NW-SE directed fault, which is parallel to the NAF. Spring has 18 l/s discharge rate and 36.7 °C temperature. Hot water is analysed by Hacettepe University, Hydrogeochemistry Laboratory. According to the analyse results total dissolved ion matter for Ladik spring 339 mg/l, Hamamayağı River 192 mg/l and Kocapınar cold water spring 378 mg/l are obtained. The hot spring are classified according to the following criterias:

-according to the structural properties “fault spring”
-according to the temperature “medium hot water”
-according to the geothermal energy “low entalphy geothermal system”
-according to the hot water analyse result cation and anion trend of the springs are;
  -for Ladik hot water spring, Kocapınar cold water spring and Hamamayağı River
    rCa2+>rMg2+>rNa+>rK+ and rHCO3->rSO42->rCl-
  -Saturation indexes of the hot and cold water springs have been calculated in PHREEQC program. Springs are not saturated with respect to the calcte, dolomite and aragonite. According to the Schoeller and Pipper Diagrame, springs and river waters have similar chemical properties but Ladik hot spring has high Mg2+, Na+ and K+ ion values. The reason of these high concentrations have been assumed that the hot water add the ions of the recristallized limestone and limestone.

References
Laser ablation inductively coupled plasma mass spectrometry -
The role of the ion source for quantitative analysis

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Abstract
Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is frequently used for spatially resolved chemical characterization of a wide variety of minerals, soils and many other samples. Despite its successful use, accurate quantification of elemental concentrations can still be problematic, due to effects commonly summarized under the term “elemental fractionation”. This is most pronounced when matrix matched calibration standards are not available, which may result in variations of the relative sensitivities of the elements. This has been mainly attributed to non-representative laser sampling due to variations in the ablation process, causing preferential vaporization of elements. Recent reports, however, indicate that vaporization, ionization of the aerosol inside the ICP as well as the transfer of ions through the vacuum interface of the ICPMS are affecting the relative responses of individual elements significantly [1, 2, 3]. To describe these effects in detail the dependence of relative elemental sensitivities on the operating parameters of the ICPMS was studied for different samples using different laser ablation units (266 nm and 193 nm lasers). It can be shown that the relative sensitivities can vary significantly with the particle size distribution of the laser generated aerosol and the total mass load presented to the ICP. These variations are least pronounced when helium is used as carrier gas with 193 nm laser ablation which produces the generated aerosol and the total mass load presented to the ICP. What comes around goes around: Mantle convection and the meaning of mantle isochrons

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The perceived significance of isotopic data arrays for oceanic basalts has long occupied a middle ground between the endmember interpretations of mixing and age. Brooks et al. [1] were the first to attach age significance to the correlations between parent-daughter ratios (e.g. 87Rb/86Sr) and daughter isotope ratios (e.g. 87Sr/86Sr) that are a regular feature of the geochemistry of OIB and MORB [e.g. 2,3]. Pseudo-isochrons derived from mixed mantle can still have age significance if the various packets of source material have been physically juxtaposed for long periods of time, yet the current paradigm has generally been to focus on daughter ratios alone, and to interpret their variations in terms of multi-component mixing.

Numerous high-quality geochemical data sets now exist, and continue to be generated, for specific regions of OIB and MORB volcanism. In order to take the next step in a more accurate interpretation of this data, a forward model is needed that delimits the bounds of chemical variability and isotopic correlations expected to arise from the major processes operative during terrestrial mantle convection. In this talk, we will present the results of cylindrical 2D convection models with force-balanced plates [4] and examine specifically the role of subduction and convective mixing of oceanic crust.

In these models, melting occurs at divergent plate boundaries and geochemical evolution is recorded by millions of passive (harzburgite) and active (basalt) tracers that record the times, extents of melting, and extents of degassing at every melting event, allowing the geochemical evolution of any isotope system to be easily calculated (and recalculated) in a post-processing algorithm that operates on the tracer data independently from the dynamic calculations. We will explore the range of isotopic variability in these models as functions of partition coefficients, chemical density of basalt tracers, and convective vigor. In particular, these models reveal relationships between mantle isochron “ages” and true tracer ages that is not obtainable from statistical box-model calculations incorporating idealized mixing scenarios [e.g. 3-5].

References:
Giant impacts, late veneers and the gradual hydration of the earth’s mantle by subduction

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The likelihood of one or more giant impact events occurring during the accretion of the Earth is very high [1,2], and most of these late-stage impact events impart enough energy to completely melt the silicate portion of the proto-Earth [3,4]. Despite the uncertain nature and composition of the terrestrial atmosphere immediately after such impacts, it seems inescapable that the Earth’s mantle suffered a catastrophic loss of volatiles (including H2O, CO2 and noble gases) within the first 100 Ma of the planet’s history.

For these volatile species, the subsequent evolution of the Earth’s mantle has thus involved a gradual re-hydration from without, via the subduction of lithosphere altered by water from an exosphere whose existence has been dated to 4.4 Ga [5,6]. The estimated composition of this exosphere shows many similarities to a mass-fractionated proto-atmosphere mixed with volatiles released during impact degassing of a chondritic late veneer.

We will present the results of forward-modelling the evolution of volatiles in the Earth’s interior via subduction hydration of an initially dry mantle, with an emphasis on H2O. The model estimates the extent of (de)hydration of subducted hydrated lithosphere, and any associated isotopic (D/H) fractionations, based on studies of altered oceanic crust and Mariana arc magmas [7,8]. A defining characteristic of these models is the prediction of an initially high mantle viscosity, with gradual growth of a low-viscosity upper mantle due to the introduction of water at subduction zones. The fraction of the mantle that exchanges water with the exosphere thus grows with time, but the details of this growth depend on the extent of mixing between a hot, dry primordial mantle and a cooler and wet subduction-modified mantle. Nevertheless, virtually all conditions are expected to result in temporal shifts of the D/H ratios of the mantle and atmosphere that never reach steady-state, even over the age of the Earth.

References

Determination of trace metal-nanoparticle associations in contaminated riverine systems using analytical TEM

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Analytical electron microscopy (AEM) is being used to study the associations between trace metals and nanoparticulate material in riverine systems. Seven samples have been taken from the Clark Fork River system in western Montana, USA, over a distance of 200 river kilometers, and during normal summertime flow. This river is being used as a model system because it is contaminated with toxic trace metals (principally Pb, As, Zn, and Cu) from over 150 years of copper and silver mining activities, and it has been studied in great detail. All samples were digested and analyzed using Inductively Coupled Plasma Mass Spectroscopy (ICPMS) to determine total metal concentrations and it was found that every sample contained significant amounts of at least two of the toxic metals of greatest interest. To date, extensive AEM analysis using an FEI Titan high resolution scanning/transmission electron microscope (S/TEM) (equipped with EDS and EELS detectors) on one water sample has been performed. Grains of aragonite, titanium oxide and hematite, bearing Zn, Pb and As, respectively, have been identified. These particles range in size from 8 to 200 nm in diameter, show various stages of crystallinity, and are often heterogeneous even on a nanometer scale. The nanometer size range is important not only because grains this small represent a disproportionately large amount of surface area available in the biogeochemical system, but also because the properties of these materials are expected to be dramatically altered from larger grains of the same material. These property changes, along with a potential for increased activity, may have a large impact on the bioavailability and toxicity of trace metals in natural systems. Further sampling and AEM analysis of existing samples will lead to a better understanding of trace metals in riverine systems and how nanoparticles are likely influencing their fate and availability.
Basalt weathering rates on Earth and the duration of water on Mars

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Understanding the duration of time that Martian rocks were exposed to liquid water is of great interest because it influences the interpretation of the climate history and the potential for life on that planet. The presence or absence of primary minerals may provide constraints for the presence, duration and characteristics of liquid surface water on Mars.

Weathering rates are very sensitive to the pH of the reacting fluid. If pH values of terrestrial and Martian weathering solutions were similar, then mineral persistence ages on Mars are likely to be ≥ those on Earth. We present a compilation of field terrestrial persistence ages for 8 common rock-forming phases (plagioclase, volcanic glass, quartz, feldspar, micas, pyroxene, amphibole, and olivine) collected from dated chronosequences representing a wide climatic spectrum ranging from -10°C to 30°C mean annual temperature and 400 mm to 4500 mm mean annual precipitation. The extent to which these minerals persist may help constrain the rates at which primary phases weather under field conditions on Earth, and likely represent minimum mineral persistence times on Mars if pH values were similar.

However, Mars weathering solutions may have been more acidic than on Earth. Relative mineral dissolution rates at different pH values can be predicted from laboratory dissolution experiments. Here we compare relative mineral weathering rates observed in the field with laboratory predicted trends. Relative mineral weathering rates observed for basalt in Svalbard (Norway), Pennsylvania, and Costa Rica are explainable by pH. These results suggest that the pH-dependence of laboratory rates can be used to interpret relative mineral persistence on Mars to yield information about the pH of the reacting fluid.

We also interpret both terrestrial and Martian weathering profiles using reactive transport modeling, which can yield insights into the duration of weathering. The interpretation of weathering profiles on Mars is a promising approach to study that planet’s aqueous history, and highlights the need for additional depth profiles.

The generation and evolution of the continental crust

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Detrital and inherited zircons encapsulate a more representative record of igneous events than the rock record, and their hafnium isotope ratios reflect the time since the source of the parental magmas separated from the mantle. O and Hf isotope ratios on well-dated zircons are used (i) to distinguish crust formation ages that reflect involvement in the sedimentary cycle, and those that do not, and (ii) to reconcile the crust formation ages of material whose isotope ratios reflect evolution in the igneous and sedimentary reservoirs.

Global peaks in juvenile igneous activity have been identified at 2.7, 1.9 and 1.2 Ga from the geological record. An initial study on samples from the Lachlan Fold belt revealed sharp peaks in Hf model ages in zircons with δ¹⁸O of < 6.5 per mil at 1.9 Ga and 3.3 Ga. It is rare to find zircons with similar crystallization and Hf model ages. At issue are the links between such peaks in the geological and zircon records, and the time periods between initial crust formation and the generation of high silica magmas that might crystallize zircon in different tectonic settings.

The sedimentary record shows no evidence for major pulses of crust generation, and one interpretation is that it can take up to one billion years for new crust to dominate the sedimentary record. The residence times of material in the lower crust appears to be much lower than in the upper crust. Finally, the development of granulite facies rocks, and their effects on the deformation history of the continental crust, will be briefly explored.
Paleoproterozoic post-orogenic evolution of the North China Craton: Geochemical and isotopic constraints from the Xiyanghe Group along the southern margin of the North China Craton

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There is now a coherent outline of the timing and tectonic processes involved in the Palaeoproterozoic amalgamation and much intensive knowledge concerning the pre-collisional history of the North China Craton. However, much of the post-collisional history of the craton remains unknown. The Xiyanghe volcanics, together with the Xiong’er volcanics, constitute a large Paleo-Mesoproterozoic volcanic belt along the southern margin of the North China Craton. In this study, we provide geochemical and Sr-Nd isotopic data for the Xiyanghe volcanics, which provide important constraints on their petrogenesis and tectonic environment.

The Xiyanghe volcanics could be subdivided into three units: BA1 (basaltic andesites-1), BA2 (basaltic andesites-2) and andesites, all of which show consistent εNd(t), La/Nb and Th/Nb values irrespectively of SiO₂, precluding significant crustal contamination during ascent. Based on the covariation between La and La/SmN, the basaltic andesites show the trend of partial melting processes with the BA1 unit representing the major products of a magma chamber, whereas the andesites may fractionally crystallize from the BA1. The BA1 rocks and andesites show HSFE enrichments (especially Nb>6 ppm) and high Fe-Ti contents, comparable with Nb-enriched basalts, suggesting that the Xiyanghe volcanics were derived from a met-metasomatized mantle source. The BA2 unit is characterized with variable Ti/Eu, Zr/Sm and Nb/La ratios, suggesting that amphiboles have been involved in a partial melting process, which implies that the Xiyanghe volcanics were derived from hydrous magma. A large range in initial Sr (0.7039 to 0.7111) and a relatively narrow range in 143Nd/144Nd (εNd≈-6.8~--10) suggest inheritance of the enriched Nd-isotopic composition from the mantle wedge metasomatized by slab derived fluid. On the primitive mantle normalized trace-element diagrams, the Xiyanghe volcanic rocks show enrichments in the LILE and LREE and negative anomalies on the Nb-Ta-Ti, similar to arc-related volcanics produced by the hydrous melting of the metasomatized mantle wedge. The arc-related characteristics of the Xiyanghe volcanic rocks suggest that the southern margin of the North China Craton may have recorded the outbuilding history of the Columbia Supercontinent during Paleo-Mesoproterozoic time.

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Np(V) coprecipitation with calcite

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The actinide elements U, Np and Pu form oxo-cations (’actinyl-cations’) in oxidizing aqueous environments. The environmental behaviour of the actinyl ions U(VI), Np(V) and Pu(V,VI) is to a large extent controlled by sorption reactions (adsorption, coprecipitation / structural incorporation) with minerals. We study the structural incorporation of Np(V) into the host mineral calcite by coprecipitation in mixed flow reactors under steady-state conditions at room temperature. In this way reaction rates and partitioning coefficients can be determined under varying conditions. We found that homogeneous partition coefficients for Np in calcite (0.5 - 11) are significantly higher than those reported for U(VI) (0.01 - 0.2 [1]). The local structural environment of incorporated Np(V) is characterized from the Np L3 EXAFS. Measurements are performed at the INE-Beamline at ANKA (Forschungszentrum Karlsruhe). Our data suggest that the Np(V)-ions occupy calcium lattice sites, but with two missing carbonate groups in the first coordination sphere. The two axial oxygen atoms of the linear neptunyl-ions are likely oriented towards these vacant sites. Consequently, only four carbonates are observed to coordinate the Np(V)-ion. Np-O and Np-C interatomic distances (2,41Å, 3,34Å, respectively) indicate slight structural relaxation of the carbonate groups from their ideal sites. A similar structural model was reported for U(VI) incorporated into natural calcite [2].

References
Geochemistry and mechanic emplacement of Late proterozoic dyke swarms, Eastern Desert, Egypt

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Geologic and geochemical data of intraplate Late Pan-African (493±7Ma) dykes assemblage in the Eastern Desert of Egypt are presented. The dyke swarms consist of a bimodal mafic-felsic suite of transitional alkaline to subalkaline chemistry and exhibit a broad compositional range. Geochemical studies show that they can be subdivided into three distinct chemical groups with two distinct compositional gaps and correlate fairly well with other occurrences of late Pan-African dykes in Egypt. This bimodal suite bears a genetic relation to corresponding rock types in the study area. These dykes trend predominantly in NW and NNW directions and less frequently in NW and N orientations; parallel to the major fracture pattern and lineament trends. Despite of the small geographic area and limited time interval in which the dykes were extruded, their complex geochemistry requires multiple sources together with varying amounts of open system fractionation assimilation. It is believed that the crystallization of the studied dykes follow the one-step emplacement either in open or closed system under both brittle and ductile crustal conditions. The time (ts) required to solidify these types of dykes is generally longer in the acidic than the basic variety.

Nb-depleted calc-alkaline dacites from Iceland: Implications for Archean crust formation

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Samples from the dacitic Kroksfjordur volcanic center, NW Iceland, have calc-alkaline compositions contrasting the alkaline to tholeiitic composition commonly observed for felsic rocks from ocean islands or plateaus (Jónasson, 2006). New major, trace element, and isotope data show that these samples display a distinct depletion of Nb (La/NbPM = 2.7 ± 0.4; 1σ) and enrichment of Pb (Ce/Pb PM = 0.7 ± 0.1) in primitive mantle normalized trace element plots, and high Na/K ratios (3.6 ± 0.3).

The Sr-Nd-Hf-Pb isotopic compositions preclude the involvement of old continental lithosphere in the petrogenesis of the dacitic melts. The limited variation in major element data and the small though systematic variation of La/Nb and Ce/Pb ratios with TiO2 and Ce concentrations, respectively, suggest that the dacites were derived by partial melting of a mafic protolith comprising plagioclase + clinopyroxene + amphibole + Fe-Ti oxides. Inverse modelling shows that the calculated trace element composition of the source is similar to that of mafic crustal xenoliths hosted by one of the dacitic bodies. This observation suggests that partial melting of Icelandic mafic lower crust, most likely during magmatic underplating, has produced the calc-alkaline dacites at Kroksfjordur.

The major and trace element composition of the dacites closely resembles that of Archean tonalite - trondjemite - granodiorite (TTG) associations. Depletion of Nb and enrichment of Pb in TTG associations have hitherto been interpreted as evidence for their exclusive formation in Archean subduction zones (e.g. Drummond and Defant, 1990; Martin, 1999). The new findings from the Kroksfjordur volcano demonstrate that partial melting of mafic protoliths in an oceanic intra-plate setting can also lead to chemical signatures similar to that of magmatic rocks generated in subduction zone environments. This provides evidence that the Archean continental crust could have been formed in a variety of geodynamic settings including intra-plate as well as plate margin settings.

References
Mineralized microbial mats with extreme lanthanum enrichments in the tunnel of Äspö, Sweden

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Microbial mats precipitating iron oxides and thereby accumulating trace and rare earth elements (REE) are widely recognized [1, 2, 3]. A key role in that biomineralization process is assigned to negatively charged organic surfaces (cell surfaces and extracellular polymeric substances, EPS) binding cations and forming complexes [2,3,4]. Depending on the nature of these surfaces, a fractionation of specific cations may occur, thus giving the resulting minerals an inorganic “biosignature”. Bacteriogenic iron oxides covering granitic surfaces in the 450m deep Äspö Hard Rock Laboratory (Sweden) were analysed for inorganic biosignatures using LA-ICPMS. The study revealed an extreme enrichment (about 1000fold) in lanthanum (La) compared the other REE (Fig. 1). According to the similar chemical behaviour of the light REE (La - Nd), this phenomenon cannot be explained by an inorganic precipitation of REE. Likewise, the REE concentration of the water supplying the microbial mat did not show a positive La anomaly. This points to a biologically driven, selective fractionation of La by the bacterial community involved. The resulting biosignature may help to build a better understanding of modern and fossil microbially induced minerals and rocks, even in the absence of fossil remains and organic molecular indicators.

Figure 1: REE plot of mineral precipitates (line 2a-2e on the mineralized microbial mat), and the supplying water (H2O).

References

Fe isotopes in siliceous igneous rocks: Evidence for fluid-rock interaction in plutons

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The average δ²⁶Fe value of bulk plutonic rocks (PR) with >70wt% SiO₂ is 0.18±0.08‰ (1-SD; n=19; data from Poitrasson and Freydier 2005 CG; Poitrasson 2006 EPSL; this study). In contrast, the average δ²⁶Fe value of bulk volcanic rocks (VR) with >70wt% SiO₂ is 0.02±0.07‰ (1-SD; n=6; data from Beard et al., 2003 CG; Beard and Johnson, 2004 GCA; this study). We have conducted a detailed study of minerals and bulk PR and VR samples using high-precision Fe isotope analysis (±0.06‰, 2SD) to evaluate the origin of these differences.

Magnetite in PR has consistently higher δ²⁶Fe values (δ²⁶Fe= +0.13 to +0.51‰) than its host rock, whereas VR magnetite has lower δ²⁶Fe values (-0.05 to +0.27‰). Silicates in both PR and VR have δ²⁶Fe values that fall within the range for mafic VR (δ²⁶Fe= -0.14 to +0.10‰). Fractionation factors between magnetite and silicates are larger for magnetite-biotite pairs in PR (Δ²⁶Femag-bt= +0.15 to +0.58‰) than for magnetite-silicate pairs in VR (Δ²⁶Femag-sil= -0.02 to +0.19‰, one at +0.34‰). Both are positively correlated with the δ²⁶Fe values of magnetite and show a weak negative correlation with those of silicates, but in PR they are also correlated with δ²⁶Fe of the host rock. The positive correlation between Δ²⁶Femag-sil and bulk δ²⁶Fe in PR indicates that magnetite and bulk PR underwent open-system Fe exchange; the near-zero δ²⁶Fe values in VR indicate that high δ²⁶Fe values in silicic igneous rocks do not reflect crystal fractionation.

Open-system Fe isotope exchange in PR is influenced by cooling rates, Fe content, crystallization temperatures, fO₂ conditions, Fe diffusion rates in minerals, and interaction with late-stage exsolved fluids and/or saline hydrothermal fluids. There is no correlation between δ²⁶Fe and δ¹⁸O values for PR, indicating that Fe was not mobilized by dilute meteoric fluids; the largest range in δ²⁶Fe values of minerals and bulk samples occurs in PR that have been mineralized. Fe isotope shifts likely occurred during exsolution of Fe-rich brines during solidification and deuteric alteration. The relatively high δ²⁶Fe values of magnetite from PR probably reflect sub-solidus isotopic equilibration upon cooling and the high Fe diffusion rates in this mineral relative to silicates. Exsolved Fe-chloride solutions will have low δ²⁶Fe values as compared to silicates or magnetite based on theory (Polyakov and Mineev, 2000 GCA; Schauble et al., 2001 GCA), suggesting that the remaining pluten will increase in its δ²⁶Fe value; this effect will be most significant in low-Fe, high-SiO₂ rocks, matching the observation that δ²⁶Fe values for bulk samples and magnetite in PR are higher at higher SiO₂ contents.
Synthetic forsterite grain boundaries: Tilt [100] and 9.9° to 21.5°

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Forsterite is a main constituent of rocks in the Earth’s mantle. The refractory nature of forsterite makes it suitable for ceramics used in thermal insulations. The properties of rocks and ceramics are largely determined by their grain boundaries. Structure and transport properties of grain boundaries in rocks are still poorly understood. In general grain boundary structure, grain boundary energy and grain boundary properties depend on orientation. Low angle grain boundaries show dislocations, have low grain boundary energy and their transport properties (e.g. grain boundary chemical and thermal diffusion, grain boundary migration and sliding) are slow. High angle grain boundaries do not reveal dislocations, have high grain boundary energy and their transport properties are fast. In oxides, the transition from low to high angle grain boundaries is not studied in detail, but the transition to a high angle grain boundary is commonly defined at an angular lattice misorientation of ~ 10°-15°.

We synthesized a series of symmetric tilt grain boundaries in forsterite bicrystals with tilt axis a and increasing tilt angle from 9°-21° by direct bonding (Heinemann et al. 2001, 2005). For each bicrystal two oriented and polished synthetic forsterite single crystal plates were joined at room temperature and annealed at 400°C in vacuum for one week. All bicrystals were cut in two parts and one part was annealed further at 1650°C for 48h. Specimens were prepared for investigations in the TEM with focused ion beam (FIB).

HRTEM investigations of the grain boundaries parallel to tilt axis a show symmetric tilt grain boundaries with arrays of regular spaced edge dislocations between undisturbed crystal regions for all annealing temperatures and all tilt angles. The grain boundary structure developed below 400°C and did not change till 1650°C. All grain boundaries with tilt angles from 9°-21° are low angle grain boundaries. The Burgers vector of the edge dislocations is a. The regular dislocation spacings decrease with increasing tilt angles and dislocation cores do not overlap up to a tilt angle of 21°.

The dislocation model of low angle grain boundaries can be applied and the observed dislocation spacings d are related to tilt angle θ and Burgers vector length b by Frank’s formula:

\[ d = b(2\sin(\theta/2))/b = \theta \]

with tilt angles increasing from 9° to 21° the dislocation spacing decreased.

Using Frank’s equation and a rough estimation of the dislocation core radius of \( r_0 \approx 0.4nm \approx 2/3b \) we propose that in forsterite the transition between low and high angle grain boundary occurs at a misorientation of ~ 42°.

References
Evaluating the role of superoxide (O$_2^-$) and hydrogen peroxide (H$_2$O$_2$) in the dissolution of Saharan dust in the Tropical Atlantic

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Method and Theory

The major source of iron to the Tropical Atlantic is through aeolian deposition of Saharan dust. Presently within SOPRAN (German SOLAS) we are investigating, at the TENATSO site in Cape Verde, water column processes that control the dissolution of Saharan dust deposited at the seawater surface. The thermodynamic solubility of Fe(III) in surface seawater is thought to be controlled by the presence of iron complexing organic ligands. However in tropical waters, where high fluxes of superoxide (O$_2^-$) may exist, due to photochemical reactions of dissolved organic material, there exists the possibility of a kinetic controlled reduction of Fe in colloids and particles to the more soluble Fe(II) [Kustka et al., 2005; Rose and Waite, 2006].

\[ \text{Fe}^{III} + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{Fe}^{II} + \text{H}_2\text{O}_2 \]

Photochemistry may not be the only source of O$_2^-$ in seawater as recent work suggests a significant biological source also [Kim et al., 2004]. Overall these processes may lead to longer residence times for dissolved Fe in surface waters [Croo et al., 2004].

Discussion

Current work focuses on laboratory work evaluating analytical methodologies and focuses on three key aspects:

(i) The influence of temperature on the dismutation rate of O$_2^-$ in seawater.

(ii) How O$_2^-$ can alter the Fe organic speciation in seawater.

(iii) Assessment of the enhancement of Fe dissolution from Saharan dust via increased O$_2^-$

Conclusion

Using this approach we hope to be able to critically examine the role in which photochemistry and biology play in solubilizing Fe from Saharan dust in Tropical seawater. Overall this information will help in better assessing the key processes controlling iron bioavailability in natural seawater.

References


The reactivity of ferric (oxy)hydroxides toward dissolved sulphide between pH 3 to 9

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The reaction between H$_2$S and ferric (oxy)hydroxides exerts a major role for the sulphur and iron cycle as for the electron and carbon flow in many aquatic systems (e.g. Canfield, 1992). The reaction mechanism is reasonably well understood (Dos Santos Afonso et al., 1992; Peiffer et al., 1992). The reaction rate depends on pH which can be explained by a surface speciation model according to which the electron transfer is preceded by an adsorption step of a sulphide species to the neutral ferric oxide surface $>$FeOH.

In a recent study, steady-state experiments have been performed at low pH ($<5$) using a fluidized-bed reactor that is supplied with a constant flow of electrochemically generated hydrogen sulphide (Peiffer & Gade, 2007). The surface area normalized experimental reaction rates depended on bulk properties of the used minerals and decreased in a sequence Gt $>$ 2lfh $>$ 6lfh. These observations are in contrast to results from batch experiments obtained at pH 7.5 where mineral reactivity seemed to be related to the free energy of their formation (Poulton et al, 2004). Under these conditions Fe$^2+$ strongly adsorbs to the mineral surface and thereby interacts with dissolved sulfide.

In this study we attempt to resolve these contradictions. Using the same experimental approach as described in Peiffer & Gade (2007), we have extended the experimental pH range to study the steady-state reactivity of various iron (hydr)oxides to values between 3 and 9. In this poster we will present the first results from these experiments.

References


Investigating the dependence of feldspar dissolution rates on Gibbs free energy in the presence of high pCO₂

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Here we report on results from an ongoing experimental investigation of the dissolution kinetics of albite feldspar at 100 °C in aqueous solutions significantly enriched in dissolved carbon dioxide (pCO₂ = 9 MPa). The purpose of this study is to measure CO₂-water-rock interactions as a function of solution saturation (ΔG), thereby providing data needed to model physico-chemical interactions associated with mobile CO₂-plumes in subsurface environments. Over the fluid saturation range of –70 to –40 kJ mol⁻¹ the dissolution rates can be characterized by a dissolution rate plateau, where the rates are roughly equal and independent of dissolved Na, Al, and Si. At higher solution saturation states, the rates begin to decrease sharply. In addition, the stoichiometry of dissolution changes from stoichiometric to non-stoichiometric, and is most probably due to the precipitation of an Al phase. Current experiments are being run to measure the kinetics at ΔG > -30 kJ mol⁻¹. The present data set, even though incomplete, is in general accord with many other studies that show a sigmoidal dissolution rate-free energy relation (e.g. Hellmann and Tisserand, 2006; and refs therein). Most importantly, the data also deviate dramatically from the behavior predicted by transition state theory (TST).

Reference

Lower mantle phase-boundary variability

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A lower mantle S-wave triplication with a Scd branch occurring between S and ScS appears to be explained by a recently discovered Perovskite (PV) to Post-Perovskite (PPV) phase-change. It is predicted to have a positive Clapeyron slope (γ) between 5 to 13 MPa/K with a small S-velocity jump (1.5 to 4%) and an even smaller 1 to 2% jump in P-velocity. Seismic observations indicate that Scd arrives earlier and stronger beneath fast regions indicating a positive γ (circum-Pacific) than slow regions (super plumes). However, it proves difficult to separate effects produced by down-welling (slab debris) from up-welling (plumes) in refining the actual physical properties. Here we model dense record sections collected from USAArray and existing PASSCAL data to isolate effects produced by lower mantle structure as evidenced by P and S-waves, to better define the seismic phase-change properties beneath Central America. We find that the PV-PPV velocity jump is twice as strong beneath slow regions than fast regions requiring distinct reference heights indicative of changing chemistry. Moreover, the edges of the supposed buckled slabs delimited by both P and S-waves display very rapid changes in phase-boundary heights producing Scd multipathing. These features can explain the unstable nature of this phase with easy detection to no detection commonly observed. The fine structure at the base of the mantle beneath these edges contains particularly strong reflections indicative of local ultralow velocity zones, which is predicted in some dynamic models.

References
Different origin for mafic and intermediate/felsic lavas from Moorea island (Society, French Polynesia)

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Moorea, a Quaternary volcanic island in the linear Society chain (French Polynesia) is made up of shield (alkali basalt to trachybasalt) capped by intermediate lavas (basaltic trachyandesites, trachyandesites, tephri-phonolites) and alkali trachytes. These intermediate to evolved lavas were emplaced between 1.55 and 1.35 Ma, just after the end of the shield stage which started at 1.72 Ma. The Moorea alkali basaltic suite cannot, however, be easily explained by closed-system fractionation processes because (i) the suite is bimodal in terms of rock abundances (60% mafic lavas and 40% intermediate/felsic ones), and (ii) fractional crystallisation tests fail to account for the transition between these two types.

In order to understand the relationship between basalts and felsic lavas, we determined trace element concentrations, as well as high precision Pb isotope ratios, and Hf, Sr and Nd isotopic compositions of a selection of 18 samples representing the various lava types. Basalts have relatively uniform ²⁰⁶Pb/²⁰⁴Pb (~ 19.2) but variable Nd, Hf and Sr ratios (i.e., ⁸⁷Sr/⁸⁶Sr between 0.7044 and 0.7052). In contrast, the felsic lavas have uniform Nd and Hf isotopic ratios but variable Sr and Pb ratios. The high precision Pb isotopic data define a straight line for the felsic lavas while the basalts form a cluster. Interestingly, the felsic lava straight line does not intersect the basalt cluster.

The composition of the basalts can be explained by conventional models involving partial melting of a garnet peridotite within a plume with EMII characteristics. The composition of the felsic material requires a completely different origin. We suggest that the felsic lavas originate from melting of a basaltic component and not from fractional crystallization of the plume derived basalts. This basaltic component is isotopically heterogeneous but its location is uncertain: it could be located at the base of the oceanic crust below the island or it could be an integral part of the plume.

Schwertmannite transformation to hematite by heating: Implications for pedogenesis, water quality and CO₂/SO₂ export in acid sulfate soil landscapes

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Naturally occurring schwertmannite (Fe₈O₇(OH)₅.₅(SO₄)₁.₂₅), a product of acid sulfate soil oxidation and severe acidification, has been identified as a labile source of iron, sulfate and acidity. Schwertmannite forms surface accumulations on coastal flood plains of eastern Australia that are subject to wild fire events. We report experimental evidence that fire in acid sulfate soil landscapes will convert schwertmannite to hematite (α-Fe₂O₃), consequently reducing the potential acidity store whilst liberating Greenhouse gases. At ≥ 800°C, naturally occurring schwertmannite was transformed completely to hematite. Thermal gravimetric analysis of this transformation process showed that CO₂ and SO₂ evolved simultaneously at relatively low temperatures (200-250°C and 300-340°C respectively). Aqueous dissolution experiments with samples of the initial schwertmannite and the resultant hematite showed that there was a significant decrease in the acidity potential associated with the heating-induced conversion to hematite. The data clearly shows natural fires may convert schwertmannitic surface accumulations to hematite. Hematite surficial layers have been observed previously in these landscapes and this study provides an explanation for their pedogenesis. Theoretical acid loads, based on this research, indicate fire can greatly reduced potential acidity. Relatively low temperature fires in these landscapes can combust schwertmannitic accumulations resulting in the discharge of CO₂ and SO₂. These results have implications for the assessment of acidity and the sustainable management of acid sulfate soil landscapes.
Evidence for natural, non-thermal annealing of fission tracks in apatite

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Apatite fission-track (AFT) analyses using a LA-ICP-MS based approach on samples from Finland and Canada provide evidence for a non-thermal AFT annealing process that is dependent on the present-day concentration of alpha-emitter actinides (U, Th, Sm) within grains. In one example, 118 grains were dated from a sample from central Finland (see below).

Because all of the dated grains are from a single hand sample, the inverse correlation between the concentrations of alpha-emitter actinides and AFT age cannot be explained simply by intra-grain variations in temperature history. Electron microprobe analysis of the dated grains indicates that chemical elements that are known to control the annealing rates in apatite (Cl, Mn, Fe, REE, etc.) do not show a similar correlation.

Electron beam induced annealing of fission tracks in apatite (Paul and Fitzgerald 1992) and studies of phosphates as nuclear waste forms (e.g. Ewing and Wang 2002) indicate that processes other than thermal annealing can cause fading of fission tracks under laboratory conditions. The above example from Finland represents a natural example of non-thermal, radiation-induced annealing.

Modelling of AFT data from cratonic settings with annealing models that do not incorporate non-thermal annealing processes will lead to overestimation of palaeotemperatures.

References
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Trace element distributions and coral skeleton micromorphology following a bleaching event

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The massive tropical corals commonly used as palaeoclimate archives, such as Porites sp., contain zooxanthellae (symbiotic photosynthesizing algae). Coral bleaching occurs when these pigmented zooxanthellae are expelled from the coral tissue. In this study we investigate how the biomineralization process and trace element distribution within the coral skeleton are impacted by zooxanthellae population dynamics following a bleaching event. The non-destructive, high resolution in-situ mapping capabilities of synchrotron µ-XRF is an ideal tool to investigate differences in trace element partitioning that correspond to the fine-scale architecture of coral skeleton.

A healthy ~30 year old Porites australensis colony was collected 2 ½ years after the February 1998 mass coral bleaching event from the inshore central Great Barrier Reef, Australia (18.48°S, 146.26°E). During the 1998 coral reef bleaching event ~80% of coral to a depth of 10m bleached at this reef, and bleaching mortality subsequently reduced coral cover by ~20%. At the time of collection (August 2000) there were no signs that the specimen had bleached, however, x-ray images show a marked and sustained skeletal growth response with lower extension and calcification rates and higher skeletal density.

Synchrotron µ-XRF mapping was carried out at Beamline X26A (NSLS, BNL) with the beam set at 16.5 keV to target elements up to Sr and a 10µm spot size. Sr, Ca, Br, Zn, Ni, Cu, Fe Pb and Ba were mapped in 20µm steps (equivalent to daily growth rate) down the width of a single corallite for a 4-year period of skeleton growth including the 1998 bleaching event. Skeletal structures are compositionally zoned, with a strong response 6 months after the start of the bleaching event. An adjacent CT-X-ray microtomography scan recorded the contemporary morphological changes in skeleton micro-architecture. Bulk analyses of Sr/Ca, Mg/Ca, δ¹³C, δ¹⁸O were measured on a parallel milled transect. To isolate the role of tissue smoothing on the seasonal signal µ-XRF elemental maps were also collected across the most recent skeleton deposited within the tissue zone of specimens collected in both summer and winter seasons.
Tourmaline in evaporites and meta-evaporites: Perspectives from Namibian metasediments

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Tourmalines associated with evaporitic or meta-evaporitic rocks commonly exhibit a compositional trend where there is low Al in the structural formula that is compensated by the introduction of Fe i.e., Al = Fe3+ exchange. This compositional trend has been found in the few occurrences of known evaporitic tourmalines: the caprock of a salt dome in the Gulf of Mexico, a brecciated and metamorphosed cap rock from Alto Chapare (Bolivia), an amphibolite-facies metaborate deposit from eastern Liaoning (China), and some tourmaline in tourmalinites from the meta-evaporitic sequence of the Duruchaus Formation (Damara Belt, Namibia – this study). These tourmalines follow a trend that defines a complete solid solution between dravite (NaMg3Al6(Si6O18)(BO3)3(OH)3(OH)) or “oxy-dravite” (Na(MgAl2)(MgAl5)(Si6O18)(BO3)3(OH)3O) and povondraite (NaFe3+(3Fe3+2Mg2)(Si6O18)(BO3)3(OH)32). These trends are interpreted to represent tourmalines developed in an Al-poor, Fe3+-rich environment, consistent with evaporitic settings.

Although some of the tourmalines from the Duruchaus Formation follow this Al for Fe3+ trend, a number of clearly meta-evaporitic tourmalines do not. The tourmalinites in two of the three localities studied are interlayered with biotite- and muscovite- semipelite and with calcite-dolomite marble. Despite their derivation from evaporitic sediments (tourmalinites preserve pseudomorphs after a variety of primary evaporitic minerals), the tourmalines in these tourmalinites exhibit an Al- and Mg-rich composition that appears to reflect a local compositional influence from the semipelitic interlayers. In fact, these Al-Mg-rich compositions are similar to those found by Prof. Werner Schreyer and his colleagues in tourmalines from the ultrahigh-pressure rocks of the Dora Maira massif (Italy) that they interpreted as meta-evaporites.

Geochemistry of cold vent fluids at the Central American Convergent Margin

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The active continental margin offshore Central America is characterised by a high number of cold vent sites associated with typical sea floor features such as mud volcanoes and diapirs (mounds) or submarine slides. Over the past couple of years a solid geochemical database of fluid samples has been collected from various locations along the Costa Rica - Nicaragua forearc. Similar to pore fluids from other, mostly accretionary convergent margins, these fluids are typically less saline than normal seawater. There is clear evidence (using oxygen and hydrogen isotope ratios) that chloride-depleted fluids originate from clay-mineral dehydration processes at elevated temperature and pressure conditions. This interpretation is supported by a number of additional observations such as the occurrence of thermal methane and highly elevated boron concentrations. Due to the lack of suitable conditions for the presumed processes within the sedimentary sequence of the overriding plate, it has been hypothesized that the fluids may originate from mineral dehydration in subducted sediments at about 10 km depth (Hensen et al. 2004). This is supported by mass balance estimates between input of mineral-bound water by subducting sediments and output through known vent sites. At many sites, however, the geochemical signature does not reveal clear evidence for a “deep” origin, such as the abundant occurrence of shallow biogenic gas. Conspicuous differences in the geochemical composition of fluids from various locations allow a general subdivision into regional, potentially structurally-controlled, types. We will present a comprehensive description of the available data set – covering the main element composition and various isotope systems (δ18O, δD, δ13C, 87Sr/86Sr, δ44Ca, 129I/I) – and discuss fluid sources and potential ages as well as processes of formation and alteration. In addition, we will present an outline of current efforts to drill key sites of the most prominent dewatering structures within IODP (633 full2, Costa Rica Mounds).

Reference
The application of granular activated carbon on remediation in trichloroethylene contaminated groundwater

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The objective of this study is to evaluate the effect of ionic strength and hardness of trichloroethylene (TCE) contaminated groundwater on remediation using granular activated carbon (GAC). The sorption rate of TCE by GAC was observed by batch experiments. The sorption kinetic of GAC was analyzed by kinetic models. As the ionic strength and hardness of the synthetic groundwater increased, the TCE sorption rates of GAC in the synthetic groundwater decreased. The TCE sorption rates of GAC in synthetic groundwater were 100%, 93.0%, 90.2%, and 86.2%, respectively. These results showed that the TCE sorption rates were affected by the relationship between the ionic strength and the hardness of the synthetic groundwater. The Elovich model ($r^2=0.99$) is more precise than Pseudo first order model ($r^2=0.96$). This indicates that the Elovich model is well represented in the contaminated groundwaters which have various factors like ionic strength and hardness. The surface area of the GAC was 958.98 m²/g and the calculated sorption areas of TCE & ions were 318.38 m²/g, which were 32.2% of the GAC surface area. Therefore, the ionic strength and hardness of groundwaters must be considered in the remediation of TCE-contaminated groundwater using GAC.

Accessory phase control on the trace element signature of subduction zone fluids

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In order to understand the general trace element signature of arc lavas, phase and melting relations in metapelites at sub-arc depth are of first order importance. Here we present results from experimental studies on a trace element doped, hydrous (2-7 wt.% H₂O), synthetic pelite and granite in the range 20-45 kbar and 600-1050°C, i.e. conditions relevant for the slab at sub-arc depth. In the metapelite, a hydrous melt that quenches to a glass is present at conditions above 700°C, 25 kbar; 750°C, 35 kbar and 800°C, 45 kbar. At lower temperatures, a solute-rich aqueous fluid is present that is not quenchable. This fluid has been captured in diamond traps in the experiments and the quench material as well as the glass have been analysed with LA-ICP-MS.

One surprising feature in the run products is the presence of accessory phases at subsolidus as well as at suprasolidus conditions, even at large melt proportions of 50%. Rutile, apatite and zircon have been found over the entire investigated P-T range. Allanite is present at 2.5 GPa up to 800°C, and at 3.5 and 4.5 up to 750°C. At higher temperatures, monazite is stable up to 1000°C. This has profound bearings on the trace element characteristics of the fluid phase. In a residue consisting of garnet, clinopyroxene, phengite and coesite all trace elements in the fluid phase are governed by partitioning behaviour. In contrast, in the presence of accessory phases, several trace elements are buffered (Ti by rutile, P by apatite, Zr by zircon, LREE by monazite/allanite). Additionally, other HFSE and REE are preferentially retained in the residue with respect to a system without these accessory minerals. This is documented in the measured composition of the fluid phases. For example LREE display only incompatible behaviour at the highest temperature investigated (950-1000°C) whereas at 800°C, LREE are compatible in the residue due to the presence of monazite or allanite. In the aqueous fluid LREE are about an order of magnitude lower than in the hydrous melt at 750°C. Zircon is able to fractionate geochemical twins such as Zr and Hf. Hf decrease in the melt is less pronounced than Zr decrease with decreasing temperature and thus hydrous melts at 750-800°C leaving the slab have a Zr/Hf significantly lower than the primitive mantle value. Aqueous fluids are very dilute in all trace elements and even LILE are higher in the residue than in the fluid. For example Ba is more than 10 times lower in the aqueous fluid than in the residue. This provides evidence that hydrous melts and not aqueous fluids are needed to significantly recycle incompatible elements from the slab to the mantle wedge. This observation provides evidence that top slab temperatures ≥ 750°C are required below arcs that show significant LILE and LREE enrichment or a Hf contribution from sediments.
Validation of normalisation concepts for in situ µ-EDXRF data

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Column experiments were performed to study hard pan formation processes in mining dumps. The special focus of this study was to develop a better understanding concerning the time-dependent transport behaviour of element towards the capillary fringe. Therefore, three 50 cm long vertical columns were filled with homogenized tailings material from Freiberg/Germany (35cm) and purified silica sand (top part of column). At the bottom of the columns water is injected and because of capillary transport a continuously fluid transport occurs. The resulting changes in the local chemical conditions (e.g. Eh, pH) create the environment for dissolution, transport and precipitation. Hence, an enrichment of mobile behaving elements like Cu, Zn and Fe are expected to occur in the upper levels and accordingly a decrease within the bottom parts of the column.

The measurements were performed by using the µ-EDXRF method, which has been described in detail by Rammlmair et al (2006). The experiment was set up for a period of six month. Within this time frame 20 runs were achieved to record the changes in the elemental concentrations. The results were calculated by using the Q-Spec 6.5 software (COX Analytical Systems).

There is no way to compare scans of different dates directly, since we havened found a proper way to calibrate the method yet. In the frame of a student research project the collected µ-EDXRF data are studied for comparison using various normalizing methods. Hence, effects due to e.g. matrix or water content changes can be shown.

Reference

A high-resolution study of diatom oxygen isotopes in a Late Pleistocene to Early Holocene laminated record from Lake Chungará (Andean Altiplano, Northern Chile)

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Lake Chungará (18°15' S, 69°09' W, 4520 m a.s.l. 22.5 Km2 and 40 m of water depth) is a hydrologically closed lake located on the Andean Altiplano. The lake is polyemic, meso to eutrophic and currently primary productivity is mainly governed by diatoms and chlorophyceans.

Three laminated intervals were selected for detailed petrographical studies as well as a high resolution diatom oxygen isotope analysis. These laminated sediments are made up of bands of white and dark mm-thick laminae and thin layers of diatomaceous ooze with variable carbonates and amorphous organic matter.

Assuming no significant changes in the isotopic compositions of the water sources and according to the diatom microstratigraphy of the laminae, two alternating environmental scenarios can be described. Lower-level water conditions are interpreted during the intervals of white laminae deposition (high values of δ18O), since those conditions are more favourable for the massive short-term deposition of monospecific large centric diatom blooms and δ18O enrichment. These white laminae are probably the result of exceptional periods of mixing of the shallow water column during lowstands, which recycle nutrients from the hypolimnion. Lower δ18O values, and therefore deeper water conditions, are more favourable for the development of dark laminae (normal annual cycle of the lake with alternating phases of stratification and mixing).

These conditions would lead to the development of a complex diatom community, among other algal groups.
The energy balance at the core-mantle boundary

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Cooling of Earth’s core occurs because relatively cool rocks sink to the core-mantle boundary (CMB) and absorb heat by conduction in a continuous cycle of sluggish mantle convection. A thermal boundary layer (TBL) is formed where heat is conducted from the core into the mantle and is characterized by an increased geothermal gradient in the D′′ region. The recent discovery of post-perovskite (pPv) and increasing seismic evidence for a double-crossing of the pPv phase boundary by the TBL geotherm provides auspicious new constraints on the heat flow in D′′, yielding lower bounds in the range 5-15 TW. However, if a several km thick layer of partially molten material just above the CMB was much thicker in the past when Earth’s deep interior was hotter, then it is possible that the layer fractionally crystallized over time to achieve its present state and could therefore retain a significant budget of incompatible radioactive species. The power released by radioactivity (on the order of several TW) in this ultralow-velocity zone (ULVZ) layer would contribute to overall D′′ heat flow and have potentially important consequences for the structure and dynamics of the mantle and core. Numerical models of mantle convection including a thin dense radioactive layer show that significant lateral variations in the thickness of the ULVZ arise which enhance variations in heat flux at the top of the core, with the thickest and hence most internally heated patches swept up beneath upwelling plumes. On the other hand, inclusion of larger modestly dense chemical piles (or “crypto-continents”) moderates the excess heat that would otherwise be transferred into upwelling plumes.

An integrated NMR and FTCIR mass spectroscopic study to characterize a new and major refractory component of (marine) natural organic matter (NOM) at the molecular level, CRAM: Carboxyl-rich alicyclic molecules

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Advances in organic structural spectroscopy have enabled a direct molecular level analysis of very complex natural mixtures such as the very abundant natural organic matter (NOM), a key contributor to the global carbon cycle and other element cycles (N, P, S,…). NOM often defines the chemical environment and the bioavailability of toxic and nutrient metal ions in the biosphere. Little is known about the chemical composition of NOM and the reason for its refractory nature. Recently we have identified a new and major constituent of NOM, namely carboxyl-rich alicyclic molecules (CRAM), using nuclear magnetic resonance spectroscopy and ultrahigh resolution mass spectrometry [Fourier transform ion cyclotron mass spectrometry (FTICR-MS)]. CRAM are compositionally and structurally more heterogeneous than other NOM constituents (like peptides and carbohydrates), and are comprised of a complex mixture of carboxylated and fused alicyclic aliphatics with a carboxyl:C:aliphatic-C ratio of 1:2 to 1:7. The structural diversity found within CRAM and their substantial content of alicyclic rings and branching contribute to their resistance to biodegradation and refractory nature.

CRAM are expected to constitute a strong ligand for metal binding, and multiple coordination across cations could promote aggregation and marine gel formation thereby affecting CRAM reactivity and the bioavailability of nutrients and trace metals. It appears CRAM are ultimately derived from biomolecules with structural similarities to sterols and hopanoids. The occurrence of CRAM in freshwater and terrestrial environments seems likely, considering the global distribution of biomolecules and the similarities of biogeochemical processes among environments.
Modelling the geochemical variation of granitic mushes

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Straightforward Rayleigh-type fractional crystallisation models have merits to outline the main factors that caused geochemical evolutionary trends of granites, but the implied complete separation of mineral phases from residual liquid is at best a poor approximation of reality. A more elaborate crystallisation model of granitic ‘mushes’ tracks the trace element variation in two subsystems - a ‘congealed mush’ and a ‘residual mush’ - that develop as crystallisation proceeds. It takes into account any separation of less-viscous, water-rich melts and fluid phases from the residual mush during the final stages of solidification. Special attention is paid to the role of accessory minerals on the evolution of the Rare Earth Element (REE) patterns. Petrography learns that accessories are often present as clusters of minerals that crystallised from pockets of trapped interstitial melts. These accessory minerals crystallised too late to significantly affect fractionation trends. Moreover, these clusters frustrate efforts to estimate effective crystallisation rates from modal abundances. Parameters of the model are the fraction of crystals trapped in the congealed mush, and the crystal-to-trapped liquid ratio in the congealed mush. Calculations are based on a ‘finite step’ numerical simulation of crystallisation and melt expulsion processes.

The model calculations will be illustrated with results for two closely related leuco-granitic series from the Variscan Northern Vosges (France): the Natzwiller granite and the highly evolved Kagenfels granite. The variation trends of the Natzwiller granite demonstrate the crucial role of the accessory minerals apatite, sphene, allanite and zircon. The pronounced decrease of the concentrations of the middle REE (relative to Light and Heavy REE) of the Kagenfels granite cannot be explained by models based on reasonable values of modal abundances of accessory minerals and of partition coefficients. It is argued that the Kagenfels granite matches the composition of expelled liquids from the residual mush at 50 to 60% solidification of the Natzwiller body. The expulsion of interstitial liquids is presumably promoted by tectonic activity.

The first Lu-Hf garnet ages of North Penninic alpine eclogites

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Despite a large geochronological database there are still various models for the tectonic evolution of the Alps. Current rapid progress in dating metamorphic minerals such as garnet has given this technique a key role in the ongoing discussion. Recently, [1] recognized the so called Balma Unit in the upper Sesia valley, previously interpreted as part of the Zermatt-Saas Zone (South Penninic Ocean), as a fragment of the North Penninic Ocean. Most previous studies dating peak metamorphism of Alpine ophiolites have focussed on the Zermatt-Saas zone. Here, we present the first Lu-Hf garnet data for eclogites from the North Penninic Ocean.

Electron microprobe analyses show typical prograde zoning profiles in garnet. A selective digestion procedure for garnet was applied, where zircon and rutile inclusions are not dissolved. The garnet-whole rock Lu-Hf ages obtained for three samples are 42.19 ± 0.47 Ma (MSWD: 1.8), 43.19 ± 0.36 Ma (MSWD: 1.2) and 45.4 ± 1.1 Ma (MSWD: 2.3), which is significantly younger than all Lu-Hf ages established so far for South Penninic Units. Notably, existing SHRIMP U-Pb zircon ages [2] of 93.4 ± 1.7 Ma (synmagmatic core) and 40.4 ± 0.7 Ma (synmetamorphic rim) for the sample in which the Lu-Hf age of 42.19 Ma was obtained, indicate that growth of metamorphic zircon postdates garnet growth.

Despite the fact that all three samples originate from the same tectonic unit, their Lu-Hf ages differ outside of error. The cause of this is not yet known, but if the garnets grew over a long time interval (several million years) it is possible that varying core-to-rim distributions of Lu in garnet could result in the observed age range. Such Lu zoning can occur by Rayleigh fractionation during garnet growth [3] or by diffusion-limited garnet growth [4]. Our new Lu-Hf data indicate that garnet growth, and possibly peak pressure conditions in the North Penninic ophiolites postdates those in the South Penninic ophiolites.

References
Convective Dissolution of CO₂ in Saline Aquifers

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Dissolution of CO₂ into the brine is one of the major trapping mechanisms that increases storage security. The increase in density of the brine that occurs when CO₂ dissolves drives convective motion that enhances the dissolution rate of CO₂. We present the results of a hydrodynamic stability analysis that describes the onset of convective motion. We have obtained expressions for the critical time necessary for the onset and the initial wavelength of the fastest growing disturbance. In high permeability aquifers onset of convection will be rapid (<1 yr), but wavelength are very small (~1 m). Resolution of these small length scales is a challenge standard reservoir simulators.

We present numerical results of the long term evolution of the convection in the brine and the dissolution rate of the CO₂. The numerical simulations show three mass transport regimes, an early diffusive regime, followed by an infinite-acting convective regime, and finally a finite-acting convective regime. The infinite acting convection regime is characterised by a constant dissolution rate. The depth of the aquifer determines the duration of this highly efficient convective mass transfer regime. As the plumes of CO₂-rich brine reach the bottom of the aquifer mass transfer decays rapidly, despite continued convective motion (finite acting convection).

We conclude that dissolution trapping will be an important mechanism in high permeability aquifers, because the onset time is short, the dissolution rate is high. In large aquifers the high infinite-acting dissolution rate can be maintained longer and therefore dissolution trapping will be more important in large aquifers.

Reference

Microbial life in a hydrothermal spring rich in arsenic compounds

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The geothermal spring Champagne Pool in Waiotapu, New Zealand has an estimated volume of 50,000 m³ and discharges fluid at 75° C, which is oversaturated with arsenic and antimony compounds such as orpiment (As₂S₃) and stibnite (Sb₂S₃) that precipitate and form orange deposits. Although Champagne Pool is geochemically well characterized only few studies addressed its role as a potential habitat for microbial life. In the current investigation, a combined approach of first culture-independent studies followed by culturing experiments was applied to describe microbial density and diversity within Champagne Pool. ATP measurements and epifluorescence microscopy showed relatively low biomass in Champagne Pool compare to other terrestrial hot springs within New Zealand and relatively low cell numbers of 5.6 ± 0.5 x10⁶ cells per ml. Denaturing Gradient Gel Electrophoresis and 16S rRNA gene clone libraries analyses indicated low microbial diversity and the abundance of hydrogen-oxidizing and sulfur-dependent populations, which were dominated by members belonging to the order Aquificales. On account of the results culture media were designed and two novel bacteria and a novel archaeon were successfully isolated. Experiments suggested that the observed relatively low biomass and biodiversity might be due to the presence of volatile components (H₂S, methyl and hydride derivatives of arsenic and antimony) within the spring which are inhibiting microbial growth.
Carbon is isotopic compositions of acetate as proxies for biogeochemical processes in gas hydrate bearing sediments

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A large fraction of methane in marine gas hydrates results from biogenic sources, but the processes that generate methane in the deeply buried sediments remain to be elucidated. IODP Expedition 311 drilled a transect across the Cascadia Margin, NE Pacific, to study the distribution and evolution of gas hydrates in an active continental margin. In our post-cruise research, we seek to identify processes and reactants involved in methane formation by compound-specific isotopic analysis (CSIA) of dissolved carbon-bearing compounds such as acetate. So far, deep pore-water profiles of acetate concentration are rare and δ13C values of acetate are largely lacking due to analytical obstacles.

Our recent survey of a wide range of natural sediments and sediment incubations has revealed a large variability in the carbon isotopic compositions of acetate and incubation experiments suggest a systematic link between the carbon isotopic composition of acetate and the dominant carbon transforming processes of the sediments, i.e., fermentation, methanogenesis and homoacetogenesis (Heuer et al., 2006).

At the Cascadia Margin, both concentrations and δ13C of acetate vary considerably. Acetate concentrations increase from <5 µM at the sediment-water interface to 670 µM at 250 meters below seafloor. δ13C values of acetate range from -50 to -8‰ vs VPDB. Given uniform δ13C values of dissolved organic carbon (DOC) close to -23‰, the low values of acetate require either partial production of acetate from a 13C-depleted pool of precursors such as biomass from methanotrophs or partial production of acetate by CO2 reduction (homoacetogenesis). On the other hand, the high values of δ13C of acetate in some hydrate-bearing sediment intervals likely point to aceticlastic methanogenesis as an important sink of acetate. CSIA of dissolved organic compounds provides novel information on the molecular-scale processes in deeply buried sediments that lead to formation of methane and ultimately methane hydrate.

Reference

Biological fractionation of Ca isotopes (δ44/40 Ca): A study in Göttingen minipigs

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Calcium is an essential element in human physiology and plays an important role in many processes. Due to its important role Ca concentrations are kept within small limits in the extracellular space. This Ca homeostasis is maintained by three organs, the gastrointestinal tract (input of Ca), the skeleton (store of Ca) and the kidney (output of Ca). Physiological ageing processes and many chronic diseases are associated with disturbances of the calcium metabolism.

In a study at the Federal Research Centre for Nutrition and Food several animal trials with the Göttingen miniature pig for generation of osteopathies have been carried out. The Göttingen miniature pig was chosen for these trials as their physiology is comparable to human physiology (e.g. Scholz-Ahrens et al., 2007). We analyzed food, feces, blood, bone and urine samples of six animals from these trials in order to study the calcium metabolism with respect to stable Ca isotopes and their fractionation.

Feces had δ44/40Ca values similar to the δ44/40Ca of the semi-synthetic diet (0.42‰) or exhibit a fractionation which tends to result in lower δ44/40Ca values in feces. Blood δ44/40Ca values vary from 0.06‰ to 0.68‰ and are on average 0.68‰ heavier than the bone δ44/40Ca values (-0.60‰ to -0.03‰). This difference between the δ44/40Ca values of blood and bone is only half of the difference between soft and mineralized tissue reported by Skulan and DePaolo (1999).

δ44/40Ca values of urine samples range from 2.05‰ up to 2.68‰ and are approximately 2‰ higher than the corresponding blood δ44/40Ca values of the same animal. Presumably, the observed fractionation between blood and urine mainly occurs in the kidney. This enrichment of heavy Ca in urine may be due to preferential transport of 40Ca by Ca transporters in the renal tubules, by which more than 98% of the calcium of the primary urine is reabsorbed (Hoenderop et al. 2005) in a repetitve process.

References
Continental crust as a source component for NW Central American Arc lavas?

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Our group evaluates along and across arc geochemical variations from various volcanoes and volcanic centres in the NW Central American Volcanic Arc from NW Nicaragua to Guatemala. Additional data from several Guatemalan continental crust samples as well as Cocos Plate sediments help to clarify the potential endmember compositions for the observed trends.

Subduction input from the subducting Cocos Plate consists of carbonate to hemipelagic sediments, seawater altered and unaltered igneous crust and serpentinites. Slab dip decreases while the thickness of the continental crust increases beneath the volcanic front (VF) from a maximum in central Nicaragua to NW Guatemala. Continental crustal thickness also increases behind the VF.

Our comprehensive geochemical data set consists of major elements, a wide variety of trace elements and Sr-Nd-Pb-HF-O isotope data. As shown previously by the Carr group, ratios of fluid mobile to less fluid mobile elements (e.g., Ba/La, Ba/Th and U/Th) decrease and Pb isotope ratios increase systematically from Nicaragua to Guatemala. The 143Nd/144Nd and 176Hf/177Hf isotope ratios decrease systematically from Nicaragua to Guatemala. These geochemical variations suggest a decreasing role for a hydrous fluid component and an increasing role for a sediment or continental crustal melt component in volcanic rocks towards Guatemala (NW) along the VF and behind the volcanic front (BVF). Samples from the back arc in Honduras have the most mid-ocean-ridge basalt (MORB) like compositions and are believed to represent the composition of the mantle wedge. Samples from the Nicaraguan VF have similar Nd but higher Sr isotope compositions most likely reflecting enrichment with slab derived fluids containing a subducted sediment or seawater Sr component.

A positive correlation in 206Pb/204Pb vs. 207Pb/204Pb isotope ratios for VF and BVF volcanic rock samples from El Salvador and Guatemala trends towards the granitic basement in Guatemala. Combined εNd vs εHf isotope data for VF and BVF samples from Nicaragua to Guatemala tend from high εNd and εHf MORB like compositions towards continental crust like compositions with increasingly lower εNd and εHf values. Supplementary εNd vs εHf isotope data from Guatemalan continental crust and Cocos Plate sediment samples provide further support for a continental crustal component in the generation of the NW CAVA magmas.

Melt/wallrock interaction shown by silicate melt inclusions in peridotite xenoliths from Pannonian Basin

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Samples
Primary silicate melt inclusions (SMI) in clinopyroxene (cpx) rims and secondary ones in orthopyroxenes (opx) along healed fractures from two equigranular amphibole-bearing spinel lherzolite xenoliths representing the subcontinental lithospheric mantle (Szliglet, Pannonian Basin, Hungary) have been studied. Microthermometry of dense CO2-bearing fluid inclusions, associated with SMI, was also carried out.

Discussion
Electron microprobe analysis reveals in both xenoliths that cpx and opx are zoned, especially in terms of basaltic major elements. Cores of both cpxs show trace element distribution close to the primitive mantle. Rims display an overall enrichment with high positive anomalies in Th, U and moderate LREE content, as an indication for metasomatism. The pargasitic amphiboles, formed after rims of the cpx, exhibit elevated Rb, Ba, Nb, Ta and moderate LREE content. The SMI are composed mostly of silicate glass and dense CO2 bubble. The primary SMI show evidence for significant crystallization on the wall of the host cpx. The major element composition of glass in SMI, regardless of xenoliths and host minerals, covers a wide range, mostly with trachyandesitic composition. The SMI, either primary or secondary ones, are extremely enriched in incompatible elements (particularly in U, Th, La, Zr) with a slight negative Hf anomaly.

Conclusion
The development of zoned pyroxenes, and the trapping of primary SMI in the cpx rims happened after the partial melting and subsequent crystallization of cpxs, most probably due to an interaction between a hot volatile-rich mafic melt and mantle wallrock. This interaction resulted in evolved silicate melts, which filled microfractures in opxs, leading to the formation of secondary SMI and, via metasomatism, the development of zoned pyroxenes. Most probably the formation of amphiboles is not related to this evolution.
Acessing the surface area of natural nanoparticles

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Information on the reactive surface area of natural samples is essential for the application of surface complexation models (SCM). The PO₄-CO₃ interaction on oxide surfaces is used to quantify the reactive surface area of soil particles. In the approach, phosphate is used as probe ion in natural samples brought at well-chosen solution conditions enforced by a 0.5 M NaHCO₃ extract solution. This matrix suppresses the influence of Ca²⁺ ions, desorbs organic matter (further high values for the specific surface area (~200-900 m²/g). Scaling of SA on the experimental soil oxide contents shows that the natural oxide particles are embedded in an OM matrix, the correlation of OM with the Fe oxide fraction, suggesting organic matter (OM) content of the samples, which is due to extracted oxide, pointing to the presence of nanometer-sized particles (~1-5 nm).

The CO₃-P-O₄ interaction is calibrated by studying it for goethite, using the CD model [1] with an Extended Stern (ES) double layer option. The CD values are independently obtained from MO/DFT optimized geometries of iron-carbonate and phosphate complexes and are additionally corrected for dipole orientation effects [2]. The surface speciation derived from the data analysis of the CO₃-P-O₄ interaction on goethite agrees with ATR-FTIR spectroscopy. Application to data of natural samples shows SA values from ~1000-10,000 m²/kg soil. The SA correlates to the organic matter (OM) content of the samples, which is due to the correlation of OM with the Fe oxide fraction, suggesting that the natural oxide particles are embedded in an OM matrix. Scaling of SA on the experimental soil oxide contents shows high values for the specific surface area (~200-900 m²/g extracted oxide), pointing to the presence of nanometer-sized particles (~1-5 nm).

References


In situ Hf and O isotopic data from Archean zircons of SW Greenland

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We have obtained new, coupled U-Pb, O and Hf isotopic data from Archean TTG suites in Southwest Greenland in order to explore mechanisms for Archean tonalite genesis and crust formation. The dataset comprises analyses of >250 zircon spots from 11 rocks ranging in age from 3.85 Ga to 2.55 Ga, including the most ancient tonalites of the Itsaq Gneiss Complex through to late Archean granitoids of the Qørqut Granite Complex. All grains were characterized by CL, reflected and transmitted light imaging prior to analysis. U-Pb ages were determined using either SHRIMP RG or SHRIMP II; ¹⁸O/¹⁶O ratios were measured on the same zircon spots using SHRIMP II in multi-collector configuration; ¹⁸⁷⁶⁶⁸⁵Hf/¹⁷⁷Hf data was subsequently acquired by LA-MC-ICPMS (ANU Neptune).

Zircons from the oldest, ca. 3.85 Ga, tonalites record δ¹⁸O compositions within 1‰ of mantle values (δ¹⁸O mantle = 5.3 ± 0.3 [e.g. 1]) and initial εHf values largely within ±1 epsilon unit of chondritic composition (calculated using χ¹⁷⁶⁶⁸⁵Lu = 1.867x10⁻¹¹yr⁻¹). These narrow, mantle-like, O–Hf fields contrast markedly with results from studies of Phanerozoic suites [2, 3], which show diverse Hf–O isotopic arrays, displaced from mantle compositions.

Hf isotopic compositions of zircons from the youngest sample analysed, the 2.55 Ga Qørqut Granite Complex (initial εHf ≈ -25), are in agreement with earlier Pb isotopic studies [4] suggesting the origin of the Complex by the remelting of >3.7 Ga crust. The O isotope data from this suite however lie 1-2‰ below mantle compositions, again in contrast with results for Phanerozoic suites.

A striking feature of the overall dataset is the absence of high (>7‰) δ¹⁸O values highlighting the lack of recycled supracrustal material in the genesis of the TTG. Of particular note is the prevalence of low δ¹⁸O values, with 4 out of 11 samples, with ages from 3.7 to 2.55 Ga, having compositions 1-3‰ below mantle values. Low δ¹⁸O values are a relatively rare feature in granitic suites (e.g. [1]) and typically result from hydrothermal alteration by surface waters, in some cases enhanced by glaciation. The presence of low δ¹⁸O in these mid-crustal level Archean granitoids is unexpected and may reflect different surface conditions and hence fluid compositions in the Archean.

References

Confocal micro-Raman spectroscopy: A tool for the allocation of organic and inorganic components in calcified biominerals

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Mineralized biological composites have attracted increasing interest because of their outstanding mechanical properties that are well adapted to their function. Microcharacterization of these materials allows a better understanding of the structure-properties relation ship of these materials. Since the mineralized exoskeleton (cuticle) of crustaceans is composed of various types of calcified biominerals e.g. calcium phosphate, calcite, and amorphous calcium carbonate (ACC) embedded in a chitin matrix this material is an excellent model for a biocomposite. High resolution scanning electron microscopy has been extensively used to investigate the morphology of the crustacean cuticle. However, to allocate the spatial resolution of the various organic and inorganic components an additional chemical characterization is required. Scanning confocal µ-Raman spectroscopy (SCµ-RS) provides complementary important information about the spatial distribution of both the organic and the inorganic components because the Raman spectrum can be unequivocally attributed to a certain compound even when its concentration is very low. Additionally, SCµ-RS enables one to allocate the different calciumcarbonate polymorphs.

For these studies the cuticle of the terrestrial isopod *Porcellio scaber* is be used as a model system. The spatial distribution of minerals, elements, and organic compounds was studied on the sub-micrometer scale using cross sections of the cuticle. Calcite and amorphous calcium carbonate (ACC) were found to be the main biominerals within the cuticle. For the first time, it was shown that the minerals are arranged in distinct layers. Calcite is restricted to the outer area of the cuticle, whereas ACC is localized in the middle having only little overlap with the calcite layer. The proximal region of the cuticle mainly consists of chitin. Since the cuticle is subjected to periodic molting it is periodically decalcified and shed. A new larger cuticle, synthesized before shedding, is mineralized after every molt. These processes cause spatial and temporal variations of the mineral distribution. The change in mineral during the molting cycle was monitored with respect to the organic matrix. It was shown that the protective outer calcite layer is shed away during each molt, while ACC is recycled to quickly re-establish the protective calcite layer in the new cuticle. Thus, ACC is used as a transient reservoir for calcium and carbonate ions.

Demonstrating equilibrium Fe-isotope fractionation in Fe-Cl solutions

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A major problem when conducting isotopic fractionation experiments in aqueous solutions is determining if isotopic equilibrium has been reached. We have successfully demonstrated the attainment of equilibrium isotopic fractionation in a two-phase aqueous/ether system containing a mixture of Fe-Cl complexes, using the Fe three-isotope equilibrium method of Shahar et al. (2006; Matsuhisha et al., 1978). The immiscible liquid/spiked reversal procedure should also be applicable to other aqueous systems. These reversal experiments are part of our continuing integrated theoretical and experimental studies of the effects of changing bond environments on Fe fractionation. We use aqueous Fe-Cl complexes as a example of possible Fe-ligands because of the structural similarity of chloride to other potential iron-ligands, such as sulfides (e.g., pyrite, FeS2) and small organic ligands (e.g., rubredoxin, FeS2R2 similar in structure to tetrahedral FeCl4–), and the tractability of chloride in aqueous experiments.

Our experiments consist of a series of low pH solutions of ferric chloride, with total chlorinity varying from 0.5 to 5.0 M, to which an equal amount of immiscible diethyl ether has been added. As the aqueous-ether mixture equilibrates, FeCl4–, the only Fe-Cl complex soluble in the ether, moves from the aqueous into the ether phase. We use measurements of δ56Fe(aq) – δ54Fe(ether), in conjunction with a speciation model, to determine the relative fractionations among the complexes. At [Cl–]=1M the aq-ether fractionation is ~0.8‰.

To establish the attainment of equilibrium between the ether and aqueous phases, we paired an aq/ether mixture of unspiked 56Fe/54Fe with an equivalent mixture prepared with 54Fe spike. Once both mixtures had equilibrated, half the ether from the spiked experiment was added to the ether of the normal Fe experiment, so that spiked FeCl4– from the ether phase would have to pass into the aqueous phase of the unspiked experiment to reach equilibrium. We removed small aliquots from both the ether and aqueous phases after 20, 30, and 40 minutes, without disturbing the equilibrium of the mixture, and measured the aqueous-ether fractionation.

At 20 minutes, the ether and aqueous solutions were ~80% equilibrated, and they were totally equilibrated by 30 minutes. Equilibrium was demonstrated by the reversal in two ways: 1) both the aqueous and ether phases arrived at the same mass fractionation line; and 2) the final aqueous-ether fractionation of the reversal experiment was ~0.8‰, in agreement with the unspiked forward experiments.

References
Potassium as a heat source in the core? Metal-Silicate partitioning of K and other alkali metals

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The alkali metals (Li, Na, K, Rb, and Cs) are depleted to varying degrees in the Earth’s upper mantle. This is generally assumed to be due to volatility of these elements during accretion of the Earth. However, it is also often argued that some amount of K may have partitioned into the core and act as an additional heat source for the core dynamo. If K could partition into the core, it is not unreasonable to assume that the other alkali metals might also do so. Therefore, we have begun an experimental study of the partitioning of K and the other alkali metals between metals and silicates at lower mantle conditions using the laser-heated diamond anvil cell.

Our samples consisted of either pure Fe-metal or an Fe-S mix containing 10 wt. % S surrounded by either a K-silicate glass, a (Li, Na, K, Rb, Cs)-silicate glass, or a mixture of a (Na, K, Rb, Cs)-silicate glass and San Carlos olivine and overlain by an Al2O3 disk (to act as an optical window and to insulate the sample from the diamond). Pressures for the runs ranged from 23 to 110 GPa, and the temperatures for each sample were above the melting point of Fe for that pressure. Samples were recovered, polished and analyzed with the electron microprobe.

Experiments with pure Fe-metal and K-silicate glass in the pressure range 38-77 GPa showed no pressure dependence for the partitioning of K into metal. They also implied a maximum of 5 ppm K in the core.

Results from the experiments with the alkali-silicate glass or alkali–silicate glass mixed with olivine and Fe or Fe-S mix suggest that all the alkalis partition more readily into a sulfide than pure metal, and we found the general trend that DMET/SIL for Na > K ≥ Cs > Rb. However, under all conditions all the alkalis remained distinctly lithophile, and even at 110 GPa and 3200 K with 5 wt. % S and 1.5 wt. % O in the metal, the results suggest no more than 10 ppm K in the Earth’ core. Thus, K could only be responsible for less than 1% of the core’s heat budget.

Helium isotope studies in seismically-active regions of Turkey and California

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He isotopes in groundwaters and geothermal fluids are sensitive indicators of crustal-mantle interaction. Here, we present new He isotope (and associated carbon) data from two of the world’s great fault systems - the North Anatolian Fault Zone, Turkey (NAFZ) and the San Andreas Fault, California (SAF) - to further utilize He isotopes in regions of crustal unrest.

Following the catastrophic earthquakes in 1999, we initiated a periodic monitoring program (4 times/yr for 3 yrs) targeting geothermal fluids at 9 localities along an 800-km stretch of the NAFZ. 3He/4He ratios vary between 0.29 R A (Yalova, Gozlek) and 2.2 R A (Mudurnu) (R A – air 3He/4He) indicating a magmatic He contribution throughout. There were no large earthquakes over the monitoring period and little variation in 3He/4He values at individual localities. However, there are significant changes in the CO2/3He ratio and especially δ13C. We discuss these changes with respect to the regional stress pattern in Turkey.

Mantle-derived He is also pervasive in the vicinity of the SAF: 3He/4He reaches 0.11 R A (Mojave River Basin); 0.26R A (East Morongo Basin) and 3.4 R A (Monterey Bay). The whole region adjacent to the SAF is therefore leaking mantle-derived He to the surface albeit heavily diluted with crustal He. At Monterey Bay, cold seep fluids collected in long Cu-coils preserve temporal variability in He isotopes. This technique has enormous potential in future monitoring studies of earthquake-prone regions as it produces a continuous record of He isotope and gas chemistry variations.
Accessory mineral dating by ims-1270 ion microprobe

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A number of accessory minerals concentrate small amounts of U and Th and if they (initially) contain very little Pb they will be amenable to ion microprobe analysis. Each mineral presents different analytical problems not the least of which is the identification of well characterised standards. Changes between analyses in the ionisation and detection of Pb⁺ relative to U⁺ ions (i.e. in the Pb⁺/U⁺ ratio) do occur but can be shown to correlate with measured UO⁺/U⁺ ratios and corrections applied. At the EIMF we believe that measurement of a second molecular species e.g. UO₂⁺ or ThO₂⁺ can improve the correction procedures or, at least, be simply used to give confidence in the correlating ratios. Routinely, Pb, U, UO, ThO and UO₂ are all measured.

In monazite the high Th/U ratios make it possible to utilise both U and Th decay systems. Corrections are applied using a combination of Pb, Th, ThO and ThO₂ peaks. In the work to date monazite has given good reproducibility in the Pb/Th system but some open system behaviour has been observed in the Pb/U system.

Rutile, like zircon, gives good correlations for Pb/U vs UO/U or UO₂/UO ratios. However, this phase discriminates so strongly against Th that in some cases no Th signal can be detected and any ²⁰⁸Pb⁺ signal can be assumed to be common Pb. The total background common Pb, either that originally incorporated in the mineral or that added to the surface during sample preparation, can be shown to be less than 1 ppb (and ²⁰⁶Pb less than 0.03 ppb). This increases the confidence that dating rutile with relatively low U content (<5 ppm) should be possible.

Baddeleyite is the only mineral analysed so far where variations in the Pb/U ratio have been shown to be dependent on crystal orientation (Wingate and Compston, 2000). Similar effects have been observed in baddeleyite analyses made on the Edinburgh ion probe. Future EBSD work will be used to study the effects of crystallographic orientation and whether corrections can be systematically applied.

Reference


The origin of compositional variation of mafic magma and genesis of associated silicic magma in the Shirataka volcano, NE Japan: Constraints from Sr isotopic compositions of mafic inclusions and their hosts, with detailed petrologic features of the mafic inclusions

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Eruptive products of Shirataka volcano (0.9-0.7 Ma) in NE Japan are calc-alkaline andesite-dacite (57-66% SiO₂), and are divided into six petrologic groups (G1-6). Mafic inclusions, basalt-andesite (48-58% SiO₂), are always observed in G1, G2, G5 and G6. All rocks are mixing rocks formed by mixing/mingling between mafic and silicic end-members judging from many petrologic aspects, such as linear trends defined by hosts and inclusions in variation diagrams and coexistence of mafic and silicic magmas origin phenocrysts in each group. The mixing trends defined by hosts and inclusions are divided into high- and low-Cr Ni types, and both types coexist in G1, G2 and G5. Cr and Ni contents of the high type show some variation. Estimated mafic end-members are high-Cr-Ni (1120-1150°C, 47-52% SiO₂, Fo-rich olv±Mg-rich cpx±An-rich plg) and low-Cr-Ni type magmas (ca.1100°C, 48-52% SiO₂, Mg-rich cpx±An-rich plg), while the silicic end-members of both types have similar petrologic features in the same petrologic group (790-840°C, 63-68% SiO₂, hbl±qtz±Mg-poor px±An-poor plg). The high-Cr-Ni type mafic end-member magma is richer in compatible elements and poorer in incompatible elements than the low type one. Besides, ⁸⁷Sr/⁸⁶Sr data of all rocks show broad ranges (0.70377-0.70537), but the compositional range of each group is restricted. In each petrologic group, the high-Cr-Ni type mafic and associated silicic end-members have lower values in ⁸⁷Sr/⁸⁶Sr ratio than the low type ones, indicating that mafic and silicic end-members in the same type have co-genetic relationships. The MELTS and trace element model calculations suggest that the low-Cr-Ni type mafic end-member magma can be produced through <25% fractional crystallization (olv±cpx±plg) from the high-Cr-Ni type mafic end-member magma accompanied with the assimilation of basement plutonic rocks (r=0.03-0.07). In terms of associated silicic magmas, the trace element model calculations indicate that the silicic magmas can be produced through <30% partial melting of corresponding solidified mafic magmas leaving a gabbroic residue.

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Reference


The origin of compositional variation of mafic magma and genesis of associated silicic magma in the Shirataka volcano, NE Japan: Constraints from Sr isotopic compositions of mafic inclusions and their hosts, with detailed petrologic features of the mafic inclusions

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Eruptive products of Shirataka volcano (0.9-0.7 Ma) in NE Japan are calc-alkaline andesite-dacite (57-66% SiO₂), and are divided into six petrologic groups (G1-6). Mafic inclusions, basalt-andesite (48-58% SiO₂), are always observed in G1, G2, G5 and G6. All rocks are mixing rocks formed by mixing/mingling between mafic and silicic end-members judging from many petrologic aspects, such as linear trends defined by hosts and inclusions in variation diagrams and coexistence of mafic and silicic magmas origin phenocrysts in each group. The mixing trends defined by hosts and inclusions are divided into high- and low-Cr Ni types, and both types coexist in G1, G2 and G5. Cr and Ni contents of the high type show some variation. Estimated mafic end-members are high-Cr-Ni (1120-1150°C, 47-52% SiO₂, Fo-rich olv±Mg-rich cpx±An-rich plg) and low-Cr-Ni type magmas (ca.1100°C, 48-52% SiO₂, Mg-rich cpx±An-rich plg), while the silicic end-members of both types have similar petrologic features in the same petrologic group (790-840°C, 63-68% SiO₂, hbl±qtz±Mg-poor px±An-poor plg). The high-Cr-Ni type mafic end-member magma is richer in compatible elements and poorer in incompatible elements than the low type one. Besides, ⁸⁷Sr/⁸⁶Sr data of all rocks show broad ranges (0.70377-0.70537), but the compositional range of each group is restricted. In each petrologic group, the high-Cr-Ni type mafic and associated silicic end-members have lower values in ⁸⁷Sr/⁸⁶Sr ratio than the low type ones, indicating that mafic and silicic end-members in the same type have co-genetic relationships. The MELTS and trace element model calculations suggest that the low-Cr-Ni type mafic end-member magma can be produced through <25% fractional crystallization (olv±cpx±plg) from the high-Cr-Ni type mafic end-member magma accompanied with the assimilation of basement plutonic rocks (r=0.03-0.07). In terms of associated silicic magmas, the trace element model calculations indicate that the silicic magmas can be produced through <30% partial melting of corresponding solidified mafic magmas leaving a gabbroic residue.
Carbonatite-mantle interaction in the formation of highly alkalic oceanic island basalts

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In heterogeneous basalt source regions, variations in mantle composition correspond to variations in melt production, leading more enriched compositions to produce partial melts at depths where more refractory lithologies do not. Migrating melts from easily melted heterogeneities can enrich refractory surroundings, which may subsequently partially melt. Thus, there is a direct link between heterogeneity and metasomatism in basalt source regions. In the source regions of oceanic islands, carbonated lithologies partially melt to form small amounts of carbonatite at >300 km. These highly mobile melts react with mantle rocks at shallower depths to form carbonated silicate liquids. Experiments show that these silicate partial melts are stabilized in peridotite and eclogite ~130 °C and ~250 °C cooler, respectively, than the volatile-absent peridotite solidus (Dasgupta et al., 2006; 2007). Thus, migrating carbonatite produces carbonated silicate liquids when it encounters eclogite bodies at depths of >150 km. Such melts may metasomatize surrounding peridotite, which can produce highly alkalic carbonated magmas when it encounters eclogite bodies at depths of >150 km. Such melts may metasomatize surrounding peridotite, which can produce highly alkalic carbonated magmas at depths of 90-150 km that are compositionally similar to basanites, nephelinites, and melilitites common in many OIB localities. Such magmas are expected where potential temperatures are not much greater than those in the MORB-source mantle (weak plumes, the margins of hotter plumes, or petit spots). Implantation of small-degree partial melts produces peridotite that is enriched in highly incompatible elements and that has isotopic signatures of crustal recycling, characteristics typical of sources of highly alkalic OIB.

References

How nanoscience has changed our understanding of environmental geochemistry

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Naturally occurring nanoscale materials, many containing trace elements, appear to be ubiquitous in the environment, and it can be hypothesized that due to their behaviour which is unlike both molecules and bulk materials, they play roles that have not yet been appreciated, or even realized. More specifically, nanoscale particles, films, and/or confined fluids are present throughout the Critical Zone, and in the atmosphere and oceans. And it has been well established that the structural and electronic properties of these materials change, often dramatically, as a function of their size in the nanorange. As a result, chemical and physical properties of nanomaterials change as a function of size (in the case of particles) or thickness (in the case of films). Yet we do not understand these nanomaterials very well, even from a fundamental physical chemistry point-of-view. Nevertheless, it is straightforward to hypothesize about their importance because it is becoming more common to observe their deviant behavior (relative to the same material at a larger scale) in laboratory and field studies in both biologically and abiotically dominated systems. In addition, because of the minute sizes involved, the interface to bulk ratios are extremely large in these nanoscale components of bulk systems, and therefore interfaces become even more important than usual. Critical insights into local, regional, and even global phenomena await our understanding of processes that are relevant at the smallest scales of Earth science studies. More and more investigators are beginning to uncover a fascinating story of how the immense surface area, unusual properties, and widespread distribution of natural nanomaterials affect Earth phenomena in ways that are surprising.
Chromite-rich cumulates in mafic xenoliths, São Vicente, Cape Verde Islands
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Mafic xenoliths from two basanitic lavas at São Vicente have mineral compositions and textures indicating that they could be early cumulates, fractionated from magmas similar to the host of the xenoliths. In one of these lavas some xenoliths accumulated up to 25% anhedral chromite in poikilitic olivine (mg# 83-86) and ferri-titan-chromdiopside. The shape of the chromite grains as well as their high concentration has not been reported from other xenoliths from the Cape Verde Islands. We have puzzled our brains over their origin.

The chromites have cr# and fe2+/~ 40-60 and are relatively rich in Ti and Fe3+. Such composition is known from chromite in Kimberlites and is thought to be a result of fluid release from the magma during decompression. The anhedral shape could form either

1. By early precipitation and later partly dissolution of chromite in the magma. Complete dissolution of chromite was avoided by the high concentration of chromite buffering the melt, or 2. Matveev and Balhaus report an experiment on an olivine and chromite saturated basaltic melt which holds sufficient H₂O (> 4 % H₂O) to release fluid when decompressed. Chromite then precipitated as pearls inside the fluid bubbles. They rose towards the top of the magma chamber until the bubbles got overloaded with chromite and sunk. This could be the explanation for the shape and concentration of the São Vicente xenoliths although the chromite concentration maybe never passed the critical mass limit but kept flowing. Based on the primitive nature of olivine and clinopyroxene and because the necessary water may have been present we prefer the second solution.

References

Comparison of laser ablation and micromill sampling techniques for MC-ICPMS ²³⁰Th-²³⁴U-²³⁸U measurements on speleothems
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In situ laser ablation (LA) MC-ICPMS can be used to achieve U-series isotope measurements at very high spatial resolution without prior chemical separation procedures. However, matrix effects especially for mass and elemental fractionation pose significant problems for accurate determinations of ²³⁰Th/²³⁴U,²³⁸U ratios.

Procedures for accurate determinations of U-series isotope ratios using in situ laser ablation (LA) and MicroMill techniques for carbonates such as speleothems are presented. For LA analyses we are using a New Wave UP193HE laser and a new multiple ion counting detector system available for the ThermoFinnigan Neptune MC-ICPMS. Multiple ion counting increases the efficiency of low level ion beam collection by allowing simultaneous collection of all ion beams and also circumvents problems associated with unstable, transient beams. We present details of our measurement setup for LA measurements and the correction procedures for instrumental fractionation effects using a matrix matching carbonate standard.

We compare results of LA U-series measurements on a U rich (40 - 90 µg/g) speleothem from Spannagel Cave (Austrian Alps) to results on samples from the same speleothem section prepared using a New Wave MicroMill and processed through separation and purification solution chemistry. For laser ablation results, we currently obtain precisions of ²³⁰Th/²³⁸U in the range of 3 % (2σ), the solution analyses yield more precise ²³⁰Th/²³⁸U isotope ratios in the range of 1 %. Accuracy is assessed by comparison to conventional MC-ICPMS and TIMS measurements.

Key advantages of our LA technique are, for example, a matrix matching calibration standard, high spatial resolution analyses and the possibility of rapid determination of numerous coeval subsamples. We also demonstrate that LA measurements yield accurate but less precise results on speleothem samples with less than 1 µg/g U. The results on MicroMill samples are more precise but this sample preparation technique is time consuming and for a single measurement a bigger sample size is needed. For solution U-series MC-ICPMS measurements a minimum total load of about 5 ng for ²³⁰U and about 10 fg for ²³⁰Th should be used.
Evidence for Hadean mantle depletion in the sources of ~3.75 Ga subduction-related rocks, Isua, SW Greenland

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The Hf isotope compositions of Earth’s oldest zircons provide growing evidence that crust-mantle differentiation started as early as 4.4 Ga. Yet, the size of these differentiated Hadean reservoirs and their persistence over Earth’s history are still under debate. Lu-Hf studies on zircons younger than ~3.8 Ga do not reveal any evidence for the long term presence of ancient depleted mantle reservoirs [e.g. 1].

Rocks from the ~3.71-3.81 Ga Isua supracrustal belt (ISB) comprise the oldest preserved record of mafic crustal material, thus potentially providing evidence for any large scale mantle depletion in the early Archean. Here, we report Hf and Nd isotope data for the least altered samples from a suite of ~3.75 Ga old, submarine boninite-like metabasalts from the central tectonic domain of the eastern ISB [2]. These metabasalts are among Earth’s oldest preserved subduction related rocks [2]. They were metamorphosed under amphibolite to greenschist facies conditions.

Initial εHf values of the boninite-like metabasalts range from -1.3 to +7.9. The samples have 176Lu/177Hf values as high as 0.9, indicating a previous depletion of the mantle source(s) in the garnet stability field. These εHf values are clearly of primary origin, as the initial εHf, εNd and γOs [3] correlate with major and trace elements [2], exhibiting a magmatic differentiation trend. All samples follow AFC curves, suggesting assimilation of up to 30 % enriched crustal material, possibly marine sediments or igneous rocks with TTG-like composition. Two different parental mantle sources can be identified: one has an initial εHf value of ca. +7.9 and the other of ca. +1.3. In order to have an initial εHf of +7.9, a source must have an old and strong depletion in incompatible elements. Hence the presence of a complementary enriched component is required, which may be the earliest continental crust. These results provide the first evidence from mafic Archean rocks for the persistence of Hadean mantle depletion into the early Archean. As other ISB rocks do not display such strongly depleted initial εHf values, the volume of these depleted mantle domains was probably small.

References

Is D" a low-mu reservoir?

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Preservation of a “hidden” reservoir in the lowermost mantle, the D" layer, since the early Earth has recently been proposed to explain unbalanced geochemical signatures of accessible terrestrial reservoirs relative to a chondritic Earth, on the basis of xenon (Tolstikhin and Hofmann, 2005) and 142Nd isotopes (Boyet and Carlson, 2005). How could such a reservoir have formed and subsequently survive for more than 4 Ga? Here we explore the possibility that following large-scale early mantle melting, the partially molten lowermost mantle solidified by downward migration of a dense melt fraction. This is the inferred consequence of the measured crossover of melting temperatures of silicate perovskite and magnesio-wüsitê at about 1200 km depth, and the predicted Fe-rich eutectic and low melting temperatures in the lowermost mantle (Boehler, 2000). This suggests that D" formed during early solidification of the lower mantle and that it survives because of its Fe-rich composition.

The high melting temperatures of Mg and Ca perovskites in the lowermost mantle suggest that both phases remain in the residual solid. Corgne et al. (2005) have measured remarkably high partition coefficients for U and Th in Ca-perovskites. They suggested that this might provide an explanation for the “HIMU” (high mu = high U/Pb) ocean island source reservoir. In contrast, we suggest that the downward solidifying scenario should create a low-mu lowermost mantle region, because Pb is incompatible in the perovskites and is therefore enriched in the liquid, whereas U and Th are enriched in the Ca perovskite of the residual solid. Using the partition coefficients of Corgne et al. (2005) with simple fractional crystallization models yields a low-mu D" layer and a higher-mu overlying mantle. If the time scale of this lower-mantle solidification was on the order of 100 to 500 Ma, this offers a simple solution to the classic “Pb paradox” (estimated bulk silicate lead lying “to the right” of the Pb-Pb geochron) and the well-known two-stage evolution of terrestrial lead. We also explore possible solutions of other geochemical puzzles, such as the high, time-integrated Th/U ratios calculated from early Archean galenas and feldspars, the subchondritic Nb/Ta ratios of accessible terrestrial reservoirs, and the decoupled ε(Hf) and ε(Nd) values of early Archean rocks in terms of this model.

References
Sub-micron-scale variations in Ti abundance in zircon

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The Ti-in-zircon geothermometer [1,2] can constrain growth and/or re-equilibration temperatures of zircons and is particularly useful for constraining Archean and Hadean events where detrital zircon is the only surviving mineral. Zircons are often small (ca. <100 μm in the long dimension) and preserve evidence of fine-scale (sub-micron) compositional zonation. Methods for determining Ti abundances in natural zircons typically analyze domains 10s of microns across, which must average fine-scale compositional variations. Although Ti can correlate with coarse cathodoluminescence (CL) zones (e.g., [3]), it is unknown whether Ti exhibits fine-scale variations and thus may be compromised by coarse-scale measurements.

We report Ti abundances in natural and synthetic zircons down to length scales of ca. 250 nm based on measurements made with the Caltech Microanalysis Center Cameca NanoSIMS 50L. All data reported here were calibrated by comparison with primary and secondary standards previously studied in other laboratories. The external precision of our measurements for 2-μm raster images are typically 2%, relative, at 10 ppm Ti, and degrade with decreasing spot size as expected by counting statistics.

We analyzed detrital zircons from Archean metasediment in the Jack Hills (Australia) and from Proterozoic metapelite in the Adirondacks (New York). Ti concentrations commonly vary by factors of 2-3 over distances of ca. 3 μm, conformable to μm-scale CL zonation and corresponding to nominal temperatures of ~700 to ~750 °C. In some cases, banding extends down to sub-micron scales with gradients at least as sharp as a factor ~3 in concentration over 250 nm. The preservation of such gradients through granulate facies metamorphism attests to slow diffusion of Ti in zircon. Curiously, compositional variations include ca. 1-2 μm bands of very low Ti content (<2 ppm, corresponding to apparent temperatures of <600 °C). Hf concentrations commonly covary with Ti, but the sense of correlation can be either positive or negative; i.e., there is no general correlation among all data. All zircons studied to-date also contain 1-2 μm-wide bands or ca. 1 μm spots having Ti concentrations up to 80 times that of the background, corresponding to nominal temperatures up to 1200 °C. These presumably reflect sampling of micron or sub-micron inclusions of Ti-rich phases.

References

Ferrihydrite in porous media – An inner-sphere complexation and transport approach to describe multiple reactions and predict colloid mobilization

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Prediction of colloid release and transport as affected by reactive species remains a significant challenge for field applications. We report experimental and modeling results of ferrihydrite colloid release under the influence of citrate species. Using CD-MUSIC, a 3-plane surface complexation model (1), equilibrium constants were obtained for the three proposed inner-sphere complexes by fitting citrate adsorption isotherm and pH adsorption envelopes. The constants are used in a reactive transport model (implemented in ORCHESTRA (2)) for simulating reaction fronts of dissolved species during injection of citrate in ferrihydrite-coated quartz columns. Simulation results show that sorption alone may not adequately describe the breakthrough curves. Inclusions of ferrihydrite dissolution and re-adsorption of Fe(III) improve the prediction of dissolved species transport. Additionally, matrix diffusion may be needed for a better prediction. The mechanisms of colloidal iron oxide release change over time. At complete breakthrough of citrate, oxide dissolution and interfacial repulsion control particle release from sediment. However, the peak release of colloids, corresponding to the breakthrough front of citrate, was mainly brought by electric double layer forces. These particles underwent detachment-deposition-detachment cycles along the flow path, and emerged in the effluent with the major reaction front. To quantitatively predict colloid release, a semi-empirical linear correlation is proposed, linking the calculated electric potential to experimental colloid release rates. The model works well for the prediction and scaling of field experiments concerned with organic ligand injection in subsurface environments.

References
Theoretical and experimental arguments for Earth’s heat flux being 31±2 TW

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Global power (heat flux averaged over Earth’s surface) links to radiogenic content, geodynamic state and thermal evolution. Recent computations involve replacing measured flux over substantial parts of the ocean floors with calculations from 1-D cooling models. Cooling models must support through their alleged prediction of seafloor depths. But, a factor of 3 error exists in equations used to predict depth as a function of seafloor age. Specifically, 1-D models presume that temperature varies in the Z-direction only, so contraction is only in Z and is governed by linear thermal expansivity, not volumetric as mistakenly implemented. Values predicted for depth are 1/3 those measured if reasonable physical parameters are used. To reproduce depth data requires using ~3000 K as the basal temperature, which is incompatible with petrology, and provides global power of ~132 TW, not 44 TW. Other problems exist with cooling models and the database. Recent asessment of heat flow data, corrected for duplications and errors in location, limits global power to between 28.6 and 34.1 TW, with uncertainties largely stemming from the need to estimate flux in certain geographic regions. Hydrothermal circulation has been rationalized as causing the discrepancy of model with measurements, but practically speaking, measurements are made mostly in strongly sedimented areas where the confining lid prevents effects of hydrothermal circulation, local or extensive. In hydrothermal systems, temperature gradients in the rocks are reduced below ideal conductive values where the water enters the system in recharge regions far from the ridges and rocks heat from the rocks, not near the ridges where ascending hot water warms rocks and enhances conductive gradients. The rationalization thus implicitly assumes that measurement sites are preferentially located over recharge zones, which is unlikely. Harmonic expansions, up to degree 36, reveal that previous low-degree hybrid spherical harmonic analysis (wherein high fluxes near the ridges from 1-D cooling models are used in place of data) causes heat flux in the mathematical representation to be overestimated, even in continental regions, due to the importance of lowest order spherical harmonic coefficients. Enstatite chondrite models provide ~30 TW, suggesting that additional heat sources, such as K in the core or secular delay, are not necessary to explain Earth’s thermal state.

References

Timescale for metal-silicate separation by metal rainfall in a magma ocean

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The largest sequestering event in Earth’s evolution, which ultimately lead to the differentiation of Earth’s mantle and core, was the separation of metal from silicate in a magma ocean. The only separation mechanism that can explain geochemical observations is metal rainfall. Essential to the metal rainfall mechanism is that metal disperses into small droplets which chemically equilibrate with the surrounding silicate while they sink by means of turbulent density currents. Höink et al. (2006) have studied the metal rainfall mechanism under the assumption of constant silicate viscosity and found that the time scale of metal silicate separation under these conditions are on the order of the Stokes’ settling time, which for centimeter-sized metal droplets in Earth’s magma ocean corresponds to a time scale of weeks.

However, it is well known that magma dynamics are fundamentally influenced by variations in viscosity. A non-constant viscosity, i.e. a temperature dependent viscosity, or even more realistically, a temperature- and pressure dependent viscosity may alter the mechanism of metal rainfall significantly. In the present work we analyse the influence of temperature dependent viscosity and temperature- and pressure dependent viscosity on the rainfall mechanism by employing a numerical convection model combined with a sedimentation method.

We find that the metal-silicate separation time depends on the thermal viscosity contrast and also on the viscosity contrast due to pressure. For values suitable to Earth’s magma ocean, the time scale of metal-silicate separation by metal rainfall increases to the order of tens to hundreds of years. Accordingly, metal rainfall is a very rapid mechanism for metal-silicate separation in a magma ocean. This short timescale has profound implications for the timing of Earth’s evolution.

References
Comparison of the development in melt compositions in the Faroe Islands and East Greenland during continental breakup in the Paleogene

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The upper part of the Faroe plateau lavas erupted during continental rifting and can be correlated with East Greenland counterparts of the Paleogene North Atlantic Igneous Province (Søager & Holm, this conf.). Low-Ti lavas with typically La/Sm = 0.3-0.4 have fractionated Dy/Yb up to 1.25 which require substantial melting with residual garnet and thus a relatively hot source. Compared to late low-Ti lavas, the early tend to have more radiogenic Pb and occur in the northeastern parts. There is also a 7/4 decrease from 0 to -3 with time, while positive 8/4 show a rough increase with time. The low-Ti basalts with the most radiogenic Pb show a marginal overlap with Icelandic rocks. Dy/Yb has a negative correlation with 208Pb/204Pb and on formation level there is an increase in 206Pb/204Pb with time.

While the low-Ti basalts seem to be similar on both sides of the rift, the high-Ti basalts in the Faroes indicate decreasing depth of melting throughout the development, whereas the contemporaneous RFF in East Greenland has melts derived at high pressure. However, as in East Greenland, there is a change with time from IE2 to IE1 (Thirlwall & al., 2004) end-member composition. The increasing fraction of high-Ti basalts to the south could be caused by lateral variation in the mantle plume. Relatively low Dy/Yb indicates lithospheric thinning to have continued at the Faroes in contrast to East Greenland. A MORB-type source dominates the early low-Ti thinning to have continued at the Faroes in contrast to East Greenland.

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Bubble gas-exchange in an artificially aerated lake traced using noble gases

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The concentrations of dissolved atmospheric noble gases in open waters generally correspond to the equilibrium concentrations determined by temperature and salinity during atmospheric gas exchange. As noble gases are chemically inert, only physical processes may change the noble-gas abundance and hence are responsible for deviations from the initial equilibrium. Gas bubbles that are released at the bottom of a lake will affect the concentrations of dissolved gases in the water column, as the bubbles strip gases from the surrounding water and dissolve simultaneously during their ascent. The effect of these secondary gas exchange processes on the concentrations of dissolved gases varies depending on the solubility and diffusivity of the respective gas and on the initial gas concentrations in the bubbles.

We measured dissolved noble gas concentrations in Lake Hallwil (Switzerland), a small eutrophic lake, to trace the effects of gas release from an aeration system. This installation prevents anoxia in the deep water by the injection of oxygen-rich gas bubbles at the bottom of the lake. Noble gases in both the aeration gas and dissolved in the water of the lake were analyzed.

The measurements show that noble gases in the injected gas are strongly fractionated with respect to air. He, Ne and Ar are enriched, whereas Kr and Xe are virtually absent. Noble gases dissolved in the lake water show corresponding deviations from the atmospheric equilibrium concentrations. Deep-water samples taken at three different locations in the lake are supersaturated in He, Ne and Ar. The magnitude of the enrichment decreases with increasing distance from the bubble source. The observed noble gas supersaturations were also found to vary according to the operation mode of the aeration system, with higher gas flow leading to stronger noble gas enrichment. In contrast, only minor changes of the dissolved oxygen concentrations could be detected due to fast oxygen consumption.

In conclusion, the example of Lake Hallwil demonstrates that gas exchange with injected bubbles affects the noble gas abundance in the water body. Noble gas analyses allow quantifying the effectiveness of the aeration system, i.e. noble gas enrichments can be interpreted as a measure for the oxygen transfer to the lake water. Note that these findings may also help to understand natural systems like gas seeps in lakes and oceans.

References

TEM investigations of bacterial effects on biotite dissolution

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Introduction

In natural environments minerals and rocks are not only weathered by chemical and physical processes but also by biological activity. In order to understand the role and interaction between alteration processes, the interface between minerals and bacteria must be investigated at the microscopic to nanometer scale.

Methods and results

In batch culture experiments three different bacteria strains (*Bacillus subtilis* spizizenii, *Shewanella putrefaciens* and *Streptomyces acidiscabies E13*) were grown for 35 days with ground biotite as main nutrient source. The release of major and minor elements (Al, Fe, K, Mg, Mn, Si, Ti) was measured using inductively coupled plasma-optical emission spectrometry (ICP-OES). In comparison with an abiotic control the sample with *Bacillus subtilis* spizizenii showed an increase in the dissolution of Al and Mg. Compared to the control, the dissolution rates of Al and Mg in experiments with *Shewanella putrefaciens* and *Streptomyces acidiscabies E13* are however slightly decreased. These first results demonstrate that bacteria have a diverse control on the dissolution behaviour of biotite.

To understand this diversity in dissolution behaviour of biotite, we have employed transmission electron microscopy (TEM) and energy dispersive X-ray microanalysis (EDX). These techniques were used to detect changes in structure, morphology, and element chemistry of the untreated and biologically treated biotite. Pure visual TEM observations of the bacteria treated specimens provide clear evidence for intense degradation. The small bacteria treated biotite flakes show frayed rims and etch pits on surfaces, whereas untreated biotite from the control experiment displays the normal shape of unaltered starting biotite with unaffected crystal edges and surfaces. Crystal-chemical changes have been detected in experiments with *Bacillus subtilis* spizizenii, which show an K-Na cation exchange in biotite interlayers. The Na is thereby provided by the liquid media. Additionally, we found small crystals of a secondary phase, which is currently under identification.

Conclusion

Bacteria are able to influence the dissolution processes of biotite in various ways. Especially the gram-positive soil bacteria *Bacillus subtilis* spizizenii increases the dissolution of certain elements and triggers the precipitation of a secondary phase.

An evaluation of He, Ne and Ar isotope and element systematics of oceanic mantle sources

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The more radiogenic character of Mid Ocean Ridge Basalts (MORB), i.e. higher air corrected mantle ratios of \( ^{4}\text{He}/^{3}\text{He} \), \( ^{33}\text{Ne}/^{22}\text{Ne} \), \( ^{40}\text{Ar}/^{36}\text{Ar} \) compared to many Ocean Island Basalts (OIB), is commonly attributed to a higher degree of depletion of primordial noble gases within the MORB source. In addition, He/Ne and He/Ar elemental ratios found in MORB glasses are higher relative to OIBs. This had been considered as evidence for solubility controlled elemental fractionation during gas - melt partitioning. However, the generally lower He concentrations in OIBs compared to a presumed degassed MORB source appears in contradiction with this conclusion.

To resolve this issue in terms of a two-stage fractionation and binary mixing model we evaluated literature data from MORB and Loihi-Kilauea glasses and used their He, Ne and Ar isotope and element systematics and concentrations. We can describe mantle \( ^{33}\text{Ne}/^{22}\text{Ne} - ^{4}\text{He}/^{3}\text{He} \) isotope systematics by a simple binary mixing process between a MORB and a ‘plume’ endmember that differ in their \( ^{3}\text{He}/^{22}\text{Ne} \) ratios at time of admixing. The ‘plume’ endmember is a postulated component, basing on the premise that both endmembers shared a common radiogenic evolution history, i.e. the same initial \( ^{3}\text{He}/^{22}\text{Ne} \) ratio, but a different time integrated accumulation of radiogenic isotopes. Within this model a primary fractionation process must have occurred before admixing of both subcomponents. We performed a back calculation of this mixing process and extended this procedure to the Ar system assuming a linear relationship of mantle \( ^{22}\text{Ne}/^{38}\text{Ar} \) and \( ^{40}\text{Ar}/^{36}\text{Ar} \) ratios. With the implicit assumption that the composition of basalt glasses represents the melt phase and that the initial He/Ne, He/Ar compositions of the melt will only evolve towards higher values in course of solubility controlled secondary fractionation during magmatic degassing we derive upper limits for the \( ^{3}\text{He}/^{22}\text{Ne} \), \( ^{3}\text{He}/^{38}\text{Ar} \) and \( ^{4}\text{He}/^{40}\text{Ar} \) ratios of both mixing endmembers. The MORB component appears not or weakly fractionated, in opposite to the ‘plume’ component displaying a significant He deficit. A simple calculation of unfractionated initial ‘plume’ \( ^{3}\text{He}/^{22}\text{Ne} \), \( ^{3}\text{He}/^{38}\text{Ar} \) and \( ^{4}\text{He}/^{40}\text{Ar} \) concentrations and He concentrations are in broad agreement with observed MORB data. A more compatible behaviour of He relative to Ne and Ar during crystal - melt partitioning could explain the data: OIB melt could represent low degree melts from an isotopically different source region that admixes with higher degree MORB melts at shallow depths. Alternatively, a more complex magmatic fractionation scenario is addressed.
The H-, C-, N-, and O-isotopic compositions of cometary matter returned by STARDUST

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Introduction
The STARDUST spacecraft collected about 1 mg of dust during a flyby in January 2004 of comet 81P/Wild 2 in two collection media, low-density silica aerogel and Al foil (Brownlee et al., 2004). The dust collector was successfully returned to Earth in January 2006 and the cometary dust was analyzed by an international Preliminary Examination Team. These analyses showed that comet Wild 2 is an unequilibrated mixture of materials that have both solar and presolar origins (Brownlee et al., 2006). Here, I will briefly review the results obtained for H-, C-, N-, and O-isotopic compositions by the Isotope subteam (McKeegan et al., 2006; Stadermann et al., 2007).

Hydrogen
The H-isotopic composition was measured in five particle fragments. Moderate D enrichments were observed with D/H ratios of up to ~3x the terrestrial value. This is qualitatively consistent with the signature found in IDPs and insoluble organic matter (IOM) from chondrites, although the maximum D enrichments are smaller in the Wild 2 samples.

Carbon and Nitrogen
C- and N-isotopic compositions were measured in several microtome sections, particle fragments, and crater residues in Al foils. No circumstellar C- or N-rich grains were found. Two hotspots enriched in 13C and depleted in 14N were recognized, possibly the signature of labile organic material. 15N enrichments with 15N/14N ratios of up to ~2x the terrestrial value are found in bulk samples and as hotspots as similarly observed for IDPs and IOM from chondrites.

Oxygen
Most studied samples (crater residues, microtome sections) have O-isotopic compositions compatible with those of bulk chondrites. One circumstellar O-rich grain, about 250 nm in size, was found. The 17O/16O ratio of ~2.6x solar and 18O/16O ratio of ~0.9x solar suggest an origin from a RGB/AGB star. A CAI-like particle exhibits enrichments in 16O of ~4% as similarly observed for CAIs from chondrites. The presence of a CAI-like particle among cometary matter is suggestive of large-scale radial mixing in the solar nebula.

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Mineral-melt trace element equilibria in plutonic rocks studied by Laser Ablation ICP-MS

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Magmatic intrusive systems often yield very complex cumulate rocks, consisting of different solid phases and interstitial residual liquid phases. It is an intrinsic difficulty of cumulate rocks to properly interpret whole rock contents of incompatible trace element data, because the amount of trapped interstitial residual liquid might be the controlling factor. Moreover, as early formed cumulates might have been permeated by later-stage evolved liquids, there is no guarantee that whole rock data represent ‘equilibrium’ compositions. In the late stages of differentiation accessory minerals often start to crystallize and have an important impact on the behavior of trace elements during differentiation. This raises an important issue since models of fractionation are usually largely based on whole rock geochemical trends.

Equilibria at the micro-scale can be studied in situ in standard, thick polished mounts with LA-ICP-MS. The most promising minerals for the study of REE melt/mineral distributions are clinopyroxenes and plagioclase. However, accurate results require rather meticulous standardisation. Several standard materials have been tested in the present study: the commonly used NIST612 glass, USGS BCR-2 fused glasses, and a natural, very homogeneous obsidian glass from the Krafla volcanic area, Iceland. The equipment consisted of a Cetac200 266 nm UV-light of a NdYAG laser, coupled to a quadrupole based HP4500 ICP-MS. The Krafla obsidian yielded the best analytical results.

Ongoing studies include the analysis of core samples from the oceanic gabbro section of Hole735B drilled during Ocean Drilling Program Legs 118 and 176, and a section from the Tron pluton from the Caledonide Trondheim Nappe Complex, Norway. The accuracy of the LA-ICP-MS could be checked against analysis of separated pure mineral fractions analyzed by other methods. The micro-analytical data allow to calculate the liquid compositions with which clinopyroxene and plagioclase equilibrated, and to estimate the stage of solidification at which interstitial liquids were expelled. Mass balances further make it possible to estimate the amount of dispersed trapped late stage residual liquids.
Development of in situ U-Pb analysis of uranium oxides using an ion microprobe

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The chronological study of uranium minerals provides practical information on the formation of uranium deposits as well as elemental transportation in association with the alteration of uranium minerals. Moreover, the timing of uranium mineralization from the Archean to the Paleoproterozoic period is a good indicator of atmospheric oxygen evolution, because uranium is only mobilized as a uranyl ion (UO₂⁺) under oxidizing conditions (e.g., Holland, 1984). However there are some issues to estimate the 2⁰⁶Pb/²³⁸U age from SIMS analysis such as large variation of the ionization efficiency of secondary ions and standard material. In this study, we established a method for the in situ U-Pb isotopic analysis of uranium minerals in a similar manner to the conventional zircon analysis.

The Faraday mine uraninite from Bancroft, Canada was used as a standard material for the U-Pb calibration of three uranium minerals from Chardon, Ecarpière (the Armorican Massif, France) and Mistamisk (Labrador, Canada). Quantitative analysis of major elements was carried out by EPMA. In situ U-Pb analyses of uranium minerals were performed by using a SHRIMP at Hiroshima Univ. The calibrated SHRIMP ²⁰⁶Pb/²³⁸U ratios of three uranium minerals from Chardon, Ecarpière and Mistamisk show a good correlation with Pb/U elemental ratios obtained from EPMA, which indicates the reliability of the SHRIMP calibration in this study. The SHRIMP ²⁰⁶Pb/²³⁸U data of Ecarpière (285 Ma) and Mistamisk (1729 and 421 Ma) uraninite are consistent with previous chronological data obtained by TIMS. As shown in Figure, the selected SHRIMP data of the Chardon mine provide a ²⁰⁶Pb/²³⁸U age of 313 Ma, which is older than the previously reported age of 264 Ma. Considering that the analytical spots were selected to avoid impure minerals and altered phases, which were probably formed by later processes, it is interpreted that the Chardon uraninite was crystallized by the remobilization of U during the cooling of the Mortagne granite (310-313 Ma).

References

Calcite-water oxygen isotope fractionation at elevated temperatures: Experimental and theoretical study on the effect of pressure and dissolved NaCl

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We have conducted an experimental and theoretical study for investigating the effect of pressure and dissolved NaCl on oxygen isotope fractionation in the system calcite – water at elevated temperatures. First, our novel corresponding state principles approach for calculating the effect of pressure (density) on the reduced partition function ratio (RPFR) of H₂¹⁸O (Polyakov et al., 2007) shows that the RPFR increases up to 1.0 % by increasing pressure to 1 kb at 273-523°C. The RPFR of CaCO₃ increases only slightly, thus the oxygen isotope fractionation of the system CaCO₃-water decreases up to 1.0 % at 1 kb.

Our calculations of oxygen isotope fractionation factor between CaCO₃ and pure water are significantly (up to 2 %) lower than experimental values between CaCO₃ and calcite-sturated water at 300-750°C at 1 kb (this study) and 15 kb (Hu and Clayton, 2003). The cause of this discrepancy is due most likely to either errors in the calculation of ideal-gas RPFR of H₂¹⁸O (Polyakov et al., 2007), is found to be small (≤0.5 ‰).

It is very likely that pressure and dissolved CaCO₃ decrease and increase the calcite-water oxygen isotope fractionation at low and high pressures, respectively. In contrast, dissolved NaCl appears to have a small effect. However, the available data are still sketchy, and we have just begun to quantify the effects of these important variables for mineral-water isotope fractionation at elevated temperatures.

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References
The late Eocene Chesapeake Bay impact structure – Status of research, insights, and implications

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This is an overview of studies since 2000 by the USGS Chesapeake Bay Impact Crater Project and the ICDP-USGS Chesapeake Bay Impact Structure Deep Drilling Project. The ~35.5 Ma Chesapeake Bay impact structure (CBIS), on the Atlantic margin of Virginia, USA, may be Earth’s best preserved large impact structure formed in a siliciclastic, continental-shelf environment. The 85-km-wide structure formed in a layered target (seawater-sediments-rock), has an inverted-sombrero shape (deep central crater surrounded by a shallower annular trough), and is well preserved beneath postimpact sediments. Saline ground water in the CBIS affects water resources in an area of urban growth.

In 2000-2003, USGS drilled the Watkins School corehole just outside the structure, and the North, Langley, and Bayside coreholes in the annular trough, at 43, 39, 36, and 25 km from the center. These cores revealed (top to base) polymict sedimentary breccia interpreted as ocean-resurge deposits, target sediments modified by liquefaction, injection, and extensional structures, and unshocked Neoproterozoic basement. The sedimentary breccia contains shocked quartz and impact-damaged, mixed-age microfossils. In 2004, USGS drilled and partly cored the Cape Charles test hole on the central uplift, 1 km from the center. It revealed suevite, impact-melt clasts having a meteoritic component, a shock-induced TiO₂ polymorph, and hydrothermal alteration. Gravity, magnetic, seismic, and magnetotelluric surveys delineated the central uplift, moat, and outer margin. Numerical models simulated the inverted sombrero using strength contrasts of weak over strong layers.

In 2005-2006, the ICDP-USGS Eyreville coreholes were drilled to 1.77-km depth in the moat (deepest part) of the central crater, 9 km from the center. They cored (top to base) postimpact sediments, allochthonous sedimentary breccia and sediment megablocks, granite megablock(s), sediment with lithic blocks, suevite and lithic impact breccias, and brecciated schist and pegmatite with breccia veins [1]. Studies by seven science teams will allow unprecedented understanding of a shallow-marine impact and its consequences. Topics include impactor type and relation to other late Eocene impacts (Popigai?), tektite formation, shock-pressure variations with depth and lithology, layered-target influence on cratering, resurge dynamics, unknown target basement, environmental consequences and hazard implications, hydrothermal conditions, source of contained ground-water brines, subsurface microbial diversity, and habitats unique to impact structures.

Reference


Pre-Variscan Barrovian metamorphism in the eastern part of the Slavonian Mountains, Tisia Unit (NE Croatia): Application of quantitative phase diagrams and monazite age dating

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Petrological investigations, quantitative phase diagram modelling and monazite dating were carried out on medium-grade metamorphic rocks from the Kutjevačka Rijeka transect in the Slavonian Mts., Tisia Unit (NE Croatia). Micaschists contain complex zoned garnets with Mn-rich cores and Ca-rich rims. Mn decreases steadily from core to rim, but there is an abrupt increase in Ca between core and rim. This complex zoning was not observed in garnets from intercalated paragneisses and amphibolites. Quantitative phase diagrams and garnet composition isochores using bulk rock compositions revealed that the garnet cores formed at 584-592°C and 6.4-7.8 kbar. For establishing the PT conditions responsible for garnet rim formation the composition of the garnet cores was removed from the bulk data and a new effective bulk composition was established. Using quantitative phase diagrams, mineral isochores and thermobarometric methods we calculated peak PT conditions of ~600-660 °C and 11-12 kbar for the garnet rim and the matrix assemblage of biotite, muscovite, plagioclase and quartz. Staurolite mentioned in the literature was not observed in this study and the application of quantitative phase diagrams contoured for H₂O mode isochors supports our opinion that during the retrograde PT path the rock did not pass staurolite-bearing fields. PT conditions for the intercalated paragneisses and amphibolites are the same as for the micaschists.

The Th, U and Pb contents of yttrium-rich accessory monazites indicate a pre-Variscan (428 ± 25 and 444 ± 19 Ma) age for the medium-grade metamorphism. These data are 70-100 Ma older than previously published mica Ar-Ar and K-Ar ages from the study area.

This study was financially supported by the Hungarian National Science Fund (OTKA, grant number F047322 to PH) and by the Croatian Ministry of Science, Education and Sports, Projects 119-1191155-1156 (DB) and 195-1951293-3155 (BT).
Environmentally hazardous trace elements of Eocene coal deposits in the north Anatolia, Turkey

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Amasya, Bolu and Kastamonu in Northern Anatolian Region in Turkey host high-calorie lignite coals of Eocene age with reserve more than 1 million tones. In this study, distribution of environmental elements in coals, enrichment factors of these elements and total organic material-element relations were investigated.

The lignite coals in Amasya are found in 4 different fields within the Eocene clastic deposits. In these fields, concentrations of Cu, Zn and Se are generally higher than that of the Turkish coals. Considering the enrichment factor calculations with respect to world coals, Mo, Pb, Cd and Sb are depleted while Cu, Ni, Co, Mn, V, Cr, Hg, Se, Th and As elements are enriched.

Mo, V, B, Se and S% values of the Bolu field coals are higher than the average value of Turkey. Enrichment factor calculations on these coals reveal that Pb, Cd, Sb and Th are depleted and Se, Cr, Co, Zn and Cu are enriched while Mo, Ni, Mn, As, V, B, Hg, U and S are considerably enriched.

Lignites in Kastamonu are found within the Eocene marl-limestone sequence. It was determined that Cu, Pb, Zn, Ni, Co and S concentrations of this field are higher than the average value of Turkish coals. Enrichment factor calculations on the Kastamonu coals reveal that Cd, Sb and Se are depleted and Mo, Cu, Pb, Zn, Co, Mn, As, V, B, U, Th and S are enriched while Ni, Cr, and Hg are considerably enriched.

Using the environmentally sensitive elements and total organic matter values of coals from all the fields, statistical evaluation was made.

In the Amasya-Kastamonu coals, Cr-V and As-S element pairs show positive correlations while B-TOC, Th-TOC, Cu-TOC and B-Cu element pairs display negative correlations.

Except for S-Cu element correlation resembling to the Amasya field, the Bolu field does not display any similarity to any of the fields.

Zeolite-calcite-silica formation in basalt during orogenic collapse, Washington Cascades

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Regional extension and collapse of the 96 to 45 Ma Cascade orogen during the Eocene is recorded by rapid basin subsidence, mafic to intermediate dike swarms, and exhumation of a partially migmatized gneiss complex (Miller et al., 2007). Shallow hydrothermal systems developed as a response to high regional geothermal gradients (35–40 °C km⁻¹) and local intrusions. The fossil hydrothermal system in the vicinity of the largest dike swarm (Teanaway dikes) is recorded by calcite-gold veins in sandstone-shale and by zeolite-calcite-silica ± Fe-oxo/hydroxide assemblages in distal and stratigraphically higher basalt lavas and pyroclastics. Silica in distal assemblages occurs as α-quartz, chaledony, and moganite forming agate. Zeolite phases are heulandite and stilbite.

Oxygen-isotope (δ¹⁸Oₛ=$((O_{SiO})/_{(SiO)}) values for silica phases range about 10–16 ‰ and 10–15 ‰ for calcite. Values of δ¹³C它可以 for calcite range –9 to –11 ‰. Calculated temperatures of formation based on calcite-quartz pairs, calcite-water, and quartz-water thermometry indicate precipitation at 50–60 °C in a meteoric water dominated system. Field-constrained 2D thermal models indicate that these temperatures are likely to have existed for about 10⁴ years at subsurface depths of 50–100 m.

Compositional modeling using PTAX and the Geochemists Workbench indicate that zeolite-calcite-silica formation occurred at log[aCa²⁺/a²H⁺] ≈ 12–13 and low log[aAl³⁺/a²H⁺] values that evolved up to 3–4 with time. Low Na activity in the fluid meant that mordenite or phillipsite were not stable zeolite phases in the CNKASH system. Based on phase relations in the albite-anorthite-quartz-H₂O system (Liou et al., 1991), heulandite + stilbite may coexist at 50–100 m depth at temperatures less than about 105 °C which is consistent with isotopic thermometry and inferences based on field observations.

Analytical and modeling results indicate that heated meteoric fluids reacted with basalt to produce an assemblage that at first was in equilibrium with basaltic glass, but later became more Al-rich indicating equilibrium with glass + plagioclase. It appears that as for the zeolite-calcite-silica occurrences of Iceland (Neuhoff et al., 1999), porosity is an important factor in determining which zeolite precipitates during low-grade alteration-metamorphism of basalt.

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Chemical weathering, erosion, and CO\textsubscript{2} consumption in the southern Tibetan Plateau and Eastern Syntaxis of the Himalaya

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The Yarlung Tsangpo-Brahmaputra River drains a large portion of the Himalaya and southern Tibetan plateau, including the eastern Himalayan syntaxis, one of the most tectonically active regions on the globe. We measured the solute chemistry of 161 streams and major tributaries of the Tsangpo-Brahmaputra to examine the effect of tectonic, climatic, and geologic factors on chemical weathering rates. Specifically, we quantify chemical weathering fluxes and CO\textsubscript{2} consumption by silicate weathering in southern Tibet and the eastern syntaxis of the Himalaya, examine the major chemical weathering reactions in the tributaries of the Tsangpo-Brahmaputra, and determine the total weathering flux from carbonate and silicate weathering processes in this region. We show that high precipitation, rapid tectonic uplift, steep channel slopes, and high stream power generates high rates of chemical weathering in the eastern syntaxis. The total dissolved solids (TDS) flux from the this area is greater than 520 t km\textsuperscript{-2} yr\textsuperscript{-1} and the silicate cation flux more than 34 tons km\textsuperscript{-2} yr\textsuperscript{-1}. In total, chemical weathering in this area consumes 15.2 x 10\textsuperscript{5} mol CO\textsubscript{2} km\textsuperscript{-2} yr\textsuperscript{-1}, which is twice the Brahmaputra average. These data show that 15-20% of the total CO\textsubscript{2} consumption by silicate weathering in the Brahmaputra catchment is derived from only 4% of the total land area of the basin. Hot springs and evaporite weathering provide significant contributions to dissolved Na\textsuperscript{+} and Cl\textsuperscript{-} fluxes throughout southern Tibet, comprising more than 50% of all Na\textsuperscript{+} in some stream systems. Carbonate weathering generates 80 to 90% of all dissolved Ca\textsuperscript{2+} and Mg\textsuperscript{2+} cations in much of the Yarlung Tsangpo catchment.

Precipitation and aggregation of ZnS nanoparticles in the presence of low-molecular weight organic acids

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Introduction

ZnS and other metal-sulfide nanoparticles are known to exist as intermediates during precipitation and dissolution of their respective bulk mineral phases [1, 2]. However, the mechanisms that enable these nanoparticles to persist in surface waters and sediment porewaters are unknown. Humic substances and other hydrophilic organics can stabilize metal-oxide colloids in solution by adsorbing to particle surfaces and preventing aggregation [3]. This study seeks to identify whether similar processes occur for nanocolloidal ZnS.

Experimental Methods

The stability of aqueous ZnS nanoparticles was investigated by assessing the role of low-molecular weight organic ligands (oxalate, serine, cysteine, thioglycolate, and glycolate) during precipitation of ZnS. Zn(NO\textsubscript{3})\textsubscript{2} and Na\textsubscript{2}S were dissolved (2 μM each) in laboratory aqueous solutions buffered at pH 7.5 and containing one of the organic ligands. Particle formation and size was monitored over time by dynamic light scattering. Zn speciation was measured in filtered (<0.2 μm) ZnS solutions by anodic stripping voltammetry to confirm that Zn was coordinated to sulfide during the aggregation experiments and not in the form of dissolved Zn-organic complexes.

Results and Discussion

Observed growth rates of ZnS aggregates varied by orders of magnitude, depending on the type and concentration of organic ligand in solution. Growth rates were slowest in the presence of thiol-containing ligands: cysteine and mercaptoacetate. In contrast, ZnS aggregation rates were generally not affected by oxalate, serine and glycolate. These compounds contain hydroxyl, carboxylate, and/or amine functional groups. Thermodynamic stability constants for the Zn-thiol complexes are greater that those for the other Zn-organic complexes. Thus, slow aggregation of ZnS nanoparticles may be caused by specific attachment of the thiol on surface Zn sites. These results demonstrate a possible mechanism that stabilizes nanocolloidal metal-sulfides in the aquatic environment.

References

Distribution of Cesium sorption on micas and application on nuclear waste disposal

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Introduction Cs is an important radionuclide in nuclear waste. It not only 135Cs is extremely long-lived (t1/2=2.0×106) and 137Cs is a major radioactive contaminant in high-level nuclear waste (HLW), but also exhibits almost unlimited solubility, so it is very necessary to find highly insoluble phases able to fix radionuclide Cs and to have a long-term stability in geological repositories.

Natural micas are important constituents of geological formations and they also contain elevated contents of Cs, therefore we tried to make cesium sorption experiments on micas and to evaluate the ability of micas to incorporate and retard radionuclide cesium.

Experiments Four different micas, such as muscovite, lepidolite, biotite and phlogopite were hand-picked from the pegmatite and granite samples. Micas that had not been exposed to CsCl solution were analyzed by EMPA, average Cs content of muscovite and lepidolite are very lower and respectively are 0.02wt% and 0.09wt%, Cs content of biotite and phlogopite all below detectable limit.

All minerals were processed by ultrasonically washing in deionized water before absorption experiments. Cesium-absorption experiments were performed by 0.1g samples of the reaction vessels with 20ml 0.1M CsCl solution for 7 days, 14day and 21days. No additional buffer was used. Treated slab samples was simply removed from the reaction vessels, then ultrasonically washing in deionized water and allow to air dry. Treated slabs were observed and analyzed by the EMPA method.

Conclusions 1) Cs content of all treated micas became higher than untreated samples, even in the treated biotite for 21days, Cs content up to 2.05wt%. These show that the four micas are able to fix radionuclide Cs in their interlayer structure and may be the possible stable waste disposal phases in the near field of geological barrier; 2) The distribution of Cs in micas was variable, Cs was preferentially sorbed where individual sheet boundaries were crude steps and abundant on these areas; 3) The ability of bonding of cesium is different. Ferriferous micas, such as biotite and phlogopite, are likely to be higher than muscovite and lepidolite. It indicates that biotite and phlogopite are good candidates for the storage of Cs.

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Biogeochemical investigations of the Zunyi sedimentary Ni-Mo-PGE ores in the Lower Cambrian black shale formation, South China

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The metalliferous black shales and their Ni-Mo-PGE ores can be traced across a broad region of South China, mainly south of the Yangtze River, extending a 1600 km belt of main provinces. The Lower Cambrian black shales that host the ores are approximately 60 to 150 m thick and include the Niutitang Formation of Guizhou and Hunan and stratigraphic equivalents elsewhere. The Ni-Mo ore bed itself varies in thickness from a featheredge to ~30 cm and consists largely of pyrite, apatite, vaesite, gersdorffite (NiAsS), and an amorphous Mo-S-C mixed-layer phase. Lots of organic matter, including algae and bacteria are abundant and constitute up to 10% of the ores, which may have played an important role in their formation.

Combined organic petrography, elemental and stable isotope (S) analyses of samples from the Lower Cambrian shale Ni-Mo-PGE ores of Zunyi provide insight into the relationship of organic matter-ores, biogeochemical alteration of hydrocarbons, microbial sulfate reduction, and mineral deposition. In the absence of vitrinite, relative thermal maturity were determined from the reflectance of bitumen, and marine kerogen like algal remains, Ro basically in range from 2.0 to 4.1%. Elemental analyses suggest that organic matter has been oxidized throughout the study area. The sulfur isotopic composition of the metal sulfides correlates with the degree of biodegradation of hydrocarbons, with the base-metal content and with the proportion of aromatics in the organic extracts. Sulfur isotopes study shows that micro-organism took active part in the re-enriching processes of metal sulfide, barite and witherite during digenesis. Variation of conventionally determined δ34S values are great, ranging from +25‰ to -12‰ for samples from the study area in Zunyi. Individual nodules also show large variations in the drilled sulfide data of up to 15.7‰ between rims and cores of sulfide ore nodules. The high variation in isotopic fractionation of the ores may reflect the varying proportions of different sulfide minerals. On the other hand, Extreme variation of δ34S values during the formation of the Ni-Mo sulfide ores could have been caused by the effects of both biogeochemical and hydrothermal activity during the formation of these unusual ores.

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Geological and geochemical constraints on the origin of the giant Lincang coal seam-hosted germanium deposit, Yunnan, SW China

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The Lincang germanium deposit in Yunnan, SW China, contains at least 1000 tones of Ge at an average grade of ~850 ppm Ge, being one of the largest germanium deposits in the world. The deposit is hosted in coal seams of the Miocene Bangmai Formation deposited on a Ge-rich granitic batholith. The Bangmai Formation is divided into eight units among which three units are coal-bearing. The Ge-bearing coal seams are inter-layered with siliceous rocks and siliceous limestones in the basal coal-bearing unit. The coal seams of the other two coal-bearing units are not inter-bedded with siliceous rocks and siliceous limestones, and are barren. Equant or elongated germanium ore-bodies are mainly distributed at fault intersections, and are located at the top and bottom of coal seams where they mainly contact with the layered siliceous rocks or siliceous limestones. Ge is mainly associated with organic matters of coal seams. The major and trace elements, O- and C-isotopes of the siliceous rocks and siliceous limestones, the major and trace elements, and O- and C-isotopes of the siliceous rocks and siliceous limestones are similar to those of hydrothermal sediments, indicating formation by hydrothermal sedimentation. Compared with barren coals, Ge-rich coals are notably rich in Nb, Li, Sh, W, Bi and U and show substantial enrichment of HREE which increase with Ge. Ge-rich coals have the vitrinite reflectance generally higher than barren coals. They contain disseminated pyrites with δ34S from 17.2‰ to 51.4‰, similar to the pyrites in barren coals, and thin vein-like pyrites with δ34S from 1.9‰ to -5.4‰, similar to the sulfides in granite-related quartz veins. We propose that circulating hydrothermal fluids leached abundant Ge and other elements from Ge-rich granite in the basement, and then discharged into the basin mainly along fault intersections to form layer-like siliceous rocks and siliceous limestones by depositing Si and Ca, and to form germanium deposit through interaction between germanium in the fluids and organic matters in coal seams.

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Oxygen and carbon isotope composition and implication of Early Palaeozoic dolomites in Keping, Tarim Basin

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In order to approach to the formation environment and fluid condition, carbon and oxygen isotopes are analyzed of Early Palaeozoic dolomite sequences in Keping, northwest of Tarim Basin, for the dolomite sequences are important reservoir rocks in the basin.

104 field dolomite samples were collected from the outcrop of Early Palaeozoic in Keping. This outcrop is consisted of algal dolomite, bedding dolomite, calcareous dolomite, and some limestone. Evaporates and many siliceous aggregates were found in the middle Cambrian, which might be related to special environments. In order to figure out variations of the isotopes in the samples with different composition and texture, micro-area sampling was conducted by Hand Grinder with 1mm in diameter. The analysis was performed on CF-IRMS in Nanjing University.

The isotopic result is mainly consistent with ancient seawaters of that age. The δ13C of the samples ranges from -1.6‰ to 1.6‰, with an average of 0.515‰, and the δ18O from -12.7‰ to -5.7‰, with an average of -7.23‰. The δ18O varies larger in different samples than the δ13C, and the δ18O become depleted with increasing ages. The δ13C and δ18O have relatively lower values in middle Cambrian dolomites. But they rise to -1‰ and -7‰, respectively, and become relatively stable in upper Cambrian and Ordovician dolomites. In addition, the obvious variation of the isotopes can be found between different algal dolomite layers in middle Cambrian, but such a variation becomes small in the younger algal dolomites in upper Cambrian and Ordovician.

The depleted δ18O in middle Cambrian, most less than -10‰, is likely related to hydrothermal activity. On the other hand, evaporation process during middle Cambrian could make the δ13C and δ18O of the seawaters enriched, and the δ13C and δ18O rise in the related dolomites. Because the above two aspects had different constraints on the variation of the isotopes in the seawater, the δ13C and δ18O of middle Cambrian dolomites go up and down frequently. There was no effect of hydrothermal fluids and evaporation process in upper Cambrian and early Ordovician, and little variation of the δ13C and δ18O can be seen of the younger dolomites, just showing δ13C of about -1% and δ18O of about -7‰ consistent with the seawaters at that ages.

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Effect of geologic and biologic cycling on Se variability in a soil ecosystem with high level of nonagenarians

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Introduction
The spatial variability of Se in soils is affected by geologic and biologic cycling and has the potential to induce human health problems through food chains. The objectives of this study were to determine the effect of sedimentation and pedogenesis on the spatial variability of Se in an agriculturally soil ecosystem with high level of centenarians in Rugao County, Jiangsu province, China and discuss the Se bioavailability to rice and human longevity.

Materials and Methods
342 surface soil samples and 9 of soil profiles in the studied area with 1,450 km² of land area and 1.54 million populations were taken. Total and water soluble Se (H₂O-Se) in profile soil samples were determined using atomic fluorescence spectrometer (AFS). 97 of rice grain and drinking water samples were taken for Se determination using AFS. The ratio of population of nonagenarians over total population (90-rate) was calculated using the data of the national census in 2002.

Results and Discussion
The results showed that the total Se concentrations (0.127±0.021 mg kg⁻¹, n=203) had a narrow variation in topsoils derived from paleo-alluvium, lacustrine deposits or neo- alluvium, while H₂O-Se (2.42±1.09 µg kg⁻¹, n=342) had a wide variation among the soils derived from different parent materials. The concentrations of H₂O-Se in the soil series on lacustrine deposit with fine texture and long-term development were greater than those on paleo-alluvium with long-term development but coarse texture or neo-alluvium fine texture but short-term development. Increased H₂O-Se in the topsoil of soils was, in part, related to the changes of soil properties due to weathering, pedogenic processes, and human activities. Correlation analysis between Se in the soils and rice Se or 90-rate in the study area showed that H₂O-Se in topsoil had a significant relationship with rice Se or the 90-rate at village level (p<0.01), but total Se had no any relationship between them (p>0.05). Similar variation of Se in drinking water to H₂O-Se in soils was found as well.

Conclusions
In conclusion, the geologic and biologic cycling in the studied area didn’t cause the significant variation of total Se in soils, but significantly affected the variation of H₂O-Se in soils, and further Se uptake by crops, Se in ground water, and human health. It suggested that H₂O-Se in soils of the agricultural ecosystem might be one of the most important geochemical factors affecting human health or longevity.

Mg and Fe isotopes as tracers of temperature gradient driven diffusive differentiation

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The development of high precision MC-ICP-MS has led to breakthrough observations which have fundamentally called into question our current understanding of melt-mineral equilibrium and chemical differentiation processes. Although the mafic terrestrial igneous earth appears to have a near constant Fe isotopic composition with δ⁵⁶FeIRMM of ~ 0.07‰, a majority of granites and rhyolites with SiO₂ content > 71 wt.% have a significantly heavier Fe isotope signature than the mean mafic earth with δ⁵⁶FeIRMM up to 0.4% (e.g. [1]). This has generated vigorous debate [2], since the origin of Fe isotope variation with differentiation remains unclear.

A thermal migration experiment using wet andesite (AGV-1) along a temperature gradient from 950°C to 350°C over 2 cm in a 3/4” piston cylinder apparatus for 66 days at 0.5 GPa produces silicic solid, melt + solid, and more mafic melt from the cold bottom to the upper top of the charge, respectively. Major-trace elements and mineralogy vary with temperature due to temperature gradient driven chemical differentiation (thermal migration). Most importantly, Fe-Mg isotopes of the experiment vary consistently as a function of position. The bottom solid portion does not deviate significantly from the starting material, AGV-1. However, the heavy isotopes of Mg and Fe are depleted in melt at the hot end and enriched in the middle melt + solid portion. δ⁵⁶FeIRMM and δ⁵⁶MgIRMM vary by 2.8‰ and 9.9‰, respectively. These total variations in Fe-Mg isotopes are much greater than those observed in the terrestrial igneous Earth. These variations are not caused by kinetic diffusion or equilibrium isotope fractionations. Instead, they appear to result from Soret diffusion, in which light isotopes are known to be enriched in the melt + solid portion. These total variations in Fe-Mg isotopes are much greater than those observed in the terrestrial igneous Earth. These variations are not caused by kinetic diffusion or equilibrium isotope fractionations. Instead, they appear to result from Soret diffusion, in which light isotopes are known to be enriched in the melt + solid portion. These total variations in Fe-Mg isotopes are much greater than those observed in the terrestrial igneous Earth. These variations are not caused by kinetic diffusion or equilibrium isotope fractionations. Instead, they appear to result from Soret diffusion, in which light isotopes are known to be enriched in the melt + solid portion. 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References
C and S isotope records in Doushantuo Formation: Implication for Redox Fluctuation of the Ediacaran Ocean

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Carbon and sulfur isotope evidence from Oman and iron speciation data from Newfoundland suggested a stepwise oxidation of the Ediacaran ocean from ca. 635 Ma to ca. 542 Ma (Fike et al., 2006; Canfield et al., 2007). New isotope data obtained from the Ediacaran Doushantuo Formation, however, reveal alternative oxidation events from ca. 653 Ma to ca. 551 Ma that suggest stepwise oxidation of the Ediacaran ocean, with significant ocean anoxia following each oxidation event. No Δδ34S values exceed 46‰ in the Doushantuo Formation, indicating the absence of sulfur disproportionation before 551 Ma and a complete oxidation of deep oceans did not occur until the latest Ediacaran or early Cambrian. Our data of δ13Corg, δ13Ccarb, δ34SCAS, and δ13S provide an alternative environmental interpretation for the evolution of early animal life and subsequent Cambrian explosion.

Increases of δ13Ccarb and Δδ34S, with occurrence and diversification of Doushantuo-Pertatataka acritarchs (DPA), in the lower and middle Doushantuo Formation after the Nantuo (or Marinoan) glaciation indicate the first oxidation event to cause oxic water column in the shelf. Constant δ13Ccarb values (down to –29‰) with variable δ13Corg (–6.93‰ ~ +6.17‰) are consistent with the existence of DOM (dissolved organic matter) rich deep-ocean. Following negative shifts in δ13Ccarb (down to –9.62‰) and δ34SCAS (down to +9.5‰), a temporary anoxia occurred between the middle and upper Doushantuo Formation that is concordant with DPA’s extinction. Another oxidation in the upper Doushantuo Formation, where multicellular, macroscopic algae (the Miaohu biota) were found. The prominent negative δ13Ccarb (down to –8.98‰) excursions and associated decline of δ34SCAS (from +43.5‰ to +10.2‰) imply both oxidations of DOM and sulfide from anoxic water column of deep-ocean. Unusually low δ13Corg values (down to –38‰) and increasing δ13Ccarb (from –8.16‰ to –2.00‰) in the uppermost Doushantuo Formation (ca. 551 Ma) suggest involvement of anaerobic methane oxidation, possibly associated with the upwelling of anoxic deep-ocean seawater. Eventually, another anoxia possibly occurred at the near Dengying-Doushantuo boundary.

References


Geochemical structure of the Hawaiian plume: Inferences from Mahukona volcano

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Young, <2Ma, Hawaiian volcanoes define two parallel spatial trends, Loa and Kea. Most Loa- and Kea-trend shield lavas are geochemically distinct in major and trace element compositions and radiogenic isotopic ratios. Lasiter et al. (1996), among others, proposed a radially concentrically zoned plume with Loa shields forming closer to the plume center than Kea shields. Abouchami et al. (2005) proposed that Pb isotopic ratios are the best Loa-Kea discriminant, e.g., Pb/206Pb* > 0.95 for Loa lavas; they proposed a bilaterally asymmetrically zoned plume with geochemical differences between the northeast and southwest halves of the plume. These models are oversimplified because they do not consider local (Ren et al., 2005) or vertical heterogeneities (Blichert-Toft et al., 2003) in the plume; nevertheless the alternative large-scale zonation models can be evaluated with geochemical data for shields formed at varying distances from the plume center; e.g., Bryce et al. (2005) suggested that when active the submarine Mahukona volcano was southwest of the current location of Mauna Loa, a Loa-trend volcano; hence Mahukona lavas should be Kea-like in the concentrically zoned model and Loa-like in the bilaterally zoned model.

We report major and trace element compositions, Pb and Hf isotopic ratios for 18 Mahukona lavas; these include three transitional to slightly alkaline basalts from the large 125–350 m cones that may represent preshield lavas based on their 3He/4He ratios of ~20 R/Ra (Garcia et al., 1990). Consistent with this inference, the cone samples overlap with the distinctive Pb isotopic field defined by preshield lavas from Loihi seamount. All other Mahukona lavas are tholeiitic basalt that define three groups based on CaO content at a given MgO content. The high CaO group, >12%, has unusually low 206Pb/204Pb (<18.0) and may be derived from a peridotite source (Herzberg, 2006). All other tholeiitic lavas straddle the Loa-Kea boundary in Pb isotopic space with 206Pb/204Pb* between 0.940 and 0.951 compared to the range of 0.947 to 0.956 for Mauna Loa lavas. In a 176Hf/177Hf vs 206Pb/204Pb* plot (Huang et al., 2005), the inverse trend of Mahukona lavas also straddles the Loa-Kea boundary. Their Zr/Nb ratios (12.1-14.8), another Loa-Kea discriminant, are also at the Loa-Kea boundary. Clearly, Mahukona tholeiitic basalt has a weaker Loa geochemical signature than Mauna Loa lavas. This result may require modification of the simple large-scale zonation models.
Inter-diffusion of Mg/Ca in synthetic polycrystalline carbonates at elevated temperature and pressure

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The transport rates of MgCO$_3$ from dolomite into calcite were measured within synthetic dry dolomite-calcite polycrystalline aggregate at 1.6 GPa and isothermally at 800, 850, and 900 °C over different run durations. Aragonite in the starting dolomite-aragonite aggregate was first transformed rapidly to calcite, which, then, reacted with dolomite to form Mg-calcite progressively rich in Mg at slower rates.

The average contents of Mg in calcites determined by XRD increase with run time, which can be described empirically by the first-order rate law. The temperature dependence of the overall transport rate of MgCO$_3$ from dolomite into calcite can be estimated by the kinetic parameters ($E = 231$ kJ and $A_0 = 22.7$ hr$^{-1}$). The extrapolation using the Arrhenius equation to the prograde metamorphic conditions reveals that the formation of Mg-calcite saturated with Mg from dolomite-calcite aggregate in the absence of metamorphic fluid may not completed at temperatures below 600 °C over different run durations. Aragonite in the starting dolomite-aragonite aggregate was first transformed rapidly to calcite, which, then, reacted with dolomite to form Mg-calcite progressively rich in Mg at slower rates.

The extrapolation of the rate to the conditions during exhumation of UHPM rocks, at which the P-T path entered calcite stability field from dolomite-aragonite field, indicates that the reaction of dolomite with calcite can be completed in a geologically short period (< 1 my).

The SEM-EDS analysis of individual calcite grains shows that the Mg contents in calcite grains progressively decrease with increasing the distance from dolomite-calcite grain boundary, suggesting a diffusion control of the reaction. The Mg/Ca inter-diffusion coefficient at 850 °C calculated using the diffusion equation is around 3 x 10$^{-16}$ m$^2$/sec. The calculated closure temperatures for Mg/Ca inter-diffusion as a function of cooling rate and grain size in calcite reveal that the Ca/Mg resetting in calcite in dry polycrystalline carbonate aggregate may not occur at temperatures below 600 °C at geological cooling rate (> 100 °C/my), unless other processes were involved.

Reference

Pressure dependence of viscosity of hydrous rhyolitic melts

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Knowledge of viscosity of silicate melts is critical to the understanding of igneous processes. Numerous viscosity measurements have been carried out on the natural and synthetic silicate melts under ambient pressure, but only a few investigations have examined the pressure dependence of viscosity of silicate melts. “Hydrous species reaction viscometer” (Zhang et al., 2003) based on the concentrations of two hydrous species in the melts after a known cooling history is applied to investigate pressure dependence of viscosity of hydrous rhyolitic melts at near glass-transition temperatures.

The samples used here are natural obsidian glass with about 0.85 wt% water and hydrated natural obsidian glasses with higher water contents (2 wt% and 4 wt%). The experiments were conducted in piston cylinder apparatus at 1, 2 and 3 GPa. A prerequisite for viscosity inference with this “viscometer” is to know the temperature dependence of the equilibrium constant $K$ of the interconversion reaction at a given pressure. Hence, pressure dependence of the speciation of dissolved water in these samples was investigated. Comparing with speciation model at ambient pressure (Ihinger et al., 1999), equilibrium constant changes with pressure nonlinearly, decreasing from 0.1 MPa to 1 GPa and then increasing from 1 GPa to 3 GPa.

Cooling rates varied from ~ 100 K/s to 0.1 K/s in the cooling-rate experiments. Viscosity (in Pa·s) at the apparent equilibrium temperature of the hydrous species reaction (i.e., glass transition temperature) is obtained as 10$^{11.45/q}$ where $q$ is cooling rate in K/s. So the total range of viscosity inferred from this method in this study is 3 orders of magnitude. Preliminary results show that viscosity of hydrous rhyolitic melts increases by about 1.4 log unit from 0.1 MPa to 3 GPa. The behavior of viscosity as a function of pressure for hydrous rhyolitic melts with water content of 0.8 wt% or more at low temperature range is similar to that of depolymerized melts.

References
Nucleation, growth, and phase transformation of titanium oxides in hydrothermal solution

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Fine grained titanium oxide minerals are environmentally important in soils, where they take part in a variety of geochemical processes. They are also industrially important as catalysts, pigments, food additives, and dielectrics. Recent research efforts have focused on an apparent reversal of thermodynamic stability between TiO2 phases at the nanoscale that may be caused by the increased contribution of a surface energy term to the total free energy. We have performed time-resolved X-ray diffraction experiments at the National Synchrotron Light Source (NSLS) at Brookhaven National Labs (BNL) in which titanium oxides crystallize from aqueous TiCl4 solutions between 100 and 200 °C, as diffraction patterns were collected at intervals of ~ 4 minutes. These experiments confirm that anatase is the first phase to nucleate from solution within the first ~ 20 minutes of heating, and then slowly begins converting to rutile. Whole pattern refinement of diffraction data reveals that lattice constants systematically change during particle growth for both phases throughout the crystallization process. The unit cell dimensions eventually converge to values close to those of the bulk phases.

Using the Vienna Ab-initio Package Simulation (VASP) with soft pseudopotentials, we modeled the energetics of bulk anatase and rutile using our refined structures of the evolving nanoparticles. The density functional theory (DFT) calculations indicate that the change in free energy between the incipient nanoparticles and bulk crystals was on the order of 0.5 kJ/mol for each phase, as compared to the 9 kJ/mol difference in free energy of formation between the two phases. To the extent that the structures of the nanoparticles that first nucleate in our experiments reflect the surface structures of bulk anatase and rutile, our results indicate that the energetics of the bare surface do not dictate the relative stabilities of nanoparticulate anatase and rutile.

Predicting Raman spectra of aqueous silica and alumina species in solution from first principles

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Dissolved silica and alumina play an important role in lithospheric fluid chemistry. Silica concentrations in aqueous fluids vary over the range of crustal temperatures and pressures enough to allow for significant mass transport of silica via fluid-rock interaction. The polymerization of silica and alumina could afford crystal-like or melt-like sites to otherwise insoluble elements such as titanium, leading to enhanced mobility. Raman spectroscopy in a hydrothermal diamond anvil cell has been used to study silica polymerization at elevated pressure and temperature [1, 2], but Raman spectra of expected solutes are not fully understood. We calculated Raman spectra of H4SiO4 monomers, H6Si2O7 dimers, and H6SiAlO7 dimers, from first principles using hybrid density functional theory (B3LYP). These spectra take the variation in Si-O-X bridging angle that the dimers will have at a given temperature into account, thereby broadening the main dimer peak. Solution effects are incorporated in two separate ways - by using a polarizable continuum model and adding explicit water molecules. Both methods are in excellent agreement with each other. However, the results are in contradiction with earlier results based on gas phase models, in which the bridging angle variation broadens the 630 cm⁻¹ silica dimer peak enough to explain the broad peak observed at high temperatures. In the solution phase, whether by a polarizable continuum model or adding explicit water molecules, the peak is not broadened enough to explain experimental results. The observed broadness, therefore, is most likely caused by additional, higher order polymers that have peaks within the broad observed peak. Ring polymers in particular may provide much of the observed broadness. The synthetic spectrum of the silica-alumina dimer suggests that there may be a higher ratio of complexed alumina to free alumina in solution at highly basic pH than previously estimated [3].

References
Paleoaltimetry from “clumped” $^{13}$C-$^{18}$O bonds in carbonates, Colorado Plateau

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The elevation history of Earth’s surface is a key element linking tectonic, geodynamic, climatic, and surface processes, but remains difficult to reconstruct from the geologic record. In contrast to conventional stable isotope paleoaltimetry approaches, the new “clumped” $^{13}$C-$^{18}$O paleothermometer independently determines carbonate growth temperature and the $\delta^{18}$O of water from which the carbonate grew, potentially enabling the effects of altitude, climate, and seasonality to be distinguished. This approach has been successfully applied to paleosol nodules. Here, we examine what other materials may potentially access paleoelevation information using this technique, including gastropods, the bivalve anomia, oysters, barnacles, soil, marl, and limestone from Cretaceous to Pliocene deposits from and adjacent to the Colorado Plateau, southwestern USA.

The abundance of $^{13}$C-$^{18}$O bonds in diverse carbonate materials from related sediments records temperatures between 20-84°C and $\delta^{18}$O$_{\text{smow}}$ water values of -2 to 12‰. Temperature estimates for independent preparations of the same sample are reproducible to within ±0.55-2.2°C (2 s.e.), and average temperatures determined for different materials from the same deposit exhibit negligible variations (±0.05°C).

While samples at the lower end of the observed temperature range represent reasonable Earth surface conditions that may be interpreted in terms of paleoelevation, samples yielding temperatures in excess of ~33°C likely provide a record of carbonate recrystallization/replacement during burial metamorphism (“resetting”). Clear examples of resetting include gastropod fossils in which original aragonite is completely replaced by calcite (yielding apparent temperatures of 76.5±1.7°C) and a suite of more cryptically reset Pliocene molluscs from tidal flat facies that yield temperatures of >42°C. Most apparently unreset samples are fine-grained (impermeable) micrites, which consistently yield temperatures within the plausible Earth-surface range. This suggests that resistance to diageneis is grain size dependent – a promising result given the abundance of well preserved fine-grained lacustrine and marine carbonates found throughout the geologic record. Results for micritic carbonates from Middle Miocene to Pliocene age record reasonable spring to summer depositional temperatures and oxygen isotopic values relative to modern lake waters on the Colorado Plateau.

Simulations of dry-out and halite precipitation due to CO$_2$ injection

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Although CO$_2$ is not very soluble in supercritical CO$_2$, a continuous stream of CO$_2$ being injected into a formation, will result in a region around the injection well to dry out. As the water of the formation brine is continuously extracted, the irreducible water saturation may attain practically zero. Enhanced injectivity is the result in a low salinity brine environment. In formations saturated with highly saline brine (e.g. Northern German Basin) the outcome is opposite: injectivity is impaired. In this case, the brine becomes supersaturated as continuously H$_2$O evaporates into the CO$_2$ phase and salt (halite) precipitates in the pores. The porosity and permeability diminish, which can lead to the loss of a injection well.

We present simulations of these processes as an example of pre-injection study for a CO$_2$ injection and storage site. The simulation tool consists of a commercial compositional code used extensively in the oil and gas industry to simulate the flow of multiple phases (oil, water, gas) in porous or fractured media. The mutual solubility of CO$_2$ and H$_2$O with a correction for salinity is implemented as described in Spycher and Pruess (2005). The brine salinity is adjusted accordingly until the saturation threshold is reached and halite is precipitated. The severity of this process can be evaluated for a specific site and also remediation strategies (injection of dilute fluids) tested.

Reference

Method measurement of Ar isotopes in He stream (conflo) for K/Ar geochronology

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Mass-spectrometric methods of measurement of Ar isotopes for K/Ar geochronology after of some key development (Inghram et al., 1950, Standacher et al., 1978) are developed on a way of perfection low background equipments. Achievement low background conditions measurement of Ar isotopes is extremely a challenge, requires greater efforts and a lot of time. Here, we report a new laser GC-MS method that incorporates helium carrier gas and chromatography methods (conflo) that allow for rapid analyses for small samples. The Ar gas is swept into the mass spectrometer in a helium carrier gas, allowing for extremely small samples to be quantitatively transferred (<5 .10-13g). The laser GC-MS technique consists of six components: the overall high vacuum extraction line, the system of input tracer 38Ar, the sample chamber, the laser, the gas chromatograph, the interface to the mass spectrometer and the mass spectrometer via a split interface (Matthews, Hayes, 1978). To separate the Ar from any other gas, and admitted into the mass spectrometer, Extracted Ar together with tracer (38Ar – 0.5105g) passes through U-shaped a trap (T =196) and is adsorbed onto activated coal in a loop at temperature of liquid nitrogen. He is passed through the loop (He, 99.9999%) and the loop is heated up to 100°C. The Ar gas is entrained in a helium stream (1-2 mL He/min), passes through the gas chromatograph to separate the Ar from any other gas, and admitted into the mass spectrometer via a split interface (Matthews, Hayes, 1978). To separate the Ar from other gas we use the capillary chromatographic column (HP-MOLSIV). Samples are analyzed using a dynamically pumped mass spectrometer. In general, Ar extraction by laser can be made every 15-20 min. The laser GC-MS system has been used successfully to analyze samples containing <510-13 g. Ar. Smaller samples can be analyzed with the use electron multiplier for 38Ar. Laser GC-MS method may be used and for 40Ar/38Ar geochronology.

References

On the nebular origin of water in the Earth

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Although the chondritic or cometary origin of water in the Earth has been widely accepted, we explore another possibility that the Earth acquired water from the solar nebula. Several recent theories of the final assembly of the terrestrial planets in the solar system (e.g., Kominami and Ida 2002; Nagasawa et al. 2005) suggest that there existed the nebular gas until the formation of the terrestrial planets was completed. When that is the case, the planets collect large amounts of hydrogen from the solar nebula.

Our simulations of the structure of the atmosphere on terrestrial planets embedded in the solar nebula (Ikoma and Genda 2006) demonstrate that the planet’s surface temperature is rather insensitive to the parameters and almost always higher than the melting temperature of silicate. In that situation the atmospheric hydrogen efficiently reacts with oxides contained in the magma ocean to produce water on the planet. From the chemical equilibrium constants (Robie et al. 1978), we find it possible that the reaction yields water comparable in mass to hydrogen. Although the exact amount of hydrogen that the primitive Earth acquired is unable to be determined at present because of the uncertainties in the heat flux and the grain abundance in the primitive atmosphere, our simulations show that production of water comparable in mass to the Earth’s current sea water is possible for wide ranges of the values of the quantities.

We have also tackled the well-known problem of the discrepancy between the D/H ratios of the Earth’s current sea water and the nebular gas (e.g., Drake and Righter 2002). We have simulated the evolution of the D/H ratio of sea water in the case the Earth had a relatively massive hydrogen atmosphere, which was neglected by previous studies, and found that the D/H ratio of the sea water increases by a factor of 3 to 9, depending of the escape rate of the atmospheric hydrogen (Genda and Ikoma 2007); this is consistent with the current D/H ratio of the Earth’s sea water.

In the presentation we will discuss the advantages and disadvantages of the nebular hypothesis about the origin of water in the Earth.

References
Time-series analysis of Magnesium isotopes in speleothems

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Magnesium-isotope time series MC-ICP-MS analyses from NW Africa (Morocco) speleothems are reported. In addition, high-resolution C, O and Sr-isotope data, and Mg and Sr element abundances were compiled. The analytical results show clearly co-variant, systematic and cyclical fluctuations for all proxies collected along the growth axis and - with respect to the analytical error - invariant data within one growth increment. Magnesium-isotope ratios ($\delta^{26}\text{Mg}$) fluctuate between -4.39‰ ± 0.02σ and -4.17‰ ± 0.05σ. The difference of 0.22‰ is significantly beyond the error of the external reproducibility of ± 0.03‰ σ for $\delta^{26}\text{Mg}$. Considering the analytical error, neither a purely kinetic nor an equilibrium fractionation process explains the observed isotope pattern. Two external factors might drive the speleothem Mg-isotope cyclicity: (1) climate-driven (arid versus humid) variances in the precipitation rate of a carbonate phase from meteoric water; and (2) changing rates of silicate versus carbonate weathering. Both of these processes fractionate the Mg-isotopic composition of runoff/seepage water.

Fractionation of iron isotopes in shallow-marine ferromanganese concretions

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Fe-isotope data for ferromanganese concretions indicate a trend from positive to negative values going from the freshwater environment, via the Arctic Ocean to the Atlantic and Pacific Ocean nodules, possibly following the redox related separation pathway of Fe from Mn in the exogenic cycle. However, the database is still small and additional Fe-Mn concretion data is needed, especially from continental margins, to verify if such a trend exists.

Shallow marine Fe-Mn concretions from the Baltic Sea and the Barents Sea analysed in this study show large variations in $\delta^{56}\text{Fe}$, from -1.55 to +1.0, thus spanning the whole range of $\delta^{56}\text{Fe}$ values presented so far for ferromanganese concretions. There are also large variations in $\delta^{56}\text{Fe}$ in concretions from the same area. Large positive $\delta^{56}\text{Fe}$ values are obtained only close to the reduced-oxidised interface in the sediment. Samples taken at some distance from the reduced-oxidised interface with low Fe/Mn ratios generally show negative values. It can be concluded that the local redox conditions strongly influence the Fe-isotope signal in the concretions.

This study indicates that dissolved heavy Fe-isotopes preferentially are trapped close to the reduced-oxidised interface and any dissolved Fe that might escape from the sediment up into the bottom water during early diagenesis should have a clear negative $\delta^{56}\text{Fe}$ value. Hence, early diagenetic cycling of Fe-oxyhydroxides in shallow marine sediments acts as a sink for heavy Fe-isotopes and as a source of lighter ones.
A U-series study on groundwaters from southwestern France

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U-series have been investigated in groundwaters from one demonstrative water body named the Eocene sands aquifer (Adour-Garonne district, southwestern France). This work was done in the framework of a research project (CARISMEAU, Négrel et al., 2007), related to the UE Water Framework Directive (WFD, 2000/60/EC). The Eocene sands aquifer extends north and south of the Garonne River. Groundwaters have been recovered both in spring and fall, in order to check for seasonal variations.

The $^{234}$U/$^{238}$U activity ratios are in any case higher than 1 (equilibrium value), some of them being very enriched in $^{234}$U (up to 11 in the northern part). Only slight isotopic variations of the $^{234}$U/$^{238}$U activity ratios have been evidenced between spring and fall waters. In the southern part, the highest $^{234}$U/$^{238}$U activity ratios correlate roughly with the oldest measured $^{14}$C ages (> 25 ka, André et al., 2005) while recharge areas have the lowest $^{234}$U/$^{238}$U activity ratios, closer to the equilibrium value. Hence it is not possible to apply a "simple" model featuring a decay of excess $^{234}$U through time during groundwater circulation to put chronological constraints on the residence time of waters in the aquifer.

Thorium isotopes have been measured successfully in some of these groundwaters, due to recent analytical improvements in Th isotopic analysis (Innocent et al., 2006). $^{230}$Th/$^{232}$Th activity ratios range between 0.4 ($^{230}$Th deficit) and 9.2 (large $^{230}$Th excess). $^{230}$Th/$^{234}$U activity ratios are very low ($\leq 0.01$), except for recharge areas (0.6). High $^{230}$Th/$^{232}$Th roughly correlate with $^{234}$U/$^{238}$U close to the equilibrium. A open-system model, combining these three activity ratios is presented, potentially constraining groundwater residence times in the aquifer.

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Spatial and temporal variation of anthropogenic lead inputs to the western Pacific

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A continuous record of anthropogenic lead affecting on the western Pacific has been less studied compared to the North Atlantic. In this study, Pb contents and isotopic compositions in the annually banded coral (Porites sp.) from Ogasawara, Japan was used for reconstruction of Pb variation since the late 19th century. We also determined Pb in corals collected from several sites in the western Pacific to examine spatial distribution of Pb in sea surface. Determinations of Pb contents and isotope ratios were conducted using inductively coupled plasma mass spectrometer (ICP-MS) and multiple collector ICP-MS, respectively (Inoue et al., 2006; Tanimizu and Ishikawa, 2006). The spatial distribution of Pb showed a clear dilution pattern of Pb from Asian continent to the open ocean. In addition to the spatial distribution, Pb contents in Ogasawara coral have gradually increased during last 108 years. Although Pb emitted from Japan seems to be main source during the period of 1960 – 1980, that from China might be predominant source of Pb affecting on the western Pacific for the last 20 years based on the variation of Pb isotope ratios in the coral core.

References


Peridotite xenoliths from the andesitic Avacha volcano, Kamchatka – Any signatures of subduction metasomatism?

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We report chemical data, Os- and Li-isotope ratios, PGE abundances and \( f_{O_2} \) estimates for peridotite xenoliths from the active Avacha volcano in southern Kamchatka peninsula, Russia. The rocks are large, fresh and homogeneous spinel harzburgites that contain accessory interstitial cpx and amphibole as well as highly variable amounts of fine-grained, second-generation orthopyroxene (opx). None of the samples have intrusive magmatic or metasomatic veins.

Major and trace element compositions were obtained for 17 peridotites. The whole-rocks contain 0.4-0.9% \( \text{Al}_2\text{O}_3 \), 0.5-0.9% \( \text{CaO} \), <0.03% \( \text{Na}_2\text{O} \), <0.01% \( \text{K}_2\text{O} \); Mg\# = 0.906-0.916. They are highly refractory rocks produced by high degrees of melt extraction, but their Mg\# are lower than in many other (Ca,Al)-poor mantle peridotites. The Avacha xenoliths have low HREE and are depleted in LREE and MREE relative to HREE. The rocks show minor enrichments in Rb, Ba, U and Sr relative to adjacent REE but no significant Zr, Nb or Ti anomalies. Overall, they show no enrichment patterns considered typical of “subduction” metasomatism.

The rocks have 2.7 to 9.6 ppb Os; \( ^{187}\text{Os}/^{188}\text{Os} \) range from 0.1235 to 0.1319 and are positively correlated to Al contents. This “alumichron” is not likely to be related to ancient melt extraction. Rather, it may reflect a correlation between the amounts of slab-derived radiogenic Os and those of late-stage amphibole and pyroxenes added by percolating fluids. Li abundances in whole-rocks, olivine and opx range from 0.8 to 1.8 ppm, i.e. match estimates for melting residues. \( \delta^7\text{Li} \) range from -2 to +4.7‰, with averages for olivine, opx and WR from +1.7 to +2.7‰, i.e. are within the range reported for oceanic basalts and “normal” mantle. \( \Delta \log f_{O_2} \) determined using measured \( \text{Fe}^{3+}/\text{Fe}^{2+} \) in spinels are FMQ +0.1 to +1.8.

Relatively high \( f_{O_2} \), Os abundances and \( ^{187}\text{Os}/^{188}\text{Os} \) in several Avacha peridotites might be related to enrichments by slab-derived fluids but these are decoupled from trace element and Li-isotope signatures, which show no or little evidence for metasomatism. The slab-derived fluids may be largely consumed by reaction with wall-rocks in the lower mantle wedge, with only small amounts of residual fluids occasionally reaching the shallow uppermost mantle sampled by the Avacha xenoliths.

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Re-Os evidence for ancient mantle beneath the Ontong Java Plateau

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We have carried out a Re-Os isotope study of a suite of peridotite xenoliths from Malaita, Solomon Islands in order to better understand the nature and formation of oceanic lithosphere beneath the Early Cretaceous Ontong Java Plateau (OJP). Thermobarometric and petrochemical evidence reveal that the xenoliths represent virtually the entire section of subplateau lithospheric mantle (<120 km) which is stratified in compositional [1]. Os isotope data have been obtained for samples covering the whole range of \( P-T \) and depletion.

Whole-rock analyses of peridotites from the shallow part of the lithosphere (<95 km) yield an average \( ^{187}\text{Os}/^{188}\text{Os} \) ratio of 0.1247 (n=15) and a range from 0.1223 to 0.1272, illustrating an affinity with abyssal peridotites (whole-rock mean ~0.1246) [2]. This is consistent with previous Sm-Nd results indicating a recent (Jurassic) mid-oceanic ridge origin for the shallow lithosphere [3]. By contrast, the deep-seated peridotites (>95 km) show much greater variation in Os isotope composition that is correlated with differences in rock types: garnet lherzolites have limited \( ^{187}\text{Os}/^{188}\text{Os} \) variations (0.1244-0.1254); spinel harzburgites record unradiogenic \( ^{187}\text{Os}/^{188}\text{Os} \) ratios (0.1174-0.1196); Fe-rich garnet lherzolite from the deepest portion possesses the most unradiogenic ratio (0.1156). These unradiogenic ratios yield Proterozoic model \( T_{BD} \) ages of 1.2-1.8 Ga, demonstrating the existence of ancient mantle in the basal section of subplateau lithosphere.

There are several potential explanations for the diversity of ancient Os signatures found in these OJP peridotites. (i) Continental mantle was tectonically incorporated to the newly forming oceanic plateaux, analogous to the scenario suggested for the Kerguelen plateau mantle [4]. (ii) The OJP lithosphere may be sampling the inherent isotopic variability of the oceanic mantle as represented by abyssal peridotites, which overlaps the range reported here (extending to \( ^{187}\text{Os}/^{188}\text{Os} \) as low as 0.110 in sulfide grains from abyssal peridotites [5]). (iii) The depleted Os isotope compositions may reflect recycled heterogeneity within the upwelling plume source, as suggested recently for Hawaii [6]. Option (iii) may best explain the absence of old continental materials around the OJP, the contrasting Os isotope ratios between shallow and deep lithosphere, and the presence of recycled pyroxenite of Proterozoic age in the basal lithosphere [7]. Thus, the OJP may have been generated by mantle plume consisting of a mix of ancient, depleted, recycled Proterozoic lithosphere.
Amphibolite-facies metamorphism of the subducted slab and boninite magma genesis: An inference from the Oman ophiolite

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The Oman ophiolite contains boninite and other arc-related volcanic rocks generated after the magmatism of spreading-ridge ceased. The initiation of subduction of a young, hot oceanic lithosphere (and obduction of the future Oman ophiolite) near the spreading ridge and the resultant melting of the hydrous shallow mantle wedge represent the most favorable mechanism for the genesis of the Oman boninites. On the other hand, this ophiolite is underlain by a thin sliver of amphibolite-granulite-facies metamorphic rocks. These rocks (metamorphic sole) are believed to represent oceanic crust overridden and “ironed” by the ophiolitic lithosphere, and may be analogous to the subducted slab that contributed to producing the geochemical signature of the Oman boninites. Thus the Oman ophiolite provides a best opportunity for investigating the link between the amphibolite-facies metamorphism of the slab and the boninite magma genesis in the mantle wedge.

The amphibolites in the 230 m-thick metamorphic sole in Wadi Tayin area show significant variation in fluid-mobile element concentrations across the transect of the sole. The observed variations suggest that the amphibolites (>600°C in peak metamorphic temperature) near the contact with the overlying peridotite were equilibrated with evolved, B-Rb-K-Ba-rich fluids formed through successive fluid-rock interactions during prograde metamorphism. The estimated amphibolite-derived fluids are characterized by striking enrichments of B, Rb, K and Ba and moderate to minor enrichments of Sr, Li, Be and Pb. It is also suggested that at higher temperature (up to 700 °C), the fluids become considerably enriched in light REE and Nb in addition to the above elements. Model calculations showed that the trace element characteristics of the Oman boninites, including their U-shaped REE patterns and relatively low Ba/Rb ratios, are successfully explained by partial melting of the highly depleted mantle that had been metasomatized by the amphibolite-derived fluids. The Sr and Nd isotope compositions of the boninites and related volcanic rocks in the Oman ophiolite are also consistent with the involvement of such fluids. The compositions of the fluids liberated from the amphibolite-facies slab are likely to vary dependent on the metamorphic temperature, and the evolution and hybridization of such fluids may produced considerable variations in trace element and isotope compositions observed in the boninites.

The magmatic plumbing of the submarine volcanic chain of an oceanic island arc volcano: Long distance lateral magma transport?

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Recent geophysical observations on basaltic composite volcanoes in Izu arc reveal the process of long distance lateral magma transport within the arc crust. Such intrusion events sometimes caused flank fissure eruption and also triggered a formation of collapsed caldera (Miyakejima 2000). To clarify a long-distance magma transport system of the basaltic volcano in volcanic arc from geological and petrological aspects, we investigated a submarine volcanic chain (Hachijo NW chain) and satellite cones nested Hachijo Nishiyama volcano, a frontal composite volcano in the northern Izu arc.

Basalts from the Hachijo NW chain generally have more primitive composition compared to those from the Nishiyama. The bulk compositional trend of Hachijo NW chain magma is controlled by crystal fractionation while plagioclase accumulation was indicated by aluminum-rich character of the Nishiyama volcano and its subaerial and submarine satellite cones other than NW chain edifices.

Trace element ratios unaffected by melting or crystal fractionation (e.g., Nb/Zr) and isotopic compositions are not significantly different between the Nishiyama and the Hachijo NW chain. This implies that the sources of magma for these volcanic systems are identical. However, Hachijo NW chain shows lower LREE/HREE and Zr/Y. These differences in trace element ratios could be ascribed to difference in degree of partial melting of the source or crustal assimilation. Assuming difference in degree of partial melting, Nishiyama magma, which is much more voluminous than Hachijo NW chain magma, should have lower degree of melting relative to Hachijo NW chain. Instead we prefer a model considering larger extent of crustal assimilation for Nishiyama magma, where assimilated crust is expected to have higher LREE/HREE and Zr/Y, but similar isotopic composition to basaltic primary magma.

Nishiyama magma is assumed to form shallow crustal magma chamber where it experienced crustal assimilation and plagioclase accumulation. Satellite cones other than NW chain can be explained by magma transport from this magma chamber in the shallow crustal level. On the other hand, Hachijo NW chain was tapped by the same primary magma as Nishiyama volcano, but experienced much less crystal fractionation and assimilation in the crust during ascent without forming shallow magma chamber. Long distance magma transport is assumed to have occurred in the lower crustal level, which is consistent with the depth of hypocenters of seismic event in 2002.
Adsorption of As(III) and As(V) onto vivianite – Evaluation as a sink for arsenic in Bengali aquifers

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Although microbially mediated reduction of Fe(III) oxy-hydroxide phases is thought to be critically implicated in the mobilisation of arsenic in shallow aquifers in Bengal (Islam et al., 2004), Cambodia (Rowland et al., 2004) and other parts of world, there is substantial evidence that mobility of arsenic in such aquifers is also controlled by the nature and distribution of secondary Fe-bearing phases. Secondary Fe-sulfides, magnetite, siderite and vivianite have all been suggested as potential arsenic sinks. Whilst there are considerable data on the adsorption and/or incorporation of arsenic into Fe-sulfides (Farquhar et al., 2002; Wolthers et al., 2005) and magnetite (Dixit and Hering, 2003; Coker et al., 2006) there is a dearth of such data for vivianite. In this study, we report the sorption behaviors of both arsenite and arsenate on vivianite under anaerobic conditions as a function of solution pH and dissolved arsenic oxidation state and concentration.

Natural well crystallised vivianite was characterised by ESEM/EDS, XRD, EPMA and BET and then mixed (1:8 wt/wt) with 1, 10 and 100 µM of As(III) or As(V) in a background electrolyte of 0.1 M NaNO₃ with pH adjusted from 3 to 11 with HNO₃ or NaOH. Solutions were purged with nitrogen and the studies were conducted under a modified atmosphere of 5% H₂ + 95% N₂ in an anaerobic cabinet at ambient temperature (T = 23 +/- 3°C) and pressure. Fe, P and As in the aqueous phase after 40 hours were measured by ICP-AES.

The adsorption of As(III) was found to be pH dependent, increasing from 10% of a 100 µM solution at pH 3 to 33 % at pH 10 and 75% at pH 11. Implications for the scavenging capacity of vivianite for As(III) in shallow reducing groundwaters in Bengal are discussed.

References

Fossilized microorganisms from Emperor Seamounts: Evidence for a deep sub-seafloor biosphere

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Fossilized microorganisms have been observed in drilled samples of seafloor basalts collected during ocean Drilling Program (ODP) Leg 197. During that leg three different seamounts belonging to the Emperor Seamounts in the Pacific Ocean were drilled: Detroit (81 Ma), Nintoku (56 Ma) and Koko (48 Ma) Seamounts respectively. A wide variety of microbial-like structures were found in veins, attached to mineral surfaces and embedded in minerals like calcite, aragonite and gypsum. Morphologically, the microfossils vary a lot. Globular cell-like coccoids, sheaths, segmented filaments, twisted filaments and branched filaments were found. With ToF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) fatty acids and lipids were detected in the microfossils. This is, to our knowledge, the first time such compounds have been found in association with microbial remnants from sub-seafloor environments. ToF-SIMS further showed concentrations of C₅H₄ and PO₃ in the microfossils. The biogenicity was also supported by dying the microfossils with the pigment PI (propidium iodide) that binds to dead bacteria cells and remnants of DNA. EDS-analyses showed that they contain slight amounts of elements like Si, Al, Mg, K and Na but very high amounts of carbon (~10-50 wt % C) and iron (~10-50 wt % Fe). The high iron content as well as a close association with iron oxides and deposition of iron oxides onto the filaments indicate that the microorganisms were involved in iron oxidizing reactions and that iron probably served as an energy source for the metabolism of the microorganisms.

Our observations show that all three seamounts drilled during ODP Leg 197 have been supporting a deep sub-seafloor biosphere during their volcanically active period of time when hydrothermal activity was present and fluids circulated the rocks.
Determination of production rates of cosmogenic nuclides based on data from large landslides in the Alps

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We are analyzing samples from boulder and bedrock surfaces associated with large prehistoric landslides in the Alps for ¹⁰⁷Be, ²⁶Al and ³⁶Cl. In addition to determining the ages for undated landslides, we are examining cosmogenic nuclide production rates based on results from landslides with independent age constraints (for example Flims, Graubuenden Switzerland and Koefels, Tirol, Austria). We focus on ¹⁰⁷Be, ²⁶Al in crystalline regions with abundant quartz, while ³⁶Cl is used in areas underlain by calcareous rocks. Potential complications include pre-exposure, post-slide rock fall, and shielding by soil or snow. Results from several sites as well as the problems encountered will be discussed.

Independent component analysis of isotopic compositions of oceanic basalts

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Isotopic variations in oceanic basalts indicate possible interactions among several distinct mantle components, such as DMM, EM, FOZO, C, HIMU, etc. Increasing number of data for various isotopic systems now allows us to systematically search the structure hidden in the multivariate compositional space by independent component analysis, ICA [1]. Principal component analysis (PCA) has been regarded to be the most efficient way to display the extreme mixing end-components. However, it has a fundamental problem: PCs are independent only when the data distribution follows the Gaussian distribution, which is not in this case. ICA is the method to deconvolute a data set into independent components that maximize the non-Gaussianity of the projected distribution of the data. Based on ICA, we have explored the isotopic compositional space of the oceanic basalts from Atlantic and South Indian Oceans, based on the data from literature [21] and GEOROC database. We show that the two independent compositional vectors/directions (referred to as independent components or ICs) are involved to create the variations with six isotopic ratios of Pb, Sr, Nd and Hf. One of the two ICs clearly divides OIBs and MORBs, while another IC distinguishes the geographical distribution including DUPAL anomaly. This feature supports that the two ICs are indeed independent. We also show that the conventional mantle end-components are not appropriate to represent the compositional space. Instead, two independent processes that create vectors parallel to DMM-FOZO or towards EM are proposed to explain the independent compositional space. Since the average composition of the oceanic basalts is similar to that of the average DMM, around which MORBs and OIBs are roughly symmetrically distributed in the IC space, we argue that these processes occur as two dominant but independent differentiation processes within the depleted mantle domain. Considering these nature, one IC is likely to be produced by recycling and stirring of MORB and its residue, while another IC is possibly created by the subduction zone processes. According to the ICs, the criterion of DUPAL anomaly is re-defined. As a result, distribution of the enriched region is modified, showing that the enriched signature disperses into the northern hemisphere.

References

The simulation experiments on hydrothermal formation of organic globules in carbonaceous chondrites

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Organic globules were found in the Tagish Lake meteorite (carbonaceous chondrite fallen in 2000). Since then, further characterizations of these globules in meteorites have been conducted. However, the formation processes of organic globules remain unclear. In order to simulate the globule formation processes, a series of hydrothermal heating experiments of an OH-bearing amino acid (threonine: Thr) have been conducted in the presence of some rocks (rhyolite, basalt).

40 ml of Thr solution with a rock piece was heated in a hydrothermal vessel at 160°C for 4 days, globules of 2 to 20 micrometers in size were observed under Scanning Electron Microscope (SEM) on the rock surface. By elemental analysis of the globules, they are found to be carbon rich substances. This result suggests that the organic globules found in Tagish Lake meteorite might be formed by organic-inorganic interactions during the aqueous alteration of the chondrite parent body.

In order to study quantitatively the globule formation processes, hydrothermal heating experiments of Thr solutions have been conducted with the silicate glass slide having smooth surfaces. SEM images of glass surfaces showed that diameters and numbers of globules increased with the heating duration and with the temperature. By image analyses, grain size distributions and mean diameters of globules have been determined. Growth rates of organic globules at different temperatures were evaluated by means of their mean diameters. Based on these results, formation of globules of about 300 nm in diameter would need several hundred years under the temperature of aqueous alteration (20°C). These results can be used to estimate temperature conditions and time scales of organic globule formation in the meteorite parent body.

Processes of biomineralization in freshwater cultured pearls

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Freshwater cultured pearls formed by the mussel *Hyriopsis* represent excellent examples to study processes of biomineralization in molluscs. They are grown by inserting a piece of epithelial tissue from the mantle lobe into the mussel where processes identical to those forming the mussel shell occur.

Resonance Raman Spectroscopy of polished pearl cross-sections revealed that ca. 50% of the samples contain vaterite in addition to aragonite. Vaterite is the thermodynamically most unstable polymorph of CaCO$_3$ and is often discussed as a precursor phase in the mineralization of aragonite or calcite by organisms (Weiss et al., 2002). Vaterite forms relatively small areas in high quality pearls (1-1.5 mm diameter) which are spherical to irregular and always in close proximity to the center of the pearl. However, in low-quality pearls, they can be much larger, sometimes comprising the major part of the pearl, including the surface (Ma and Lee, 2006; Qiao et al., 2006).

To further study the micro-structure of the vaterite zones, cross-sections were etched with Mutvei’s solution (Schoene et al., 2005). This etching method dissolves the calcium carbonate surface with acetic acid, while the organic matrix is stabilized with glutaraldehyde and Comassie Blue colours the organic material in intensities which correspond to the concentration of the organics. SEM analyses of the etched surfaces show that growth rings transect the vaterite areas, implying that vaterite and aragonite grew simultaneously, and that vaterite may not have been an initial template for aragonite growth.

LA-ICP-MS and electron microprobe were used to quantify minor and trace elemental differences between the calcium carbonate polymorphs. Vaterite areas have about 1400 ppm Mg and 1000 ppm Na, versus around 30 ppm Mg and 1650 ppm Na found in aragonite. The Sr concentration in vaterite (250 ppm) is about half of that found in aragonite, while for Mn, Zn and Ba no significant differences were detected.

References
Thermodynamic assessment of the magnesium-olivine-pyroxene system using a lattice vibrational technique

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We are currently constructing a thermodynamic database providing phase diagrams, thermophysical and therchemochemical properties for materials with a geophysical relevance, applicable in the pressure and temperature regime of the Earth’s mantle. The computational technique is based on Kieffer’s (1979) approach to model the vibrational density of states of a substance, a key property to derive the Helmholtz energy. It allows the calculation of $V_T$ and $V_A$ sound wave velocities. The developed thermodynamic framework uses model input properties related to Raman and infrared spectroscopic data. It puts tighter constraints on therodynamic properties compared to methods based on polynomial parameterisations of thermal expansivity, heat capacity and isothermal bulk modulus. Jacobs and de Jong (2005) and Jacobs et al. (2006), showed that this framework entails a description of properties free from physical anomalies for close-packed materials. In addition it discriminates, based on internal consistency, between the quality of disparate sets of experimental therchemochemical, thermophysical and phase diagram data.

The present work focuses on the application of vibrational modeling to the magnesium-olivine-pyroxene system, which constitutes over 90% of the Earth’s mantle and which is intimately linked to the magnesium-olivine system by the common phases wadsleyite, ringwoodite and perovskite. We show how our approach is used in a thermodynamic assessment of experimental data. The results, presented here, were used in a numerical model of convection in the Earth’s mantle to reveal, effects of phase transitions on the degree of layering, mineral distribution and sound wave velocities in the transition zone, around 660 km depth in the Earth.

References


Accretion and early differentiation history of the Earth based on extinct and long-lived chronometers

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Jacobsen and Harper (1996) showed that isotopic variations due to decay of extinct nuclides ($^{129}$I, $^{244}$Pu, $^{182}$Hf and $^{146}$Sm) could be used to study early evolution of terrestrial reservoirs and provide observational constraints on the timescale of accretion of the terrestrial planets. Measurable variations in $^{182}$W/$^{183}$W, $^{142}$Nd/$^{144}$Nd, $^{129}$Xe/$^{130}$Xe and $^{136}$Xe/$^{138}$Xe in the Earth (compared to bulk planetary values inferred from primitive meteorites) provide a preserved record of accretion, core formation, early crust, atmosphere formation and evolution. The $^{182}$Hf-$^{182}$W system is the best accretion and core-formation chronometer because it is identifiable with chemical fractionation during the accretion process itself. This system yields a mean time of Earth’s accretion and core formation of 10 Myr, with a total timescale of accretion being 30 Myr. New experimental data pertaining to the conditions that existed in the Earth’s deep mantle ($P > 100$ GPa and $T > 6000$ K) subsequent to the giant Moon-forming impact show that metal-silicate equilibrium will be rapid enough for the Hf-W chronometer to reliably record this timescale (Petaev et al. 2007). Although the $^{206}$Pb/$^{204}$Pb chronometer has been used to argue for a more protracted timescale (~100 Myr) of accretion and core formation, Yin and Jacobsen (2006) showed that these data do not require a longer time scale. Using the coupled $^{146}$Sm - $^{147}$Sm chronometer, the age of the initial silicate differentiation in the mantle source region of some of the Earth’s oldest surviving crustal rocks can be constrained to ~4.47 Ga. Attempts to use this chronometer for dating proto-crust formation at ~30 Myr are unreliable because of the uncertainties in the initial Nd isotopic composition inferred from heterogeneities in Ba and Nd isotopes in primitive meteorites (Ranen and Jacobsen 2006). The presence of a large $^{129}$Xe excess in the deep Earth is consistent with a very early formation and a short time interval for the accretion of the Earth.

References

δ$^{44}$Ca evolution during water-rock interaction in a carbonate aquifer

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To improve understanding of Ca isotope transport during water-rock interaction on the continents, we measured δ$^{44}$Ca values along a 236 km flow path in the Madison aquifer, South Dakota, where fluids have chemically evolved according to dolomite and anhydrite dissolution, calcite precipitation, and Ca-for-Na ion-exchange over a timescale spanning ~15 kyr. We use a reactive transport model that employs rate data constrained from major ion mass-balances to evaluate the extent to which calcite precipitation and ion-exchange fractionate Ca isotopes. Elevated δ$^{44}$Ca values during the initial and final stages of water transport may result from calcite precipitation under supersaturated conditions and Ca-for-Na ion-exchange, respectively. However, for the bulk of the flow path, δ$^{44}$Ca values evolve by mixing between dolomite and anhydrite dissolution, with no fractionation during calcite precipitation under saturated conditions. We attribute the absence of Ca isotope fractionation to the long timescale of water-rock interaction and the slow rate of calcite precipitation, which have enabled fluids to chemically and isotopically equilibrate with calcite. We therefore conclude that the equilibrium Ca isotope fractionation factor between calcite and water (Λ$_{calc-w}$) is very close to zero. We further reason that instances of $^{44}$Ca enrichment attributed to calcite precipitation must stem from kinetic isotope effects. To the extent that the Madison aquifer typifies other groundwater systems, our study suggests that groundwater δ$^{44}$Ca values can be modelled according to simple mixing theory, without the need to invoke isotope discrimination during calcite precipitation. We suggest that groundwater may play an important role in transmitting the pristine isotopic signature of Ca mineral weathering to the oceans, by way of surface–groundwater interactions in tributary networks of large rivers.

Diatom δ$^{13}$C, δ$^{15}$N, and C/N since the Last Glacial maximum in the Southern Glacial Ocean: Evidence for regional and ecological influences

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The carbon and nitrogen isotopic composition (δ$^{13}$C and δ$^{15}$N) and C/N ratio of diatom-bound organic matter is commonly used to reconstruct oceanographic processes that contribute to variations in atmospheric CO$_2$ over glacial-interglacial cycles. This organic material is presumed to be part of the diatom cell wall and the template for biomineralization, entombed upon silicification and protected from diagenesis. However, this material has not been well characterized and there is no strong sense yet for how variable its composition is between species or among members of the same species growing under different conditions. In addition, the studies that have been carried out on isotopic fractionation by diatoms have focused on the “whole cell” isotopic composition and not specifically that of the material occluded within the matrix of the silica. Some investigation of this matters would go a long way towards refinement of these proxies for nutrient utilization and primary production.

Towards this end, measurements of δ$^{13}$C, δ$^{15}$N, and C/N on diatom-bound organic matter were made over the Holocene and Last Glacial Maximum (LGM) from 3 piston cores in the Southern Ocean, one from each of the three sectors. The site in the Atlantic sector differs considerably from the other two sites by having markedly lower δ$^{13}$C, more variable δ$^{15}$N and C/N ratios, and a sedimentary diatom assemblage that is never dominated by Fragilariopsis kerguelensis. The proportion of F. kerguelensis in the samples, and to a lesser degree, the carbon content of the organic matter, have a strong influence on δ$^{13}$C. Extreme values of δ$^{13}$C, δ$^{15}$N, and C/N at the Last Glacial Maximum are also related to the abundance of resting spores of Eucampia antarctica. These results suggest that methods for the separation of specific diatom species out of opal sediments would considerably aid in the reconstruction of paleoceanographic conditions from diatom stable isotope and elemental records.
Formation of hydrozincite, Zn layered double hydroxide and Zn phyllosilicates in contaminated calcareous soils

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The incorporation of Zn into layered mineral structures such as layered double hydroxides (LDH) or phyllosilicates may reduce its mobility and bioavailability in soils. The quantity and structure of Zn bearing layered phases forming in soils depend on soil physicochemical properties and contamination level. To date, most spectroscopic studies on the speciation of Zn considered neutral to acidic non-calcareous soils. In this study, we investigate the reactivity and speciation of Zn in contaminated soils developed from calcareous and dolomitic parent material.

Five soils developed from limestone and one developed from dolomite were sampled below power line towers made from galvanized steel that had been constructed 30 to 50 years ago. All soils have been contaminated by input of runoff water containing dissolved Zn from corrosion. The soils cover a wide range in clay content (90-450 g/kg), inorganic carbon content (10-89 g/kg), and Zn concentration (1'300 - 30'000 mg/kg). They have pH values between 6.1 and 7.5. The molecular scale speciation of Zn in the soil matrix was investigated by Zn K-edge EXAFS spectroscopy on powdered soil samples. Thin sections from two calcareous soils (1'300 and 30'000 mg kg\(^{-1}\) Zn) and the dolomitic soil (1'400 mg kg\(^{-1}\) Zn) were further studied by µ-X-ray fluorescence (µ-XRF) and µ-EXAFS spectroscopy. Principal component analysis and target testing indicated that octahedrally coordinated Zn in layered minerals and tetrahedrally or octahedrally coordinated sorbed Zn are likely candidate species. In the dolomitic soil, pure Zn-phyllosilicate was identified in Zn-rich spots. In the calcareous soil containing 30'000 mg kg\(^{-1}\) Zn, the Zn was diffusely distributed in the soil matrix with a spectrum similar to Zn-LDH. Crusts on calcite particles from the same soil were identified as hydrozincite using powder X-ray diffraction and EXAFS spectroscopy. Linear combination fits to the bulk EXAFS spectra indicate that LDH- and phyllosilicate-type precipitates account for a considerable fraction (17-53%) of the total Zn in all soils. To quantify the reactivity of Zn, the soils as well as synthetic references were fractionated using a 7-step sequential extraction procedure (SEP). Between 32-65% of the total Zn in the soils was extracted in the first two fractions (1M NH\(_4\)NO\(_3\) and 1M NH\(_4\) acetate at pH 6.0, respectively), suggesting that most Zn occurred in labile species. Zn-LDH, Zn-phyllosilicates and hydrozincite showed similar chemical reactivity with 46 to 84% of the total Zn mobilized in the first two fractions.

Solving the mystery of SNC meteorites

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Rb-Sr, Sm-Nd and U-Th-Pb isotopes have been intensively studied on SNC meteorites. There is a general consensus that these meteorites are magmatic rocks. While in terrestrial magmatic rocks the Rb-Sr system usually shows a greater melt-residue fractionation than the Sm-Nd system, it is just the reverse in the case of the SNC meteorites. While the whole rock SNC meteorites scatter along a 4.5Ga Rb-Sr reference isochron showing only a slight disturbance, the Sm-Nd isotopes for the same whole-rocks are strongly fractionated, with a considerable depletion of Nd for the shergottites and an enrichment of Nd for the nakhlites. One would expect that a magmatic fractionation would cause a strong enrichment in Rb, but only a moderate enrichment in Nd. The shergottites, however, which clearly originally crystallized from melts, show no significant enrichment in Rb but, by contrast, a strong depletion in Nd. The nakhlites, which are mafic cumulates with a residual major element chemistry, experienced a significant Nd enrichment. Model-calculations that are able to explain the Sm/Nd evolution cannot be extended to the other REE and completely fail to explain the observed Sm/Yb and La/Nd ratios. A mixing model reveals the need for three components to explain the composition of shergottites and nakhlites, but does not contribute to an understanding of a realistic magmatic process.

Recently we developed a magmatic model that consistently explains the observed petrographic and isotopic data for SNC meteorites. It is based on the premise that the basaltic shergottites, Shergotty, Zagami, and Los Angeles, have typical crustal compositions and were differentiated very early at 4.4 Ga, while nakhlites and olivine-bearing shergottites, Que, SAU, Y89, and others, derive from a nearly homogeneous mantle source [1].

Minor heterogeneities in the Sr and Pb isotopes are insufficient to argue against a common mantle source, and reported W isotopic differences might be caused by terrestrial contamination (the intrinsic W contents of the shergottites, as estimated from the W/La in these meteorites, may be unmeasurable). To explain their unusual fractionation pattern, we postulate the presence of two phosphates in the Martian mantle: xenotime and monazite. At the time of fractionation, xenotime partitions into the olivine bearing shergottites while monazite partitions into the nakhlites. This phosphate chemistry has little effect on the Rb-Sr system, strongly fractionates between the light and heavy REE. Because in such an environment the trace-elements do not follow Henry’s law, commonly employed melting models cannot be applied.
Differences between preserved vs. delaminated lower crust: Evidences from the Kohistan arc

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Delamination and foundering of the lower continental crust (LCC) into the mantle are important crust forming mechanisms. However, knowledge of the composition and mineralogy of the preserved and/or delaminated LCC remains scarce. We provide a synopsis of recent research within the Kohistan arc (Pakistan). We show that hydrous and “less-hydrous” liquid lines of descent related to flux and decompression melting, respectively, produced compositionally different lower crustal rocks in the Kohistan arc. These observations allow a new model for CC formation where delaminated and preserved LCC differ in mineralogy and composition.

Within the Kohistan arc two mantle-lower crustal sections are exposed: the older Jijal section and the younger, rifting-related Chilas section. We describe lithologies of these sections and argue that fractionation mechanisms that produced them document two liquid lines of descent with largely differing initial water contents. The Jijal liquid line of descent is typical for a hydrous, high-pressure fractionation sequence (e.g. pyx, grt, Fe/Ti-oxides, amph, An-rich plag). The composition of the Jijal lower-crustal gabbroic rocks differs markedly from bulk lower crust estimates but is complementary to silica-rich rocks (tonalite, granite etc.), exposed within the Jijal section and within the so-called Kohistan Batholith.

The Chilas liquid line of descent is typical for a “less-hydrous” fractionation sequence (e.g. ol, pyx, plag, amphib). Gabbro-norite to diorite rocks are dominantly composed of plagioclase, clinopyroxene and orthopyroxene (±quartz, ±amphibole). Despite the similarity of the Chilas gabbroic rocks to typical lower crust compositions, the “less hydrous” fractionation results in massive amounts of gabbroic material and small volume of silica-rich rocks. This mass balance and their mineralogy precludes them to represent the magmatic equivalent of the upper crust.

We propose that the upper, non-sedimentary CC is dominantly formed by hydrous high-pressure fractionation with subsequent delamination of the complementary garnet-pyroxene-amphibole-rich LC cumulates. This LC The delaminated amphibole-rich lower Jijal crust has trace element content and mineralogy adequate to explain certain characteristics of OIB. In contrast, the LCC, which is preserved over geological timescales, is formed by “less-hydrous” parental melts. We suggest that the bulk crustal composition is a mixing between these two compositional end-members.

Plastic deformation of orthoenstatite and the ortho- to high-P clinoenstatite transition studied by atomistic simulation

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Atomistic computer simulation techniques are used to study plastic deformations of orthoenstatite, MgSiO3, at high pressure, P, and high temperature, T. The combination of molecular dynamics with metadynamics allows the direct observation of the structural changes at the atomic scale during the creation of stacking faults in the (100) planes. The respective slip deformations consist of at least four partial deformations crossing high energy intermediate structures. Although the low energy structures that may be observable experimentally suggest a dominant (100)[001] single slip system, the partial deformations also have contributions in (100)[010] direction.

Choosing conditions in the stability field of high-P clinoenstatite (T=1000 K, P=15 GPa), one sequence of plastic deformations in orthoenstatite leads to reformation of perfect orthoenstatite, whereas a second sequence results in the formation of the thermodynamically stable high-P clinoenstatite. From experiments (Lin, 2003; Kung et al., 2004) it is known that due to the high kinetic barrier of the partly reconstructive phase transition, the formation of high-P clinoenstatite is prevented at ambient T in a wide pressure range up to at least 22 GPa. We are able to identify some of the possible metastable high-P polymorphs of orthoenstatite, which lead to anomalous behavior of the elastic properties (Kung et al., 2004) and to changes in the Raman spectra (Lin, 2003).

References
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The influence of metasomatized mantle wedge related to flat-subduction processes in extra back-arc basalts in Patagonia, Argentine

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During the Cenozoic age, there were relatively large volumes of basaltic lava eruptions in the eastern Andes along the Chile trench, South America, which generated extensive volcanic plateaus in a geotectonic environment of continental “extra” back-arc. The outcropping volcanic products in the studied area are displaced from 34ºS to 46º30’S and host ultramafic xenoliths. Twenty-three samples of volcanic basalts from 11 different localities were analyzed. These rocks are basanites-tefrites, trachybasalts and basalts of the alkaline series, with phenocrysts and/or xenocrysts of olivine, orthopyroxene and clinopyroxene. In general, REE patterns for these rocks present similar variation with an expressive enrichment in light REE in relation to the heavy REE. The multi-elemental diagram analyses allow the individualization of the basalts into two groups with distinct behaviors. Group I shows OIB-like characteristics with Th enrichment and Pb depletion, while Group II presents OIB-like characteristics with Pb, Ba and Sr enrichment, which is related to some influence of the subduction zone. Isotopic data for both group present low \(^{87}\text{Sr}/^{86}\text{Sr}\) isotopic ratios (0.7031-0.7049) and moderate \(^{143}\text{Nd}/^{144}\text{Nd}\) values (0.512689 to 0.512983) that are comparable to typically mantle basalts with OIB characteristic, according to Hart and Zindler (1989). However, Group I generally exhibit higher \(^{143}\text{Nd}/^{144}\text{Nd}\) and lower \(^{87}\text{Sr}/^{86}\text{Sr}\) isotopic ratio compared to the majority of samples from Group II. These characteristic are similar to the ones observed to Pliocene-Pleistocene post-plateau basalts studied by Gorrings and Kay (2001). However, our data suggest that some of these basalts in Group II are generated from depleted mantle wedge with some influence of the subduction event when flat-subduction of Nazca plate might be temporally occurring under the South American plate during the Miocene. Our conclusions are very close to the one reached by Stern et al. (1990) who classified the basalts in “cratonic” and “transicional” observing a geographic distribution for them. However, our basalts from both groups resemble the “cratonic” basalts of Stern et al. (1990), and we address the difference from one to the other to different contribution proportion of fluids originated from the subducting slab. We do not observe samples with “transitional” characteristic or any geographic distribution for them.

Controls on weathering rates by reaction-induced hierarchical fracturing

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Weathering takes place through several stages that include mechanical disintegration of the rocks, and subsequent interactions between the exposed rock surface, the hydrosphere and the biosphere. Here we demonstrate how physical and chemical weathering processes are intimately coupled during weathering of basaltic intrusions (dolerites) in the Karoo Basin in South Africa. Incipient chemical weathering of the dolerites occurs around water-filled fractures originally produced by thermal contraction or by externally imposed stresses. This chemical weathering causes local expansion of the rock matrix, which generates elastic stresses. On mm to cm scales, these stresses lead to mechanical layer-by-layer spalling, producing the characteristic spheroidal weathering patterns. However, our field observations and computer simulations demonstrate that in confined environments, chemical weathering drives a much larger scale hierarchical fracturing process in which fresh dolerite undergoes a continuous domain division that effectively regenerates fresh surfaces in a self-accelerating manner. This process produces the characteristic weathering patterns seen in Karoo and a wide-range of other geological environments, and provides a first-order control on the total weathering rate.
The mechanism of oxidation and “leaching” of ilmenite during natural and experimental alteration

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Ilmenite (FeTiO$_3$) undergoes weathering through oxidation and removal of Fe to form an apparently continuous series of compositions from ilmenite to pseudorutile (ideally Fe$_2$Ti$_3$O$_9$), and with further weathering, to leucoxene (essentially rutile and/or anatase). We have carried out an experimental study of ilmenite alteration in autoclaves at 150°C in HCl solution, and studied the resulting products by X-ray diffraction, scanning and transmission electron microscopy, electron microprobe and Raman spectroscopy. In some experiments the solution was initially enriched in $^{18}$O and the distribution of the isotope in the alteration products mapped from the peak shift in the Raman spectra. The results indicate that the alteration proceeds in two distinct stages, each with a sharp interface between the parent phase and the product. The alteration begins at the original ilmenite crystal surface and along cracks through which the fluid can migrate. The first alteration product is pseudorutile - no phases intermediate between ilmenite and pseudorutile were detected. The textural relationship between ilmenite and pseudorutile suggests a coupled dissolution-reprecipitation mechanism rather than a solid state continuous oxidation and Fe diffusion mechanism. The second stage involves a further dissolution-reprecipitation step to form rutile. Raman spectroscopy shows that the $^{18}$O is incorporated in the rutile during the recrystallisation. Throughout the alteration process the original morphology of the ilmenite is preserved although the product is highly porous. The rutile inherits crystallographic information from the parent ilmenite, resulting in a triply-twinned rutile microstructure.

The role of crustal assimilation and fractional crystallization in the generation of a hybrid composite dikes suite in the Arabian-Nubian Shield, southwest Jordan

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A suite of hybrid composite dikes from the Arabian-Nubian Shield (ANS) in southwest Jordan is investigated. The petrogenesis of these dikes is discussed on the basis of field, petrographic, geochemical and Rb-Sr isotopic data. These dikes originated from the interaction between basaltic magma and the granitic basement. This interaction ranges from brecciation and partial assimilation of the host alkali feldspar granite to almost complete assimilation of the granitic material. Field structures range from intrusive breccia (i.e. angular granite fragments in a mafic groundmass) to hybrid composite dikes. The rims are mafic (basaltic andesite) in composition with alkali feldspar ovoids (up to 1 cm in diameter); while the central parts are of trachydacitic to dacitic in composition again with alkali feldspar ovoids and xenoliths of the dike rims.

A seven points Rb/Sr isochron from one the composite dikes yields an age of 560±7 Ma and an initial $^{87}$Sr/$^{86}$Sr ratio of 0.70332±0.00004 (2σ) and MSWD value of 0.59.

Geochemical modelling using major, trace elements and isotopes suggest the generation of the hybrid composite dikes through the assimilation of 30% granitic crustal material by the basaltic magma, while the latter was undergoing fractional crystallization deep in the continental crust.
Changes in the $\delta^{15}$N of nitrate in Greenland ice: Implications for source changes over the last 500 years

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Recent increases in atmospheric nitrogen oxides may have a profound effect on terrestrial and lacustrine ecosystems through increases in the deposition of nitrogen. These nitrogen oxides, emitted from both anthropogenic (e.g., fossil fuel combustion) and natural (e.g., biomass burning, lightning, and soil emissions) sources, also affect the lifetimes of greenhouse gases such as methane and carbon dioxide through atmospheric interactions with ozone and OH. Developing an understanding of natural variations in atmospheric nitrogen oxides over the Holocene will aid in the interpretation of long-term records of climate and ecosystem change. One possible source of such information is the record of nitric acid ($\text{HNO}_3$, or nitrate, $\text{NO}_3^-$), the primary sink of nitrogen oxides, obtained from ice cores in polar ice sheets.

We present isotopic measurements of nitrate ($^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$) deposited and preserved in ice at Summit, Greenland. Previous studies have suggested that the $\delta^{15}$N of nitrate in precipitation contains a source signal while the $\delta^{18}$O of nitrate contains information regarding chemical pathways of nitrate production prior to deposition. Our measurements from a 100-meter ice core, which contains approximately 300-500 years of climate information, show a large shift in $\delta^{15}$N between the top and bottom of the core. We discuss the possibility that this shift is indicative of changing sources of nitrogen oxides to the atmosphere over the industrial transition. This would imply that our ice record can be used to evaluate the contribution and extent of influence of pre-industrial sources of nitrogen oxides, providing an important constraint on the interpretation of other records of environmental change.

Trials into the effect of manganese oxide addition to composted municipal solid waste

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Procedure

Trials were carried out into the effects of amending the compost-like output (CLO) from the aerobic digestion of municipal solid waste with varying levels of waste manganese oxides. It was theorised that manganese oxide could affect humification of the decomposing CLO, with potential improvements in carbon storage in the material. Carbon emission data was recorded over the five week period of the study, and $E_4/ E_6$ ratios of a sodium pyrophosphate extraction were measured from CLO samples after five weeks of composting to assess levels of humic matter. Sand was included in the study as a control amendment with the manganese oxide, which was itself a granular material coated onto sand grains.

Results

A statistically significant effect was found between manganese oxide level and carbon flux rate, with flux rate increasing with increasing manganese oxide level. The effect was not significant between all levels however. The level of sand amendment included for comparison was found to be a significant factor only in one of the two trials carried out, where flux rate increased with sand addition. The $E_4/ E_6$ ratio for the CLO extractions were found to be unaffected by the addition of manganese oxide. The absorbancies at both wavelengths (465nm and 665nm) were found to increase significantly with increasing manganese oxide level.

Conclusions

The effect of the manganese oxide was found to have an effect on the rate of flux, although the confounding nature of environmental variations means that further work would be needed to quantify this effect with greater confidence. Attributing the increase in flux rate with manganese oxide to the physical or chemical properties of the amendment is difficult with the data collected to date.

The results from the absorbance analysis suggest that while the degree of humification of the humic matter was unchanged by the presence of manganese oxide, more humic matter in total seems to have been formed.
Deciphering the record of early life in Precambrian oceans using combined microscopy and microchemistry of organic-walled microfossils.

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Organic-walled microfossils (acritarchs) can be exquisitely preserved in fine-grained siliciclastics and chert through the Proterozoic and conceivably in the Archean. These fossils record crucial steps in the early evolution and diversification of complex ecosystems, and their morphology indicates the evolution of major biological innovations. However, the taxonomy of these fossils is often impossible to resolve beyond the level of domain.

Acritarchs are conventionally interpreted as algal cysts but most probably include a larger range of organisms such as prokaryotic sheaths, heterotrophic protists or even parts of multicellular beings. The organic remains can be studied in thin sections with optical microscopy and with Raman micro-spectroscopy to prove endogenicity. They can then be isolated from the rock by gentle acid maceration to be further studied by FTIR micro-spectroscopy, SEM and TEM microscopy to reveal morphological and ultrastructural details, and biopolymer composition, permitting in some cases to determine their biological affinities by comparison with extant clades. We present how combining microscopy (light microscopy, Scanning and Transmitted Electron Microscopy) with micro-spectroscopic analyses of individual Proterozoic microfossils (FTIR and Raman micro-spectroscopy) offers further insights into the paleobiology and evolution of early microorganisms in Precambrian oceans.

Such a multidisciplinary approach offers new possibilities to investigate the record of early life on Earth and beyond.

The most probable Earth composition

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Redox and isotopic criteria for Earth primitive materials clearly select a unique chondrite family, which, whatever its conditions of formation, can be modelled simply by a mixture in variable proportions of three mineral types: silicates (enstatite with minor amounts of oligoclase and free silica), metal (Si-bearing kamacite) and sulfides of Fe, Ca and Mg (evolving to metal, oxides and silicates with increasing temperature and decreasing fS2).

The modelling of a million such mixtures results in well defined elemental correlations, which can be used efficiently to test the obtained compositions versus high pressure mineralogy and seismological data. About a quarter of them have Fe contents compatible with the Earth’s Core/Mantle ratio and mantle range of densities. Their composition is perfectly compatible with the geophysical constraints in their present state of accuracy.

They predict Lower Mantle iron derives largely from the reaction:

\[
\text{SiO}_2 + 3\text{Fe} \rightarrow \text{FeSi} + 2\text{FeO}
\]

This results in a strong correlation between bulk mantle iron content and core silicon content (Si_n = 1.5 Fe_m - 5.9).

There is also a well marked anticorrelation between silica saturation and iron content of the lower mantle (Perovskite% = 100 (1.07-0.015Fe_m%)). That is, the denser it is , the softer it is.

Finally the Lower Mantle is strongly depleted in major radioactive elements (U~7ppb).

From the presently available experimental high pressure melting experiments a primitive pyrolitic upper mantle is obtained by an average 25-40% partial melting of the original solid silicate part.

Earth envelopes' compositions hence are as follows:

Primitive Upper mantle: pyrolitic

Lower Mantle: Mg_{0.8} Fe_{0.15} Al_{0.03} Ca_{0.03} Si_{0.07} Al_{0.03} O_3

Core: 85.3% Fe, 5.7% Ni, 6% Si, 3% O.
A multiproxy approach to constrain the origin of the natural fertilisation on the Kerguelen plateau

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The Kerguelen Ocean and Plateau compared Study (KEOPS) took place during the austral summer (19 Jan-13 Feb 2005, R/V “Marion-Dufresne”, 68°-78°E/ 49°-52°S sector). One of the KEOPS objectives was to determine the mechanisms responsible for the bloom occurring on the Kerguelen plateau and allocated to natural fertilisation due to island inputs.

Coupled with physical measurements, a multi-proxy investigation was carried out in order to better constrain the sources of iron, but also the water mass and particle pathways. REE concentration and Nd isotopes suggest that weathering of Heard Island brings significant amounts of iron to plateau waters (Zhang et al., in rev.), in agreement with radium isotopes (van Beek et al., in rev.) and consistent with total dissolved and particulate iron results. Th isotopes allow the quantification of particle settling velocities on and off the Kerguelen plateau and the identification of strong boundary scavenging along the south-east Kerguelen slope, likely due to the occurrence of nepheloid layers (Venchiarutti et al., subm.). Slow particle settling velocities are observed on the Kerguelen plateau, consistent with the high mineralization rates characterizing this area, deduced from the barite concentrations which were used as proxy for twilight zone mineralization of organic matter (Jacquet et al., in rev.).

This talk highlights the main results deduced from each proxy, underlining both coherences and contradictions. A synthetic and simplified scheme of the potential sources and sinks of iron over the plateau is finally discussed.

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Geochemical monitoring of CO\textsubscript{2} storage: Natural analogues studies using isotopic composition of gases and travertines

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Studies of natural analogues can be used to understand long-term processes affecting CO\textsubscript{2} in geological storage, because CO\textsubscript{2} can remain trapped for geologically significant times.

Noble gases are useful tools for tracing CO\textsubscript{2} and track its leakage toward surface. They also provide information about the origin of CO\textsubscript{2}; its migration, physical processes such as diffusion, solubilization in water and residence time.

We collected gas samples from natural CO\textsubscript{2} reservoirs and surface seeps in French carbo-gaseous province: Sainte Marguerite seeps (Allier, France), Montmiral natural CO\textsubscript{2} field (Drôme, France), and in the Colorado Plateau (Green River seeps (Utah), Springerville St Johns natural CO\textsubscript{2} field (Arizona)).

The preliminary results obtained provide strong evidence for a mantle-derived magmatic source for CO\textsubscript{2} in all sampled accumulations, and show various physical processes affecting CO\textsubscript{2} during its migration.

For example, natural CO\textsubscript{2}-degassing springs near Sainte Marguerite, Allier, France show evidence of Rayleigh fractionation on argon, neon isotopes and elementary ratio of atmospheric-derived noble gases. This distillation process highlights rapid migration of CO\textsubscript{2} toward surface, consistent with small accumulation of radiogenic/nucleogenic isotopes.

The Helium concentrations range between 0.28 and 8.22 ppmv, consistent with a magma degassing at depth. Such low concentrations imply that solubilization of CO\textsubscript{2} in water occurs at shallow depth, thus CO\textsubscript{2} migration mainly occurred in the gaseous state.

Active and fossil travertines were present in all sampled areas. They represent geological record of the movement and discharge of CO\textsubscript{2} and associated fluids to the Earth’s surface. They also provide information about the origin of CO\textsubscript{2} from which they precipitate. We present here our first petrographical observations as well as isotopic results for the travertines, including $\delta^{13}$C and $\delta^{18}$O. The samples from Green River have $\delta^{13}$C values typical of thermogene carbonates and presumably associated with deep magmatic degassing. On the contrary in Montmiral, the $\delta^{13}$C values are more typical of the meteogene travertines, associated with atmosphere-derived CO\textsubscript{2}.
Nitrate reduction, sulfate reduction and sedimentary iron-isotope evolution during the Cenomanian-Turonian Oceanic Anoxic Event (OAE2)

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Organic-carbon rich shales from localities in England, Italy and Morocco, which formed during the Cenomanian-Turonian Oceanic Anoxic Event (OAE), have been studied for their total organic carbon values (TOC) together with their carbon-, nitrogen- and iron-isotope ratios. Carbon-isotope stratigraphy ($\delta^{13}C_{\text{org}}$ and $\delta^{15}N_{\text{org}}$) allows accurate recognition of the strata that record the Oceanic Anoxic Event, in some cases allowing characterization of isotopic species before, during and after the OAE. Within the black shales formed during the OAE, relatively heavy nitrogen-isotope ratios, which correlate positively with TOC, suggest nitrate reduction, extant sulfur-isotope data and molecular fossils of green sulfur bacteria signify the development of free H2S in the water column by sulfate reduction. Black shales deposited before the onset of the OAE in Italy have unusually low bulk $\delta^{57}Fe$ values, unlike those found in the black shale (Livello Bonarelli) deposited during the Oceanic Anoxic Event itself: these latter conform to the Phanerozoic norm for organic-rich sediments. Pyrite formation in the pre-OAE black shales has apparently taken place via dissimilatory iron reduction (DIR), within the sediment, a suboxic process that causes an approximately -2 % fractionation between a lithogenic Fe(III)oxide source and Fe(II)aq. In contrast, bacterial sulfate reduction (BSR), at least partly in the water column, characterized the OAE itself and was accompanied by only minor iron-isotope fractionation. This change in the manner of pyrite formation is reflected in a decrease in the average pyrite framboid diameter from ~10 \(\mu\)m to ~6.5 \(\mu\)m. A gradual, albeit irregular increase in Fe-isotope values during the OAE, as recorded in the Italian section, may demonstrate limited isotopic evolution of the dissolved iron pool, consequent upon ongoing water-column precipitation of pyrite under euxinic conditions.

An important implication of the low $\delta^{57}Fe$ values measured in this study is that they decrease the gap between the lowest values observed for Phanerozoic sediments in which DIR is indicated to exert a strong control of isotopic fractionation and the very low Fe-isotopic compositions observed for Archaean rocks.

Speciation of arsenic in the coprecipitated As(V)-Fe(III) solids

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Lime neutralization and coprecipitation with ferric iron is the common method for the removal and immobilization of arsenic from industrial mineral processing effluents. The nature of the arsenate in the coprecipitated As$^{V}$-Fe$^{III}$ solids is not fully understood though it is generally believed that arsenate is adsorbed as surface complex on ferrihydrite. In this study we used infrared spectroscopy and X-ray diffraction to characterize the coprecipitates with an attempt to shed some more light on this issue.

A suit of As$^{V}$-Fe$^{III}$ coprecipitates were synthesized by neutralization of acidic solutions of various Fe/As molar ratios to pH 4-8 using both sodium hydroxide and slaked lime as base. The synthesized samples were subjected to powder X-ray diffraction and Fourier transformed infrared analyses. Lab synthesized scorodite, poorly crystalline ferric arsenate and 2-line ferrihydrite were used as reference materials. The speciation of arsenate was determined based on the As-O stretching vibration bands located at 650-950 cm$^{-1}$ and the characteristic XRD bands of poorly crystalline ferric arsenate and ferrihydrite.

Both infrared spectroscopic and X-ray diffraction data showed that poorly crystalline ferric arsenate is the dominant arsenate phase in the As$^{V}$-Fe$^{III}$ solids coprecipitated at pH 4 using NaOH as base. At pH 8 the arsenate is present basically as adsorbed surface complex in ferrihydrite. The results are similar to the arsenate-ferrihydrite adsorption system in which poorly crystalline ferric arsenate surface precipitate is formed at acidic pH while bidentate surface complex is the major arsenate species on the surface of ferrihydrite. Crystalline yukonite (Ca$_3$Fe$_2$(AsO$_4$)$_4$(OH)$\cdot$12H$_2$O) was generated in the coprecipitated solid when the CaO neutralized system was subjected to heat treatment at 75 °C.

References

Geochemistry and genetic models for tin deposits in South China

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South China is one of the most important tin producers in the world. Except for the classical granite-related magmatic-hydrothermal tin deposits, there are many other types of tin deposits in this region, such as sediment-hosted massive sulfide type and migmatitic hydrothermal-related tin deposits. In addition, A-type granite related tin deposits are also found in South China recently.

The Dachang tin deposit in Guangxi Province is the second largest tin producer in China. Although some researchers have suggested that this deposit is a skarn or replacement type associated with the Yanshanian magmatic hydrothermal event, our detailed geochemical investigation including major, trace, rare earth elements, Pb, S, Sr, Nd, B, H, O, He, and Ar isotopes have indicated a submarine exhalative-hydrothermal origin for the bedded and massive sulfide ores in the deposit.

The Yunlong tin deposit in Yunnan Province is a medium-sized tin deposit, which occurs mainly as cassiterite-quartz-tourmaline ore veins hosting in a suite of metamorphic rocks and migmatite. Previously many researchers considered this deposit as a typical granite-related tin deposit, with a blind granite body at depths or it is genetically related to a S-type granite body occurring just outside the deposit. Our recent fluid inclusions, geochemical and isotopic (H-O, S, Pb, B) studies in the deposit indicated that metamorphic hydrothermal fluids generated by dehydration of the regional Chongshan group rocks were possibly responsible for the formation of this tin deposit. Hence, we proposed that the Yunlong tin deposit belongs to a new type of tin mineralization, i.e., migmatitic-hydrothermal type.

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The Furong tin deposit in Hunan Province is a newly discovered large tin deposit. Tin mineralized bodies mainly occur as veins in the crush zone of the Qitianling granite that genetically related to chlorite alteration, although less important small greisen and skarn orebodies also occurred in the contact of granite with country rocks. Our study shows that the Qitianling granite is distinctly different from common S-type tin granite in the world but rather similar to A-type granite. Tin mineralization is suggested to be related to post-emplacement chloritization of the Qitianling granite. Sn-rich mafic minerals (amphibole, biotite and titanite) in the granite released tin and other metals (e.g. Ti) into the hydrothermal fluids when these minerals were altered to chlorite. Then cassiterite and rutile precipitated together when the physical and chemical condition of Sn- and Ti-rich fluids changed. It is a special model for granite-related tin mineralization.

Geochemistry of Late Mesozoic lamprophyre dikes from the eastern North China Craton: Implications for subcontinental lithosphere evolution

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Mineral chemical, element geochemical and Sr–Nd–Pb isotopic data have been determined for the late Mesozoic lamprophyre dikes from the Jiaodong and Liaodong Peninsulas. Together with the published data, three late Mesozoic lamprophyre belts in the northwestern Jiaodong Peninsula, also suggest that the Sulu lamprophyre belt (belt 1), Guojialing–Linglong lamprophyre belt (belt 2) and Dashiqiao–Laizhou lamprophyre belt (belt 3), respectively. These lamprophyre dikes are potassic and ultra-potassic rocks and have high MgO and compatible element contents. They are all enriched in LREE and LILE and depleted in HFSE. The belt 3 lamprophyre dikes have similar Sr–Nd–Pb isotopic compositions to the EM 2-type mantle. From the belt 3 through belt 2 to belt 1, the lamprophyre dikes show a trend towards the EM 1-type mantle in terms of Sr–Nd–Pb isotopic compositions. In addition, the Sr–Nd–Pb isotopic compositions of each lamprophyre belt show a trend towards those of MORB. Furthermore, the belt 1 lamprophyre dikes have super-chondritic Nb/Ta ratios (>17.5) whereas the belt 2 and belt 3 lamprophyre dikes show sub-chondritic Nb/Ta ratios (<17.5). All these features, together with comparison to the Late Triassic (201 Ma) Sulu mafic dikes that have similar Sr–Nd isotopic compositions to the EM 1-type mantle and also show super-chondritic Nb/Ta ratios, suggest that the eastern NCC lithospheric mantle near the Sulu Orogenic Belt was hybridized by the melt derived from the subducted Yangtze continental slab during the Triassic collision of the Yangtze Craton with NCC and then all the subcontinental lithosphere beneath the eastern NCC was metasomatized by slab-derived fluid during the late Mesozoic Palaeo-Pacific plate subduction. Detailed elemental and isotopic data, together with our recent studies on the origin of the late Jurassic (160–153 Ma) Linglong suite and Early Cretaceous (130–126 Ma) Guojialing suite in the northwestern Jiaodong Peninsula, also suggest that the Early Cretaceous lamprophyre dikes were derived from partial melting of the delaminated lithospheric mantle plus additional input from the upwelling asthenospheric mantle. Such a delamination is a consequence of the progressive slab roll-back associated with the subduction of the Palaeo-Pacific plate.

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Shallow crystallization and deep magma storage: Insights from U-Th and $^{40}$Ar/$^{39}$Ar geochronology

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Precise $^{40}$Ar/$^{39}$Ar age determinations and $^{238}$U/$^{230}$Th analyses from volcanoes atop vastly different thicknesses of crust in four subduction zones reveal new insights about the temporal and physical development of arc magmatic systems over several tens of thousands of years. Analytical advances yield $^{40}$Ar/$^{39}$Ar ages and U-Th mineral isochrons for latest Pleistocene to Holocene lavas and tephras with uncertainties of only a few thousand years. Thus, quantifying the length of time between crystallization and eruption has become more robust and crystallization-eruption intervals may be calculated over the lifetime of an individual volcano; this represents a significant advance in linking volcanic evolution to magmatic processes as compared to restricting U-Th geochronology to historical eruptions. Our most compelling discovery is that minerals (opx, cpx, mt, plag, ol), matrix glass, and whole rocks measured in dozens of basaltic to rhyolitic lava flows and pyroclastic deposits erupted over the last ~150 ka define $^{238}$U/$^{230}$Th isochrons whose age cannot be distinguished from that of the eruption. This finding indicates that the observed phenocrysts began to grow less than 1 to 2 ka prior to eruption and that processes including crystal fractionation and magma mixing—required to explain the spectrum of basaltic to rhyolitic compositions erupted at these volcanoes—took place prior to growth of the erupted crystals. The short crystal residence times are consistent with inferences from trace-element zoning and diffusion profiles in phenocrysts and $^{226}$Ra-$^{230}$Th disequilibrium data from recent eruptions at several volcanoes, each of which likely reflect exceptionally rapid transit of evolved melt through the crust, during which crystallization of the erupted phenocrysts occurs en route due to decompression.

The duration of magma storage and processing in the deep crust, although more difficult to constrain, can be tracked using initial ($^{238}$Th/$^{232}$Th) ratios in sequences of lavas and tephras erupted over $10^4$-$10^5$ year periods of volcano growth that have been precisely dated using $^{40}$Ar/$^{39}$Ar geochronology. Our large set of $^{238}$U/$^{230}$Th data suggests that the duration of deep crustal storage, differentiation and mixing of magma may vary greatly, ranging from a few thousand years to longer than 100 ka. In most cases, it appears that the deep crust buffers mafic magma flux from the mantle, which may explain our finding that long-term arc volcano growth rates are modulated to within a narrow range, despite gross differences in crustal thickness or age.

Oxygen isotope record of Devonian and Carboniferous biogenic apatite

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Oxygen isotope ratios of conodont apatite (n=1286) were studied in order to reconstruct the palaeotemperature and ice volume history during the Devonian and Carboniferous. Oxygen isotope ratios are around 18‰ V-SMOW in the Early Devonian, increase gradually during the Pragian and Emsian, show comparatively high values around 20‰ V-SMOW in the Middle Devonian, decrease during the early Frasnian to minimum values around 18‰ V-SMOW at the Frasnian-Famennian transition, and increase again to 19‰ V-SMOW in the Famennian. The Early Carboniferous record is characterized by a first major increase to values around 21‰ V-SMOW in the middle Touraisian to earliest Viséan, high values around 21‰ V-SMOW in the Viséan and a second major increase in the Serpukhovian to maximum values around 23‰ V-SMOW. Oxygen isotope values of Pennsylvanian and Early Permian conodont apatite vary between 19 and 22‰ V-SMOW.

The $\delta^{18}$O fluctuations recorded in the Devonian are interpreted as palaeotemperature changes with the Early and Late Devonian revealing relatively warm climatic conditions, whereas the Middle Devonian is characterized by a cooler climate. The positive shifts in the oxygen isotope ratios in the Touraisian and Serpukhovian are too large to be explained solely by a change in sea water temperature and/or salinity. Instead, the positive shifts in the oxygen isotope ratios in the Touraisian and Serpukhovian points to an intensified ice build-up during the latest Mississippian. The relatively large variance in the oxygen isotope ratios of Pennsylvanian conodonts is explained by the waxing and waning of Gondwanan ice sheets.

The comparison of the conodont apatite with published brachiopod calcite $\delta^{18}$O records (taking into account the different thermodynamic oxygen isotope fractionations for apatite and calcite) reveals that $\delta^{18}$O values of apatite are in many cases significantly higher than calcite $\delta^{18}$O values. Apatite $\delta^{18}$O values translate into realistic palaeotemperatures by assuming a modern $\delta^{18}$O value for Palaeozoic sea water and do not support the idea of a secular change of the oxygen isotope composition of sea water.
Reactive fluid flow in slabs –
A metamorphic view on the origin of the slab component

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Subduction zones are the places on Earth where quantitatively the largest mass transfer rates exist and element fractionation occurs between crust and mantle. The agents, which are central to these processes, are aqueous fluids, supercritical fluids, and melts. Field evidence found in formerly subducted rocks shows that the preferential flow field of released slab fluids is highly channelized and that these fluids tend to react with parts of their wall rocks. Thereby they are able to serve as agents for mobilization and transport for most trace elements. I will describe a model for fluid flow within slabs that suggests that slab melting must not necessarily be invoked for mobilization of so-called fluid-immobile trace elements. For this model it is critical that permeabilities in the subducting slab appear to be too low and dihedral angles between fluid and relevant minerals too high to allow for pervasive porous flow, hence the fluids tend to localize while flowing. I will outline how fluid channelization controls reaction rates and element redistributions during metamorphism of the subducting plate as well as trace element composition of subduction-related fluids during flow. Channelized fluid flow predicts that most formerly subducted material will show only very limited evidence for fluid flow, consistent with the rarity of observed high fluid fluxes in subduction-related rocks. Aqueous fluid produced by dehydration reactions will not percolate through large rock volumes, but rather will be carried away from the dehydration sites by a veining network. Indeed evidence for significant aqueous-fluid fluxes have been found in high-pressure veins with adjacent selvages. In such selvages, LILE’s generally show the highest mobilities, followed by light REE’s and then heavy REE’s and HFSE’s. Equilibrium between aqueous fluid and surrounding rock will only be approached at sites of fluid production and mineral reaction. However, this fluid can be significantly modified while moving upwards through a veining network where the wallrocks are out of equilibrium with the passing fluid. In a subducting slab, such reactive fluid flow can preferentially dissolve minerals and release their trace elements. The degree of change in aqueous fluid composition will depend on the fluid composition itself, the amount of fluid–mineral surface interaction and the ratio between the kinetics of the mineral reactions and the velocity of the passing fluid. In this talk I will focus on field evidence for reactive fluid flow in localized channel networks in high-pressure metamorphic terranes and its distinct chemical signature that is a direct counterpart to that in arc magmatism.

Interplay of deformation, fluid infiltration and eclogitization

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It is a common observation that during increasing metamorphic conditions dry coarse-grained rocks often fail to react because of sluggish mineral reactions. The crucial trigger mechanism to start the delayed metamorphic reactions is the infiltration of fluids. But how do fluids flow within dry rocks with very low permeability and how fast do the system react? The Kråkenes Gabbro is a partially deformed and transformed igneous body located in the Western Gneiss Region (Norway). The body is transected by a swarm of cm-wide hydrous eclogite-facies shear zones. The shear zones have cores of intensely deformed material surrounded by a dm-wide reaction halo where deformation is less obvious. The water-bearing minerals are highly concentrated in shear zones and their modal abundance progressively decreases with increasing distance to the deformation front. Fluid infiltration into the undeformed parts apparently occurred both along grain boundaries and through reactive minerals. Thereby, olivine appears to have been too reactive and thus shielded by corona formation, whereas clinopyroxene mainly reacted along its grain boundary and the magmatic plagioclase reacted to a micron-sized hydrous symplectite. It is interesting to note that these symplectites lack deformation features, indicating that they formed under static conditions. The subdomains can be regarded as tiny batch-experiments in which the fluid was rapidly supersaturated in the precipitating mineral phases, so that the replacement products inherited the chemical variations of the subdomains. In this manner magmatic zoning of plagioclase grains have been preserved. These findings imply that the kinetics of the reactions were faster than the fluid flow. From less transformed subdomains it is evident that element transfer was controlled by discrete transport pathways. At the terminations of such transport pathways the stable mineral assemblage precipitated. Real eclogite formed only if the element exchange between different subdomains was efficient, otherwise “metastable” phases formed. Obviously, the dynamic formation of porosity and permeability is crucial for the described observations, because it allows fluid access to the reaction interfaces and mass transfer even in undeformed parts. However, even though the suggested fluid pathways are wide, in cases up to several hundred microns, the final effective porosity is low. Thus, beside the deformation enhanced fluid infiltration along the shear zones effective porosities only exist while minerals react – then the newly formed mineral assemblage closes the pathways. Formation of porosities is either reaction enhanced along grain boundaries or occurs in form of porosity waves associated with mineral reactions through reactive domains.
Iron isotope compositions of 2.5 Ga banded iron formations (BIFs) from the Hamersley Basin and Transvaal Craton identify the iron sources and formation pathways during BIF genesis. $^{56}\text{Fe}$/$^{54}\text{Fe}$ ratios for magnetite reveal a strong inheritance from Fe(III) hydroxide precursors, with a peak about $\delta^{56}\text{Fe}=0$. Near-zero $\delta^{56}\text{Fe}$ values for the Fe(III) hydroxide precursors may be produced by complete or near-complete oxidation of Fe(II)$_{aq}$ derived from marine hydrothermal fluids, suggesting the existence of a significant oxidant in the upper water column at 2.5 Ga. Transformation of the Fe(III) hydroxide precursors to magnetite occurred through several diagenetic processes that produced a range of $\delta^{56}\text{Fe}$ values: 1) addition of marine hydrothermal Fe(II)$_{aq}$, 2) reduction by bacterial dissimilatory Fe(III) reduction (DIR), and 3) interaction with excess low-$\delta^{56}\text{Fe}$ Fe(II)$_{aq}$ that was produced by DIR.

The range in $\delta^{56}\text{Fe}$ values for siderite reflects a mixture of iron sources including seawater Fe(II)$_{aq}$ and Fe(II)$_{aq}$ produced by DIR. The inferred Fe sources and pathways for magnetite and siderite from adjacent bands, however, are distinct, and these minerals did not generally form in Fe isotope equilibrium. Instead, the Fe isotope variability of magnetite and siderite document fine-scale isotopic heterogeneity that reflects a strong component of diagenesis. Support for an important role of DIR in siderite formation in BIFs comes from previously published C isotope data on organic carbon and siderite, which may be explained as a mixture of C produced by bacterial and seawater sources.

Several factors likely contributed to the important role that DIR played in formation of the 2.5 Ga BIFs from the Hamersley Basin and Transvaal Craton, including high rates of ferric hydroxide formation in the upper water column, delivery of organic carbon related to photosynthesis, and low clastic input. We infer that DIR-driven Fe cycling was much more important during deposition of these BIFs than in modern marine systems. Low pyrite contents in oxide-facies BIFs suggest that bacterial sulfate reduction (BSR) was minor, and the absence of sulfide allowed preservation of magnetite and siderite; low BSR also provided a competitive advantage for DIR. When compared to BIFs that formed prior to 3.0 Ga, the Fe isotope signature for DIR is absent in the older sequences, suggesting that this metabolism may have been absent in the Early Archean. Moreover, the generally positive $\delta^{56}\text{Fe}$ values for the older BIFs suggest that oxidants were more limited, which in turn would limit DIR activity.

**Iron isotopes constrain the roles of biologic and abiologic processes in formation of banded iron formations**

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To investigate volatiles (H$_2$O, CO$_2$, S, Cl) and magma formation in subduction zones, we have analyzed olivine-hosted melt inclusions from 10 basaltic centers at varying distances from the trench in the Michoacan-Guanajuato Volcanic Field in central Mexico. Our data from these primitive basaltic cones (most contain Fo87-90 olivine) reveal the surprising result that H$_2$O contents are high (3.0-5.2 wt%) from the volcanic front to ~140 km behind the front. The high H$_2$O across the arc, combined with high S and Cl, suggest that flux of volatiles from the subducted plate has affected a broad region of the underlying mantle.

To understand the depths over which subducted slab components dehydrate beneath the arc, we have modeled the thermal structure of the mantle wedge and slab using a 2D numerical model (Manea et al., 2005). We then use phase equilibria to evaluate dehydration of subducted sediment, altered oceanic crust, and hydrated lithospheric mantle in the slab (Rupke et al., 2004). An important constraint is that volcanism has migrated towards the trench over the last 3 Ma, suggesting an increase in slab dip angle. Thus our studied cones farthest from the trench are older than those closer to the trench, and their volatile contents likely reflect mantle hydration resulting from a different slab geometry than the present-day configuration.

For the present-day slab model (13 Ma oceanic crust at trench), maximum mantle wedge temperatures beneath the volcanic front (1200-1300°C) agree with petrological calculations. The model results predict dehydration of subducted sediment and altered oceanic crust beneath the forearc, the volcanic front, and extending ~50 km behind the front. Subducted lithospheric mantle, if hydrated, would undergo dehydration beneath the arc ~50 km behind the volcanic front. In addition, chloride formed by hydration of the overlying mantle wedge would no longer be stable ~100 km behind the volcanic front. Thus the width and high magmatic H$_2$O in the Quaternary arc may be due partly to dehydration of subducted serpentinized mantle and the stability of chloride in the overlying mantle wedge.

For the present-day slab model, subducted sediment and oceanic crust dehydrate largely beneath the wide forearc during near-horizontal subduction. The main source of H$_2$O to flux the wedge beneath the volcanic front at 2-3 Ma comes from dehydration of serpentinized lithospheric mantle in the slab. Thus our results for both the present-day and 3 Ma slab configurations suggest a role for deserpentinization of the downgoing slab in magma generation beneath Mexico.

**Slab dehydration beneath central Mexico inferred from melt inclusions and geodynamic modeling**

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Springtime Deposition and Emission of Mercury from Arctic Snow

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Atmospheric mercury depletion events (MDEs) provide a pathway for gaseous elemental mercury (Hg0) to be rapidly oxidized to Hg2+ and deposited to terrestrial surfaces. MDEs occur between polar sunrise and spring melt in many high-latitude locations. Projected changes in the Earth’s climate this century will alter contaminant transport pathways (Macdonald, 2005) and may enhance Hg deposition and bioavailability in high latitude ecosystems (Lindberg, 2002).

We investigated net Hg deposition by MDEs to the Arctic cryosphere near Barrow, Alaska by (1) monitoring Hg concentrations in surface snow for 18 days, (2) quantifying emission of total gaseous mercury (TGM) from snow in flux chambers and (3) applying a newly developed analytical technique to measure Hg isotopic fractionation during (photo)chemical reactions. A nine-day MDE occurred during our intensive sampling campaign.

Daily monitoring of the upper 1 cm of the snowpack at two locations showed an increase in total Hg concentration throughout the MDE to maximum levels of 147 and 237 pg/g Hg. Twice-daily sampling at one site revealed a secondary trend of night-time Hg deposition. Mercury concentration in surface snow typically rose after exposure to darkness (~12 hours), while it remained unchanged or slightly decreased after exposure to daylight (~12 hours). Within two days of MDE cessation, Hg in surface snow returned to near-baseline levels and is probably the result of both Hg0 emission and physical mixing of the snowpack (high-Hg surface layer diluted by low-Hg snow column).

Flux chambers were employed to elucidate the rate and mechanism of TGM emission from natural snow. The TGM emission pattern was typical of light and/or temperature dependent reactions: emission peaked shortly after solar noon and ceased overnight. Peak TGM emission from MDE and non-MDE snow reached > 15 ng/m²/hr and ~8 ng/m²/hr, respectively. Blocking direct UV radiation decreased TGM emission by only 25%; UVB was not wholly responsible for this flux. Hg isotopic ratios of snow samples before and after flux chamber incubation are being measured to help identify an isotope signature of Hg (photo)chemical reduction.

References

Modeling glyphosate and metal-glyphosate speciation at solution-mineral interfaces

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Glyphosate (N-(phosphonomethyl)glycine, PMG, H₃L) is a widely used organophosphorous herbicide. It interacts with metal ions and mineral surfaces, which may affect its mobility, degradation and bioavailability in the environment. However, so far these interactions are far from fully understood.

This paper is a discussion on the complexation of PMG with metal ions in aqueous solution and the adsorption of PMG and Cd(II) on different mineral surfaces. EXAFS, ATR-FTIR, and XPS measurements showed that PMG adsorbs to the surfaces of goethite (α-FeOOH), aged γ-alumina (γ-Al₂O₃) and manganite (MnOOH) through one oxygen of its phosphonate group to singly-coordinated OH-surface sites.

The coadsorption of PMG and Cd(II) on the surfaces of goethite and manganite results in the formation of ternary mineral-PMG-Cd(II) surface complexes, as suggested from EXAFS results. In addition to the surface reactions in the binary Cd(II)-mineral and PMG-mineral systems, a single ternary complex with the stoichiometry ≡MeL₁Cd(OH)₁.₅ was sufficient to explain coadsorption data.

Surface complexation models consistent with the different spectroscopic results were fit to adsorption data using the 1pK reaction formalism involving charge distributions.
Sorption of arsenic under oxic and anoxic conditions: Possible origins of elevated arsenic in groundwater

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In Bangladesh and West Bengal, millions of people are using groundwater with elevated (> 50ppb) concentrations of arsenic. The origin of the elevated arsenic levels is still unclear. Both As(V) and As(III) are strongly sorbed to iron(III) (hydr)oxides. We have developed surface complexation models for sorption of As(III) and As(V) on goethite and ferrihydrite. These models predict that sorption should limit As concentrations to acceptable levels even when As(V) is reduced to As(III) and ferrihydrite transforms to goethite. One hypothesis for the elevated As concentrations is that sorbed As is released during bacterial reductive dissolution of Fe(III) (hydr)oxides. However, this should yield a strong correlation between dissolved Fe and As but this is not observed. The formation of secondary Fe(II) or mixed Fe(II)/Fe(III) minerals such as siderite (FeCO₃), green rust (GR) and magnetite has been suggested to reduce the aqueous concentration of Fe while leaving the concentration of As high in the Bangladesh and West Bengal aquifers. To test this hypothesis we have studied the adsorption of arsenite and arsenate to siderite, carbonate GR and magnetite as a function of pH using EXAFS and batch adsorption experiments.

EXAFS spectra show that As(V) sorbs to GR, magnetite and siderite by forming bridging bidentate inner-sphere surface complexes. The adsorption is similar to that of As(V) on Fe(III) (hydr)oxides and the adsorption decreases with increasing pH. No evidence of As(V) reduction is found. Hence, reduction of As(V) could release As(V) into solution but the formation of GR, magnetite or siderite would immediately re-adsorb the released As(V), keeping the aqueous As(V) concentration low. EXAFS spectra show that As(III) forms strong inner-sphere surface complexes on magnetite and GR, similar to that of As(V). No evidence of As(III) oxidation is found. On siderite, however, As(III) sorbs only by forming a weak outer-sphere complex and adsorbs much less strongly than to GR, magnetite or Fe(III) (hydr)oxides.

We propose that the elevated groundwater concentrations of As in West Bengal and Bangladesh result from the reduction of iron(III) (hydr)oxides to siderite in conjunction with the reduction of As(V) to As(III).

Magnesite dissolution in the presence of organic and inorganic ligands

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Quantitative and predictive modelling of CO₂ sequestration in deep aquifers requires precise knowledge of carbonate mineral reactivity at conditions pertinent to CO₂ storage. Whereas the effect of temperature, salinity, pH, and pCO₂ on Ca- and Mg-carbonate dissolution is extensively studied, the understanding of the influence of organic and inorganic ligands, omnipresent in deep sedimentary basins, remains very limited. Organic and inorganic molecules can exert various influences on the kinetics of growth and dissolution of crystals. The ligands can promote or inhibit growth and dissolution and can control crystal morphology.

Here, a combination of mixed-flow reactor experiments and in-situ hydrothermal atomic force microscopy experiments has been used to investigate the effect of organic (acetate, oxalate, citrate, succinate, EDTA) and inorganic (sulphate, phosphate, borate) ligands on the surface morphology of magnesium and on the molecular mechanism and kinetics of magnesite dissolution at different pH values and NaHCO₃ concentrations.

Since AFM enables to observe monolayer step motion on the surface as well as the step formation frequency by pit nucleation, the effect of ligands on the rate of detachment at specific surface sites can be determined. Thus, AFM data can be interpreted towards a determination of the consequences of adsorption at specific sites on the dissolution kinetics of magnesite in a molecular scale. Comparisons of these data with the dissolution rates of the (104) surfaces and with the dissolution rates of entire crystals (obtained by mixed-flow reactor experiments) allow one to link the molecular-scale effects to the macroscopic effects of ligands on magnesite dissolution.

At circum-neutral pH, the experiments showed a most pronounced effect in citrate- and EDTA-bearing solutions. For citrate, the modification of the reactivity of a distinct kink-site could be detected. More pronounced than the effect of organic ligands was the effect of 0.01 M NaHCO₃ (at pH around 8) which caused a general decrease in reactivity at far from equilibrium conditions. The ligands phosphate, oxalate, citrate, and EDTA were found to weaken but not to fully compensate the retardation of the reactivity generated by NaHCO₃.
Voltammetric determination of Te(IV) and Te(VI): Sorption behaviour on Fe and Mn oxides

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Sorption experiments by Koschinsky et al. (2004) had shown an extremely fast and effective enrichment of tetravalent tellurium (Te(IV)) on Mn and Fe oxides, but no comparable enrichment of the geochemically very similar Se(IV). This Te enrichment was related to a surface oxidation process of Te(IV) to Te(VI) on the Fe-Mn oxide surfaces, which apparently does not take place for Se(IV). In order to compare the behavior of tetravalent and hexavalent Te and Se species, which can both exist in natural waters, new sorption experiments were carried out with the hexavalent species of Te and Se.

Te(IV) was determined by differential pulse cathodic stripping voltammetry (DPCSV) using a 0.1 M HCl and 1 mg L−1 Cu2+ medium according to Ferri et al. (1998). As Te(VI) cannot be reduced electrochemically, a UV-reduction step was required after the sorption experiments and before the voltammetric analysis. For the UV-irradiation procedure, best results were obtained by using a 0.4 M HCl medium for 3 ½ h irradiation time at 90°C (Hg-high pressure lamp, 500 W).

The results of the sorption experiments indicate sorption of Te(VI) on all Mn and Fe oxides used in the experiment, however, the sorption rate was significantly lower than in the experiments with Te(IV). This supports our assumption that Te(IV) is preferentially removed from aqueous solution by Fe and Mn oxide phases compared to Te(VI) and compared to Se(IV) and Se(VI). Comparison of solid phase concentrations of Te and Se in marine oxides indicates that this different sorption behaviour leads to a significant fractionation of the two elements in the marine environment.

Reference


Trace element distributions in hydrothermal quartz: Fluid or structural control?

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Quartz is probably the most common hydrothermal vein mineral and its isotopic composition and the chemical composition of its included fluids are widely used for petrogenetic interpretations. In contrast, its own chemical composition is often close to being pure SiO2. A number of studies have, however, shown that some trace elements may enter its structure. While the factors governing such an incorporation are, as yet, not clearly understood, it is obvious that they can potentially be useful for petrogenetic interpretations.

A number of Alpine fissure quartz crystals having formed from chemically different fluids were analyzed for a range of possible trace elements (Li, Na, Mg, Al, P, K, Ca, Ti, Fe, Ge, and H) using different in situ methods (electron and ion microprobes, LA-ICP-MS, and FTIR spectroscopy) after cathodoluminescence (CL) analyses to determine the growth zones. CL bright zones were associated with high Al (up to 7000 ppm), Ge, and Li contents, these elements being strongly correlated, in particular within zones of discontinuous grown crystals. No correlation was found between Al and Na and K. The Al-Li-Ge correlation remains the same in quartz analyzed from different localities as well as along the same growth sector within any one crystal, suggesting that differences in the chemical composition of the fluids (also monitored through the oxygen isotope compositions of the quartz) do not control this correlation. However, the Li/Al ratio (i.e. compensating ion/ substituting ion) can be changed along a growth sector and within different crystals and it never appears to approach unity. While significant quantities of H (deduced from OH− absorption spectra) are also present within the quartz, with high amplitude IR-spectra corresponding to Al-Li rich zones, the H-content alone does not compensate for the charge difference between a Si4+ and (Al3+,Li+) coupled substitution. Also, while no significant differences in trace element content have been observed between the two rhombohedral faces (r and z, where z generally grows faster than r), the prismatic face (m) always has lower trace element content compared to r and z.

It can be concluded that the incorporation of trace elements into hydrothermal quartz is strongly influenced by the growth mechanism, structure, and probably by surface effects, but less so by the chemical composition of the fluid.
Considerations in dating impact craters using the $^{40}$Ar/$^{39}$Ar method: The problem of inherited $^{40}$Ar*

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A large number of impact structures on Earth remain to be dated accurately and precisely (e.g. http://www.unb.ca/pasc/ImpactDatabase/index.html) and [1]. A very versatile and powerful chronometer is the $^{40}$Ar/$^{39}$Ar method, because of its sensitivity to thermal input, the availability of internal reliability criteria such as age plateaux and/or isochrons, and the possibility to obtain compositional parameters (i.e., Ca/K, K/Cl and $^{40}$Ar*). Apart from alteration and/or metamorphic processes that can strongly bias the measurement of the age of a sample, accurate $^{40}$Ar/$^{39}$Ar age determinations are often challenged by the presence of inherited $^{40}$Ar* (i.e., Ar not completely degassed from the target rock during the impact) in the sample.

Here, through the study of 2 impact structures (Tswaing, South Africa and Jänisjärvi, Russia) and comparison with results from 4 other structures, we study the cause and consequence of the presence of inherited $^{40}$Ar*. For example, in the case of Tswaing impact glass particles, no ages approximating the previously accepted impact age of 250 ± 104 ka [2] could be obtained, whereas the Jänisjärvi impact melt rock yielded a statistically robust global isochron age of 682 ± 4 Ma.

The main characteristic controlling the apparent age bias (for a given proportion of inherited $^{40}$Ar*) is the age difference between the impact and the target rocks. The buffer effect for a given crater structure can be predicted knowing the age of the impacted basement and having a rough estimation of the age of the crater structure itself. The occurrence of $^{40}$Ar* inherited is likely influenced by (1) the degree of polymerization (i.e., silicate structure complexity) of the target rock and presumably related to the diffusivity of Ar in the melt/glass, (2) the Ar partial pressure at grain boundaries, (3) the quantity of energy involved in the impact, and (4) the porosity of the target rocks. In addition, the degree of polymerization will control the degree of homogenization of the melt and the rate of $^{40}$Ar* diffusion in the melt. Homogenization of the inherited $^{40}$Ar* ratio at the grain scale (i.e. 150-250 µm) facilitates accurate age determination through isochron analysis, although in completely melted rocks a homogenization of atomic scale environments for inherited and radiogenic Ar eliminates the possibility to resolve the two components thermally, i.e., by step-heating.

References
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Plagioclase lamellae in peridotite-hosted orthopyroxene

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The solubility of low-Ca orthopyroxene (opx) in calcic clinopyroxene (cpx) and vice versa is temperature dependent. During cooling, pyroxenes develop subparallel exsolution lamellae. Deviations from this canonical behaviour are very rare. Here we present results from porphyroclastic plagioclase lherzolites from the Ozren ultramafic massif (Dinaride orogenic belt) that contain plagiozise (plag), which seems to be texturally exsolved from opx.

Plag lamellae are parallel to cpx exsolution lamellae and occupy up to 10 vol-% of opx. Spacing is irregular between different porphyroclasts and within the single porphyroclast, but generally ranges between 30 and 500 μm. Some plag lamellae are interrupted by trace amounts of spinel, cpx or amphibole (very rare). In places, opx porphyroclasts are devoid of plag lamellae, but instead contain irregular plag blebs and trails. Opx have very well developed alumina concentration gradients around the Na-poor (An90) plag lamellae and blebs.

Opx-hosted plag exsolutions are very difficult to recognize, both in thin section and BSE images. They are easily overlooked and probably more widespread than commonly assumed. We have also observed them in harzburgite opx near a highly evolved gabbro dike (Central Indian Ridge). To our knowledge they have been described only in peridotites from the Ronda massif (Obata 1980). In contrast, cpx-hosted plag exsolution lamellae are apparently more widespread in peridotites (e.g. Rampone et al. 1993). Closed-pyroxene exsolution requires additional silica in form of Eskola component to produce plag (2CaAl2SiO6+2Ca0.5(-0.5)Fe0.5AlSi2O6). Plag residua is known from HP and UHP mafic rocks. However, Eskola pyroxene is not expected in silica undersaturated rocks. Alternatively, spinel exsolution from pyroxene could provide the Si to produce plag, but spinel contents are too low to balance all observed plag. A third possibility is that the peridotites were lithospheric and that heating was sufficiently fast to reach near-solidus conditions to allow for grain boundary melt migration without rehomogenizing exsolved pyroxenes.

References

Speciation and long-term sequestering of Zn in a naturally enriched soil

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Recent XAS investigations of Zn-impacted soils have identified Zn-phyllosilicates, Zn/Al-Layered Double Hydroxides, Zn sorbed on Mn and Fe oxides and Zn complexed to soil organic matter as the most probable chemical forms for anthropogenic Zn in soils (e.g. Kirpichtchikova et al., 2006 and reference therein). However, the long-term stability of these Zn species has been rarely investigated. This question, which is of primary importance to assess the fate of anthropogenic Zn, can be partly addressed by studying the chemical forms of Zn occurring in naturally Zn-enriched soils overlying geochemical anomalies. Such approach has already allowed us to identify chemical forms of lead and arsenic able to resist to long-term weathering (Morin et al., 2001; 2002).

In the present study, the selected soil has developed upon sulfides mineralized sandstone (Ardeche, France) and exhibit Zn concentrations (up to 500 mg/kg) similar to those found in impacted soils. Molecular-level information gained by EXAFS indicate the occurrence of two main Zn species [Zn-bearing clay minerals and Zn-sorbed Fe oxides], with varying proportions as a function of depth. In the topsoil (A0- and Bs-horizons), about 50 % of Zn is hosted by the clay minerals, whereas this proportion decreases to less than 10 % at depth (C-horizon) where no clay minerals could be detected by XRD. These results suggest that Zn-sorption onto Fe oxides represents the first-stage of weathering of the ZnS-mineralized sandstone (C-horizon). After longer weathering (A0- and Bs-horizons), Zn is progressively incorporated in neoformed clay minerals which likely represent long-term hosts for this element in soils.

References
Trace element SIMS investigation of multistage garnet – Constraints on partial melting processes in crustal rocks

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The basement dominated granulite-facies part of the central Damara orogen (Namibia) hosts abundant migmatites that originated by partial melting of metapelitic or, less abundant, meta-igneous sources. A migmatitic orthogneiss shows the growth of garnet within the host gneiss (A), the leucosomes (B) and cross-cutting granite dykes (C). Based on microstructural features and microprobe data, garnet A is considered to be metamorphic and garnet B and C are considered to be anatectic and igneous, resp. Rb/Sr and Sm/Nd whole rock isotope data confirm the suggestion that the gneiss belongs to the Pre-Damara basement. Sr isotope data are heterogeneous but assigning an age of 550 Ma for the gneiss, 500 Ma for the leucosomes and 493 Ma for the dykes results in similar initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ca. 0.730. These results suggest high-grade metamorphic conditions at ca. 550 Ma, followed by in-situ partial melting at ca. 500 Ma and intrusion of granitic dykes at ca. 493 Ma. All garnets have a $10^5$-$10^6$ CI-normalized range in REE abundances and steep LREE-depleted and HREE-enriched element patterns. Garnet from A, B, and C are zoned in Y, HREE, Sr and Ti in which garnet A shows a small core with HREE, Y, Sr and Ti enrichment and a broad rim with trace element depletion. Garnet B has a core enriched in Yb+Y but depleted in Er and Dy and an outermost rim even more depleted in these elements. Garnet C has a broad core with enrichment in Yb+Y and depletion in Er and Dy. The rim is enriched in HREE+Y. LREE (Sm, Nd) profiles are similar to HREE profiles for garnet B and C but garnet A shows the opposite of HREE zoning with a LREE-depleted core and a LREE-enriched rim. These features indicate that HREE fractionation of garnet A follows a Rayleigh fractionation scheme but Nd and Sm concentration profiles are modified by volume diffusion at high temperatures. Garnet B shows evidence for a two-step growth history (melt absent vs. melt-present?) evidenced by the marked hump between core and rim. The trace element pattern of garnet C can be explained by a combination of a Rayleigh fractionation process and a liquid diffusion controlled process. The data show that trace elements may potentially be more sensitive to chemical changes in rocks than major elements in which an accurate interpretation leads to an improved understanding of p-T paths of metamorphism and melting.

High-precision Lu-Hf garnet ages from granulite-facies migmatites (Damara orogen, Namibia)

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The basement dominated granulite-facies part of the central Damara orogen (Namibia) hosts abundant migmatites formed by partial melting of metapelitic sources during intrusion of hot granitic melts. Centimeter-sized garnet is a common product of incongruent melting reactions and has been dated with the Sm-Nd and U-Pb methods. In addition, the U-Pb ages of matrix monazite have also been determined for the majority of the samples. In general, Sm-Nd garnet whole rock ages are precise (better than 1%) and agree with the Pb-Pb ages of the garnets, although the latter are relatively imprecise (2-8%) due to low $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Collectively, the Pb-Pb garnet data define an age of 540±40 Ma, whereas the Sm-Nd garnet-whole rock ages range from 530±3 Ma to 506±2 Ma. These age estimates agree with previous Sm-Nd grt-WR ages and U-Pb monazite ages from elsewhere in the orogen and are interpreted to constrain the time span of high-grade metamorphism and melting. To better resolve the relationship between high grade metamorphism and melting and garnet growth, and to improve upon the precisions of the Sm-Nd and Pb-Pb age determinations, garnets were dated with the Lu-Hf technique. All garnets display similar Lu-Hf isotope systematics, with high Lu (16-40 ppm) and high Hf (0.9-1.5 ppm) contents, moderately high $^{176}\text{Lu}/^{177}\text{Hf}$ ratios (1.7-7.3), and radiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ ratios (0.30059-0.35467). Due to these characteristics, the internal isochron ages are precise (0.2-1.0%), and range from 531±1 Ma to 514±5 Ma. For all samples, the Lu-Hf grt-WR ages are similar to—or lower than—the U-Pb monazite ages and are also similar to (with one exception) the Sm-Nd grt-WR ages from the same sample. The similarity among Lu-Hf and Sm-Nd grt-WR ages, Pb-Pb garnet ages, and U-Pb monazite ages imply relatively fast cooling rates immediately after the peak of regional metamorphism, which was probably related to fast uplift of the basement-dominated part of the orogen.
Geochemical and isotope geochemical investigations on Palaeozoic sedimentary rocks

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Palaeozoic natural gas reservoirs in the Central European Basin (CEB) regionally contain high percentages of molecular nitrogen (N2). The highest nitrogen contents are found within Rotliegend reservoirs of the North East German Basin (NEGB) where thick, highly mature Palaeozoic sedimentary sequences are present.

The release of molecular nitrogen from coals and sedimentary rocks with low contents of dispersed organic matter was investigated by means of non-isothermal open system pyrolysis, elemental analysis and stable isotope mass spectrometry. The principal goal was to explore the contents, isotopic composition (δ15N) and the speciation of nitrogen in organic and inorganic constituents of these sequences.

Total nitrogen contents of Namurian shales from four deep wells (4400 - 7000 m) in NE Germany ranged from ~500 to ~2700 ppm. Between 50 and 100 % of this nitrogen is inorganic and fixed as ammonium. Although there is a clear facies trend from marine sediments in the lower part to paralic and terrestrial sediments in the upper part of the Carboniferous sequence, the corresponding δ15Nfix values are within a narrow range (+1 to +3.5‰) along the entire profile while the isotopic composition of the thermally liberated nitrogen was consistently lighter (by 3-5‰). Low nitrogen contents (as low as 460 ppm) and high δ15N values (up to +5.6‰) in one well in the basin centre suggest a significant release of nitrogen (as NH3 and/or N2) associated with 15N enrichment in the residual nitrogen.

Open-system non-isothermal pyrolysis has revealed the presence of inorganic nitrogen species with relatively low thermal stability in marine Namurian A shales. Inorganic nitrogen components in the paralic Namurian B facies show a higher thermal stability range while nitrogen in kerogen and coals is fixed in very refractory compounds decomposing in the 700 – 1200°C temperature range. The presence of significant amounts of inorganic nitrogen is also reflected in the high N/Corg (atomic) ratios (up to 0.108) of the Palaeozoic shales. Thus the on-line isotope analysis indicates the presence of precursor pools with different thermal stability and nitrogen isotopic composition.

The combination of laboratory data, field data and numerical simulations is expected to further constrain the time, temperature and fluid flow conditions and result in an improved understanding of this complex issue.

Pit lakes in Kemerovo region, Russia: Geochemical composition and ecological risk

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The open pit mining and processing of polymetallic ores in XVIII-XX centuries resulted in rise of pits with high-sulfides wastes in all over the world and Russia particularly. The pit lakes arise after pits flooding with atmospheric and underground water and are characterized by low pH, high metal and SO42- concentrations. Unfortunately investigations on pit lakes composition, development and transformation haven’t been carried out adequately in our country. The several pit lakes situated in the Salair ore field (Kemerovo region) are examined in this paper.

Results of the field researches in 2005-2006 and following analytical works allowed to ascertain the composition of water and bottom sediments in pit lakes situated in three ore deposits: Aleksandrovskoe, II Mine, III Mine. Slow interaction between water and oxidized ore bodies in the pit walls resulted in formation of acid solutions (pH=3-5) with high mineralization (5-8 g/l) and metals (Fe-up to 350 mg/l, Zn - to 100 mg/l, Cu, Cd and Pb - to 10 mg/l) and metalloids (concentration of arsenic is up to 0.3 mg/l). The concentrations of concerned elements considerably exceed the background and maximum allowable values with the greatest portion of Cu, Zn, Cd species is most toxic free ion.

The geochemical anomalies of various elements (Ti, Mn, V, Cu, Zn, Cd, Pb, As, Sb, Ag, Te) appear in the pit lake bottom sediments which are mainly in very soluble forms and of high mobility.

The data obtained point out not only an ecological risk but also indicate it is possible to extract the ore elements from these objects for the second time. But currently superficial lakes with transparent water and bottom sediments lacking in vegetation are very popular pleasure resorts for Salair’s natives. The detailed research of circulation of toxic elements will be conducted in the system «pit wall – bottom sediments – water – biota» which is essential to forecast the subsequent changes in pit lakes and find the methods of improvement of these objects.
Magmatic transport of nitrogen, hydrogen and carbon constituents from reduced planetary interiors

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In theories of the Earth’s formation, the composition of gases extracted by primary planetary magmas is accounted for the large-scale melting of the early mantle in the presence of the metallic Fe phase. The melting should have been accompanied by the formation of volatile compounds, which composition was controlled by the interaction of N, H and C with silicate and metallic melts.

In a series of experiments in the system Fe-bearing melt + molten Fe rich metallic phase (0.1-12 % Si + H2 carried out at 4 GPa and 1520-1600°C and log fO2 (oxygen fugacity) = -5 below 1W, we have characterised the nature (oxidised versus reduced) and quantified the abundance of C, H and N-compound dissolved in an iron bearing silicate melt. The speciation of components dissolved in the glass has been determined by Infrared and Raman spectroscopy.

The solubility of Si in liquid metal increases with decreasing fO2 from 0.1-0.55 wt % at ΔlogfO2(IW)= -2-3 to 10-12 wt % at ΔlogfO2(IW)= -4-5. Carbon content in iron-rich globules to be fixed between 3 and 6 wt %. The amount of H (as H2O, OH, H2, CH4) and C (as CO2, CO3, CH4, Si-C) dissolved in the glasses was measured by ion microprobe and by CNH analysis. Hydrogen content decreases with decreasing fO2 from 0.3-0.4 wt % at ΔlogfO2(IW)= -2-3 to 0.1-0.2 wt % at ΔlogfO2(IW)= -4-5 as a result of decreasing of H2O in melt. Carbon content increases with decreasing fO2 from 0.2-0.5 wt % at ΔlogfO2(IW)= -2-3 to 1-2 wt % at ΔlogfO2(IW)= -4-5 as a result of increasing of CH4. The nitrogen solubility (as N2, N+) reaches 2-3 wt % at ΔlogfO2(IW)= -2-4.)

In the light of experimental data we argue that magma in reduced environment in area of the Fe-Si alloy stability could form melts containing dissolved both oxidized, and reduced components of hydrogen and carbon species. We assume that core growth took place under reduced conditions imposed by the pristines terrestrial materials and was accompanied by the emission of CH4, H2, N2 and NH3 and minor H2O into the atmosphere.

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Colloid formation in aerated Fe(II) containing water: Effect of phosphate, silicate and Ca on morphology and structure

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The biogeochemical cycling of nutrients and pollutants is strongly influence by the formation and presence of colloids. In this study we focused on the microscopic analysis of colloids formed due to iron oxidation and hydrolysis in synthetic carbonate-buffered groundwater (pH 7, 2-30 mg/L Fe(II)). We investigated the influence of phosphate (2-20 mg/L P), silicate (2-20 mg/L Si), and Ca (2.5 mM Ca- or 8 mM Na-bicarbonate) on colloid formation. The morphology, chemistry and crystallography of the colloids were characterized using HR-TEM (high resolution transmission electron microscopy), TEM-EDX (energy dispersive x-ray analysis) and SAED (selected area electron diffraction).

When Fe(II) is added to a Na-bicarbonate-buffered water, idiomorphic lepidocrocite (Lp) crystallizes, as confirmed by SAED. Individual sheet-like crystals are between 100 - 200 nm long and a few nm thick. These crystals agglomerate to ‘spherical’ entities with a diameter of up to 500 nm. Several of these ‘spherical’ entities aggregate again to fractal-like aggregates.

At high Si/Fe ratio, the crystallization of Lp is suppressed and ferrihydrite (Fh) forms instead. The Fh crystals are platelets of ~5 nm showing lattice fringes in HR-TEM images. The individual Fh agglomerate to spheres of ~200 nm and form fractal-like aggregates. SAED images of aggregates show two distinct rings at distances of 0.15 and 0.25 nm, indicative of 2-line Fh.

At high P/Fe ratios, a Fe-phosphate (Fe-P) forms. The Fe-P appears as spherical particles of ~100 nm in diameter, but no primary crystals can be observed. However in the SAED pattern, a faint ring at a distance of ~0.29 nm is observed, in agreement with XRD patterns from amorphous Fe-P references.

At lower Si/Fe or P/Fe ratios, depletion of Si or P due to precipitation of Fh or Fe-P results in the subsequent formation of Lp. The presence of Ca in solutions containing Si and P enhances Fe(III)-colloid coagulation due to a reduction of the electrostatic repulsion. Based on our microscopic investigations, it is not clear, yet, whether Ca is also directly incorporated into the colloid structures.

Despite the varying chemistry, the morphologies of all colloids are very similar. The formation can be described with the following three steps: 1. rapid formation of primary particles (Fh, Lp, Fe-P), 2. formation of ‘spherical’ entities and 3. agglomeration to fractal-like aggregates.

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Melt-rock reaction and late-stage melting in peridotite xenoliths from Marsabit (Kenya)

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Mantle metasomatism is widespread in mantle rock suites worldwide, highlighting the importance of melt- and fluid-rock reaction in the Earth’s upper mantle. Styles of metasomatism can be very complex and include a wide variety of mineralogical and geochemical signatures, reflecting both, the nature of the initial metasomatising agent (carbonate or silicate systems, melt or fluid) and its evolution through reaction with the pre-existing mantle rock. Here, we present a study on variably metasomatised peridotite mantle xenoliths (from Marsabit, Kenya) that aims to constrain either of the above parameters by integrating results from textural and in-situ (LA-ICPMS, SIMS) geochemical analysis.

The investigated xenoliths are cpx-bearing cryptically metasomatised harzburgite (LREE, Li, B, U, and Th enrichment of cpx) and modally metasomatised cpx-free harzburgite and dunite. Metasomatic phases include amphibole, plagioclase, apatite, graphite and opx. Transitional samples show that metasomatism led to replacement of cpx by amphibole. Further, in all modally metasomatised xenoliths melt pockets (silicate glass containing silicate and oxide microlites and carbonates) occur in close textural relationship with the earlier metasomatic phases. Textural, major and trace element compositions and results from thermobarometry and fO2 calculations indicate that the mineralogy and compositions reflect complex interplay between melt-rock reaction processes, trace element fractionation, pre-existing mantle heterogeneity and effects of changing P, T and fO2 during one single metasomatising event. The metasomatising agent was a SiO2-Na2O-CO2-H2O-rich liquid (possibly a fluid). The unusual style of metasomatism (composition of amphibole, presence of graphite, formation of opx) reflects low P-T conditions (ca. 750-850°C at <1.5 GPa) in the wall rock during impregnation and locally low fO2. The latter allowed the precipitation of graphite from CO2. The Si-rich fluid possibly derived from alkaline basic melts by melt-rock reaction during Tertiary-Quaternary magmatism. Melt pockets formed during late melting of the earlier phases (mainly amphibole) shortly before or during xenolith transport in the host magma and was triggered by CO2-rich fluid infiltration.

Uraniferous carbonate rocks from Mt. Kithaeron, central Greece

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The average abundance of U in carbonate sedimentary rocks is 2.2 ppm. Sandstones and shales contain 0.5 ppm and 3.5 ppm respectively while the typical U concentration in seawater is 3.2 ppb (Krauskopf and Bird 1994). Uranium in the oceans follows anoxic pathways and it is mainly removed from the water due to chemical processes taking place at the interface of organic-rich sediments. Uranium is therefore correlated to organic carbon whereas the diagenetic cycle of the element may include reduction of U(VI) to U(IV) related to sulfate bio-reduction (Mo et al. 1973, Klinkhammer and Palmer 1991). The concentration of U in marine carbonates from SE Europe and the eastern Mediterranean is reported to be in the region ca. 1 – 7 ppm. Here we present the occurrence of carbonate rocks, limestones and dolomitic limestones with variable organic content, from Mt. Kithaeron (central Greece) containing unusually elevated U concentrations up to ca. 56 ppm. We also present a relationship between the U content and radioactivity (see Figure below).

They are typical Alpine (Neotethyan) sediments, of likely Triassic age (according to existing paleontological data) belonging to the SubPelagonian zone of the internal Hellenides. The rocks were investigated using a combination of microscopic, spectroscopic and wet-chemical techniques. Our study revealed that U is probably associated to the non-carbonate part of the rocks (organic matter, Fe- and Mn-oxides, phosphates, etc.).

References

The 1991 - 1993 eruption of Mt. Etna: Timescales and nature of magma recharge and mixing

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We have quantified the timescales of magma mixing and residence before eruption by modelling compositional gradients of multiple elements (Fe, Mg, Mn, Ca) in several olivine crystals from the different lava flows that erupted during December 1991, January 1992 and March 1992 at Mt. Etna. Three different olivine populations were identified based on core crystal compositions (Fo70, Fo78, Fo80-82) and these are interpreted as open system involving mixing between three different components (magmas or crystal sources). The difference in core compositions contrasts with the common composition of most rims at Fo70-72 indicating that all crystals share their late magmatic histories. The zoning patterns of these olivine types are: (i) a dominant population of reversely zoned or unzoned crystals with cores at Fo70 and rims at Fo72-74, (ii) a less abundant, normally zoned crystal population with cores at Fo80-82 and rims Fo72-74 (occasionally Fo78), (iii) a subordinate population with crystal cores at Fo75-78, an intermediate zone of Fo80, and rims at Fo74. These types of zoning indicate two distinct mixing events. An early episode between the two high Fo magmas (e.g., cores at Fo78 and Fo80-82) followed by the remixing of this with a more differentiated magma with Fo70 crystals. The results of modelling the chemical gradients indicate that the early mixing event occurred about 100 - 200 days prior to eruption. Crystals showing evidence of this older mixing event are mainly represented in the December 1991 rocks and their proportions decrease in the latter eruptions. In contrast, the times since the last mixing episode with the more differentiated magma are present in all studied rocks, and are in general shorter. They increase from a few days or weeks for the December 1991 products to a few months for the March 1992 deposits. This sequence of events and time scales may be explained by arrival of an already mixed magma to a shallower reservoir containing the differentiated magma. The observation that the times since this last mixing event increase with eruption sequence indicates ageing of the crystals in this shallow reservoir which was simply being emptied after an initial recharge of mixed, mafic melt that may have triggered the eruption. This single recharge was apparently sufficient to sustain the eruptive activity during the December 1991 to March 1992 eruptions.

Aerobic and anaerobic microbial ecosystem recorded in the Steep Rock Group, Ontario, Canada

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The Steep Rock Group is mainly composed of ca. 3.0 Ga submarine volcanic and sedimentary rocks. Thick carbonate unite, containing stromatolite, is the well-known characteristic of this group. The stromatolite is overlain by other carbonate, black cherts, black shales and carbonaceous massive sulfides, although most outcrops were mined out.

Carbon isotope compositions of kerogen in the examined samples range from -37 to -23 ‰. The heaviest carbon isotope composition is found in the stromatolite sample. SEM observation indicate that kerogen in stromatolite samples often contain micro-crystals of Mn and Fe oxides. Such Mn and Fe oxides were most likely formed during diagenesis using dissolved oxygen in shallow water and have distinct characteristics compared to the secondary Mn and Fe oxides formed by Phanerozoic weathering. These mineral and isotopic characteristics suggest the aerobic microbial activities during the formation of stromatolite. The lightest carbon isotope composition was found in black shale samples, suggesting the activity of methanotrophs during the black shale sedimentation.

Micro-scale sulfur isotope compositions of pyrite were also determined by the laser microprobe system. Sulfur isotope compositions of pyrite in black shales and massive sulfides range from -8 to -5 ‰. Such isotope compositions, small range and pyrite texture suggest that microbial sulfate reduction in stratified ocean water followed by syngenetic pyrite precipitation from deep euxinic ocean water. Those all data indicate that variety of microbial ecosystem, corresponded to the paleo-water depth, existed in the 3.0 Ga Steep Rock oceans.
Li, Be, B and $\delta^{11}$B values from the peralkaline Ilimaussaq intrusion and its country rocks (South Greenland)

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The Ilimaussaq intrusion is characterized by four progressively more fractionated magmatic pulses: (1) augite syenite, (2) peralkaline granite and (3+4) agpaitic nepheline syenites. The peralkaline granite is interpreted as a contaminated equivalent of the augite syenite. Evidence for late-stage hydrothermal activity is present as veins penetrating all units. The intrusion is partly hosted by supracrustals, partly by the Proterozoic Julianehåb granite.

Li, Be and B contents, as well as $\delta^{11}$B ratios have been measured with SIMS (secondary ion mass spectrometry) in all important primary and secondary minerals from the different rock types of the Ilimaussaq intrusion and the Julianehåb granite to understand the behaviour of the light elements during differentiation of an alkaline magmatic system. The main Li carrier in the system is Na-rich amphibole, with a maximum Li content of 6000 µg/g in the foyaites and naujaites, but with only 50 µg/g in the early Ca-rich amphiboles of the augite syenites. The highest Be contents occur in late-stage hydrothermal aenigmatite (500 µg/g), followed by nepheline (16-100 µg/g) and sodalite (15-60 µg/g). The main B carrier of the rocks is sodalite with maximum contents of 120 µg/g. $\delta^{11}$B measured in most amphiboles is about –20 ‰ and displays closed-system behaviour in the inner part of the Ilimaussaq intrusive rocks, but rises in the augite syenites from –20 to –7 ‰ towards the contact with the Julianehåb granite. The highest Be contents occur in late-stage hydrothermal aenigmatite (500 µg/g), followed by nepheline (16-100 µg/g) and sodalite (15-60 µg/g). The main B carrier of the rocks is sodalite with maximum contents of 120 µg/g.

Melt inclusions from the Barberton Greenstone Belt, South Africa

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Melt inclusions from komatiites in Archean Greenstone Belts can increase our understanding of the origin of ultramafic magmas. However, the question of whether old inclusions preserve original magmatic compositions has to be answered first. To address this problem, we have studied melt inclusions from the southwestern part of the Barberton Greenstone Belt with visual heating experiments. Our sample is a partially serpenetised olivine cumulate with olivine relics of Fo93-94 composition.

Unheated inclusions show a variety of petrographic textures. Inclusions range from mostly glassy to crystalline. The morphology of the inclusion edges varies from smooth edges to many irregular protrusions at the edges. The origin of these different morphologies is not yet fully understood.

Inclusions that were visually inspected during heating behave similarly. Melting starts at 800-900°C. A vapour bubble forms and gets smaller with increasing heating indicating that the system is closed. At a peak experimental temperature of 1360°C a small bubble is still present, and the melt is in the olivine-only field. Inclusions were not heated to a higher temperature to avoid H2 loss during experiments. After initial experiments, subsequent inclusions were quickly heated to a temperature of 1360°C, held for 30s and quenched to try to preserve olivine rim compositions and volatile contents. The relative proportions of the bubble and inclusions sizes are approximately constant, except for a few selected altered looking inclusions where a large expanded bubble is observed.

FeO content of reheated inclusions shows a negative correlation with Fo-content of host olivine, which is indicative of re-equilibration during cooling (Danyushevsky et al., 2000). Major element compositions of inclusions have been recalculated to correct for Fe-loss. Inclusions larger than 35 microns and with ‘normal’ bubble sizes show coherent major element trends. Smaller inclusions have lower MgO outside the main trend, probably caused by poor quenching.

Compositional profiles have been analysed across the olivine rims around several inclusions in order to constrain the cooling history of the individual olivine grains (Danyushevsky et al., 2002).

We will present major, trace and volatile (H2O, Cl, S) contents of the melt inclusions and their host olivine phenocrysts and use them to estimate the composition and temperature of the parental melt and the conditions of its evolution.

References

Cell enumeration in extremely nutrient-poor sediments

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This expedition explored extraordinarily slowly accumulated sediments of the South Pacific mid-ocean gyre, farther from continents and productive oceanic zones than any other site on Earth. It provided an opportunity to study the nature of life in the most oxidized and food-limited sediments of Earth’s ocean. These sediments are relatively rich in cosmic debris and a direct terrestrial analogue for slowly accumulating energy-poor sedimentary environments on other planetary bodies (e.g. wet subsurface sediments of Mars).

So far most cell enumerations have been carried out in shelf sediments which contain variable but significant amounts of organic matter. Such sediments usually have cell abundances that range from 10^6 to 10^10 cells cm^-3 at the surface and decrease with depth to about 10^5 cm^-3 around 100 to 1000 mbsf. The sediments retrieved during this cruise have much less organic matter and also lower cell numbers. Due to the low cell abundances, ranging from 10^6 cm^-3 at the surface to 10^3 cm^-3 at 10 mbsf, it is necessary to extract the cells from the sediment and concentrate them prior to counting, using novel technique (KALLMEYER, subm.). The sediment is treated with a mixture of different detergents, solvents and complexing agents, followed by separating the cells from the sediment particles by density centrifugation. The cell extracts are then filtered and stained with SYBR Green I®, a highly dsDNA specific stain.

The cell counts show that there is a microbial community in these sediments despite the fact that there is basically no organic matter available. The cell abundances are the lowest ever encountered in the marine environment. These very low cell counts imply that current estimates of subsaeal floor biomass are far too high, because the abundance of cells in this extensive habitat is approximately three orders of magnitude lower than current estimates of average cell concentrations in subsaeal floor sediments.

Establishing high precision trace element maps of the main dust source areas of eastern and south-central Australia

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Continental-scale geochemical mapping relies on precise and accurate chemical analyses of surface samples. Eggins et al. (1997) demonstrated that appropriate analytical protocols can yield high precision (typically better than 1-2% rsd) and accurate trace element data for >40 elements by inductively-coupled-plasma mass spectrometry (ICP-MS).

Here we present such a high-precision geochemical dataset (40 trace elements) for the source areas of dust that is transported across the Eastern Australian seaboard. These source areas (river floodplains, palaeo-lakebeds, dunes, playas) have generally similar relative trace element abundances, typical of upper continental crust. However, the new ICP-MS data document geochemical provinces on the sub-catchment scale. The geochemical provinciality is largely inherited from the main erosion source lithologies and translates into provenance resolution of ca. 50 x 50 km.

When modern far-travelled (up to 4,000 km) mineral dust of known provenance (from ground observation) is compared to the surface geochemical map, we find excellent agreement with the source area for many elements (McGowan et al., 2005). Mismatching elements are those affected by: (i) density sorting (Zr, Hf, HREE); (ii) reprecipitation (Be, Sr) and (iii) air pollution (first and second order transition metals, Ti and Pb). Comparison of 210Pb activity between known source areas and far-travelled dust demonstrates clearly that the enrichment in metals like Pb, Zn and Cu happens during atmospheric transport through the coastal East Australian pollutant plumes (Marx et al., 2005).

For the purpose of dust provenancing, for which Zr, Hf and HREE are unsuitable, it is sufficient to digest surface sediments in closed beakers at 130°C. However, we also demonstrate that only high-P digestion at 200°C yields complete sets of accurate data for all elements. This factor will severely increase the effort and cost of any rigorous surface geochemical mapping project.

Reference

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Dynamics of zero-valent sulfur species, including polysulfides, in Wadden Sea tidal flat pools

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Zero-valent sulfur (ZVS) species (rhombic elemental sulfur, colloidal elemental sulfur, inorganic polysulfides (S\textsubscript{n+2}\textsuperscript{2-}) and polythionates (S\textsubscript{n}O\textsubscript{2}\textsuperscript{2-})) play an important role in a variety of environmentally, geochemically and biogeochemically important processes. Polysulfides are known to decompose halogenated pollutants by reductive dehalogenation pathway. They are the important reactants in pyrite formation and sulfuration of sedimentary organic matter during early diagenesis. ZVS compounds are also important bacterial substrates. In natural aquatic systems ZVS species can be produced by microbial as well as by chemical pathways.

ZVS species dynamics in tidal flat pools of Wadden Sea (North Sea) was studied. Concentrations of solid sulfur, colloidal sulfur and distribution of inorganic polysulfide species were detected in different pools as a function of time after detachment of the pool from the sea.

Every sample was analysed by the protocol that consists of 4 procedures: 1) detection of individual inorganic polysulfides by rapid single-phase derivatization with methyl trifluoromethanesulfonate followed by HPLC-UV detection of dimethylpolysulfanes [1]; 2) detection of colloidal elemental sulfur, polysulfide and polythionate ZVS by reaction with hydrogen cyanide followed by HPLC-UV detection of thiocyanate; 3) pre-treatment with zinc chloride solution followed by chloroform extraction and HPLC-UV detection of elemental sulfur; 4) analysis of individual polythionates by HPLC-UV. Detection limit of each procedure was ≤2 µM.

Maximum sulfide concentration detected in the pools was 273 µM. During the initial 2 hours of pool detachment from the sea the main ZVS pools were colloidal sulfur and polysulfides. Dispersed solid sulfur concentrations reached significant values only 5 hours after pool detachment. Maximum concentration of colloidal sulfur detected in the pools was 73 µM and total ZVS >100 µM. Polythionates with n=4-6 were not observed in any of the analysed samples.

Individual polysulfides with chain lengths of 4-6 sulfur atoms were quantitatively detected for the first time in marine waters. Polysulfides concentrations were found to be lower than the predicted ones by calculations based on thermodynamic values. Maximum detected sum of S\textsubscript{4}\textsuperscript{2-}, S\textsubscript{5}\textsuperscript{2-} and S\textsubscript{6}\textsuperscript{2-} concentrations was 5.9 µM.

Reference


A deep mantle reservoir inferred from isotope signatures of Kimberlites

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Based on radiogenic isotopes, depleted (DM) and enriched (EMI, EM2) mantle reservoirs together with the other one (HIMU) have been generally accepted. However, existence of BSE-like (non- or less fractionated and least degassed) mantle reservoir is a matter of debate.

Although much caution is required to get reliable data of Kimberlites, their isotope data bear characteristic features. Based on Sr-Nd isotopic systematics, Kimberlites have been classified into Group I and II (Smith, 1983). In the Sr-Nd isotope diagram, Group I Kimberlites cluster close to the value of BSE, whereas Group II Kimberlites in the enriched area. Pb isotope systematics show similar systematics. The latter can be explained by incorporation of recycled materials and their distribution is limited. Hence I concentrate my discussion on Group I Kimberlites. Based on HF isotopes of Greenland kimberlites, Bizzarro et al. (2002) suggested the existence of a hidden reservoir, since Kimberlite data systematically lie below the Nd-HF isotope mantle array. While HF isotope data themselves also cluster close to the BSE value, Sr, Nd and Pb isotope systematics of Kimberlites have often been attributed to the mixing of components between the asthenosphere and lithosphere. However, our \textsuperscript{3}He/\textsuperscript{4}He and Ne isotopic studies of Greenland and Russian Kimberlites have revealed the occurrence of Lohi-type noble gas isotope signatures in their magmas and suggest their deep mantle origin (Tachibana et al., 2006; Sumino et al., 2006).

Noble gas isotope signatures are similar to those of Lohi-type OIBs. However, solid isotope epsilon data of Kimberlites with different time and space cluster much more tightly than those of OIBs and they are close to BSE. To produce such a feature, mixing among two or more multiple components operated with the same degree even in different time and space is unlikely. Accordingly, such a feature would be attributed to the properties of kimberlite magma source itself. Thus, isotope signatures of Kimberlites suggest possible existence of a deep mantle reservoir which is close to BSE and less fractionated and less degassed than the other mantle reservoirs. However, HF isotope signatures might require an additional component to explain the trend of kimberlites.

References

Localization of hydrocarbon contamination by measuring microbially induced changes of soil magnetic properties

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Soil contamination by crude oil and other hydrocarbons represents a severe, global environmental problem, but often the location and extent of contamination is not known. Hydrocarbons, or their degradation products, can stimulate iron-metabolizing microorganisms, leading to the formation or dissolution of (magnetic) iron minerals and an associated change of soil magnetic properties. Therefore, the screening of soil magnetic properties has the potential to serve as an efficient and inexpensive tool to localize and assess hydrocarbon contamination.

In order to identify the influence of different biogeochemical factors on the microbially influenced changes of soil magnetic properties after hydrocarbon contamination, oil spills were simulated in laboratory batch experiments. The parameters tested in these experiments included soils with different geological bedrocks, type and amount of added hydrocarbon, and microbiological parameters (sterile, autochthonous or added micro-organisms). In order to follow the changes of the soil magnetic properties, the magnetic susceptibility of the samples was measured weekly.

First results show that changes in the magnetic mineralogy are caused by microbial activity, as sterile samples showed no changes. In the microbially active set-ups, depending on the water content the magnetic susceptibility increased or decreased up to 10% in comparison to the initial magnetic susceptibility within a few weeks. In one iron-rich soil even a decrease of the magnetic susceptibility of ~40% was observed. The amount and type of the hydrocarbon source did not have an influence on the changes in magnetic susceptibility. However, DGGE fingerprints of different set-ups, performed at the end of the experiment, revealed that the amount and type of the hydrocarbon source influenced the microbial communities.

These first results show that the magnetic susceptibility changes in the presence of hydrocarbons and that this change is microbially induced. This suggests that the screening of soil magnetic properties can be applied to localize and assess hydrocarbon contamination. In order to understand the biogeochemical processes better, the change of the iron mineralogy will be followed by Mössbauer spectroscopy in future batch experiments. Furthermore, iron-metabolizing microorganisms will be isolated and identified.

Effects of calcium fluxes on authigenic carbonate formation at mud volcanoes off Costa Rica

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The Costa Rican forearc is characterized by active fluid venting related to mud diapirism and volcanism. Our study aims at thoroughly investigating the major parameters controlling authigenic carbonate formation such as fluid composition and advection rate. These efforts will help further our understanding of turnover rates at mud volcanoes and better constrain the use of authigenic carbonates as archives for past fluid flow. Pore water profiles of four sites on the southern Costa Rica margin show that all fluids are low in chloride and methane rich. Fluids of Quepos Slide and Culebra Fault are enriched in calcium, barium and bromine. In contrast, fluids of Mounds 11 and 12 are low in calcium. We present results of a numerical reactive-transport model used to quantify the effects of calcium fluxes and fluid flow rates on carbonate precipitation and methane discharge. At active vent locations of Mounds 11 and 12, 98% of the methane is released into the bottom waters due to exceptionally high advection rates (100-200 cm a⁻¹); corresponding to a low efficiency of AOM. This causes a reduced alkalinity production and hence a lower degree of authigenic carbonates formation. In comparison, moderate flow rates (0.1- 40cm a⁻¹) at Culebra Fault and Quepos Slide lead to reduced methane output (7% - 40%) from the sediment. Here, higher efficiency of AOM and Ca fluxes increase the calcium carbonate precipitation rates. Thus, higher Ca fluxes from below induce more precipitation of calcium carbonate. Further steps are in progress to better constrain the impact of calcium enriched fluids on carbonate precipitation by application of systematically simulating variations of fluid flow rate and Ca²⁺ concentrations in the ascending fluids.
Trace element contents of Jurassic coals from eastern Taurides, Turkey

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In this study, trace element and organic matter-trace element relation between Jurassic coals exposing in three different fields in the eastern Taurides were examined and their enrichment levels with respect to upper crust values were computed and the coal characteristics were also compared with those from USA and other parts of the world.

In comparison to the Feke and Kızılınç coals, Pb, Zn, Ag and Hg element contents of the Gedikli coals are considerably high; Ni, As and Ge contents are moderately high and Cr, Cu, Co, Cd, Sb, Ga and Sn contents are slightly high. The element concentrations are very similar to those of other fields. In the Gedikli coals, Sr content is extremely low and Ba content is slightly low with respect to other fields. Re, Mo, U, V and B element concentrations are different for each of three fields.

The major element contents of the Feke, Gedikli and Kızılınç coals were correlated with average values of coals from USA and other parts of the world and Fe, K, Mg and Na concentrations were found to be similar. Ti and Al contents of the world and USA coals are higher while Ca and Mn concentrations are lower. Considering trace element contents of the world and USA coals, Ba is considerably high, Cu and Zr are moderately high and Ga, Rb and Sc elements are slightly high. In comparison to world and USA coals, Sr content of the Feke and Kızılınç coals are very high while those of the Gedikli coals are lower.

For major and trace elements, factors of enrichment with respect to upper crust values were also computed. Among the major elements, Ti and K are depleted in the Feke field and Na is depleted in the Kızılınç field while other elements are enriched. The highest enrichment levels were calculated for Ca and Sr. Except for Se and Rb, all other trace elements are enriched with respect to upper crust. Re has the highest enrichment level followed by Ge, B, Sb, Cd, U, As, Te and Mo. Se and Rb show the lowest enrichment level in all the fields and, Th , Ba, Ge, Sc, Cs, Hf, Nb, Zn and Li generally have lower enrichment levels in the studied fields.

The behaviour of strontium and zinc during ageing of Fe(III) hydroxide

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Oxides and hydroxides of Fe(III) are common components of soil environment and can have a significant role in toxic metal mobility and retention. Sorption of many elements, among them heavy and Earth metals, on Fe hydroxides is fairly well understood. However, little is known about the influence of ageing and transformation of Fe hydroxides on the ions sorbed from solution. The alteration of the ferric hydroxide specific surface area during crystallization and the dynamics of interaction between Zn and Sr with Fe hydroxide were investigated experimentally at 25°C using a combination of potentiometric acid-base titration and metal uptake experiments.

The maximum decrease in Fe hydroxide surface area was observed during first day. Assuming similarity of the acid-base properties of hematite and Fe hydroxide surfaces, the specific surface area of Fe hydroxide was determined as a function of ageing time. The specific surface area determined after one hour, one and ten days following the initial precipitation are 570, 450 and 420 m²/g.

We observed a significant difference in the behaviour of strontium and zinc during Fe hydroxide crystallization. Solubility of Sr increases while the hydroxide surface area and consequently, the surface site density, decreases. While increasing ageing time from 2 hours to 10 days, Sr adsorption decreases by ~15%. The fundamental reason leading to reduction of Sr concentration in the solution is the adsorption at the surface of ferric hydroxide. In the case of zinc, even at low pH, sorption on the ferric hydroxide exceeds 40% and increases during mineral crystallization. This demonstrates the predominance of Zn coprecipitation with Fe hydroxide. Such a mechanism effectively decreases mobility because incorporated cations are only remobilized by a change in chemical conditions significant enough to force dissolution of the host mineral.
Combining riverine and satellite data for monitoring the climate effect on the carbon cycle in NE Iceland

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The objective of this study is to measure and compare the CO2 sequestration rates of vegetation and weathering of rocks in 8 (glacial and direct runoff) river catchments in NE Iceland over the years 1998-2003. Furthermore to test if increase in CO2 fixation of vegetation translates into more CO2 fixation over the years 1998-2003. Furthermore to test if increase in CO2 fixation of vegetation translates into more CO2 fixation over the years 1998-2003. The study period includes 3 of the warmest measured years in Iceland and the world. The 8 river catchments are mostly basaltic, they differ in age (from present to 15 Myr), elevation, temperature, runoff, glacier- and vegetation cover (from desert to woodland) and they are unpolluted.

Riverine discharge was continuously monitored but river carbon concentrations were measured at the end of each of 50 expeditions. Dissolved inorganic carbon flux (DIC), particulate organic carbon flux (POC), dissolved organic carbon flux (DOC) were calculated from correlations between the concentrations and the discharge at the time of sampling for each catchment (Kardjilov et al. 2006a, 2006b). Satellite remotely sensed gross primary production (GPP) and net primary production (NPP) are based on MODIS GPP and NPP products.

DIC, POC and DOC fluxes of the glacial feed rivers are depend on temperature, while for the direct runoff rivers they are precipitation dependent. The gross primary production of the vegetation is temperature dependent for all of the river catchments, while the net primary production of the vegetation shows fluctuations. There is a strong feedback between the vegetation NPP fixation of carbon and the riverine fluxes in the coldest catchments indicating that the effect of climate change for the carbon cycle is more severe for the coldest, driest and least vegetated catchments.

References

Petrogenesis of the most-recent Quaternary volcanism with implications for post-collisional lithospheric thinning of Eastern Turkey, Erzincan

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Geochemical and Sr, Nd and Pb isotope data are presented for a representative suite of the Quaternary Erzincan Volcanics (QEV) along the North Anatolian Fault Zone in order to understand the origin of the most recent volcanism in Eastern Turkey. Unspiked K-Ar and 40Ar/39Ar dating of lavas from the QEVs yielded ages of 102 ± 2 to 1060 ± 78.9 ka. The QEVs range from high-K low silica trachyandesite to rhyolite in composition, with rhyolite volumetrically the most abundant. All rocks show high K-calc-alkaline affinity, a geochemical signature common to many post-collisional magmas. They display the following geochemical signatures: (i) enrichment in large ion lithophile elements (LILE) (Rb, Ba, K, Th), light rare-earth elements (LREE) (La/Yb)CN=3-33), and depletion in high field strength elements (HFSE) (Ta, Nb, Hf, Sm, Y, Yb), (ii) pronounced negative Nb and Ti anomalies, and (iii) small negative Eu anomalies in andesite to dacitic and significant Eu anomalies in rhyolite samples. These rocks have homogeneous and relatively low 87Sr/86Sr =0.70404-0.70587 and slightly depleted Nd isotopic compositions (εNd from -0.9 to 2.8), with significantly varied Mg# ranging from 1.7 to 53. However, Pb isotopic compositions [206Pb/204Pb] = 18.90-19.02, [207Pb/204Pb] = 15.64-15.70, [208Pb/204Pb] = 38.91-39.97) reveal a profound enriched source signature (EM II), which implies that some portion of metasomatized lithospheric mantle could have contributed to their genesis. Compositional and textural disequilibrium and the negatively correlated of Sr and Nd isotopic ratios suggest that mixing of basic and acid magmas played an important role in magma genesis. A possible scenario for the genesis of these volcanic rocks is: basaltic magma formed as a result of partial melting of a subcontinental lithospheric mantle (SCLM) source responding to a possible upwelling of astenospheric mantle; underplating of these high-temperature basaltic magmas sparked melting of a juvenile lower continental crust producing rhyolitic melts; then magma mixing between basaltic and the rhyolitic magmas followed. Fractional crystallization (FC) coupled with contamination by upper continental crust could have played an important role in the evolution of mixed magma. Modelling based on Sr and Nd isotope data suggest that less than 10% of an isotopically depleted basic magma, which was chemically enriched in LILEs and LREEs due to metasomatism by fluids released from a subducting slab, was involved in the generation, but a juvenile lower continental crustal reservoir contributed about 90% of the source material for the QEVs.
Geochemistry of the Neoproterozoic Ikorongo Group of clastic sedimentary rocks, NE Tanzania: Implications for provenance, tectonic setting and upper crust composition

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Geochemical data are presented for the Neoproterozoic clastic sedimentary rocks from the Ikorongo Group in northern Tanzania in an attempt to constrain their provenance, tectonic setting and infer the composition of the Neoproterozoic exposed upper crust of the Tanzania craton. The Neoproterozoic Ikorongo Group is comprised of shales, siltstones and sandstones lying unconformably on the late Archaean Nyanzian Supergroup of the Tanzania Craton. The REE patterns of the Ikorongo mudrocks show fractionated REE patterns ((La/Yb)CN = 7.41-38.30), relatively flat HREE ((Gd/Yb)CN = 1.42-5.16) and negative Eu anomalies (Eu/Eu* = 0.71 on average) which characteristics are similar to the average post-Archaean Australian Shale (PAAS). The La-Th-Sc systematic together with the PAAS-like REE patterns and trace element ratios of La/Sc (2.02-13.84), Co/Th (0.09-1.58), Cr/Th (1.39-18.24), and Th/Sc (1.39-18.24), indicate that the source area was dominated by a mixture of mafic and felsic rocks. The geochemical considerations and palaeocurrent studies suggest that the provenance of the Ikorongo group include high-Mg andesites, dacites, rhyolites and granitoids from the Neoarchaean Musoma-Mara greenstone belt of the Nyanzian Supergroup. Major and trace element tectonic setting discrimination diagrams suggest a continental setting for the Ikorongo Group.

In situ boron isotope analysis in foraminifera: Implications for palaeo-pH predictions

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The most significant consequences of the current increase in atmospheric CO₂ are future global warming and ocean acidification; oceanic pH is predicted to drop ~ 0.3 pH units over the next 250 years. To understand the link between ocean pH and ecosystem response an accurate determination of past pH is critical. Foraminiferal tests are a key component of marine carbonate and their boron isotope composition is a widely used proxy to reconstruct oceanic pH and hence past atmospheric CO₂ concentrations. To assess the robustness of the proxy and the precision of the pH and pCO₂ reconstructions we need to understand the factors that influence the incorporation of boron into foraminiferal calcite.

In this study we used in-situ and high-spatial resolution secondary ionization mass spectrometry (SIMS) to investigate the nature and extent of boron isotope variation within the tests of a number of planktonic foraminifera specimens from sediment traps and sea surface sediment samples (e.g. G. sacculifer, G. ruber, G. truncatulinoides, G. tumida and G. menardii). The sediment traps have a biweekly resolution and hence allow assessment of seasonal variability in boron isotopes. They cover bloom phases of this species, i.e. optimal environmental conditions, and also times when the species are rare and tiny, representing suboptimal environmental conditions. Furthermore, these traps were deployed for several years and hence allow assessment of inter-annual variability.

Distinct chamber and chamber-wall layer analyses within individual tests showed consistent average B-isotope values of G. truncatulinoides tests over a size range from 460 to 670 μm. In contrast, there was a significant change in the B-isotope ratio from chamber to chamber within a specimen with lower values in the last chambers of the specimen and higher values in the older part of the test. The highest B-isotope composition and concentration are found in the earlier chambers, whereas the gametogenetic crust has lower B-isotope values. The B-isotope changes within a specimen of G. ruber are in agreement with predicted values based on model calculations by Zeebe et al [2003]. Due to the spatial resolved analyses, it is possible to discriminate between the processes influencing the B-isotopic fractionation and to improve the palaeo-pH reconstruction.

Reference
Secular variation of halogen concentrations in Yugama crater lake water, Kusatsu-Sirane Volcano

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Mt. Kusatsu-Sirane is an active volcano located along the volcanic front on Honshu Island, Japan. Crater lake water in Yugama, located at the top of Kusatsu-Sirane volcano, contains high concentration of chloride. It was observed that variation of chloride concentration in Yugama water reflected the volcanic activity (Ohba et al., 2000). However, there are limited data on other halogens. In this study, concentrations of I and Br in Yugama water were determined to know their levels and their relationships to chloride.

54 water samples, which were collected from Yugama lake during 1988-2006 were used in this study. Some other samples collected surroundings of Yugama were also used. Concentrations of I and Br were measured by ICP/MS.

Concentration ranges of I, Br and Cl in Yugama water samples collected during this period were 0.3-6ppm, 2-9ppm and 1500-3500ppm, respectively (data for Cl; Ohba et al., 2000). It is interesting to note that concentration of I in Yugama water is about 100 times higher than that of sea water. Secular variations of I and Br are similar to that of Cl. The concentrations of these three elements increased markedly during 1989-1992, with a special reference to I, which increased about 10 times. Relationships between the halogen concentrations and the volcanic activity (e.g. frequency of earthquakes) of Mt. Kusatsu-Sirane were observed, although the timing of I increase was 1-2 years later than that of Cl and Br.

In this area, there are some hot springs which are supposed to be originated from the same source as Yugama water. Variations of their halogen concentrations and also I/Cl ratios were found to be wide in those samples, while their Br/Cl ratios were relatively constant.

Figure 1: Secular variation of halogen concentrations in Yugama water

Reference

Reconstruction of the past biogeochemical cycles based on compound-specific N and C isotopic analyses of sedimentary porphyrins

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Porphyrrins are thought to have derived from biomolecules such as chlorophylls and heme, among which eoxophyllo-erythroetoporphyrins (DPEP) and its analogues are structurally related to chloropigments. These compounds thus preserve stable isotopic compositions of N and C of structotrophs of the past environment. We have developed methods for precise determinations of N and C isotopic compositions of individual sedimentary porphyrins and maleimides, which include isolation and purification of individual alkyloporphyrins and porphyrins acids by dual-step HPLC preparation (Kashiyama et al., 2007a). We have analyzed various alkyloporphyrins and porphyrin acids from organic-rich Miocene sediments of the paleo-Japan Sea (Onnagawa Formation) as well as Cretaceous black shales (Livello Selli and Livello Bonarelli, Italy) deposited in the western Tethys during the Ocean Anoxic Events (OAEs). The N isotopic composition of DPEP, which should have derived in chlorophylls in general, ranged from -6.9 to -3.6‰ (n=7) in the Miocene shale and -6.6 to -3.9‰ (n=5) in the OAE black shales, indicating that the N2 fixation was a major process for N assimilation hence the dominance of diazotrophic cyanobacteria in primary production in these paleo-oceans. Furthermore, DPEP were relatively enriched in 13C in both environments (-17.9 to -15.6‰ in the Miocene shale and -20.5 to -17.9‰ in the OAE black shales), which suggests relatively small carbon isotopic fractionation during photosynthesis and supports significant contribution of cyanobacteria-derived chloropigments. We also determined isotopic compositions of source-specific porphyrins such as 17-nor-DPEP (derived from chlorophyll-c), 8-nor-DPEP (possibly derived from divinylchlorophyll; Kashiyama et al., 2007b) as well as DPEP with extended alky side chains and their equivalents among porphyrin acids (derived from bacteriochlorophyll c, d, and e; analyzed as maleimides). The latter two porphyrins had variable and rather unique isotopic compositions compared to DPEP. Such an approach should allow reconstruction of community structures of phototrophs and associated biogeochemical processes associated with the photosynthesis in the past oceans.

The Barents Ecogeochemistry Project – Ecogeochanical Mapping of 1,500,000 km² in NE-Europe

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Scientists from Russia, Finland and Norway have jointly carried out a geochemical research and survey project in NW-Russia, Finland and NE-Norway. An important aim of the Barents project was to define the anthropogenic influence in relation to the natural variations of geochemical baseline over a large area containing both several world’s largest industrial emitters and Europe’s most pristine wilderness areas.

Terrestrial moss, the upper organic soil layer, the soil C-horizon and stream water samples were collected in 2000-2001 from 1085 sites in Russia and 288 sites in Finland.

Both total and aqua regia extractable element concentrations were determined from <2 mm fraction of minerogenic samples. Total element concentrations were measured in the plant and organic soil samples. Concentrations of more than 50 elements were determined from the samples.

The maps showing the distribution of 48 elements were shown in the Atlas. The geochemical patterns of minerogenic C-horizon are strongly controlled by element distribution in the bedrock. Some new metallogenic provinces were found in the area. Stream water data are mainly controlled by geological formations and structures both for major and trace elements. Anthropogenic activity is well reflected by anomalies in moss and organic soil layer near major industrial centres. Since the project area covers different bioclimatic zones from arctic tundra to subboreal forest, respective latitude dependence is visible on many elements distribution for moss and the organic soil layer.

Parallel to multimedia sampling and analysis, a qualitative visual estimate of the state of the ecosystem was performed for each studied site. Although this area is the most pristine in Europe, only 20% of the studied sites had no visual signs of human impact.

The replacement of calcium carbonate by hydroxyapatite

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The replacement of calcium carbonate by apatite is an important process in the growth of diagenetic apatite and also in biomimetic materials chemistry where apatite-replaced coral is being developed as a bone implant material. In the latter case the material properties depend on being able to pseudomorph the fine-structure of the coral. We have investigated the mechanism and the kinetics of the replacement of aragonite by apatite using the cuttlebone of Sepia officinalis, commonly known as the cuttlefish. The cuttlebone has an open chamber-like architecture with plate-like pillars (~5 microns thick) supporting parallel thin sheets, constructed from aragonite in association with an organic framework. Our samples, collected from various beaches in NSW Australia, have been thoroughly sun-dried and bleached. Scanning electron microscopy was used to characterise the morphology of the cuttlebone and aragonite was verified by X-ray powder diffraction. The amount of remaining organic component was determined after acid-dissolution.

Experiments were carried out using cut pieces of the cuttlebone sealed in autoclaves with (NH₄)₂HPO₄ solutions of varying concentration over a range of temperatures up to 170°C. The aragonite was completely converted to hydroxyapatite which was verified by X-ray powder diffraction and IR spectroscopy. Scanning electron microscopy showed that the fine-structure of the cuttlefish bone was maintained after the replacement process. The process of replacement is described in terms of a coupled dissolution-reprecipitation mechanism.

To determine the activation energy of the replacement mechanism, hydrothermal experiments were carried out over a range of lower temperatures to partially replace the aragonite, and the quantities of each phase determined by Rietveld analysis of powder X-ray diffraction patterns.

Atomic Force Microscopy was used to study the reaction of organic and inorganic calcium carbonate surfaces with (NH₄)₂HPO₄ solutions in situ in a fluid cell at room temperature to attempt to directly observe the dissolution and reprecipitation process.
Hydrogen generation at clay minerals of sandstone cements

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Hydrogen availability is crucial for the activity of anaerobic chemolithoautotrophs. These microbes are able to tolerate extreme environmental conditions, prevailing in e.g. hydrothermal vent systems, deep aquifers, underground mines and mine residues. If microbial or hydrothermal H₂ supply is lacking, mineral - water reactions could sustain anaerobic chemolithoautotrophic metabolism. In sandstones, iron rich clay minerals of the cements are suspected to be the most reactive minerals in respect to H₂ formation, since water reduction is commonly related to oxidation of mineral bound ferrous iron.

Methods

Rock samples from the Westfäl C sandstone formation (2,800 m depth) were analyzed for their cement minerals using XRD and sequential extractions. Milled rock samples and iron rich chlorite samples were reacted in headspace vials with a pH=3.5 buffer solution for 30 days. The headspaces were analyzed for H₂ by gas chromatography. Non-sterile and sterile test systems were used. Additional tests with Westfäl C sandstone rock samples and groundwater were performed at 90 bar and 40°C in a high pressure reactor (CO₂/Ar gas phase) for 5 months. The gas phase was sampled regularly for GC analysis of H₂.

Results

In all test systems, hydrogen generation was observed at levels of 100 to 500 nmol H₂ / g sample. Test systems unfavourable for autochthonous microbial activity (sterile mineral tests, low pressure rock sample tests) contained higher H₂ concentrations than test systems that favour autochthonous autotrophic metabolism (non-sterile mineral tests, high pressure rock sample tests). In addition, H₂ levels declined with time, indicating microbial H₂ consumption during the tests by autochthonous autotrophs. The figure shows H₂ concentrations over time in sterile and non-sterile Fe-chlorite - water interaction tests. Dissolved hydrogen concentrations in the test systems (10-60 µmol / L) clearly exceeded literature reported environmental H₂ levels of e.g. sulphate reducing or methanogenic aquifers and of basaltic ground waters. Generated H₂ concentrations are comparable to calculated H₂ fluid concentrations of midocean ridge basalt.

Figure 1: H₂ generation from Fe-chlorite - water interaction

Geochemistry of barium in sediments of the western Black Sea

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During two cruises with RV POSEIDON and RV METEOR to the western Black Sea (west of Crimean Peninsula) in 2004 and 2007, respectively, sediment cores were taken along a transect from 500 to 1700 m water depth. Pore water and solid phase investigations aimed at unraveling the geochemical behaviour of barium in this anoxic water column and sedimentary environment. In particular, our study focussed on the following questions: (1) In which way does the anoxic water column of the Black Sea control the flux of particulate barium phases to the seafloor?, (2) Does barite form in the anoxic water column and - if so - is the amount of barite reaching the sediment surface dependent on water depth as reported for oxic marine depositional environments?, (3) Can barium/barite be used as a sedimentary tracer of past productivity in the Black Sea?, (4) How is barium redistributed post-depositionally at the sulfate/methane transition (SMT) which is typically located around 2 m sediment depth?, (5) Can we use diagenetic barite to trace the downward migration of the SMT which occurred in the Black Sea deposits since the transition from the last glacial freshwater lake situation to the Holocene anoxic marine period? Understanding the geochemistry of barium in sediments underlying anoxic water bodies – like is the case in the Black Sea – will significantly contribute to improving interpretations of fossil sedimentary records laid down under oxygen-depleted water column conditions, like below or within oxygen minimum zones or during Cretaceous Oceanic Anoxic Events.
Nucleation and growth of the (Mn,Ca)CO₃ solid solution in double diffusion systems

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Introduction

Nucleation and growth of the (Mn,Ca)CO₃ solid solution was studied under conditions of double diffusion in silica hydrogel at 25°C. Three sets of experiments were carried out in U-shaped tubes of different lengths using Na₂CO₃, and MnCl₂-CaCl₂ aqueous solutions.

Results and Discussion

Using the excess Gibbs energy function of McBeath et al., 1998, two wide miscibility gaps were calculated. Experimental results show that nucleation takes place under nonequilibrium conditions when a specific value of high supersaturation β(x) is reached. Under these conditions, preferential partitioning of Mn in the solid phase has been observed. The fact that measured manganese mole fractions [X(Mn,ss)] are not restricted to the equilibrium miscibility range, can be attributed to kinetic factors. Moreover, since there is no agreement in bibliography upon the mixing properties of this solid solution, the miscibility limits at equilibrium are still under discussion.

Figure 1: Equilibrium values and experimental results plotted on a Roozeboom diagram.

Compositional profiles of crystals are characterized by alternations of Mn-rich and Ca-rich regions from core to rim, resulting in oscillatory zoning. Crystal morphologies are highly dependent on the Mn²⁺/Ca²⁺ ratio of initial aqueous solution. Even low concentrations of Mn²⁺ are capable of eliminating the {10-14} rhombohedron, by favoring the growth of rounded blocky crystals, spheres, and spherulites.

The observed reaction paths corresponding to the growth process could be used to explain crystallization behaviour and Mn/Ca distribution coefficients in natural systems.

References


Late Archean biospheric oxygenation and atmospheric evolution

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High resolution geochemical analyses of organic-rich shale and carbonate through 350 m of the ABDP-9 core through the > 2,500 Ma Mt. McRae, Mt. Sylvia, and Wittenoom formations in the Hamersley Basin of northwestern Australia record changes in both the oxidation state of the surface ocean and in atmospheric composition. Carbonate δ¹³C compositions through the strata vary systematically with lithofacies between 0 and -10‰, suggesting a strong carbon isotope gradient in Neoarchean seawater. High resolution sulfur-33 abundance data was obtained through a modified bulk powder EA combustion technique monitoring m/z 48, 49 and 50 on the SO analyte (Baublys et al., 2004). Based on observations from SO analyses, we have additionally measured many samples by standard SF₆ techniques. We observe wide variations in δ¹³C, δ¹⁸S, Δ³³S and Δ³⁶S through the stratigraphic record with specific correlations between δ¹⁸S/Δ³³S and of Δ³³S/Δ³⁶S that are temporally resolved. In the upper Mt. McRae Formation we see a change to negative δ¹⁸S with positive Δ³³S that is interpreted to capture activation of the oxidative sulfur cycle, for perhaps the first time in Earth history. In the lower Mt. McRae the δ¹⁸S/Δ³³S and the Δ³³S/Δ³⁶S relationships are different, and we interpret this as a change in atmospheric source reactions. The data suggest that oxygenation of the surface ocean preceded that of the atmosphere by 50 million years or more. Correlation of the time series sulfur isotope signals in northwestern Australia with equivalent strata from South Africa suggests that changes in the exogenic sulfur cycle recorded in marine sediments may have been global in scope, and linked to atmospheric evolution.

References

Records of A-type and I-type plutonism from the northern Aravalli craton, NW India: Age, petrogenesis and regional tectonic implications

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The northernmost segment of the Aravalli craton in NW India records two significant, discrete granitoid emplacement events at ca. 1711-1660 Ma and ca. 1822 Ma. The most unusual feature of 1711-1660 Ma plutonism is the occurrence of almost pure albite, classifying these rocks as alkali-feldspar granites. The individual plutons are predominantly composed of hastingsite or annite-bearing microcline-albite granites. The albite granites, which represent the subordinate facies, contain actinolite and magnesio-ferrohornblende or clinopyroxene. They are further characterised by low K2O (~0.5 wt%) and high Na2O (~7.0 wt%) abundances, whereas the microcline-albite granites show normal concentrations of alkali elements. The occurrence of virtually pure albite in these rocks has been attributed to varying extents of albitisation from moderately albitised microcline-albite granite to completely albitised albite granite. These granitoids are ferroan, metaluminous, typical within-plate A-type granites, and are derived from high-temperature melts (850-900°C). Initial ε(Nd) values range from -1.3 to -6.2 and correspond to mean crustal residence ages of 2.5 to 2.1 Ga. The geochemical and geochronological data for the A-type granitoids, and their comparisons with other correlative events documented in rocks farther south and southeast, signify a widespread and prominent rift-related regime during the late Palaeoproterozoic in the Aravalli craton. The 1822 Ma older plutonism, different from that of the A-type granitoids, is recorded by foliated biotite-bearing peraluminous, calc-alkaline, I-type monzogranites, which carry signatures of continental-arc setting. These rocks exhibit a restricted range of initial Nd values between -4.8 and -5.1 which correspond to a mean crustal residence age of 2.5 Ga. The lack of petrological and geochronological information for the 1822 Ma magmatism in the adjoining areas limits the scope of regional correlation of such an event.

Upscaling reaction rate laws in geochemical reactive transport using pore-scale network models

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Reliable predictions of reactive transport in geological porous media are important in carbon geosequestration studies and other engineering applications, including aquifer remediation and nuclear waste disposal. Given the size of geological systems to be used for CO2 geosequestration (in excess of 100’s of km²) and the long time horizon for predictions (10²-10³ years), explicit resolution of system heterogeneities at the micro-scale (i.e., the pore scale) is infeasible. Consequently, practical geochemical reactive transport models invariably operate at the continuum scale, in turn requiring various assumptions of homogeneity over averaging volumes far exceeding pore and grain sizes. However, sub-grid heterogeneities can undermine the macro-scale model accuracy, e.g., mineral weathering rates predicted from lab-scale data can overpredict observed field-scale rates by several orders of magnitude. This study focuses on reaction rate laws describing acid-driven mineral dissolution and examine whether reaction rates applicable at the pore-scale are applicable at the larger continuum scale. We use a pore-scale advection/diffusion/reaction model that includes kinetic precipitation/dissolution of anorthite/kaolinite clays and simulates the inflow of acidic CO2-rich brine under high-pressure conditions relevant to carbon geosequestration. The 4 mm³ pore network structure was estimated using X-ray computed tomography of sandstone cores, while the statistical distribution of reactive minerals was estimated using back-scatter electron imaging and energy-dispersive X-ray spectroscopy. The cores are from the Viking formation in the Alberta sedimentary basin (Canada), which is a potential site for CO2 storage.

We investigate whether the averaged concentrations of species and the mineral dissolution rates in the distributed pore network can be adequately approximated using a lumped model with volume-averaged parameters. For the anorthite/kaolinite system, the discrepancy between the pore-scale simulation and its lumped approximation increases with the acidity of the inflow brine and the heterogeneity of the reactive mineral distribution. The scaling effect can be reduced by replacing the volume-averaged mineral surface areas in the lumped model with “effective” reactive area parameters (calibrated a posteriori) that implicitly compensate for variations in active reactive areas due to sub-grid heterogeneities in the mineral distribution and reaction rates.
Rare earth element geochemistry of Kestelek (Bursa) borate deposit, West Anatolian, Turkey

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In this study, rare earth element geochemistry of the Kestelek borate deposit, one of the Western Anatolian borate deposits, is investigated. The known borate deposits of the Turkey were deposited in the lacustrine environment during Miocene when the volcanic activity occurred since Tertiary to Quaternary. All of the Turkish borate deposits are classified as volcanic related deposits. Rare earth element analyses of borate (colemanite) samples with different depth and textural compositions which are collected from the three different ore zones of Kestelek borat deposit are evaluated. In this situation upper crust normalized distribution diagrams of rare earth elements are made to determine physicochemical conditions and original relations of the Kestelek borate occurrence environment. Borate samples present two different groups at REE distribution diagrams which are made one by one for three different ore zones in Kestelek borate deposit. At the REE distribution diagrams, two different grouping of the curves signs that at least there are two different precipitation regimes. REE are generally constant at environment conditions which supply occurring straight lines. Second group curves, show clear anomalies, present negative Ce and positive Eu anomalies that exhibit hydrothermal source and precipitation regime with high oxygen fugacity ($f_{O_2}$). Some samples show middle rare earth element enrichment. MREE enrichment is characterized at hot naturel fluids and acid leaching. At the same time, mid-acidic source originated REE components show positive Eu and MREE enrichment. According to REE analyses results of borate samples belong to the three different ore zones, positive Eu anomalies and ranges of borate samples (where La/Lu > 1) sign mid-acidic and high temperature conditions.

References

Petrological and geochemical constraints on origin of St. Helena HIMU basalts

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Alkali basalts on St. Helena Island are characterized by elevated $^{206}Pb/^{204}Pb (>20.5)$ and $^{187}Os/^{188}Os$, coupled with depleted Sr and Nd isotopic signature. As a result they are representative of a mantle component referred as HIMU. In order to evaluate magmatic processes and source compositions of HIMU basalts, a detailed petrological and geochemical study was conducted on the shield building lava flows and dikes of the island.

The basalts show continuous compositional variation, which correlate well with petrographical features, such as modal abundance and crystal size of olivine and clinopyroxene phenocrysts. The compositional and petrographical diversity for alkali basalts can be explained by fractional crystallization of olivine and clinopyroxene at shallow depth (~1kb), and by subsequent changes in melt/crystal ratios when magma batches were extracted from a partially crystallized magma chamber.

Primary magma compositions for St. Helena basalts estimated by simulating the reverse path of fractional crystallization, show constant TiO$_2$/Al$_2$O$_3$, Yb/Tb, and highly incompatible element ratios, suggesting a homogeneous mantle source for these magmas. Examination using both pMELTS software (Ghiorso et al., 2002) and compiled data from high-pressure experimental studies for mafic rocks suggests that the primary magma can be in equilibrium with clinopyroxene and/or garnet at >ca. 2 GPa. This is the depth of the lithosphere/asthenosphere boundary beneath the island. It should be stressed that Ca and Al-rich eclogite or pyroxenite on silica-deficient in nature, not lherzolite, could be the mantle source for St. Helena basalt magmas. In order to form the source, contribution from recycled crustal material is necessary. This hypothesis is consistent with high $^{187}Os/^{188}Os$ of St. Helena basalts.

The primary magmas are characterized by low (Rb, Ba, Th, U)/Nb and Th/U ratios, and the absence of positive Sr and Eu anomalies. Together, these suggest that upper gabbroic portions of the less altered oceanic crust, rather than the lower plagioclase-rich cumulate gabbro, was recycled and involved in the mantle source of St. Helena basalt magmas.
Pressure solution deformation of Shimanto accretionary complex: Its mass transfer and temperature dependent feature

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Pressure solution (PS) is an important mechanism for mass transfer and for release of accumulated strain energy, which was formed through successive processes of dissolution, material transport and deposition. Pressure solution seams (PSS) has been observed in accretionary complexes of subduction zone, which would causes mass transfer. We evaluated mass transfer by PS as calculating volume change, and investigated relationship between intensity of PS and temperature, using microscopic observations, chemical analyses and paleotemperature. Studied samples are natural deformed shales associated with two distinct types of deformation, that is shear-dominated type (type S) and compaction-dominated type (type C). The PSS density is used as a quantitative index of PS intensity.

We obtained three results as following. (1) Ti concentrated within PSS for both type, implying that Ti is less soluble than other elements during PS deformation. (2) Positive correlation existed between PSS density and TiO₂ for both types and whose inclination of correlations are parallel to each other, indicating that TiO₂ concentration associated with development of PSS are always stable despite the different deformation types. (3) Positive relationship was figured out between PSS density and paleotemperature, implying that development of PSS depend on temperature.

From the former two results, volume change (ΔV) was calculated on the basis of compositional change of Ti using PSS density (γ) as,

\[ \Delta V = -2.4 \cdot \gamma \left( 2.4 \cdot \gamma + 1 \right) \]

From the last result (3), we estimated activation energies for each type by assuming duration of PS. Activation energies (type S: 18 kJ/mol, type C: 45 kJ/mol) are estimated to be lower than previous results (e.g. Schutjens, 1991) and dissimilar between two types. Possible reasons for the low values and the variation would be related to grain comminutions.

References

Anomalously low D/H ratio of H₂ gas from high temperature hydrothermal fluids in the Mariana Trough

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Previously reported δD values of H₂ gas (δD₂) in high temperature hydrothermal fluid (>300°C) ranged from -400‰ to -300‰ [1]. It has been thought that those δD values result from hydrogen isotope equilibrium between H₂ and H₂O, which makes δD₂ value -400‰ to -300‰ around 300°C to 400°C [1, 2].

In contrast, we discovered uniquely deuterium-depleted H₂ molecules (δD₂ = -800‰ to -700‰) in high temperature hydrothermal fluid at Southern Mariana Trough (SMT) arc and backarc systems in the western Pacific. The δD₂ in the SMT hydrothermal systems are so light that the fractionation during the hydrogen isotope equilibrium cannot explain these values at measured fluid temperature [2]. Assuming that the hydrogen isotope equilibrium is negligible in the SMT hydrothermal systems, we should consider kinetic isotope fractionations during some potential H₂ production processes in order to investigate an origin of such light H₂ in the SMT.

Degassing of H₂ from mantle would induce heavy δD values due to extremely high temperature, at which kinetic isotope fractionations are generally too weak to make such light δD value. Serpentinitization of ultramafic rocks has been thought as a major H₂ source in hydrothermal systems, while serpentine rock has not been collected in the SMT. Volcanic rock in the SMT is rather acidic than general MORs so that H₂ production by serpentinization may be little in the SMT hydrothermal systems.

On the other hand, it has been reported that chemical reaction between H₂O and crushed rock, caused by fault activity, enables to make large amounts of light H₂ (-770‰ to -470‰) [3, 4, 5]. Similar chemical reactions are expected to occur at low temperature by fracturings in plate subduction zones, close to the SMT hydrothermal systems, which is a possible origin to explain the uniquely deuterium-depleted H₂ discovered in this study.

References
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Endolithic aspartic acid as an proxy of fluctuations in the growth of coral skeleton

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Coral skeleton has been widely investigated for monitoring past fluctuations in marine environments. Although stable carbon isotope ($\delta^{13}C$) data appear to record coral metabolism, their interpretations differ from place to place and are sometimes controversial, because of the influence by carbon isotopic composition of dissolved inorganic carbon in seawater. Association of an organic matrix with biological carbonates has been reported in many previous studies. With the help of high-resolution micro-sampling of coral skeleton and advanced technique for amino acid (AA) quantification in low-volume sample, we indicate that aspartic acid (Asp) in coral skeleton varies with distinct seasonal pattern, and is useful in understanding why corals calcify faster in summer than in winter. Since Asp containing organic matrix in the coral skeleton is synthesized by the coral, changes in mole concentration of Asp relative to other AAs of the skeleton make it a potential indicator for monitoring fluctuations in coral physiology in the past.

Kornerupine sensu stricto associated with mafic and ultramafic rocks in the Lützow-Holm Complex at Akarui Point, East Antarctica: What is the source of boron?

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Prof. W. Schreyer had a long-standing interest in the MgO-Al2O3-B2O3-SiO2-H2O system, which includes kornerupine, a borosilicate rarely found in mafic or ultramafic settings. We report a new occurrence in two ruby corundum-plagioclase lenses at the same structural level as boudinaged ultrabasic rocks in hornblende gneisses and amphibolite. Ion microprobe analyses of kornerupine give 13-59 ppm Be, 181-302 ppm Li, and 5466-6812 ppm B, corresponding to 0.38-0.47 B per 21.5 O; associated sapphirine also contains B (588-889 ppm). Peak metamorphic conditions are estimated to be 770-790°C and 7.7-9.8 kbar. Kornerupine encloses tourmaline and plagioclase, which suggests the prograde reaction: tourmaline (1) + plagioclase (>An34) + sapphire + spinel $\rightarrow$ kornerupine + corundum (ruby) + plagioclase (<An82) + fluid or melt. Kornerupine later reacted with H2O-CO2 fluid in cracks: kornerupine + plagioclase + (Na, K, $\pm$Si) $\rightarrow$ tourmaline (2) + biotite + corundum (sapphire) + magnetite + andalusite + (Ca). Secondary tourmaline differs from the included tourmaline in having less Ti and higher Na/(Na+Ca+K). There are two possible scenarios for introducing B into the lenses: (i) infiltration of boron-bearing aqueous fluids released by prograde breakdown of muscovite in associated metasedimentary rocks, and (ii) hydrothermal alteration of mafic and ultramafic rocks by seawater prior to peak metamorphism. The latter scenario is consistent with the suggestion (Hiroi et al. 1991) that Akarui Point could be part of an ophiolite complex.

Reference
Cathodoluminescence characterization of shocked plagioclase

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Introduction

Shock-metamorphosed plagioclase in meteorite and impact crater have been less studied in spite of importance of planetary sciences, up to date. In this study, cathodoluminescence (CL) of the shock-induced synthetic plagioclase has been measured to clarify an effect of shock-metamorphism.

Sample and Methods

The unshocked synthetic plagioclase (Andesine-An40) and experimentally shocked samples at 20, 30 and 40 GPa (by rail gun experiment) as well as natural plagioclase (An50) from Ries Crater, Germany (occurred in suevite at shock stage IV<40 GPa) were selected for the CL measurements.

Result and Discussion

Synthetic plagioclase exhibits four CL peaks: (1) UV peaks at 330 nm related to defect center, (2) blue peaks at around 420 nm assigned to Mn²⁺ center and (4) red peaks at 740 nm assigned to Fe³⁺ center (Fig. 1). Peak positions of blue and yellow peaks respectively shift from 420 to 380 nm and 560 to 630 nm and intensity of all peaks decrease as function of the increasing shock pressure. This indicates that shock wave can cause a change of crystal field and emission processes leading to peak shift and decrease of intensity. These effects by impact shock are also observed in natural plagioclase samples from Ries Crater except for peak shift of yellow peak, which might be at least partly responsible for heating effect at natural shock event.

Gas chemistry of a hydrothermal plume at 8°18’S on the Mid-Atlantic Ridge

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Plate tectonic processes play an important role in the hydrothermal venting of gases such as helium, methane and hydrogen on mid-ocean ridges. While spreading rate (magma supply) primarily determines the rate of mantle helium degassing, venting of methane and hydrogen may be enhanced by extensional tectonics of slow spreading ridges, through the serpentinization of uplifted ultra-mafic rocks. Here we report the deep-water distribution of these gases in the region of a recently discovered hydrothermal vent at 8°17.9’S, 13°30.4’W. The measurements were carried out on Meteor cruises 62/5 and 68/1 in December 2004 and May 2006, as part of the German Priority Program 1144. The vent, a powerful, “odorless” black smoker inside a 2-meter deep crater, is located at the northern end of a narrow ridge within the MAR segment between the Ascension and Bode Verde fracture zones. The methane plume was detectable as far as 12 km from the vent, but the ³He signal was relatively weak, with clear anomalies only within a 2 km² area surrounding the site at the end of the ridge. ³He/⁴He, hydrogen and methane were observed to be well correlated near the plume, with molar ratios of H₂/CH₄ ≈ 15 and CH₄/³He ≈ 4 × 10⁻⁸. The latter is one of the highest CH₄/³He ratios observed in hydrothermal plumes. Measurement of hydrogen and methane in the vent fluid yielded a H₂/CH₄ ratio of 8:1, which is lower than the ratio observed in the plume. The distribution of methane in the region varied temporally, but during the first week of December 2004, it appeared that the plume trended mainly WSW from the vent. LADCP measurements (Stöber, 2005) indicated that currents at the plume depth during the ebb phase of the TPX0.5 tidal model were also in this direction. Excess methane inventories in 3 sections normal to the plume axis appeared to be about 12 to 14 mol m⁻². As the the current velocity at this time typically was about 5 cm s⁻¹, it appears that the methane source was about 0.7 mol s⁻¹. From the plume ratios above, it appears that the ³He and H₂ sources were about 2 nmol s⁻¹ and 10 mol s⁻¹ respectively. We also use the distribution of these tracers to estimate rates of methane oxidation in the region and of plume dispersion according to a Gaussian model.

Figure 1: CL spectra of synthetic plagioclase.
Geochemistry and petrogenetic significance of natrocarbonatites at Oldoinyo Lengai, Tanzania

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Oldoinyo Lengai, Tanzania, is the only active carbonatite volcano on Earth. However, Oldoinyo Lengai carbonatites are unique in most aspects of their petrological and geochemical characteristics and are distinguished from pre-modern carbonatites elsewhere as extremely alkali-rich natrocarbonatites, with Na₂O+K₂O generally >40wt%. No magmatic calciocarbonatites have been found at Lengai (Zaitsev and Keller, 2006). We present and discuss the composition and chemical variation of natrocarbonatites sampled in regular intervals from 1988 to 2006. Oldoinyo Lengai is a young, upper Quaternary volcano, and natrocarbonatites represent only the very recent stage of its evolution. Silicate lavas and pyroclastics constitute far more than 90% of the cone.

All silicate lavas of Oldoinyo Lengai show a high degree of peralkalinity and are highly evolved (low Mg, Ni, Cr etc). Prominent examples in the Recent evolution are the unusual wollastonite-combeite nephelinites (Klaudius and Keller, 2006). Bulk geochemical composition, trace element systematics and Sr, Nd, and Pb isotopic ratios suggest a liquid immiscible separation of natrocarbonatite from combeite-wollastonite-bearing nephelinites. Primitive olivine melilolites in the vicinity of Oldoinyo Lengai are the only candidates for primary mantle-melt compositions (Keller et al. 2006). Geochemistry and isotope systematics reveal different lineages. The spread in Sr, Nd, and Pb isotopic ratios of olivine melilolites, phonolites, combeite-wollastonite nephelinites and natrocarbonatites is explained as mixing line between HIMU and EM1-like mantle components. Liquid immiscible separation of natrocarbonatite melts is interpreted to occur a very shallow level within the volcano.

References

Constraints from Earth’s heat budget on mantle dynamics

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One of the largest challenges in modeling mantle convection is the need to reconcile the global heat budget with the time and spatial scale of geochemical heterogeneity observed in mid-ocean ridge basalts (MORB) and oceanic island basalts (OIB). Most models include at least one reservoir that is enriched in radiogenic elements relative to the mid-ocean ridge basalt (MORB) source, as this appears to be required to account for most current estimates of the Earth’s heat budget. This reservoir would also be responsible for the geochemical signature in some ocean island basalts (OIBs) like Hawaii, but must be rarely sampled at the surface. Our current knowledge of the mass- and heat-budget for the bulk silicate Earth from geochemical, cosmochemical and geodynamical observations and constraints enables us to quantify the radiogenic heat enrichment required to balance the heat budget. The current work has two parts. First, without assuming a specific model for the structure of the reservoir, we determine the inherent trade-off between heat production rate and mass of the reservoir. Using these constraints, we then investigate the dynamical inferences of the heat budget, assuming that the additional heat is produced within a deep layer situated initially above the core-mantle boundary. We carry out dynamical models of layered convection using four different fixed reservoir volumes, corresponding to deep layers of thicknesses 150, 500, 1000, and 1600 km, respectively, and including both temperature-dependent viscosity and an intrinsic viscosity jump between upper and lower mantle. We then assess the viability of these cases against some of the multiple criteria that must be satisfied by any model of mantle convection: stability of the deep layer through time, topography of the interface, effective density profile, intrinsic chemical density and a positive heat flux at the core-mantle boundary.
Insights into crustal anatexis from zircon-garnet REE behaviour

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Studies of the REE behaviour of zircon and garnet during high-grade metamorphism and anatexis have shown that the compositions of these minerals are sensitive to fluctuations in coexisting melt compositions and therefore to the timing of individual mineral growth relative to melt evolution. Zircon-garnet REE distribution behaviour is therefore critical to not only dating partial melting, but also to the assessment of the effects of melt generation, migration, drainage and recharge in migmatites within the deep crust.

A detailed study has been carried out on superbly exposed pelitic migmatites from the Brattstrand Bluffs, Prydz Bay, east Antarctica. The pelites underwent biotite-controlled vapour-absent partial melting at metamorphic conditions of ~6 kbar and ~860°C. Melting resulted in production of semi-restitic to restitic Sil-Spl-Grt melanosome and segregation of quartzofeldspathic leucosome with variable abundances of entrained residue. Transport of partial melts occurred on a range of scales, from a few centimetres to beyond 100m. Field observations suggest that some melt was still mobile during deformation associated with post-peak decompression.

Zircon, which is concentrated both within restitic melanosome and along contacts between leucosome and melanosome, was analysed in-situ along with garnet for REE and other key trace and major element data. Zircon and garnet REE patterns and partitioning data suggest that growth of new zircon on corroded detrital grains occurred in equilibrium with peritectic garnet in the melanosome. Similar REE evidence indicates that zircon present in larger melt accumulations and veins most likely grew at the site of melting before being extracted, to variable degrees, along with the melt. Integration of our field and thin section observations with mineral REE data leads to the general conclusion that zircon growth in migmatitic granulites predominantly occurs early in the progression of partial melting, at close to peak conditions. In contrast late zircon growth during post-peak decompression and cooling is limited.

Tracing the lost arcs: Granitic zircon as a geodynamic indicator?

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Subduction-related magmatism has long been acribed a central role in the generation of Earth’s continental crust, based in part on modern arc analogues. Yet, radiogenic isotope evidence implies that much of the present-day continental mass formed early in Earth history, and attempts to understand the geodynamic drivers are hampered by fragmentary preservation of ancient geological terranes. Recent studies have exploited the detrital zircon archive to chart the growth of crustal segments and even to infer Hadean subduction [1], but whether zircon-derived isotope information can reliably diagnose tectonic setting remains unknown.

We address this issue with reference to two case studies of areas formed in subduction-related settings, the Paleozoic Tasman Orogenic Belt of Eastern Australia, and the Cenozoic Hidaka Metamorphic Belt of Hokkaido, Japan. The Tasmanides preserve the record of 300 Myrs of accretionary tectonic processes outboard of the eastern Gondwana cratonic margin. Geological evidence argues that the voluminous and diverse granites of the Tasmanides formed behind a long-lived, retreating subduction system that was punctuated by episodic contraction. Isotopic data confirms the involvement of multiple source materials in granite genesis, the nature and proportion of which changed with time. The Hidaka belt comprises a remarkably complete arc sequence that encompasses upper mantle to shallow crustal depths. Formed in a trench-proximal position adjacent to the Eurasian margin, the Hidaka belt evolved from a continental arc to oceanic back arc realm with the opening of the Japan Sea at 25 Ma, prior to exhumation during collision between the Japan and Kuril arcs. Granitic rocks are abundant at all crustal levels.

We examine the micro-isotopic (U-Th-Pb, 18O/16O, Lu-Hf) systematics of granite-hosted zircon from both areas to deconvolve the magma sources as a function of tectonic evolution, and for the Hidaka, crustal depth. The goal is to capture the ‘signature’ of crustal growth and reworking in these arc settings from a zircon perspective, and thus to place the zircon record into a geodynamic context. We will explore the extent to which this signature manifests in isotope arrays generated from old zircons, and discuss the implications for the tectonic mode of crustal growth in ancient orogens.

References
Piccaninny, WA, and Matt Wilson, NT: Two possible complex impact craters in Australia

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We present results of field analysis, microscopy, and remote sensing mapping of two circular structures in Australia of which the meteorite impact origin is not yet confirmed.

**Piccaninny, Western Australia (17°25’S, 128°26’E, 7.5 km diameter):** The circular structure (Beere 1983; Shoemaker and Shoemaker, 1985) forms a plateau in the Purnululu National Park that is built up by Devonian conglomerates and sandstones. It is framed by beehive-like domes and the Piccaninny Gorge, both make the access to the elevated plain difficult. The structure is defined by a centerward dipping circular monocline (5-15° dip), a very gentle ring syncline, and a weak central rise with a stratigraphic uplift of 40-50 m. The distinct regional cleavage pattern outside the plateau displays a systematic deflection towards the center of the structure. On the plateau the vertical cleavage planes are reactivated as faults. These fault zones typically contain comminuted decimeter-wide gouge zones and meter-wide process zones in which anastomosing subsidiary fault networks occur. Some of the interconnected shear zones resemble breccia dikes. Strata are offset by faults. Minor strata tilting and the apparent lack of shock features suggest a considerable amount of erosion (>2 km) of the possible impact crater.

**Matt Wilson, Northern Territory (15°30’S; 131°10’50”E):** The outline of this possible impact crater is elliptical (4.5 x 6.5 km) with the long axis trending NE-SW. It has been formed in Mesoproterozoic rocks and consists of a crater rim monocline, a ring syncline and a central uplift 1.5 km across. The structure is described in detail by Sweet et al., 2005, who also present microstructures indicative for shock. The central uplift of the structure shows an imbrication of thrust slices in a bilateral arrangement. Such a pattern is known from other craters like Upheaval Dome or Spider (Scherler et al., 2006). The NE-SW trending symmetry axis is delineated by major faults. The fault pattern, preferred NE strata dipping in the central uplift, and the elliptical crater outline may indicate an oblique impact from NE.

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References
Cenozoic topographic and climatic change in the western U.S. from a paleosol carbonate record in Montana and Idaho

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Oxygen, carbon, and strontium isotope records from a Paleocene to Pliocene paleosol carbonate stratigraphy in southwestern Montana and eastern Idaho show evidence that significant changes in topography occurred between ~50 and 47 Ma. δ18O values of calcite decrease by 7-10‰, while δ13C increases by ~3‰, and strontium shifts to more radiogenic values. These changes reflect a reorganization of drainages with an increase in elevation of 2.5-3.5 km. This rise in elevation is roughly contemporaneous with the emplacement of the nearby Challis Volcanics, and the formation of metamorphic core complexes in the hinterland of the Sevier thrust belt. Moreover, when compared to previous oxygen isotopic studies that show oxygen isotopic shifts of similar magnitude occurring later (in the late Eocene to early Oligocene in northeastern Nevada, and late Oligocene to Miocene in southern Nevada), the results of this study add to a growing body of evidence for a spatial and temporal migration of high surface elevations from north to south in the Great Basin of the western United States. This surface uplift history supports tectonic models calling for north to south removal of the Farallon slab or delamination of the mantle lithosphere. Superimposed on this tectonic framework we find a high-resolution climate record with evidence of rapid Cenozoic climate fluctuations. Oxygen and carbon isotopes show major climate fluctuations at the Eocene-Oligocene boundary, and pulses of Pliocene cooling and Pleistocene warming. This adds to a growing body of literature that shows spatial variability in how global climatic changes are expressed in the terrestrial record. Understanding the larger tectonic framework is essential to making interpretation of climate based on these isotopic records.

Th/Nb evolution of the Archean mantle

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Values of Nb/Th in komatiites and basalts have been used as proxies for extraction of continental crust from the mantle. Ratios of 8-16 for ~ 2.7 Ga Yilgarn komatiites and basalts were interpreted either as large scale extraction of the continental crust early in Earth history, or extensive extraction of crust from small mantle domains, where bulk Archean crust has Nb/Th=2 [1]. In an alternative model, the ratio evolved from near primitive mantle values of 8 in the early Archean to MORB like values of 19, reflecting progressive crustal extraction. A new compilation of high precision data for komatiites of the Superior Province gives a range of 7-11 at 3 Ga but 7-21 at 2.7 Ga. Associated basalts span 5-13. These results are interpreted as large scale extraction of continental crust, as TTG, from melting of oceanic crust in convergent margins post 3 Ga, and recycling of the high Nb/Th residue into the mantle source of plumes from which the komatiites and basalts later erupted.

In the Neoarchean Wawa subprovince, oceanic plateau basalts are characterized by near-flat REE patterns, and Nb/U and Nb/Th ratios generally greater than primitive mantle values, consistent with positive εNd values. They are associated with komatiites, the association being interpreted as an ocean plateau sequence erupted from a mantle plume. High Nb/U and Nb/Th ratios of plateau tholeiitic basalts are interpreted as a complementary reservoir to arc magmatism (low Nb/U and Nb/Th), hundreds of millions of years prior to recycling of oceanic lithosphere through a subduction zone (high Nb/U, Nb/Th), and its incorporation into a mantle plume from which 2.7 Ga plateau tholeiites erupted.

References
Geochemistry of quaternary lavas from the Main Ethiopian Rift – Constraints on continental breakup and rifting

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The Main Ethiopian Rift (MER) is part of the Afro-Arabian Rift System and is located within a transitional zone between continental and oceanic rifting. A bimodal suite of samples from eight volcanic centres within the rift-valley (Ayelu, Dofan, Hertali, Fantale, Kone, Bosetti, Gedemsa and Aluto, from NE to SW) have been analysed on their major and trace element as well as isotopic composition to constrain the spatial distribution and temporal evolution of their magma sources. This may provide insights on the mantle processes that are likely to control continental breakup and rifting within such a transition zone. Furthermore, the magma distribution within the lithosphere potentially controls their heat budget and thus their strength, which directly affects continental breakup and rifting.

Trace element patterns show a great similarity for samples within as well as between individual volcanic centres, suggesting a fairly homogeneous mantle source over the entire sampled range. REE patterns display steep slopes with La/Yb ratios between 5.7 and 14.7 in basalts, reflecting low degrees of partial melting of an enriched mantle source. Trace element patterns of evolved rocks from all locations indicate substantial olivine, clinopyroxene and plagioclase fractionation, which is confirmed by petrographical observations. Negative Sr anomalies, however, are insufficiently explained by fractional crystallisation and require additional processes such as crustal assimilation. The large amount of crystal fractionation observed indicates a long-term residence of primary magmas within the lithosphere and thus most likely considerable heating.

The $^{87}\text{Sr}/^{86}\text{Sr}$ values range from 0.70354 (Hertali) to 0.70493 (Fantale), $^{143}\text{Nd}/^{144}\text{Nd}$ ratios vary between 0.512741 (Aluto) and 0.512944 (Hertali). An overall correlation between Nd (and Sr) isotope ratios and latitude exists, with increasing $\varepsilon_{\text{Nd}}$ values towards the northeast, which might reflect a slightly higher influence of a MORB source mantle close to the triple junction as was also suggested from geophysical data (Keranen et al., 2004). Beside the first order geographical correlation, a relatively wide spread within the isotopic ratios is observed for some volcanic centres. This supports the hypothesis of crustal assimilation during magma ascent and crystal fractionation.

References
Coastal uplift, sea level changes and active tectonics of the southeastern Black Sea: Evidences from Quaternary marine terraces, Trabzon coast, NE Turkey

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The data obtained from landsat imagery, airphotos, geological and geophysical records show that there are three distinctive lineaments in the vicinity of Trabzon, trending northeast-southwest (NE-SW), northwest-southeast (NW-SE) and east-west (E-W), analogous to North Anatolian Fault (NAF) and Northeast Anatolian Fault (NEAF) systems. According to current seismic data, the faults, which have three distinctive directions, show active properties. As a result of these, Boztepe, Erdogdu, Fatih (NE-SW directions), Yenimahalle and Faroz faults (NW-SW directions), forming the fault system of the Trabzon coast section, cut and raised the Quaternary marine terraces to the surface. In order to be able to reveal the motion rates and activity of these faults, field surveying, geomorphological studying, airphoto interpretation and geochronological measurements of seven different marine terraces on the Trabzon coast of the southeastern part of Black Sea was carried out. According to available data, the Holocene and Pleistocene marine terraces, at elevations ranging from 1-3 m to 4-300 m, are the result of the interaction between regional scale uplift and subsidence, interglacial sea level changes, and local fault movement. The mollusca shells, collected from these terraces at elevations ranging between 1-3 m (H), 4-14 m (T-1), 22-34 m (T-2), 60-80 m (T-3), were dated by ESR method. The ESR results showed that the ages of H, T-1, T-2 and, T-3 are 5.141 ± 0.294 ka, 124.8±26.0 ka, 292.5±49.8 ka and 407.998 ± 67.475 ka, respectively. The terraces were correlated to the OIS 1, 5e, 9, 11, which correspond to the 5.141 ka, 124.8±26.0 ka, 292.5±49.8 ka and 407.9 ka highstands of the paleo-sea-level curve. Considering the new ESR results, subsidence rate of the East Black Sea Basin and the abrupt drowning of the Black Sea self at 7150 years ago, mean uplift rates of the Holocene and Pleistocene marine terraces are ranging from 0.5 to 1.4 mm/year. The average motion rates of the faults, forming the fault system of the Trabzon coast section, are 0.5-1.4 mm/year while this rate is 16-25 mm/year for NAF and 9 mm / year for NEAF. This indicates that the motion rates of the faults decrease towards the plate. As a result of these mean uplift rates, the recurrent of the maximum earthquake (M=7) is predicted to be a few thousands years.

References
Potential environmental issues of CO₂ storage in saline aquifers: Geochemical results from the Frio Brine pilot tests, Texas, USA

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Deep saline aquifers in sedimentary basins provide advantageous locations close to major anthropogenic sources of CO₂ and large potential capacity for the storage of huge volumes of this greenhouse gas. To investigate the potential for the long-term storage of CO₂ in such aquifers, 1600 t and 300 t of CO₂ were injected, respectively, into the “C” and “Blue” sandstone sections of the Frio Formation, a regional reservoir in the U.S. Gulf Coast. Fluid samples obtained before CO₂ injection from the injection well and an observation well 30 m updip showed a Na-Ca-Cl-type brine with ~100,000 mg/L TDS at saturation with CH₄ at reservoir conditions, but CO₂ was low at 0.3% of total gas. Following CO₂ breakthrough, ~50 h after injection, samples showed sharp drops in pH (from 6.5 to as low as 3.7 with in-line probe), major increases in alkalinity (from 100 to up to 3200 mg/L as HCO₃⁻) and Fe ++ (from 30 to 1200 mg/L) and Feoxyhydroxides caused by low pH values (~3.0 initially) of the brine in contact with the injected supercritical CO₂.

These geochemical parameters, together with perfluorocarbons (PFTs) and other tracer gases, proved powerful tools for tracking the migration of the injected CO₂ in the injection sandstones and into the overlying Frio “B”, composed of a 4-m-thick sandstone bed and separated from the “C” by ~15 m of shale and siltstone beds. Data on brine and gas compositions of samples obtained from the Frio “B” 6 mo after injection show significant CO₂ (2.9 % compared with 0.3% CO₂ in gas) migration into the overlying “B” sandstone. Except for two PFT tracer gases, which could be explained by desorption, results of samples collected 15 months after injection show no additional CO₂ migration into the “B” sandstone. The presence of injected CO₂ in Frio “B” has important environmental implications as it shows initial leakage through the remedial cement behind the well casing or migration through the shale and siltstone beds. Environmental impacts could be major if large volumes of buoyant and reactive CO₂ and/or brine with mobilized metals and organic migrated into overlying potable groundwater resources. Sampling and geochemical analyses of fluids in deep monitoring zones together with geophysical imaging, if properly carried out, are potential early detection methodologies that could trigger remediation action should leakage of CO₂ and/or brine take place.

Hydrochemical and isotopical tracers in groundwaters from coastal zone of the Primorye, Far East of Russia

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The deep saline and brackish waters in coastal zone of the Primorye region have been studied in this investigation. Razdol’noe manifestation of deep brackish waters is located in coastal zone of the Primorye region (Far East of Russia) and it was discovered with drilling during geothermal exploration in 1992. Wells are situated in the mouth of Razdol’naia River, about 25 km from seashore. Wells disclose two different types of cold (13°C) waters: Ca-Na-Cl and Na-HCO₃.

Aquifer with Ca-Na-Cl type water occurs in Miocene sedimentary rocks at 30-130 m depth and has TDS 4.5–13.7 g/l. Ratio of major ions Ca/Mg (1.3); Ca/SO₄ (2.1) and Na/Cl (0.4), Cl/SO₄ (0.98) are close to seawater ratios. Aquifer with Na-HCO₃ type water occurs in Mesozoic sedimentary rocks at 130-500 m depth, has lower TDS - 2.5–6.0 g/l, and is being used by local spa and bottled as well. Numerous tectonic fractures are spread across the study area and located under the cap of the Miocene – Quaternary sediments in southeast and east trends. The width of the fault zone is not less then 100-150 m.

Na-HCO₃ water has prominent hydraulic continuity with upper saline water aquifer, and is enriched by B (9.37 mg/l), F (6.00 mg/l), Li (up to 1.50 mg/l), Sr (up to 0.7 mg/l), Br (0.25 mg/l) and has low contents of I (0.002). Ratio of Ca/Mg is 1.1; Ca/SO₄ ~57.5; Na/Cl −10.1 and Cl/Br is 364.2 (much higher than in seawater). Positive correlations between Sr and Ca, Na, Mg, Cl, Fe and B (r=1.00); Ca-Mg (r=0.99), SiO₂-Al (r=1.00), K-Cl (r=0.81) and negative correlation between SiO₂ and major cations (Ca, Na, K) and F (r=1.0) are observed for both types of water. δ¹⁸O and δ2H isotopic ratios show that brackish water has a meteoric origin. The main recharge zone of this aquifer occurs in the north where the sediment complex outcrops.

Received data indicate that saline waters are result of mixing of ancient seawater with infiltrate waters and brackish water has a meteoric origin and mineralization is forming as a result of water-rock interaction. Mass balance calculation and bedrock investigations proves that the albite dissolution, with or without deep-seated mantle origin of CO₂, is a dominant factor controlling the chemical composition of groundwater.
Charateristics of syn-collision magmatism, NW Iran

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Quaternary lavas from the NW Iran are related to the ongoing Arabia-Eurasia collision, which represents continued plate convergence after the end of north-dipping subduction of the Neo-Tethyan ocean at ~35 Ma. The lavas are erupted across the Turkish-Iranian plateau, which ceased crustal thickening before the establishment of a number of volcanic centres within Iran and eastern Turkey, such as Ararat and Tendurek, beginning at ~10 Ma. Local active tectonics involve right-lateral strike-slip faults and pull-apart basins, but there is no simple spatial relation between the basins and volcanic centres. Here we report geochemical and Sm-Nd/Rb-Sr data for 20 samples from a ~200 km long, N-S traverse through the main volcanic centres. Samples are transitional alkali/tholeiitic basalts and basaltic andesites. Samples fall between two end-member compositions, a “depleted”, low Nb, low LILE type with 143Nd/144Nd ~0.51290 and an “enriched”, high Nb, high LILE type with 143Nd/144Nd ~0.51265. Depleted compositions occur in the north and enriched compositions in the south. Therefore enrichment decreases with distance from the Arabia-Eurasia suture to the south of the study area. There is petrographic evidence for greater crustal contamination in the southern samples, but this is not reflected in major and trace element compositions. A previous model for similar compositional variation in Anatolian syn-collision magmatism has invoked slab-breakoff beneath the plateau (Keskin, 2003). An alternative explanation is that the degree of melting decreases southwards towards the suture, because of the reduced thickness of mantle wedge above the Tethyan ocean slab.

The impact of Fe isotope fractionation by plants on the isotopic signature of soils

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Plants play an important role in the biogeochemical cycling of iron. Enhanced mineral dissolution by root exudates, Fe uptake by plants, and decomposition of Fe-containing plant material significantly influence the speciation of Fe in soils. We investigated stable Fe isotope fractionation during the cycling of Fe from rock/soil to plants and to soil organic matter in an alpine glacier forefield (Damma glacier, Central Alps, Switzerland). Its rather uniform lithology (Aare granite) and the well-defined soil formation chronosequence (max. 150 years) provide a well-constrained natural setting for our studies. Fresh granite rock and its main Fe-bearing minerals (biotite, magnetite), soil samples, soil organic matter and various plant species were analyzed for their Fe isotopic composition. Plant species under investigation acquire Fe either by Fe(III) reduction (strategy I) or by exudation of siderophores and uptake of Fe(III)-siderophore complexes (strategy II). Iron isotope ratios were measured by MC-ICPMS (Nu Plasma) using a standard-sample bracketing method (IRM-014). The reproducibility of samples was generally better than ±0.15‰ (2SD) in δ⁵⁷Fe.

While unaltered granite samples exhibit a heavy isotopic composition (0.3-0.4‰ in δ⁵⁷FeIRMM-14), biomass of strategy I plants shows an enrichment of the light isotope of up to ~2‰. A clear trend of increasingly lighter composition from roots to stems, leaves and flowers indicates strong fractionation during Fe translocation within strategy I plants. Average δ⁵⁷Fe values for whole plants, obtained from Fe elemental and isotope mass balance, are up to 0.8‰ lower than for the lightest and most labile mineral of the granite (biotite: 0.2‰ in δ⁵⁷FeIRMM-14), demonstrating a significant fractionation already during uptake. Variations in δ⁵⁷FeIRMM-14 of grasses (mainly strategy II) did not exceed ~0.3‰ and minimum values are around -0.8‰. Nevertheless, the average isotopic composition of the aboveground biomass of grasses is still ~0.4‰ lighter than biotite. This characteristic enrichment in light Fe isotopes in the plant biomass is also reflected in the isotopic signature of organic matter and soils. Organic-rich horizons exhibit up to 0.2‰ lower δ⁵⁷Fe values than mineral-dominated horizons. The distinct isotopic composition of Fe associated with organic matter and mineral phases in soils implies that Fe isotopes can be used to assess the impact of plants on the Fe cycle in soils.
Long-term changes in water chemistry of crater lakes of Kusatsu-Shirane volcano, Japan

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Kusatsu-Shirane volcano is located at central Japan and has three crater lakes named Yugama, Mizugama and Karagama on its summit. Yugama, the largest and the most acidic (around pH 1) among the three, is well known as an active crater lake. Volcanic fluids are discharged constantly into Yugama from its bottom, and thus chemistry of Yugama water reflects the volcanic activity of Kusatsu-Shirane volcano. Therefore many researchers have studied its water chemistry as an indicator of the volcanic activity of the volcano. To the contrary, very few researchers note the other two crater lakes, because their acidity (around pH 3) is lower than that of Yugama, and volcanic fluids directly discharged into them have not been observed. Those two are thus recognized as non-active crater lakes at present. Recently, two crater lakes, because their acidity (around pH 3) is lower than that of Yugama, and volcanic fluids directly discharged into them have not been observed. Those two are thus recognized as non-active crater lakes at present. Recently, however, we have grasped some evidence that their water chemistries also reflect the volcanic activity of Kusatsu-Shirane volcano. In this study, we have discussed the long-term changes in water chemistry of the crater lakes of Kusatsu-Shirane volcano accompanying its volcanic activity.

Five phreatic eruptions had occurred at the edge of Yugama in 1982-83. A remarkable increase in concentrations of dissolved components of Yugama water was observed after the eruptions, which has been considered to be due to the influx of highly-concentrated fluids into Yugama water. Secular change in water chemistry of Mizugama resembles that of Yugama, although the absolute concentrations of the former are much lower than those of the latter. A similar trend in secular change is also observed for Karagama and Yumiiike, a marsh embracing the old crater beside the pyroclastic corn. It was thus possible that the same fluid that was discharged into Yugama was also supplied to the other lakes during the eruptions. In addition, the concentration of the chloride ion had increased in Mizugama, Karagama and Yumiiike waters immediately after the 1982-83 eruptions. Since the influx of the chloride ion generally suggests the existence of volatiles from the magma, those observations must be an evidence that their water chemistry reflects the volcanic activity. On the other hand, such as increase in the concentration of the chloride ion after the eruptions had not been observed in Yugama. This may be interpreted as follows. The influx of the volatiles could not change the water chemistry of Yugama because its water always kept high salinity, and consequently was insensitive to the influx of the volatiles unlike the other lakes. Thus, the waters of Mizugama, Karagama and Yumiiike may be more sensitive indicators for the volcanic activity of Kusatsu-Shirane volcano compared with Yugama.

Particle size effects on heavy metal distribution, speciation, and correlations in mine wastes

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Centuries of mining have left a legacy of metal-contaminated mine wastes across the world’s mineralized regions. These wastes often contain highly elevated levels of many hazardous metals in addition to the primary ore metal. Characterizing trends in metal concentrations, metal speciation (the dominant chemical form of the metal), and correlations between metals as a function of particle size can provide insight into the mechanical and chemical processes that distribute metals in the environment and impact their availability to living organisms. A combination of physical size separations, bulk chemical analyses, X-ray spectroscopic methods, and empirical leach tests aids the identification of such trends as well as the pathways that control metal transport from mine impacted sites.

Samples of both mine wastes and background soil samples from mine sites throughout California were collected and weighed prior to particle size separation using stainless steel sieves to generate 11 size-specific fractions (from >2830 μm down to <20 μm). Each fraction was weighed and analyzed using ICP-MS to determine the bulk concentrations of a standard suite of 48 elements. Results of elemental concentrations as a function of particle size were plotted and categorized based on their size-dependent behavior, resulting in groupings of elements that share similar trends and therefore possible geochemical associations.

Bulk and microspectroscopic methods were then applied to selected size fractions of mine wastes, utilizing X-ray fluorescence (XRF), extended X-ray absorption fine structure (EXAFS) spectroscopy, and X-ray diffraction (XRD) to assess the speciation, distribution, and correlation of metals of interest. The microspectroscopic methods in particular can allow the analysis of samples previously inaccessible by bulk spectroscopic techniques due to sample concentration limitations.

Results from bulk concentration analyses demonstrate that many heavy metals are concentrated in the finer grain size fractions, sometimes by over an order of magnitude, increasing their mobility and potential availability by ingestion or inhalation. However, changes in metal speciation corresponding to preferential weathering of more soluble phases may offset the potential toxicity of such metals in fine-grained fractions; this is tested through selective leach extractions. Consistent correlations between certain metals, such as iron and arsenic, were identified and further investigated with XRF, where specific As:Fe ratios could be associated with discrete phases. Such species appeared to increase in diversity with decreasing particle size, suggesting secondary mineralization or sorption processes.
Biosorption of heavy metals by using *Pseudomonas* sp. MF254A, bacterial strain isolated from the oil contaminated soil

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**Experimental method**

Batch experiments were performed to investigate the heavy metal removal efficiency of biosorption by using a bacterial strain which was identified as *Pseudomonas* sp. MF254A. *Pseudomonas* sp. MF254A was isolated from the oil contaminated soil at a military site in Korea. For the experiments, the initial concentration of heavy metals such as As, Cd, Cr, Cu, Pb, and Zn in the distilled water was titrated as 5 mg/L. The freeze-dried biosorbent (Pseudo-monas sp. MF254A) was added to the solution and the reaction mixture was shaken on an rotary shaker at 125 rpm for 120 min (30 °C). The mixture was centrifuged and its supernatant was analyzed on ICP/MS for residual metal concentration. Various amounts of biosorbent (from 0.01 g to 3 g) were applied for the batch experiment to investigate the sorption efficiency of the biosorbent. The effect of pH on the biosorption capacity of the bacterial biomass for Pb, Cd, and Cu was investigated in the pH range of 1.0 – 12.0 by using 50 ml solutions containing 5 mg/L of metal ions.

**Results and discussion**

From the results of experiments, for Pb, Cd, and Cr, more than 98 % of initial metal ions in the solution was removed with 3 g of biosorbent. For Cu and Zn, the removal efficiency was 99 % and 91 % using 3 g of biosorbent, respectively. At pH value between 3.0 and 5.0, removal efficiencies of Pb, Cd, and Cu on biosorption were 95 ~ 99 %.

**Conclusion**

From the batch experiments, it was investigated that the bacterial strain, *Pseudomonas* sp. MF254A is a suitable biosorbent to remove heavy metals from the aqueous solution.

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Spatio-temporal variations of winter CO₂ and CH₄ fluxes along a Alaska pipeline

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**Research Aims**

The purposes of researches are to estimate 1) how much winter fluxes of CO₂ and CH₄ along a trans-Alaska pipeline (total ca. 1000 km), 2) what are influencing factors in determining winter CO₂ and CH₄ estimates, and 3) what is implication in carbon budget as a region scale.

In order to conduct these purposes, we carried out winter transect observation during January 2005, Feburary to March 2006, and Feburary 2007.

**Discussion of results**

The spatio-temporal variation of winter CO₂ and CH₄ fluxes showed in Figure 1. Winter CO₂ fluxes in boreal forest are higher than those in tundra; on the other hands, winter CH₄ is no variation at a time and space.

**Figure 1.** Spatio-temporal variation of winter CO₂ and CH₄ fluxes along a trans-Alaska pipeline

In special, winter CH₄ flux trends to emit through the snowpack to the atmosphere along a latitudinal transect. Kim *et al.* (2007) demonstrated that winter CH₄ emitted to the vascular plants at top of tussock in snow-covered boreal forest. The area of tussock in Northern Hemisphere is 6.5X10¹³ m²; Whalen and Reeburgh, 1992). The average winter fluxes of CO₂ and CH₄ were 0.51±0.03 gCO₂-C/m²/day (average ± SE) and 2.7±0.3 mgCH₄-C/m²/day, respectively. Therefore, the winter CH₄ emission should not be overlooked in estimations of the regional/global carbon budget.

**References**

Metal reduction and formation of nanometer-sized magnetites by facultative iron-reducing bacteria isolated from inter-tidal flat sediments

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Although microbe-metal interactions play important roles in the metal geochemistry and organic matter degradation in the tidal flat sediments, studies of microbial metal reduction and iron biomineralization are beginning to be studied. The objectives of this study were to explore Fe(III) and metal reduction by the facultative metal-reducing bacteria isolated from the inter-tidal flat sediments, Southwestern coast of Korea as well as to examine microbial reduction of Fe(III) oxide hydroxides and biomineralization of Fe iron oxides by fermentation processes. Taxonomic characterization of the strains isolated from inter-tidal flat sediments indicated that they belong to genus of *Shewanella* sp. The bacteria were able to reduce FeCl₃, Fe(III)-citrate, FeOOH and metals including As(V) and Se(V) using short chain fatty acids as the electron donors. The Fe(III)-reducing bacteria were capable of reducing both akaganeite and ferrihydrite during glucose fermentation. By comparison of iron minerals formed by *Shewanella* sp.during reduction of the iron oxyhydroxides at room temperature, it was shown that *Shewanella* sp. formed 2~3 nm-sized magnetite (Fe₃O₄) particles by akaganeite reduction, whereas the bacterium formed mainly X-ray amorphous iron oxides by ferrihydrite reduction. These results suggest that microbial reduction of metals and formation of nm-sized magnetites by fermentation processes at near ambient temperatures may influence the biogeochemical cycles of carbon and metals in subsurface environments. Knowledge concerning such bio-solid state processes may be important in the synthesis and production of nm-sized ferromagnetic materials.

Using copper isotopes to distinguish biotic and abiotic effects on acid mine drainage

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Recent experiments have shown that abiotic leaching of chalcopyrite causes greater Cu isotope fractionation between original mineral (Cu₉₉ico) and leachate Cu (Cu₉₉aq) (Δ₉₉aq-min = δ⁶⁵Cu₉₉aq - δ⁶⁵Cu₉₉ico = 0.92-1.63 ± 0.23‰) than in the presence of *Acidithiobacillus ferrooxidans* (Δ₉₉aq-min = 0.10-0.53 ± 0.23‰), a known Fe- and S-oxidizing Proteobacterium. Additional mineral-free experiments show that Cu associated with *A. ferrooxidans* cells (Cu₀) is isotopically enriched relative to Cu₉₉aq in the medium (Δ₀-aq = 2.2 ± 0.23‰). Thus, cells are a sink for enriched Cu₉₉aq, accounting for the smaller biotic Δ₉₉aq-min fractionation during chalcopyrite dissolution.

In an effort to find similar abiotic and biotic fractionation signatures in a natural setting, we surveyed the Cu isotopic composition of primary minerals and stream water affected by acid mine drainage in an enargite- and chalcopyrite-containing drainage located in southwestern Colorado, USA. The δ⁶⁵Cu values measured for local enargite (δ⁶⁵Cu = -0.01 ± 0.12‰) and chalcopyrite (δ⁶⁵Cu = 0.16 ± 0.12‰) are within the general range of previously reported values for terrestrial primary Cu sulfides (-1 < δ⁶⁵Cu < 1). These mineral samples show lower δ⁶⁵Cu values than stream waters (δ⁶⁵Cu = 1.36 - 1.74 ± 0.12‰). The average fractionation between chalcopyrite and stream samples (Δ₉₉aq-min = 1.4 ± 0.17‰) is similar to that for previous abiotic chalcopyrite leach experiments.

Interestingly, the observed biotic Δ₉₉aq-min fractionation signature is not detected in the field. Mass balance supports the likelihood that the fraction of leached Cu that associates with microorganisms is less significant in the open field system compared to the closed batch experiments. Experiments designed to test potential Cu isotope fractionation during sorption of Cu₉₉aq onto *A. ferrooxidans* cells and onto mineral surfaces are ongoing. Our results suggest that Cu isotope measurements are a useful tool for better understanding Cu sources and mobility in the environment, and will aid in both ore prospecting and toxic metal remediation.
Hf isotope records of mélangé mixing and blueschist-facies metamorphism within the Catalina Schist

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Prograde metamorphic mélangé zones developed within the Catalina Schist (CA, USA) record progressive digestion and assimilation of peridotites, basalts, and sediments into a hybridized composition that is probably characteristic of the subduction zone slab/mantle interface (Bebout, 1991; Bebout and Barton, 1993, 2002). Of the isotopic records available, most reflect some degree of fractionation or mixing due to the effects of fluid flow or mineral partitioning attending metamorphism (Bebout, 1991; King et al., 2006, 2007). We present new Hf isotope data for zones of lawsonite-albite (LA) and lawsonite-blueschist (LB) facies metamorphic mélangé matrix with the goals of reconstructing sources and patterns of mass transfer occurring during prograde mélangé formation as well as recognizing potential mobility of HFSE such as Hf along and across the slab/mantle interface.

The syn-metamorphic Hf-Nd isotopic array defined by the LA-LB mélangé matrix is broadly similar to modern arc data (εHf= +12 to -2, εNd= +12 to +2). These compositions predominantly reflect mechanical mixtures dominated by MORB vs. terrigenous components, with a minor influence of high Lu/Hf pelagic sediment. Within the LA-LB mélangé dataset, high Hf concentrations (>2ppm) define a restricted Hf isotopic composition (εHf= +6 to +8); this is most likely the signature of the coeval Peninsular Ranges Batholith, as PRB trench fill dominates detrital zircon age spectra for LA-LB mélangé (Grove et al., 2007; King et al., 2007).

LA-LB mélangé samples bearing lower Hf concentrations (<2ppm) preserve more varied isotopic compositions. Most notable are a suite of high Mg-Cr samples (MgO >14wt.%; Cr >1000ppm) with surprisingly low Hf isotopic ratios (εHf= +4 to -2). Association of this more continental isotopic signature within mélangé matrix dominated by Mg-Cr-rich mantle material suggests that redistribution of Hf by metamorphic fluids occurs and is recorded by these more “receptive” ultramafic mélangé zones. Petrologic descriptions and geochemical analyses of similar types of ultramafic rock within metamorphic subduction complexes represent the most promising target for recognition of metasomatic processes occurring during subduction.

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The chemistry of Earth's dynamic surface

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Physical erosion and chemical weathering shape many aspects of the living environment: the topography of the surface, the fertility of soils, the chemistry of natural waters, and, over long time scales, the composition of the atmosphere and thus the climate of the Earth.

Researchers studying the physics and chemistry of the Earth's surface are currently exploring questions such as: What processes regulate rates and patterns of physical erosion and chemical weathering? How episodic are erosion and weathering, over timescales from minutes to millions of years? How sensitive is chemical weathering to variations in climate, and thus how strong are the feedbacks regulating climate through geologic time? How much do chemical weathering rates depend on rates of mineral supply from physical erosion? And conversely, how much does physical erosion depend on weakening of rocks by chemical weathering?

Questions like these are now being probed using a range of geochemical techniques. Cosmogenic nuclide methods, in particular, have proven useful for studying rates and patterns of surface denudation over thousands of years, at spatial scales ranging from individual outcrops to small catchments. When coupled with the bulk composition and mineralogy of parent materials and the soils that are formed from them, cosmogenic nuclide measurements can also be used to infer rates of chemical weathering over millennial time scales.

These geochemical techniques are opening new windows through which we can observe the evolution of the Earth's surface. These methods have recently shown, for example, that denudation rates are surprisingly episodic over a wide range of time scales. They have also shown that chemical weathering rates may be closely coupled with rates of physical erosion, and may be relatively insensitive to climatic variations. This presentation will outline these and other insights into the physics and chemistry of Earth's surface, as revealed within the past decade by cosmogenic nuclide methods and related geochemical techniques.

References
Detrital signal of early exhumation of the Central Ranges, Taiwan

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The Coastal Range contains the earliest sedimentary archive of active, mountain building in eastern Taiwan. The sediments were deposited in a collisional basin adjacent to the developing accretionary wedge to the west during the Plio-Pleistocene. In this study we combine low temperature fission track thermochronology and higher temperature U-Pb dating of detrital zircons to reveal the history of the region pre- and syn-exhumation.

The new provenance data show that the sediment was derived primarily from south-east China and is thermally unrest by the collision of the Philippine Sea Plate with the passive China Margin. This suggests that early exhumation rates of 5-7 mm/year, determined in previous studies, are overestimates. A requirement of the data in this study is for accelerated exhumation to be a recent feature initiated in the Late Pliocene. This is consistent with a regional hiatus in sedimentation that marks a period of relative quiescence between ~3-2 Ma prior to a change in regional tectonic forcing.

Paired δ⁴⁴/⁴⁰Ca, Mg/Ca and Sr/Ca in cultured G. ruber

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δ⁴⁴/⁴⁰Ca, Mg/Ca and Sr/Ca ratios were determined on a single species of cultured planktonic foraminifera (G. ruber) and the culturing solutions. The foraminifera were grown in seawater at (i) constant temperature but varying salinities of 32 to 44 ‰, (ii) constant oceanic salinity but varying temperatures of 18 to 30°C. In an additional culturing experiment, the carbonate system was manipulated so as to keep the total inorganic carbon constant but to alter the pH (and hence total alkalinity).

The δ⁴⁴/⁴⁰Ca value of cultured G. ruber shows a significant (R² =0.91, p<0.02) inverse linear correlation with salinity [δ⁴⁴/⁴⁰Ca (‰) = 1.27(± 0.36) - 0.016(± 0.009)*S]. Paired Mg/Ca and Sr/Ca both have negative linear correlations with δ⁴⁴/⁴⁰Ca (R² =0.84 and R² =0.94, respectively) in these salinity experiments, indicating a common control on all three proxies.

Ca isotopes have a nearly constant degree of fractionation between 21 and 27°C (δ⁴⁴/⁴⁰Ca ~ 0.77‰), but the degree of fractionation increases (δ⁴⁴/⁴⁰Ca < 0.77‰) at higher and lower temperatures. Mg/Ca shows 8% increase per °C. δ⁴⁴/⁴⁰Ca has no apparent correlation with Mg/Ca or Sr/Ca in the temperature experiments, but appears to reveal an optimum curve. δ⁴⁴/⁴⁰Ca values of G. ruber have a weak dependence (with a slope of +0.0005 ± 0.0002 ‰/µM) on [CO₃²⁻]. At [CO₃²⁻] < 200 µM, Mg/Ca increases by ~30% per 0.1 unit decrease in pH.

The data can be explained by a model based on our understanding of the mechanisms of calcite formation in planktonic foraminifera.
Influence of hydrothermal transformation of amorphous silica on amino acid adsorption capacity

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Silica is the major component of the earth’s crust and changes its structure with different crystallinity during diagenesis. Silica has been suggested to assist the chemical evolution of life because of its adsorption and catalytic capacities for organic matter (Bujdak and Rode, 1997). However, it is not known how these properties change with diagenesis. In this study, amorphous silica was hydrothermally transformed and its adsorption capacity for amino acid diagenesis. In this study, amorphous silica was hydrothermally transformed and its adsorption capacity for amino acid (Lysine) was investigated.

Methods

Silica gel (WakoSil-25SIL) was heated at 180°C until 48 hours with de-ionized water. The infrared (IR) absorption peak height ratio (Si-OH/Si-O-Si) was used as a measure of dehydration/polymerization degree (Ito and Nakashima, 2001). After this treatment, the silica was mixed with Lysine solution. Adsorbed Lysine was determined by Ion chromatography.

Results and Discussion

With increasing heating time of silica, the Si-OH/Si-O-Si ratio and the adsorbed Lysine gradually decreased (Fig. 1). The adsorption capacity of silica decreased by dehydration/polymerization. However, the adsorbed Lysine per specific surface area remains almost unchanged (Fig. 2). If the surface concentration of amino acid is the main factor for the chemical evolution of life, a variety of amorphous silica with different surface structures might be available for the amino acid adsorption process.

Fig. 1. The relationship between the Si-OH/Si-O-Si ratio and adsorbed Lysine [mmol/g]

Fig. 2. Changes with time of adsorbed Lysine per specific surface area [μ mol/m²]

References


Detecting the origin of saline solutions in salt deposits of the German Zechstein basin

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Considering the fact that salt is soluble in water, the problem that salt mines intruded by external water encounter the risk of flooding is obvious. However, the chance that liquids were inclosed in salt deposits during or after compaction is also known, but poses a considerably lower risk. The distinction of these internal and external inflows is vital for salt companies to avoid the loss of a mine by taking appropriate preventive actions.

One method to distinguish between open and closed inflows is the comparison of δD and δ18O of the saline solutions to the global meteoric water line (e.g. Müller & Papendieck 1975). However, this method is indistinct when used stand-alone.

So far, we have analyzed 106 samples from 25 sites in 12 German mines and 11 groundwater wells for 87Sr/86Sr and the Sr concentration in addition to δD and δ18O. One approach is the comparison of 87Sr/86Sr and δ18O versus the stratigraphic position of the intruded salt rock. The isotopic oscillations of those saline solutions which are -for several reasons- considered to be of salt internal origin show approximately the same pattern. Since the two main processes -hydrothermal convection and continental runoff- that control both isotopic systems in seawater should generate anti-correlations for Sr and O isotopes in marine deposits, the genesis of the saline solutions has to be more complex. However, a link between the evolutions of 87Sr/86Sr and δ18O must exist.

Regarding the Sr concentrations in the internal solutions, the Sr content of <3 ppm is comparatively low. In contrast, the samples from most of the open system solutions show much higher amounts between 15-240 ppm, probably absorbed from detritical clays deposited in the beginning of each evaporitic cycle. In addition, their δ18O values of −12 to −10 % resemble those of the groundwater in the vicinity of the mines. The internal solutions cover a wide range of −12 to +3 ‰. Their main ingredient is MgCl2 which almost impedes the presence of Ca. Since the chemical attributes of Sr are similar to those of Ca, this could be one reason for the absence of Sr in salt internal solutions.

Based on the isotopic information, a distinction between open and closed system solutions is yet quite complex. However, the apparent usefulness of the Sr concentrations as a fast distinction tool is further to be evaluated.

References

Nano/microstructure of polymer-derived SiOC ceramics

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The formation of nanodomains in a carbon-rich SiOC ceramic was investigated depending on annealing temperature. The high carbon content of the pure SiCO system was achieved by utilizing divinyl benzene as an intrinsic cross-linking agent. The incorporation of carbon- and silica-rich regions within the amorphous matrix implies the questions about domain size and thermal stability of such local domains. The nanostructure of the carbon-rich material was studied in detail upon pyrolysis at 1000 °C and after additional thermal anneal at 1450 °C. High-resolution and energy-filtered TEM as well as electron energy-loss spectroscopy were employed to gain an understanding of the intrinsic micro/nanostructure of such polymer-derived ceramics. Although a progressive structural rearrangement within the SiOC matrix was confirmed with increasing temperature, the sample heat treated at 1450 °C remained predominantly amorphous. Based on the experimental observations, a structural model is presented, which is consistent with the high-temperature mechanical response.

Fe-Ni-O-S phase relations during serpentinization (MAR 15°N)

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The strongly reduced nature of the vent fluids in ultramafic-hosted hydrothermal systems is due to the production of hydrogen by hydrolysis of ferrous iron in the host rock. The specific fluid-rock reactions and phase relations involved, however, are incompletely understood. To further our understanding of hydrogen production during serpentinization, we investigate the composition and phase relations of oxides, sulfides, native metals, hydrous silicates, and hydroxides in serpentinites. These phases are not only indicative of redox conditions, temperature and fluid flux during serpentinization, some of them are also important surface catalysts for organic synthesis reactions.

On thin section scale, opaque phases, except for Cr-spinel, are generally not randomly distributed. They are developed either in mesh rims or associated with serpentine and serpentine-magnetite veins. Primary opaque phases are Cr-spinel (Cr# ca. 0.5) and cobaltian pentlandite. While Cr-spinel shows only incipient alteration to magnetite, pentlandite is invariably desulfurized and altered to secondary Fe and Ni phases. The phase relations change systematically with increasing extent of serpentinization. In samples where relict olivine is present, pentlandite is replaced by an iron-nickel metal alloy, awaruite (Ni₃Fe), and/or heazlewoodite (Ni₃S₂) along with magnetite indicating very low oxygen and sulfur fugacities. In contrast, millerite is the dominant Ni-sulfide in completely serpentinized rocks. It is usually accompanied by pyrite(+/− polydymite), and the assemblage represents increased oxygen and sulfur fugacities, which develop when the reducing capacity of the rock is exhausted. These observations indicate that phase relations in the system Fe-Ni-O-S are sensitive indicators of the evolution of hydrogen and sulfur fugacity during serpentinization, as predicted by Frost (1985). Using geochemical modeling and concentration-fugacity relations, we were able to compare our observations with H₂S and H₂ concentrations determined in vent fluids from ultramafic-hosted systems. In the Rainbow and Logatchev field, those are consistent with metastable equilibria between pentlandite, awaruite, heazlewoodite and magnetite. Our calculations for the Lost City field yielded similar results, despite apparent environmental differences between these systems.

The abundance of talc in rocks with pyrite-millerite+/−polydymite assemblages indicate that high activities of aqueous silica and increased sulfur and oxygen fugacities are related. These relationships are explored in a companion paper presented in session S92.

Reference
Sr Isotopes and trace element patterns in sub-calcic garnets: A perspective on diamond-bearing fluids?

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Sub-calcic garnets are typical xenocrysts in kimberlites. They are found as inclusions in gem quality diamonds and as such have implications for the diamond growing area. This study focused on eight xenocrystic sub-calcic garnet crystals from the Ekati property, Canada. We studied the trace element and REE patterns of the garnets as well as the Sr and oxygen isotopic composition in order to investigate their origin and the nature of associated metasomatism.

Chondrite normalized REE patterns are sinusoidal, however, the slope of the curve varies (Nd/La = 1.7 to 70; Nd/Er = 1.9 to 48). The highest enrichment varies between LREE (Nd) and MREE (Eu). One crystal exhibits a pronounced Ce anomaly (Ce/Ce* = 3.3). Garnets have highly radiogenic Sr (87Sr/86Sr = 0.710371 to 0.731198). Enrichment in radiogenic Sr is coupled with increased concentrations of Ce, Sr, Nd, Sm, Pr, Nb, La, Th and U. The radiogenic Sr is not supported by the low Rb content of the garnets. The high Zr/Yb and low Sr/Yb ratios of the less radiogenic crystals indicate interaction with a Zr-rich and low Sr agent. The O isotopic composition of the garnets varies between 5.23 and 5.42‰, with a broad positive Zr-rich and low Sr agent. The O isotopic composition of the garnets indicates interaction with a low Rb content of the garnets. The high Zr/Yb and low Sr/Yb ratios of the less radiogenic crystals indicate interaction with a Zr-rich and low Sr agent. The O isotopic composition of the garnets varies between 5.23 and 5.42‰, with a broad positive Zr-rich and low Sr agent. The O isotopic composition of the garnets varies between 5.23 and 5.42‰, with a broad positive Zr-rich and low Sr agent.

We calculated the composition of possible metasomatic agents in equilibrium with the garnets using partition coefficients for carbonatitic, silicic and hydrous-silicic melts. Diamond-forming fluids show some similarities to the calculated metasomatic agents (positive Pb anomaly and negative Zr, Ti and Nb anomalies). However, REE concentrations in typical diamond forming fluids are much higher than those of the calculated metasomatic agent. Carbonatitic–silicic globules reported in lherzolitic clinopyroxene microcrystals closely resemble the trace element composition of the garnet metasomatic agent. Phase equilibria experiments indicate that sub-calcic, Cr-rich garnets have recrystallized from subducted Cr-rich protoliths. We propose that the garnets inherited an enriched Sr signature from old subducted oceanic lithosphere and were affected by extensive metasomatism of an agent not very different from carbonatitic-silicic melts and diamond forming fluids.

Hf-W chronometry and the thermal evolution of asteroids

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Hf-W chronometry has widely been applied for dating the differentiation of asteroids and terrestrial planets [1] but its potential for dating meteorites and constraining the thermal evolution of asteroids has yet to be explored. We determined Hf-W metal-silicate isochrons for various ordinary chondrites and acapulcoites and obtained the following ages: ~3 Myr for the H4 chondrite Ste. Marguerite; ~10 Myr for the H6 chondrites Kernouve and Estacado; ~6 Myr for acapulcoites Dhofar 125 and NWA 2775 (here Myr refers to time after formation of CAIs). These Hf-W ages are older than Pb-Pb ages for phosphates [2, 3] and pyroxenes [4] for the same or similar meteorites, indicating that the Hf-W closure temperature in these samples is higher than the ~780°C Pb-Pb closure temperature of pyroxenes. Hf-W ages therefore provide essential information on the earliest cooling history of meteorite parent bodies. Our new Hf-W ages combined with previously reported Pb-Pb ages for the same or similar meteorites [2-4] reveal that acapulcoites cooled more rapidly than H6 chondrites but similar to H4 chondrites. This suggests that either the acapulcoite parent body is smaller than the H chondrite parent body or that the burial depth of acapulcoites was shallower. Compared to H6 chondrites, acapulcoites were heated to higher temperatures (as is evident from the formation of FeNi-FeS melts) but cooled more rapidly, indicating that the acapulcoite parent body contained a higher amount of 26Al and hence accreted earlier than the H chondrite parent body. Acapulcoites may derive from a body that accreted as early as the parent bodies of the magmatic irons (<1.5 Myr [5]) but was too small to efficiently retain the heat produced by 26Al decay. Alternatively, the acapulcoite parent body might have accreted later than ~1.5 Myr but before accretion of the H chondrite parent body at ~3 Myr (as derived from the Hf-W age of Ste. Marguerite). The presence of relict chondrules in some acapulcoites suggests that the latter scenario might be more likely. The Hf-W data indicate that the early evolution of asteroids is largely controlled by the time of parent body accretion and hence the amount of 26Al present. This most likely reflects increasing accretion times with increasing distance from the Sun, consistent with the heliocentric zoning of the asteroid belt [6].

Is dehydration melting responsible for the evolution of high-K granitic melts throughout the Precambrian?

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Precambrian granitoid terrains mainly show two main intrusion events of granitoid rocks: a first phase of K-poor granitoid melts (granodiorites s.l.). The granodiorites (s.l.) intrude into pre-existing crust and are usually of juvenile character with higher influence of mantle material. The mechanisms of first phase granitoid melts experience a major change at the Archaean/Proterozoic boundary as indicated by the existence of TTG complexes only in Archaean times. TTG’s are special in their liquid line of descent as they are not following the main post-Archaean differentiation path (i.e. the “classical” calcalkaline differentiation) as seen in proterozoic first phase melts. In a second magmatic phase the pre-existing crust suffers an anatectic event that produces high K-granitoids. Second phase melts often intrude in a restricted time interval and field relationships indicate short transport distances for these melts. In this study K-rich granites of different precambrian granitoid terrains were compared: (i) Meso- and Neoarchaean K-rich granitoids from Barberton Mountain Land (Kaapvaal craton, South Africa/Swasiland), (ii) Paleoproterozoic K-rich granitoids from Västervik area (Baltic Shield, Sweden) and Huab metamorphic complex (Congo craton, Namibia). Archaean and Proterozoic K-rich granites show typical crustal geochemical characteristics. More importantly, Sr-Nd isotopes reveal ternary mixing relationships. Three end-members can be traced: (1) juvenile mantle material, (2) country rock material and (3) metasomatic fluids. Juvenile material is clearly under-represented and the two main contributing end-members are country rock material and metasomatic fluids. Highly radiogenic Sr initial ratios indicate mica breakdown and thus, dehydration melting as trigger mechanism for the sudden onset of the granite production factory throughout the Precambrian.

U-series crystal ages of plagioclase and zircon from the 1300 CE Kaharoa eruption, New Zealand

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The 1300 CE Kaharoa eruption of Tarawera Volcano in New Zealand offers an excellent opportunity to examine of uranium-series crystal ages of multiple phases in young rhyolitic magma. These lavas and pumices are crystal rich with abundant plagioclase feldspar and zircon (>35 volume % crystals) that can be dated using $^{226}\text{Ra}-^{232}\text{Th}$ and $^{230}\text{Th}-^{238}\text{U}$ disequilibria, allowing for a thorough comparison of the timing of crystallization for both major and trace phases in this single rhyolite eruption. The Kaharoa eruption at Tarawera produced 2.5 km$^3$ of rhyolite lava and 5 km$^3$ of pyroclastic material making it the largest eruption in New Zealand over the last 1,000 years (Nairn, 2002).

Samples from two pumice fall deposits (B and J Pumice) and the Ruawahia Dome and associated block and ash flow were chosen to examine the crystal ages of plagioclase and zircon. All of these samples have a whole rock silica content of 74-75 wt%, while their Zr contents vary: dome samples average 130 ppm and pumice average 93 ppm. This compositional difference is reflected in other trace elements. It is also seen in the An content of plagioclase grains (Figure 1). The pumice samples have a narrow range of average An content for both cores and rims (An$^{19-22}$) while the domes are much more diverse between the cores (An$^{30-45}$) and the rims (An$^{23-25}$).

Preliminary U-series analyses of whole rock samples using a Nu Plasma MC-ICP-MS at UC-Davis indicate that the pumice and dome samples have different Th isotopic compositions. Future analyses will include U-Th-Ra analyses of whole rock, glass and plagioclase separates in two different size classes (125-250 µm and 250-500 µm) along with U-Th analyses of single zircon (SHRIMP). Zircon separates will include crystals derived from the groundmass/glass and as inclusions within plagioclase. These analyses will elucidate the timescales of crystallization of major and trace phases within rhyolite magma and determine whether zircon and plagioclase ages record the same magmatic events.

Reference

Osmium isotopes as a provenance tracer? A case study from Cabrières

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La Capitelle du Broum, located in the chalcolithic copper mining district of Cabrières (Hérault, France), is the first chalcolithic copper smelting workshop known in France dating to the beginning of the 3\textsuperscript{rd} millenium BC [1]. These fahlore mines are composed of tetrahedrite, and the secondary minerals malachite, azurite and cuprite [1]. The entire chain of production from ore to slags, droplets of copper, ingots and artefacts was located on the site [1].

To determine if Osmium (Os) isotopes can be used as a provenance tracer, primary and secondary minerals from different deposits around the archaeological copper smelting site as well as three ingots and six artefacts from within the excavation site, were analysed. That no additional flux agent had been added to the smelting process, which is important for a provenance tracer, was shown by the large variety of the slag compositions [2]. This proves that there was no intention to produce a liquid slag to separate the metal and/or matte from the host rock by adding a flux agent [2]. Beside the Os isotopes also the commonly used lead (Pb) isotopic composition for provenance tracing was applied.

The ore samples show a large spread in all the Pb/Pb isotope ratios, which is typical for fahlores, but no variation between primary and secondary minerals. The Pb isotopic variation of the ingots and artefacts are much smaller and plot within the large Pb/Pb ore field, which shows that during smelting the Pb isotopic composition homogenises and that high firing temperatures of the ore (1000-1200°C) [2] did not change the Pb isotopic composition. The artefacts are therefore most likely produced from those Cabrières ores.

This is different for the Os isotopes. The \textsuperscript{187}O\textsubscript{S}/\textsuperscript{184}Os of the ores spread between 20 and 60, whereas the ingots have decreased \textsuperscript{187}O\textsubscript{S}/\textsuperscript{184}Os ratios from 20 to 23 and the final artefacts show even lower \textsuperscript{187}O\textsubscript{S}/\textsuperscript{184}Os values of around 12. Therefore Os isotopes cannot be used as a source tracer like Pb isotopes. Furthermore the [Os] decreases from around 90 pg/g for the ores down to 12 pg/g for the ingots and artefacts, due to the volatility of OsO\textsubscript{4}, which must have been produced in the smelting process, indicating a primitive oxidising environment within the smelting process. The decrease in the isotopic composition and the [Os] from ore to ingots and artefacts shows that most of the Os was lost during smelting but that an ingrowth of the \textsuperscript{187}Os by the decay of \textsuperscript{187}Re had taken place. Rhenium concentration measurements on the ingots and artefacts will finally show if the Re/Os system can be used as a dating tool for metal artefacts.

References


Mimetite formation from goethite adsorbed lead

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Immobilization of heavy metals widespread in contaminated soils is still an important issue in environmental research. High levels of arsenic are present as a contamination of agricultural soils where pesticides, herbicides, and fungicides were used (Comba et. al. 1988; Bajda et. al. 2007). These soils are often contaminated by lead as well. Bioavailability of arsenic in contaminated soils can be reduced to insignificant levels by precipitation of mimetite Pb\textsubscript{5}(AsO\textsubscript{4})\textsubscript{3}Cl. This results in conversion of bioavailable arsenate compounds into highly immobile mineral form resulting in neutralization of the toxicity without removal of As(V).

Goethite \(\alpha-\text{Fe(OH)}\textsubscript{3}\) is a mineral widespread in soil environment. It can easily adsorb arsenates or lead ions. The adsorption of lead ion onto these surface is reversible and desorption increase with decreasing pH (Cornell and Schwertmann, 1996). The objective of this study was the reaction between arsenic ions in the solution and a synthetic goethite saturated with adsorbed Pb(II). The sorption of lead ions (initial [Pb] = 50 mg/L) onto goethite at pH=4.8 caused 99% decrease of Pb concentration in the solution in 24 hours. The subsequent reaction between goethite-adsorbed lead and aqueous arsenate in the presence of CI results in crystallization of aggregates of mimetite crystals indicating homogeneous nucleation in the volume of the solution. Crystallization of mimetite is very rapid. The results suggest that the kinetics of lead desorption from goethite is fast, at least equal to the rate of diffusion and advection of AsO\textsubscript{4}\textsuperscript{3-} ions in the solution and the crystallization of mimetite. The decrease of As concentration in the solution after 48 hours of reaction indicates that apart from mimetite crystallization, adsorption of goethite took place.

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Utah and Czech Mars analog concretions; Aquatic hematite and goethite characterization

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Terrestrial Jurassic Navajo Sandstone concretions from Utah show resemblance to the hematite spherules (“blueberries”) imaged by the Mars Exploration Rover (MER) Opportunity. Both the NASA MER team and terrestrial analog studies interpreted the Mars hematite spherules to be concretions precipitated from diagenetic aqueous solutions in the sediment.

Magnetic analyses of Utah and Czech hematite concretions show unusual and complex behavior of antiferromagnetic hematite-goethite composition. We developed a method allowing us to separate the magnetic signature of goethite from hematite and further show that although hematite saturates in 1-2 Tesla range, goethite continues to acquire magnetization even above 10T. Parallel Mössbauer spectra confirm the presence of both hematite and goethite in these terrestrial samples. Magnetic separation allows using the terrestrial concretions as paleofield recorders.

Magnetic signature is tied to aqueous hematite/goethite formation in the sediment. Hematite and goethite (occasionaly also magnetite), carry a record of past magnetization events. Such magnetic signatures help interpretation of their formation.

Based on field observation and laboratory analysis, we suggest that concretions may have formed along the fluctuating water table, that periodically left behind water saturated volumes. Slow evaporation of these volumes initiated precipitation of goethite/hematite from the aquatic solution. Fe isotope data reveal some lighter isotopic iron initiated precipitation of goethite/hematite from the aquatic solution.

Future Mars Rover and sample return missions should include instrumentation for in situ magnetic measurements. Hematite and goethite are well-studied terrestrial magnetic minerals and have magnetic properties suitable for resolving the origin of the spherules. Ferromagnetism of hematite and goethite should record ancient magnetic fields, and has magnetic grainsize in the range that can be used efficiently as a paleotemperature recorder. Thus the magnetic signatures give us tools to study the origin of “blueberries”.

Nd isotope records of the deep south Atlantic and the interpretation of Neogene δ13C gradients

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Records of the past Nd isotope composition of the deep ocean can resolve ambiguities in the interpretation of other paleocirculation tracers. For example, recently published records of Neogene δ13C gradients from the deep Atlantic [1, 2] can be interpreted either in terms of changes in the strength of deep water export from the North Atlantic, or due to variation in the pre-formed δ13C of southern-derived deep water in response to shifts in the surface paleoceanography of the Southern Ocean. Here we present the first Nd isotope data for benthic foraminifera and apply down-core deep water Nd records from this and other substrates to the resolution of ambiguities in nutrient-based tracers.

Comparison of the εNd of core-top foraminifera from a depth transect on the Walvis Ridge to published seawater data suggests that benthic foraminifera represent a reliable archive of the deep water Nd isotope composition. Though data obtained through leaching of Fe-Mn coatings often record the Nd isotope composition of local inputs to the ocean, in this case paired down-core leaching and foraminiferal analyses usually yield identical results, giving confidence in their paleoceanographic significance.

The new εNd datasets, along with Cd/Ca and Nd/Ca ratios from the same foraminiferal samples, are interpreted in the context of debates over the Neogene history of North Atlantic Deep Water (NADW) export to the south Atlantic. Our data suggest strong NADW export from 9 to 5.6 Ma, mostly in congruence with one interpretation of published δ13C gradients [1]. Where the εNd record differs from the nutrient-based records, such as between 7 and 6 and at 4 Ma, changes in the pre-formed δ13C or Cd/Ca of southern-derived deep water might account for the difference. Maximum NADW-export in the last 9 Ma is suggested by all proxies at around 4 to 3.5 Ma. Chemical conditions between 3 and 1 Ma are different suggesting, on average, the lowest NADW export of the entire record. Modern-day values are similar to average values from 9 to 4 Ma, implying NADW export today as strong as at any stage over the past 9 Myr.

Reference

The effect of \( f_O^2 \) and composition on sulphur solubility and speciation in hydrous silicate systems

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The release of volcanic gases is monitored worldwide. The flux of \( \text{SO}_2 \) in the plume and the \( \text{S}/\text{Cl} \) ratio vary systematically with the style of volcanic activity [1]. In order to relate these volcanic gas signatures to processes inside the volcanic edifice the mechanisms of sulphur incorporation in melts and the transfer into a fluid phase has to be known. Sulphur has several oxidation states and \( f_O^2 \) is a crucial control on the sulphur solubility and hence the transfer of sulphur from a magma into a vapour phase.

In this study the sulphur solubility and speciation was determined for various hydrous iron-free silicate glasses equilibrated with sulphur at geological relevant P-T-\( f_O^2 \) conditions. Glass compositions include “simple” (e.g. \( K_2\text{Si}_4\text{O}_9, Rb_2\text{Si}_4\text{O}_9 \)) and more complex compositions (Albite, Trondhjemite). Experiments were performed in CSPV and with \( K_2\text{Si}_4\text{O}_9, Rb_2\text{Si}_4\text{O}_9 \) and more complex compositions (Albite, Trondhjemite). Experiments were performed in CSPV and with \( K_2\text{Si}_4\text{O}_9, Rb_2\text{Si}_4\text{O}_9 \) and more complex compositions (Albite, Trondhjemite). Experiments were performed in CSPV and with \( K_2\text{Si}_4\text{O}_9, Rb_2\text{Si}_4\text{O}_9 \) and more complex compositions (Albite, Trondhjemite). Experiments were performed in CSPV and with \( K_2\text{Si}_4\text{O}_9, Rb_2\text{Si}_4\text{O}_9 \) and more complex compositions (Albite, Trondhjemite). Experiments were performed in CSPV and with \( K_2\text{Si}_4\text{O}_9, Rb_2\text{Si}_4\text{O}_9 \) and more complex compositions (Albite, Trondhjemite). Experiments were performed in CSPV and with

The total sulphur solubility is a function of the degree of polymerisation of the silicate glasses and increases with increasing NBO/T. At reducing conditions (QFM) highly depolymerized glasses dissolve twice the amount of S (up to \( \sim 2 \) wt. %) compared to oxidising conditions (QFM+4). In runs that were saturated with sulphur, sulphate/sulfide blebs were identified, indicating the presence of an immiscible sulphate/sulfide liquid.

The oxidation state of sulphur dissolved in the glasses and the relative abundances of S-species were determined by XANES. Stable S-species in the glasses are sulfide (\( \text{S}^- \)) and/or sulfate (\( \text{SO}_4^{2-} \)) as previously demonstrated [2]. The occurrence of sulfite (\( \text{SO}_3^- \)) in the XANES experiments is demonstrated to be due to beam damage. The \( \text{S}^+/\text{S}^2- \) ratio in the glass is a function of \( f_O^2 \). At \( f_O^2 \geq \text{QFM}+1.5 \) sulphur is dissolved as \( \text{S}^0 \). At \( f_O^2 \sim \text{QFM} \) sulphur is dissolved as a mixture of \( \text{S}^0 \) and \( \text{S}^- \). The lowest fraction of \( \text{S}^0 \) was \( \sim 0.25 \) at \( f_O^2 \sim \text{QFM}-0.7 \). The relatively steep change of \( \text{S}^+/\text{S}^2- \) ratio with \( f_O^2 \) is in the range of QFM-1. This is at two orders of magnitude lower \( f_O^2 \) than previously reported for Fe-bearing systems (QFM+1, [2]). Thus, for a fixed \( f_O^2 \) at ~QFM sulphur is dissolved as mostly \( \text{S}^2- \) in Fe-bearing systems and as \( \text{S}^0 \) in Fe-free systems. This is of importance for natural processes that result in a dramatic change of the prevailing Fe/S ratio (e.g. slab melting, metasomatism, immiscible S-liquids) and has to be implicated in models aiming to quantify the sulphur flux at volcanoes.

Reference

Jarosite and goethite identified by Mössbauer spectroscopy on the surface of Mars: Mineralogical evidence for aqueous processes

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The Mars Exploration Rovers (MER) Spirit and Opportunity have explored the Martian surface at Gusev Crater and Meridiani Planum for more than 3 Earth years, traveling more than ~ 10km (Opportunity) and ~ 7km (Spirit), each carrying our Mössbauer Spectrometer (MBS) MIMOS II [1]. Each of the instruments have analyzed more than 100 targets during their ongoing missions (>1100 sols). More than 15 different minerals have been identified so far by the Mössbauer instruments on board the two rovers [2,3,4]. Mössbauer spectroscopy identified the secondary Fe\(^{3+}\)-bearing minerals jarosite, hematite, and nanophase iron oxides in the sulfate-rich outcrop rocks at Meridiani Planum [3]. The sulfate rich outcrop material covers the whole area Opportunity traveled across so far, without significant changes in the mineralogical composition. At Gusev Crater rocks are much more diverse, ranging from little altered basaltic material in the plains to pervasively altered basalt in the Columbia Hills [2,4]. Secondary minerals include the Fe\(^{3+}\)-bearing minerals hematite, goethite, nanophase iron oxides, and an unspecified iron sulfate phase. The relation between primary and secondary minerals varies over short spatial scales. Recent results from Gusev Crater indicate the presence of hematite in greater abundance than in many targets at Meridiani.

In particular the minerals jarosite and goethite [5] found at Meridiani Planum and Gusev Crater, respectively, are clear mineralogical evidence for aqueous weathering processes active at both landing sites in the past.

References
A possible laser ablation xenotime U-Pb age standard: Reproducibility and accuracy

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With the in-situ U-Pb dating of phosphates by SIMS and LA-ICP-MS new possibilities of linking geochronological and petrological data have been opened up. But wide application of the method is presently hampered by the absence of any accepted xenotime standard for U-Pb dating.

In order to establish such a well defined age standard, xenotime was separated from a Weinsberg granite sample (type Plochwald) from the Bohemian Massif (Austria). This xenotime has a concordant U-Pb TIMS age of 315 ± 2 Ma. No elemental zonation in the crystals was visible using BSE and CL imaging.

Instrumental and analytical setup: New Wave 193 nm solid state laser ablation system with He as carrier gas, Nu Instruments HR multi-collector double-focusing ICP-MS, Nu Instruments DSN-100 desolvating nebulizer. The MS was setup to allow the simultaneous acquisition of the masses $^{238}\text{U}$,$^{233}\text{U}$,$^{229}\text{Th}$,$^{207}\text{Pb}$,$^{206}\text{Pb}$,$^{206}\text{Pb}$,$^{205}\text{Ti}$,$^{204}\text{Pb}$,$^{203}\text{Pb}$. During analysis a $^{235}\text{U}$-Tl spike solution was added to the ablated material as a dry aerosol.

Data reduction: Raw signal intensities are corrected for gas blank using 40 sec of signal acquisition prior to sample analysis. Power law and $^{206}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{205}\text{Pb}$ ratios. The U/Pb elemental fractionation is corrected for using an intercept method applying linear regression. The calculated intercept values are corrected for mass discrimination using standard bracketing.

115 measurements on 15 xenotime crystals of 150 to 200 µm size were performed on three consecutive days. Lines with 5µm spot size and 30 µm length were rastered with 5 µm/sec. 12 passes resulted in a total of 72 sec of ablation per analysis.

No significant day-to-day or grain-to-grain variations in age could be detected, nor did the orientation of the laser raster parallel to the prominent {110} cleavage or parallel to crystal faces result in any age discrimination.

Results: All analyses resulted in concordant data points. On average, ages from single line analysis have 2-sigma precisions of 7.6%, 8.3%, and 5.7% for the $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, and $^{208}\text{Pb}/^{206}\text{Pb}$ ages, respectively. The total mean age of all analyses (without rejections) is 313.4 ± 1.9 Ma (2-sigma), in absolute concordance with the conventional TIMS data.

We propose that the investigated xenotime can effectively be used as a standard for in-situ LA U-Pb age dating with a spatial resolution as low as 5 µm.

External accuracy of laser ablation U-Pb zircon dating: Results from a test using five different standards

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Using a state-of-the-art 193nm-LA-MC-ICP-MS system and thorough control on analytical procedures, the long term (months) external accuracy and reproducibility for Phanerozoic zircons using standard bracketing is 1% to 2% 2RSD for the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages. This is true when using only one standard zircon, such as 91500, for the matrix matched calibration. When using different standards for the calibration (i.e. Plesovice, Sri Lanka, Temora) suspicious systematic shifts in the obtained ages and thus a reduction in the overall accuracy of the dating method become obvious. These shifts are in the range of a few percent of the U-Pb ages and seem to vary unsystematically with age and zircon composition. Two main causes could be made responsible for the effects: 1) matrix and or ablation process-related effects stemming from (subtle?) differences in standard and sample compositions; 2) instrumental effects from the laser system or the mass spectrometer.

In order to test which of the two is responsible, a ‘test of accuracy’ experiment was conducted. Any instrumental effects were reduced as far as possible by analysing five different standard zircons mounted on one single mount and analysed during one session using the identical protocol for all analyses and without changing any instrument parameters and keeping ion beam intensities as identical as possible. Each standard was analysed 8 times with two analyses per grain resulting in a total of 80 measurements. For data reduction, every standard served consecutively as calibration standard, the others were treated as unknown variables. The known standard age and the four calculated ages using the respective four other standards for calibration were then compared. Even using such a very strict analytical Protocol age shifts were still present. They vary non-systematically and range from -1 Ma to +20 Ma (i.e. 0.3% to 10%) for the investigated age range (1064 Ma to 220 Ma).

Conclusions: Accepting the absence of any instrumental effects (i.e. no memory effects, no effects from dead-time correction, non-linearity of ion counters and inter-detector calibration,…), the observed age shifts have to be attributed to matrix and/or ablation process-related effects. Therefore, to allow the comparison of laser ablation zircon U-Pb ages on an intra- and inter-laboratory basis, more rigorous than usual matrix matching procedures have to be applied, and the resulting reduction in the overall accuracy has to be included into the error propagation schemes for the final age data.
Fluid venting at a Cretaceous seamount, Canary Archipelago

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Henry Seamount is a 8-km-wide, 660-m-high edifice rising from 3700 m deep seafloor southeast of El Hierro, the youngest of the Canary Islands (1.1 Ma). Sonar and seismic data revealed that the seamount is an old volcano with radiating gullies and a sediment cover of several meters (Gee et al., 2001). Dredging during Meteor cruise M66/1 in 2005 recovered (i) slightly to heavily altered trachyte fragments covered by thin Mn-crusts; (ii) a fresh porous barite block overgrown by a coral stem; (iii) abundant shell fragments of vesicomyid clams up to 15 cm in size; and (iv) soft sediments and sediment rocks.

The trace element compositions of the trachytes indicate an origin by intraplate rather than ridge volcanism. Ar/Ar dating of feldspars and matrix of two trachyte samples gave an age range of 123.8 to 126.4 Ma, which is considerably older than any of the Canary Islands. The combined morphological and age data support the interpretation of Henry Seamount being an extinct volcano.

The recovery of shells from vesicomyid clams at Henry Seamount is surprising since this species is always associated with hydrothermal vents or seepage. 14C dating of two shells gave ages of 3.4 and 18.6 ka consistent with Recent venting activity. Fluid discharge at Henry Seamount is also indicated by the recovered barite block having δ34S values between 26.5 and 31.8 ‰ and δ18O values between 14.1 and 16.9 ‰. To our knowledge, this is the first reported finding of vesicomyid clams within the Canary Archipelago and also the first direct or indirect evidence of fluid venting in this area.

How can Recent fluid venting at Henry Seamount be reconciled with its early Cretaceous age? We propose that hydrothermal circulation within the Jurassic oceanic crust around El Hierro is driven by a mechanism similar to that proposed for young crust of the Juan de Fuca ridge flank (Fisher et al., 2003), the ultimate heat source being the hotspot beneath the western Canary Islands. Henry Seamount may thus work as a "breathing hole" where fluid discharge is facilitated by a rather thin sediment layer compared to the adjacent seafloor covered by thick impermeable sediment. Recharge may occur at adjacent basement outcrops such as the flanks of El Hierro island. Our results indicate that hydrothermal circulation through seamounts is not confined to young warm ridge flanks but may be a widespread phenomenon on the ocean floor.

References

Unfractionated excess air: The result of incomplete dissolution of entrapped air?

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Dissolved atmospheric (noble) gases in groundwater usually exceed their respective atmospheric equilibrium concentrations. This phenomenon is usually referred to as "excess air" in groundwater hydrology.

The formation of excess air has been suggested to result from the (partial) dissolution of entrapped air within the quasi-saturated zone. Excess air in groundwater crucially hampers the interpretation of environmental tracer data. Therefore, several lumped parameter models have been developed to parameterize the excess air component, which can then be separated from the total measured gas concentrations. However, these models do not include a mechanistic description of the gas exchange in porous media.

Excess air can be either unfractionated, i.e., the elemental composition is atmospheric, or fractionated with respect to atmospheric air. The most simple lumped parameter model was introduced by Heaton and Vogel (1981) and proposes the complete dissolution of entrapped air, leading to unfractionated excess air. Although most groundwater samples contain fractionated excess air, unfractionated excess air is also found. However, the amounts of entrapped and completely dissolved air proposed by the unfractionated excess air model are usually much smaller than typical values of entrapped air volumes observed in the field or in laboratory experiments.

Based on new experimental results and numerical investigations, we present an alternative conceptual model for the formation of apparently unfractionated excess air in the presence of a progressively dissolving entrapped gas phase. This new approach is of particular interest for the interpretation of environmental tracer data (e.g., determination of paleo-soil temperature using noble gases) and for the potential use of excess air as a proxy for the hydraulic conditions prevailing during groundwater recharge.

Reference
Excess air as a potential tracer for paleohydrological conditions

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The formation of excess air, i.e., supersaturations of dissolved atmospheric gases in groundwater as the result of the dissolution of entrapped air in the quasi-saturated zone, depends on the environmental conditions during groundwater recharge. Excess air can therefore be viewed as a potential paleohydrological tracer for, e.g., groundwater table fluctuations during groundwater recharge.

The amount of excess air in samples of paleo-groundwater from a deep sandstone aquifer in southern Wisconsin changes considerably over time. The area investigated was intermittently ice-covered during the last glaciation from about 12 to 26 kyr BP. Noble gas data, in conjunction with 14C ages and stable isotope data, indicate a soil cooling of about 6.5 to 7 °C during the last glacial period compared with the modern soil temperature.

All samples, except for those recharged before the last glacial period, show a strong correlation between noble gas temperature and δ18O. By contrast, δ18O values of samples older than about 28 kyr BP are too heavy with respect to their noble gas temperatures. This might be due to a stronger influence of an isotopically enriched moisture source before 28 kyr BP.

The amount of excess air increased shortly before and at the beginning of the glaciation of the study area. At the same time, the degree of fractionation of the excess air with respect to the composition of atmospheric air decreased significantly. Both the increasing amount of excess air and the decreasing degree of fractionation indicate hydrological changes at the onset of the glaciation, proposing increasing fluctuations of the groundwater table in response to climatic changes or hydraulic changes due to the ice advance. After glaciation, the amount and fractionation of the excess air quickly changed to those values of modern groundwater, which is characterized by relatively few and strongly fractionated excess air.

In conclusion, the results show that excess air is a potential tracer for the pressure conditions during groundwater recharge in the past.

Study of native metals and alloys in natural deposits and soils:
A contribution to the understanding of the influence of natural and industrial objects on the environment

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The application of highly sensitive (<1ppm) mineralogical methods (see details at www.natires.com) during geochemical exploration and environmental studies has revealed a wide range of native metals grains (NMG) and alloys in almost all samples of soils and natural deposits. Variable amounts of NMG have been observed in areas affected by industrial pollution, within city boundaries and also in areas remote (200-400 km) from any obvious sources of pollution.

The observed NMG include Si, Cr, Fe, Co, Ni, Cu, Zn, Pd, Cd, Sn, Sb, W, Pb, Bi, which were present as pure phases and also, in some cases as alloys of two or more elements.

Qualitative and quantitative determinations of the compositions of the NMG have shown that these depend on the locations of the samples. In some cases a precise correlation between the amount and chemical composition of the NMG and the composition of underlying host rocks has been established.

The NMG and alloys generally vary in size from n*1 to n*10µm, rarely reaching 200µm. Four morphological types of grains have been observed: spherical grains (are the most abundant), relatively isometric-angular grains, grains with irregular form and minor grains as peels.

Textural evidence of dissolution or supergene alteration of the NMG has not been observed, indicating that they form and exist stably under supergene conditions. The genesis of NMG requires further investigation, however the occurrence of these reduced native elements indicates that electro-chemical processes have been important in their formation under supergene conditions.

Detailed mineralogical studies of NMG and alloys in natural deposits and soils appears to be important in the evaluation of the influence natural and industrial objects on the environment, especially given that NMG can include toxic elements such as Cd, Pb etc (V. Cappuyns, et al., 2006).

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References
A geochemical model of arsenic sorption on clay mineral functional sites

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The Method
The mobility of arsenic species in the environment is largely controlled by solid phase sorption reactions. Quantitative evaluations of the solid phase/water partitioning of many toxic metals, including arsenic, are best accomplished by a surface complexation approach. Equilibrium-based thermodynamic modelling is currently one of the most appropriate methods to evaluate the competitive geochemical processes that affect the transport and toxicity of arsenic, including predictions regarding arsenic persistance and mobility in the environment.

Computation
The USGS numerical computer code PHREEQC version 1.6 was used for all simulations. The code was used to simulate arsenic surface complexation from a small watershed with naturally high levels of arsenic on clay mineral components (kaolinite and montmorillonite) of a stream sediment. Surface complexation mass-action coefficients were obtained from the literature in the generalized two-layer model form, or from linear free energy relationships. The WATEQ4F thermodynamic database formed the core to which surface complexation parameters were added. The code was used for the calculation of saturation indices, sensitivity analysis of parameters such as Eh, pH and temperature, modelling the mixing of stream water of different compositions. The surface complexation routine was used in the generalized two-layer model and competition between arsenic and other ions for sorbing phases for a finite number of sites was allowed. Both mineral assemblages were allowed to come to equilibrium by simulating the flushing of many pore volumes through the sediment-mineral surface assemblage.

The model output was evaluated using the ratio "R" of modeled vs. expected arsenic concentrations. Small differences in the conceptual model and data acquisition techniques can have a large effect on the simulation error. The error of neglecting competition by common compounds such as bicarbonate or silicic acid can equal or exceed the bias resulting from inappprpriate choice of mineral phases.

References

Controls on schwertmannite transformation rates and products

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The formation and transformation of schwertmannite is of geochemical significance in acid mine drainage (AMD) polluted surface waters. Sediments dominated by schwertmannite typically adjust to a pH around 3, as the mineral slowly transforms into more stable phases and thereby releases protons. At such low pH and only short supply of electron donors due to the low productivity of AMD polluted lakes, the sediments are characterized by an iron reducing regime. Sulfate reduction would be desirable to reverse pyrite weathering and sequester acidity, but was found to take place at significant extent only at a pH higher than 5, though. The impact of environmental factors such as dissolved organic carbon (DOC), high sulfate concentrations, pH or temperature on schwertmannite transformation is thus of particular interest when studying the biogeochemistry of AMD affected lake sediments.

To evaluate the effect of geochemical conditions on the fate of schwertmannite in AMD polluted sediments, we varied pH, concentrations of sulphate and DOC, and temperature in batch experiments. We quantified schwertmannite transformation by titration of released acidity and investigated the product with FTIR, XRD, SEM/EDX, and chemical extraction with 1N HCl. Transformation rates ranged from 0.0002 d-1 to 0.13 d-1 (transformed fraction / incubation time). Raising pH from 3 to 5 increased transformation by a factor of 5.8 (±2.1) and temperature from 10 to 20° C by a factor 3.8 (±1.6). Sulphate (20 mmol L-1) and DOC (20 mg L-1) lowered transformation by a factor of 2.5 (±0.4) and 2.4 (±0.5). The newly formed iron phase was less dissolvable in 1N HCl but goethite was not detected by XRD. The morphology did hardly change, even in sulphate-poor iron phases and no goethite-typical needle structures could be observed. Thus we concluded that an amorphous, sulphate depleted iron phase had formed. Most of the sulphate released from the schwertmannite structure remained bound to the solid phase. We interpreted changes in IR bands at 1108 cm-1 (ν3) and 984 cm-1 (ν2) as a relocation of sulphate.

The study documents the high potential of schwertmannite to buffer pH increase in sediments, particularly at low sulphate concentrations, and high temperatures. This coincides with the finding that strongly acidic sediments dominated by schwertmannite remain in an iron reducing state for a long time.

In contrast to other studies conducted in deionized water we could not identify goethite to be the transformation product under the conditions chosen.
Assessment of aquifer vulnerability using statistical methods and GIS

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The purpose of the study for the development of the technologies of water quality monitoring and contamination protection at water resource aquifer is to secure the groundwater as potable water resources. The regional survey of groundwater quality for small potable water supply system were performed to know the effect of geology, soil properties, and land use for hydrochemistry at Nonsan area, Korea.

The geostatistical analysis, multivariate statistical methods, and GIS technique were used for the quantitative interpretation of groundwater chemistry. The monitoring results of groundwater in the study area showed that 13-21% of groundwater samples were exceeded the portable water results of groundwater quality for small potable water supply system. The monitoring methods, and GIS technique were used for the quantitative interpretation of groundwater chemistry. The monitoring results of groundwater in the study area showed that 13-21% of groundwater samples were exceeded the portable water guideline and the main causes were turbidity, bacteria, arsenic and nitrate-N. The high Cl, NO₃ and Na at granite area are caused by the high vulnerability of groundwater at granite region where the residential area and cultivated land are concentrated. The spatial distribution of components indicated the close relationships between groundwater quality and geology, land use, and topography. The results of principal component and discriminant analysis showed the close relationships between groundwater quality and geology (Fig. 1). From PCA, the three main variables explain 73% of the total variance and PC2 which is influenced by NO₃, Si, and HCO₃ is the major factors indicating geology induced factors.

It is considered that the anomalous distribution of Arsenic is related to metasedimentary rock of Ogcheon belt with high contents of sulfide minerals.

Figure 1. The results of multivariate statistical methods.

Garnet peridotite and associated UHP eclogite, equilibrated at 4.5-5.0 GPa, occur as lenticular bodies surrounded by migmatitic gneiss at Nove Dvory area in the Moldanubian Zone, Czech Republic [1] [2]. This geological setting is similar to UHP rocks in Dabie-Sulu. It is important to identify the timing and mechanism when and how UHP rocks juxtaposed with Gföhl felsic rocks which have no HP/UHP evidence in their matrix, except for the occurrence of kyanite and show various kinds of partial melting structures. We report possible UHP evidence predated the partial melting of the felsic rocks identified from the zircon inclusions using the Raman spectroscopy and CL study.

The Raman spectroscopy for more than 1500 zircon separates from Gföhl felsic rocks at Nove Dvory area shows that the most of SiO₂ inclusions are quartz with clear and intense peaks at 464 and 393 cm⁻¹, and a few SiO₂ inclusion has a weak but clear peak at 521 cm⁻¹, and a weaker peak at 179 cm⁻¹, which are the most fundamental vibration of coesite, along with typical quartz vibration mentioned above. The Raman spectrum composed of the intense vibrations at 464 and 393 cm⁻¹ of quartz and the weak vibrations at 521 and 179 cm⁻¹ of coesite were also obtained from the quartz proximal to relict coesite from the UHP rocks of the Dora Maira Massif. The similar Raman spectrum has been reported from quartz transformed from coesite in UHP rocks recovered from CCSD drillhole, eastern China [3]. Therefore, we propose that the SiO₂ phase showing the Raman spectrum with the weak vibrations at 521 and 179 cm⁻¹ was once coesite, along with the case of the Lanterman Range, Antarctica [4]. CL image observation of zircon grains displays that most zircon grains can be subdivided into two textural domains; the oscillatory zoned core and the rim separated by discontinuous CL pattern. All possible coesite inclusions are always detected from the core, although all SiO₂ inclusions in the rim were quartz.

These facts may suggest that the zircon of Gföhl felsic rocks at Nove Dvory once crystallized at UHP depths and most UHP evidence was obliterated by resorption and secondary growth of zircons during the exhumation stage.

Reference

Raman and cathodoluminescence (CL) study of zircon inclusions derived from Gföhl felsic rocks in the Moldanubian Zone, Czech Republic

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Breakdown of hydrous ringwoodite to pyroxene and Fe$^{3+}$-bearing-wadsleyite at high P and T and oxidizing conditions

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The stability relations in the systems M$_2$SiO$_4$ (M = Mg, Fe, Ni, Co) have been the subject of numerous studies because of their significance for the mantle transition zone. In the Mg$_2$SiO$_4$ system three polymorphs exist: at ambient conditions olivine, at pressure > 13 GPa (1000 °C) wadsleyite and at P > 18 GPa (1000 °C) ringwoodite. This is quite different to the Fe$_2$SiO$_4$ system where no intervening wadsleyite phase has been observed but fayalite directly transforms to Fe-ringwoodite at 5.3 GPa (1000 °C). Experiments in the system Fe$_2$SiO$_4$ – Fe$_3$O$_4$ by Woodland and Angel (1998) at 5.6 GPa (1100 °C) revealed that Fe-wadsleyite can only be stabilised if significant amounts of Fe$^{3+}$ are incorporated. To get deeper insight into the phase relation in the endmember system Fe$_2$SiO$_4$ as well as in the system Fe$_1$Mg$_1$SiO$_4$ we investigated the phase relations as a function of P, T and f O$_2$. The experiments were performed in a multi-anvil apparatus at 7- 14 GPa at 1100 °C. Oxygen fugacities were varied using the solid oxygen buffer systems Fe/FeO, QFM and Ni/NiO. The run products were analysed with electron microprobe, Raman spectroscopy, X-ray powder diffraction and transmission electron microscopy. The X-ray data were analysed using the GSAS software. At f O$_2$ corresponding to Ni/NiO Fe-ringwoodite transforms to ferrosilite and Fe$^{3+}$-wadsleyite according to the reaction: 9 Fe$_2$SiO$_4$ + O$_2$ = 6 FeSiO$_3$ + 5 Fe$_{2.42}$Si$_{0.58}$O$_4$. Refinement of site occupancies in combinations to stoichiometric Fe$^{3+}$ calculations show that 32 % of the total Fe is incorporated as Fe$^{3+}$ according to Fe$^{2+}$_1.60Fe$^{3+}$_0.40Si$_{0.62}$Fe$_{3+}$_0.39O$_4$. Similar phase relations are observed in the system Fe$_1$Mg$_1$SiO$_4$.

Miocene oceanography of the Mediterranean area deduced from C-, O-, Sr-, and Nd-isotopes

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A detailed study of the isotopic composition of fossils and whole samples from a composite Oligo-Miocene pelagic sequence of the Umbria-Marche region in Italy has been made with the goal to constrain oceanographic and climatic conditions of the Mediterranean Sea during this period. Stable C and O isotope compositions of benthic and planktic foraminifera mimic global changes, supporting that these fossils have been well preserved and that the regional climate of this area was controlled by global changes in climate.

Neodymium and strontium isotope compositions of bulk carbonate fossils were measured and compared to those of the detrital silicate fraction of the embedding sediment. The compositions of the fossils are expected to closely relate to the former seawater composition, while the sediment would represent the hinterland. The relation between the two signals helps to evaluate oceanic circulation in the region. To broaden the spatial distribution and trace connections between different water masses, marine deposits from northern Italy and Slovenia were also investigated.

Results to date indicate a strong local influence on the $\varepsilon$Nd value and possibly a weaker influence on the Sr isotope composition of the Mediterranean seawater during the Chattian-Aquitanian. During the Burdigalian-Serravallian a mixed seawater composition between the Atlantic and Indian Ocean water masses was registered with a stronger Indian Ocean influence in the Umbria-Marche region, while analyzes from the west (Moransengo) might reflect a strengthening Atlantic effect. The $^{87}$Sr/$^{86}$Sr is still lower than that of the Miocene open ocean, probably due to erosion and influence of Sr derived from Mesozoic carbonates. The dataset also shows short-term deviations in the $\varepsilon$Nd values of the fossils coinciding with major sea-level decreases.

During the Late Serravallian-Tortonian normal open ocean Sr values were recorded, while the $\varepsilon$Nd values vary considerably. A low $\varepsilon$Nd value at 12-11 Ma could indicate inflow of water from the Atlantic Ocean, which stopped at 10 Ma due to major regression and allowed for the development of a locally controlled water mass with $\varepsilon$Nd of –8.5. Thereafter, the $\varepsilon$Nd again approaches compositions typical for the Atlantic Ocean.

Reference

Sterols in the red and green algae and their relevance for interpretation of Paleozoic steranes

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Steroids are a diverse class of lipid with high preservation potential and that are abundantly preserved in the geologic record. These molecules are among the few traits that are shared across all eukaryotes; and thus, they are also important for understanding the molecular evolution of this group. Sterols most commonly used by eukaryotes are C27, C28, and C29 molecules which correspond to C27, C28, and C29 steranes. A diversity of these molecules is found in oils and sedimentary bitumens. Because all three classes of molecules are used by evolutionarily diverse eukaryotes, it can be difficult to ascribe any particular molecular class to a single group of organisms. Many geochemists and paleontologists, however, have tried to draw connections between the presence of C29 steranes in the latest Precambrian and Paleozoic to green algae.

Though C29 sterols have a cosmopolitan distribution among photosynthetic eukaryotes, the known diversity of C29 producing organisms is restricted prior to the Mesozoic. Using a large survey of sterol profiles from the most ancient lineages of algae, we investigate the hypothesis that green algae are the likely source of C29 steranes through the Phanerozoic. We discuss the phylogenetic and ecological relationships of the distribution of C27, C28, and C29 sterols in these groups, and how this impacts the current interpretation of the importance of green algae in pre-Mesozoic ecosystems.

Geochemistry of ocean-floor serpentinites: Implications for subduction zone inventory

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Hydrated oceanic mantle is a significant carrier of H2O in subduction zones. Experimental studies and field observations demonstrate that serpentinites undergo major dehydration over a restricted -P-T interval (ca. 2-5 GPa, 650-700 °C; Ulmer and Trommsdorff, 1995; Trommsdorff et al., 1998). Fluids released during serpentinite dehydration may have a considerable effect on element recycling through subduction zones. Whole rock and mineral major and trace element data (EMPA, LA-ICP-MS) of 39 samples from 6 ODP drill sites representing different geodynamic settings (fast and slow spreading ridges, passive margins and forearcs) constrain the geochemistry of ocean-floor serpentinites, which are a proxy for the chemical inventory of subducted hydrated mantle.

The degree of serpentinization in the ODP samples varies between 65 and 100 vol%. Besides serpentine minerals (srp) and magnetite (mag), the most common secondary phases are chlorite (chl), brucite (brc), calcite (cal) iowaite (iow) and sulfides (sul). Excess brc component in srp is commonly observed in mesh rims and mesh cores. In few samples, the presence of iow has been inferred from high Cl and Fe content accompanying low silica. Minor and trace element compositions of srp in different textural settings generally reflect that of the precursor mineral (olivine and orthopyroxene). However, there are considerable variations due to varying degrees of element mobility and mass change during serpentinization. Elements like B, Sr, Rb and Ba show orders of magnitude enrichments in srp compared to the precursor minerals (B: 35-88 ppm, Sr: 1.0-1.3 ppm, Rb: 0.03-0.07 ppm and Ba: 0.1-0.7 ppm). Bastites tend to have about 1.5-4 times higher trace-element concentrations than mesh rims. This is probably related to local fluid chemistry, with relatively high dissolved SiO2 and relatively low pH around orthopyroxene during serpentinization. Boron values are highly variable even on the 100 µm scale, which may reflect structural effects besides srp mineral chemistry. By contrast, elevated Sr concentrations are fairly constant on the sample scale, which indicates that srp minerals may incorporate Sr.

Our results show that ocean floor serpentinization may be accompanied by appreciable incompatible trace-elements enrichment (e.g., B, Sr). Therefore, serpentinites may be important reservoirs for many trace elements in subducting slabs and, hence, may be of great consequence to geochemical recycling through subduction zones.

References
Fluid geochemistry in the Ivigtut cryolite deposit, South Greenland

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The 1.27 Ga old Ivigtut intrusion is part of the mid-Proterozoic Gardar Province in South Greenland. The Province represents a failed-rift structure where magmatic activity lasted from 1.35 to 1.14 Ga [1]. The Ivigtut intrusion is world-famous for its cryolite deposit [Na3AlF6] which is now mined out. The deposit is situated within an A-type granite stock where F- and alkali-rich fluids led to metasomatism and formation of cryolite, rare fluorides, sulfides and siderite [2].

Little has been known so far about the formation conditions of cryolite and the rare fluorides at Ivigtut. In order to estimate intensive parameters for the assemblages at Ivigtut, thermodynamic modelling was carried out with the computer program TWQ [3]. At a pressure of 1 kbar, most assemblages are stable below 450 °C at high water- and silica-activities.

Microthermometry of fluid inclusions shows that three types of inclusions can be distinguished: (1) pure CO2, (2) aqueous carbonic and (3) saline aqueous inclusions. Melting temperatures are about -56.6 °C for type 1 inclusions, range between -23 to -15 °C for type 2 and from -15 to -10 °C for type 3 inclusions. Most inclusions homogenise between 110 and 150 °C into the liquid.

Stable isotope compositions of CO2 and H2O were measured from crushed inclusions. δ18O values are about -5‰ PDB which is typical of mantle-derived magmas [4], δ18O (CO2) ranges between 21 and 42‰ VSMOW while δ18O (H2O) varies from -1 to -20‰ VSMOW. Theses values suggest low-temperature isotope exchange as proposed by [5]. δD (H2O) ranges from -19 to -123‰ VSMOW. The isotopic composition of inclusion water closely follows the meteoric water line and is comparable to Canadian Shield brines [6].

Our results show that the Ivigtut fluid has the typical characteristics of a hydrothermal, Na-dominated brine. Isotopic data suggest that the CO2 component is mantle-derived whereas the dominant H2O part is of meteoric origin and intensively interacted with the host granite.

References

In situ Fe isotope measurements in gabbros and basalts from the ocean crust

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Fe isotopes were measured in oxides and sulfides of gabbros and basalts drilled by IODP (Integrated Ocean Drilling Program) in recent oceans. Such studies may help to elucidate topics like state of equilibrium of the oxide/sulfide assemblages, temperature of formation, and imprint of seawater. We used the recently in Hannover developed LA-MC-ICPMS system consisting of a femtosecond laser and a multiple collector inductively coupled plasma mass spectrometer. For the analytical and methodical techniques, we followed Horn et al. (2006).

The used gabbro was a ferrogabbro from the Southwest Indian Ridge (drill hole 735B) showing ore mineral assemblages consisting of MT (magnetite), ILM (ilmenite) and PYR (pyrrhotite). The textural features suggest equilibrium formation for these assemblages. A temperature of 950°C was estimated as temperature of formation of these ore assemblages, obtained by amphibole geothermometry. In-situ Fe isotope analyses were performed both in the core and rim of the grains. No zoning with respect to Fe isotopes was observed.

The measured δ56Fe values, the relative isotopic differences between the mineral phases, and the comparison with literature data and equilibrium fractionation factors derived from Mössbauer data (Polyakov and Mineev, 2000), respectively, suggest the following working hypothesis: Below 950°C, at temperatures while PYR was still open, and MT and ILM closed for iron isotope exchange, the rock was infiltrated by a seawater-derived hydrothermal fluid shifting the δ56Fe values of PYR to significant lighter values. The temperatures for this process must have been fairly high (e.g., > 700°C), since PYR and the other Fe-Ti oxides do not show any sign of typical low- or medium temperature alteration. This method opens interesting perspectives in order to shed light on late stage and alteration processes in oceanic gabbros. Further in-situ Fe isotope measurements in gabbros and in fresh and progressively altered basalts from the IODP Expedition 312 which drilled the basalt/gabbro transition in fast-spreading ocean crust are in progress.

References
Isotopic signatures of the Siberian flood basalts and alkaline magmatism of Polar Siberia (age, genetic link, heterogeneity of mantle sources)

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A close association between alkaline magmatism and continental flood basalts is observed worldwide. Nevertheless, the problem of a genetic link between the Siberian flood basalts (SFB) and the ultramafic-alkaline rocks of the Maimecha-Kotuy province in Polar Siberia is still being debated. The SFB with a volume of 1.6x10^6 km^3 occur in the northern part of the Siberian platform. The Putorana plateau, where about 90% of all the basaltic volcanism occurred, is situated in the center of the SFB province, and some authors consider the Putorana basalts to be representative of the Siberian plume itself.

The ultramafic-alkaline Maimecha-Kotuy comprises the world’s largest ultramafic-alkaline Guli massif, the ultramafic-alkaline-phoscorite Kugda complex, and 31 smaller ultramafic-alkaline intrusions.

A whole-rock U-Pb age of 250±9 Ma was determined for the Guli massif, which lies within the range of ages previously reported for the SFB. The combined Pb, Sr, and Nd isotopic systematics of the SFB and the Guli and Kugda alkaline rocks identify several discrete source components. The first component dominates many of the Guli rocks and is characterized by low ^87Sr/^86Sr (0.7031 to 0.7038), high (Nd (+5.35 to +3.97), and relatively unradiogenic Pb (206Pb/204Pb = 18.3, 207Pb/204Pb = 15.8-15.46; 208Pb/204Pb = 37.33-37.70), which we associate with the depleted (or MORB signature). The second component dominating the Putorana plateau, where about 90% of all the basaltic volcanism occurred, is situated in the center of the SFB province, and some authors consider the Putorana basalts to be representative of the Siberian plume itself.

The ultramafic-alkaline Maimecha-Kotuy comprises the world’s largest ultramafic-alkaline Guli massif, the ultramafic-alkaline-phoscorite Kugda complex, and 31 smaller ultramafic-alkaline intrusions.

In situ detection of highly siderophile element micronuggets in peridotite by synchrotron radiation X-ray fluorescence mapping

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Abundances of highly siderophile elements (HSEs) in the Earth's mantle are key indices for understanding the Earth's formation processes and subsequent chemical evolution of the mantle. However, estimation of the primordial HSE abundances in the mantle from HSE concentrations in present-day peridotite samples is not straightforward, because the residence of HSEs in peridotite has not been well constrained. Sulfide minerals can account for whole-rock HSE abundances in some peridotite samples (e.g., Alard et al., 2000), but the existence of micrometer-scale HSE nuggets (e.g., Luguet et al., 2003; Lorand et al., 2006) implies that such HSE micronuggets could also influence the behavior of HSEs in the mantle. We report in situ discovery of HSE micronuggets from peridotite by microbeam X-ray fluorescence mapping using synchrotron radiation X-ray at SPring-8, Japan. We found a few grains of HSE micronuggets (1~10 µm in maximum dimension) included in single sulfide grains in an orogenic lherzolite from Horoman peridotite complex, Japan. Only two of sixteen sulfide grains investigated contain the HSE micronuggets, indicating strongly heterogeneous distribution of HSEs between sulfide grains. Pt-rich and Os-Ir-rich micronuggets were included in both of the two sulfide grains. HSE concentrations within sulfides themselves were below detection limits. These results suggest that distributions of HSEs within peridotite are strongly controlled by HSE micronuggets. We interpret that the coexistence of Pt-rich and Os-Ir-rich micronuggets and the strong heterogeneity of HSE distributions are not fully attributed to secondary processes such as metasomatism but are at least partly of primary signature in the uppermost mantle. Thus, HSE micronuggets may play a significant role in controlling HSE abundances in the mantle. It is essential to reveal the origin of HSE micronuggets and their spatial distribution in the mantle for understanding the HSE behavior in the mantle.

References

References
Nd and Sr isotopic characteristics of NE Aegean Ophiolites, Greece

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In this study we report on the isotopic characteristics of ophiolitic complexes located in the northeastern Aegean region. These complexes are, from north to south, the Evros and Samothraki ophiolites, commonly considered as part of the Circum-Rhodope Belt (e.g. Kauffmann et al. 1976) and the Lesvos ophiolite, which forms the western continuation of the Karakaya Complex (W Turkey) (e.g. Koglin et al. 2007).

The Evros ophiolite comprises the typical characteristics of an ophiolite suite, namely mantle peridotites, gabbros, sheeted dykes and basaltic extrusives. The ophiolite of Samothraki is built up of gabbros intruded by dolerite dykes, diorites, sheeted dykes, and massive and pillow lavas. The Lesvos ophiolite consists of mafic extrusives, ultramafic rocks with an amphibolitic sole at their base and an ophiolitic mélange. This mélange consists of gabbros, massive basaltic flows, pillow basalts, marbles, phyllites and greenschists.

The Middle to Late Jurassic Evros and Samothraki ophiolites (SHRIMP zircon ages, Koglin et al. 2007) show supra-subduction zone geochemical characteristics. The latest Permian ophiolitic rocks of the mélange indicate an OIB source influence, while the basalts of Vatera, S Lesvos, display a geochemical signature of mid-ocean ridge affinity (Koglin et al. 2007).

The basalts and most of the gabbros of the Evros ophiolite have εNd160 values between +2.9 and +7.7 with a mean of +5. Their 87Sr/86Sr160 ratios range from 0.7037 to 0.7052. The Samothraki mafic rocks have εNd160 from +3.8 to +7.2, mostly clustering around +5. Their 87Sr/86Sr160 ratios range between 0.7034 and 0.7058. The εNd253 of the Lesvos ophiolite mafic rocks vary from +3.8 to +6.4 with a mean of +5.5. Their 87Sr/86Sr253 is between 0.7043 and 0.7051.

For the Evros and Samothraki ophiolites the isotopic data indicate a depleted mantle source with a subduction-zone influence. This is concordant with the observed enrichment in Th and other LILE compared to MORB. The isotopic data for the Lesvos ophiolite are similar to those of Evros and Samothraki. However, the subduction-zone input is less pronounced and an additional OIB component has to be considered.

References:
Low temperature thermochronology of Phanerozoic kimberlites and Archaean basement, Slave Province, Canada

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In an effort to investigate the burial history of the Slave craton, NW Territories, Canada we report the first results of a low temperature thermochronology study applying apatite fission track and (U-Th)/He methods, from the Ekati (45-61 Ma), and the Jericho and Muskox (172-175 Ma) kimberlite pipes (including their crater facies sediments, and sedimentary and basement xenoliths) and their host Archaean granitic basement (2.71-2.58 Ga).

Previous vitrinite reflectance data (%Ro 0.24-0.42) and porosity analysis from unaltered shale xenoliths in the Eocene pipes of the Lac de Gras diamond field (including the Ekati pipes), suggest a maximum burial temperature of 60°C for mid Cretaceous strata with 1.2 to 1.4 km sedimentary cover in the Lac de Gras kimberlite field region prior to major uplift and erosion, which began around 90 Ma [1]. The nearest Paleozoic sediments are preserved more than 400 km southwest of the kimberlite fields in the foothills of the Mackenzie Mountains where they are typically 1-2 km thick.

Our data are used to obtain improved constraints on the thermal history of the Slave craton and provide more precise estimates on its denudation history. This will lead to new insights for assessing the long-term stability of continental interiors in relation to subtle sedimentation and denudation patterns, which may be related to dynamic topography driven by mantle convection and far-field tectonism.

References

Petrological Characteristics and LA-SF-ICP-MS U-Pb ages of S-type Granitoids from Central Turkey

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The S-type Sinandi microgranite (SMG) and the Namlikisla biotite-granite (NBG) (Aksaray-central Turkey) intrude metamorphic basement rocks and gabbroic rocks of an ophiolitic sequence and is itself cut by I-type granitoids. SMG and NBG consist of orthoclase, quartz, plagioclase, biotite, muscovite ± hornblende ± pyroxene and accessory zircon, titanite, epidote, apatite and opaque minerals. They have calc-alkaline peraluminous character, LILE and LREE enrichment, low Ce, Zr, Hf, Sm contents and pronounced Eu-anomalies (0.63 and 0.59, respectively). SMG and NBG display a crustal isotopic signature with high initial 87Sr/86Sr ratios (0.712827 and 0.715168, respectively) and low εNd values (-9.1 and -9.7, respectively).

Based on zircon typology method (Pupin, 1980) zircon populations from both granitoids are described by low to moderate A and T indexes, typical aspect for crustal originated granitoids. SMG has abundant S7-12-13-18 types and lesser amounts of S2-9-10-17-19-23-24 types, whereas the zircon population of NBG is represented by preferential development of S2-7-12 types besides S1-3-4-5-6-8-11-13-16 and L1-2-3-4-5 types in lesser percentage. Zircon crystals from SMG and NBG commonly contain rounded to subrounded inherited cores overgrown by oscillatory zones displaying intermittent resorption surfaces and some secondary structures such as recrystallization and flow domains.

Rims and outer zones of zircons from SMG give a LA-SF-ICP-MS mean 206Pb/238U age of 81.5±0.84 Ma (2σ), while those of NBG yield 83.8±0.95 Ma (2σ). Ages of inherited cores range from 526 Ma to 1566 Ma for SMG, and from 144 Ma to 2304 Ma for NBG.

Consequently we suggest that Late Cretaceous S-type SMG and NBG were formed as a result of Alpine collisional magmatism during closure of the northern branch of the Neotethys Ocean. However, wide range of ages indicating cryptic igneous events were recorded. Moreover xenocrystic inherited zircon cores represent a variety of sources including the Proterozoic crust.

References
Platinum Group Element contents of the Kop Chromitites and its possible sources, (NE Turkey)

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The average contents of PGE in the chromitites from the Kop ultramafics are Os: 43.6, Ir: 39.5, Ru: 74.4, Rh: 8.7, Pt: 38.6, and Pd: 35.4 ppb. Chondrite-normalized PGE distribution patterns of all chromitites reveal a negative trend from Ir to Pd. The PGEs are sensitive to the degree of partial melting of source regions and the S-saturation status of resultant magma. Chondrite normalized PGE patterns range from nearly unfractionated in the chromitites (Pd/Ir=0.09-4.18) from the Kop ultramafics. Total PGE content of the chromitites range from 93-710 ppb.

Crystallization of orbicular rocks from Camlikaya, NE Turkey

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Orbicular rocks crop out in a 25x100m size body in the granitic rocks at Camlikaya, NE Turkey. They have dioritic/gabbroic composition. The cores of the orbicules and the matrix between the orbicules have same mineralogical composition which may be crystallized from the orbicule-forming magma. The matrix and the cores of the orbicules are composed of pyroxene, hornblende, magnetite and andesine-labradorite and have poikilitic texture. Mafic cores are surrounded felsic shell composed of mainly plagioclase and perpendicular the core. After initial ‘normal’ crystallization of the magma, superheating probably triggered by a sudden addition of volatiles destroyed earlier formed nuclei and also affected the already crystallized part of the rock. Addition of felsic components and cooling causing plagioclase nucleation and rapid crystallization.

References
Fluid mixing at the depositional site of the Guelb Moghrein IOCG deposit, Mauritania

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The Guelb Moghrein IOCG deposit is located 250 km northeast of Nouakchott, Mauritania. The mineralization is hosted by < 30 m wide tabular tectonic breccias in a carbonate-facies iron formation. It comprises Oam, Mag, Po, Ccp, Fe-Co-Ni arsenides, Apy, cobaltite, uraninite, and Bi-Au-Ag-Te minerals in a proximal ore breccia grading into a distal ore breccia with Oam and Mag. Hydrothermal monazite and xenotime were dated at 2492 ± 9 Ma.

Fluid inclusions were studied in siderite (Sd) of the iron formation. Three generations are discriminated: Sd1 is undeformed, locally idiomorphic and up to 5 cm in diameter. Sd2 represents variably sized, angular fragments with numerous sulfide inclusions. Sd3 is recrystallized carbonate. Two types of fluid inclusions are distinguished, which are interpreted to have formed contemporaneously: Type I are aqueous two-phase L-V inclusions, 6-10 µm in diameter that form trails in Sd1 and Sd2. They are spatially closely associated with the ore paragenesis. Type II inclusions are aqueous two- or three-phase (L-V, L-V-S) and form clusters and single inclusions in Sd2 and Sd3. They are up to 50 µm in diameter. Trapped sulfides are present if the cluster is intersected by a type I trail. The Te of both types show a wide scatter between -10°C and -80°C. The Te peaks are characteristic of NaCl-H2O and NaCl-MgCl2-H2O mixtures, where type I inclusions are NaCl-dominated and type II inclusions are MgCl2-dominated. The Cl- content ranges between 0-4.5 mole/kg Cl-. Th for types I and II inclusions have, both, a maximum at about 300°C.

Type I and II inclusions (1) occur on trails in brecciated Sd2 and/or in recrystallized Sd3, (2) they are spatially associated with sulfides, (3) sulfides are trapped in type II inclusions and (4) uniform Th is consistent with trapping at 410 ± 30°C and 1-2 kbar, which are the P-T conditions of mineralization. The variable salinity and composition, the uniform Th, and the paragenesis of both fluid inclusion types with the ore minerals point to isothermal fluid mixing at the depositional site as a mechanism for ore formation. A MgCl2-dominated fluid probably equilibrated with the Fe-Mg carbonate in the host rock and mixed with an externally derived NaCl-dominated fluid during progressive deformation.

The ore fluids at Guelb Moghrein have a relatively low salinity of < 20 wt.% NaCl, and lack a carbonic phase. This is unusual especially for magmatic IOCG deposits. The geological setting of Guelb Moghrein and the fluid composition suggests that this deposit formed in a metamorphic setting by fluid mixing during regional-scale thrusting.

Iron enrichments in salt marshes of NW Germany

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Salt marshes are a major, widely distributed, intertidal landscape. The salt marshes of the summer polder area of the East Frisian barrier island Langeoog (NW Germany) were protected by a summer dike until 2004. In 2004 this dike was removed and rebuilt toward centre of the island. Thus the Langeoog summer polder is afresh under tidal influence and the opportunity was given to investigate the effects of a simulated sea level rise on pore water geochemistry.

For in situ sampling four pore water samplers (Beck et al. 2007) were installed in the salt marsh sediments. These lances are aligned on a N-S transect including sites at high salt marsh, low salt marsh and transition zone low salt marsh/tidal flat. Pore water sampling started in June 2005 and samples were taken in monthly intervals.

Iron enrichments in pore water were observed at all different salt marsh sites. The transition zone low salt marsh/tidal flat is characterized by high iron concentrations up to 373 µM at 0.5 m depth. In contrast, at the low marsh site iron enrichments were observed in greater depths. We found iron concentrations of 588 µM at 1.25 m, 328 µM at 2.5 m and 633 µM at 5 m depth. Further, there is an increase of iron concentration with increasing depth at the high marsh site. In addition to this general trend, distinct iron enrichments of 285 µM at 2.5 m and 325 µM at 4 m depth were observed.

These high iron concentrations in salt marsh pore waters likely result from reduction of their corresponding oxides and partly coincide with sediment lithology. Portnoy & Giblin (1997) described implications of seawater flooding on salt marshes after decades of diking. Amongst others this could mobilize a large pulse of iron (II). The extreme iron enrichments at this marine-terrestrial transition could provide an indication of pyrite enrichments within Holocene coastal deposits.

References

Melt inclusions from the Galápagos plume: Mirrors and mirages of the deep

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Melt inclusions provide an advantage over erupted magmas because they are samples of very small amounts of melt commonly trapped at pressures exceeding the pressure of eruption, and their chemical compositions have remained unchanged since entrapment. Thus, melt inclusions are an invaluable tool to characterize the composition of pre-aggregated lavas prior to differentiation and mixing in magma chambers, and to determine the pre-eruptive volatile contents of basalts. However, there are two serious disadvantages to using melt inclusions to evaluate mantle melting processes: 1) the composition of melt inclusions can reflect localized, grainscale, wall-rock reaction processes within the shallow magmatic plumbing system, and 2) the host crystal may not effectively isolate the inclusion as a closed system (e.g., preventing H2O diffusion).

We have analysed major, trace element, and volatile contents in more than 100 olivine-hosted (Fo81-87) melt inclusions in submarine and subaerial lavas from the Galapagos Islands. Our results indicate that enriched and ultra-depleted melt compositions coexist in the magmatic plumbing system beneath Galapagos volcanoes. Furthermore, the trace element compositional variations found in melt inclusions from a single sample reproduce the total geochemical variation defined by the whole rock data for the Galapagos lavas. Establishing the processes responsible for such variations will therefore have direct implications on the origin of the compositional variation of basalts throughout the Archipelago. Our new volatile data provide limits on the concentration of CO2, H2O, F, S, and Cl for the high 3He/4He and depleted mantle components beneath the Archipelago. The CO2- H2O data give an entrapment pressure of ~1 kbar, corresponding to a depth of ~3 km. A subgroup of inclusions is characterized by significant depletion in incompatible trace elements with unusual (Sr/Nd)PM and (Ba/Th)PM ratios greater than unity, suggesting the interaction of melts with a plagioclase-rich cumulate during melt percolation within the oceanic lithosphere. The volatile data for these inclusions suggest that a) the interaction of melt with lithospheric gabbros decreases the S and Cl content of the melt, and b) the H2O and F content in these inclusions have been modified by open system behavior due to diffusion of H and F through the olivine host.

Mercury, trace elements, and organic constituents: A combined approach to sampling atmospheric particulate matter (PM)

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Compliance with USA air quality PM regulatory standards (PM10 and PM2.5) is based on meeting average 24-hour and yearly mass-per-unit-volume limits, regardless of PM composition. In the present work, we combine filter-based sampling of particulate-bound mercury, trace elements, and organic constituents to determine compositional variation of atmospheric aerosols in three contrasting environments in the USA, and assess potential human health impacts.

Along the U.S. Gulf of Mexico coast, Hg wet deposition is especially elevated. PM sampling conducted together with a mobile lab Hg speciation unit shows a significant portion of particulate Hg bound to particles larger than 2.5 µm, including sea-salt aerosols derived from marine air masses. Mercury speciation results show a diel pattern of photochemical Hg oxidation. Adsorption of oxidized and elemental Hg on NaCl aerosols increases Hg available for deposition in this Hg-sensitive coastal ecosystem.

At an inland suburban site in the eastern USA, trace element enrichment factors in PM2.5 show elevated ratios of Se, Sb, Ag, Bi, Cd, Mo, Pb, Zn, and Tl, vs. Zr (crustal affinity), compared to crustal abundance ratios of these elements, suggesting influence from industrial, transportation, and fossil fuel combustion sources.

Studies in the Navajo Nation of New Mexico focus on human exposure to domestic coal combustion, shown to be correlated with the incidence of respiratory difficulties. Extractable organic compounds in PM2.5 include abundant alkanes and low abundances of various polycyclic aromatic hydrocarbons (PAHs). The predominance of low molecular weight alkyl-substituted PAHs is indicative of a coal source.
Thermodynamic modeling of REE fractionation during the interaction of monazite with chloride-carbonate fluid

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Monazite is the most abundant REE mineral, which forms in various geochemical conditions including rare metal deposits of hydrothermal and metamorphogenetic type. Besides, lanthanide-actinide phosphate matrixes are very perspective for radioactive waste disposal. It is worth to reveal the trends of REE fractionation depending on physical-chemical conditions of fluid/monazite interaction.

The thermodynamic data base for lanthanide phosphates of Vieillard and Tardy (1984) as well as SUPCRT98 for aqueous species were used. A model of ideal solid solution for (Ce,La,Nd,Eu)-monazite was calculated as a first step for the following numerical experiments. The behavior of xenotime in the modeling system was used to compare the leaching ability of Y-HREE group with the LREE one. Two type of initial modeling fluid containing 4.0m NaCl + 1,5m H\text{2}CO\text{3} were under attentions: acid (pH = 3.1 because of 0.1m HCl addition) and alkaline (pH = 7.3 because of 0.1m KOH addition). The following particular tasks were tested: 1) the estimation of a possible selective solubility of some LREE+Y as compared to each other during the cooling of the chloride-carbonate fluid within the 500 - 100 °C interval; 2) the calculation of the influence of fluid/REE phosphate solid phase ratio (within 10\text{−}4 – 10\text{4} interval) on possible correlations between various LREE+Y in solid phases after “leaching”.

The principal results under discussion: 1) in the acid fluid, expected concentrations of La-, Ce- and Nd are higher by two order of magnitude as compared with the alkaline one; 2) the Eu-minal of monazite demonstrates the anomalous high solubility at elevated temperatures; 3) the solubility of xenotime minal is lower by two orders of magnitude as compared with the monazite one; 4) at low ratios of fluid/REE-phosphate intensive leaching of EuPO\text{4} with the following leaching of (La, Ce, Nd)PO\text{4} takes place with leaching of YPO\text{4} at the last stage of the process only.

Extensive set of new ICP-MS and XRF-SI data about REE patterns in natural monazites will be used for verification of thermodynamic models under development.

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Decoupling photochemical Fe(II) oxidation from shallow-water BIF deposition

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Oxidized Fe minerals in Archean-Paleoproterozoic banded iron formations (BIFs) are commonly taken to indicate the presence of biogenic O\textsubscript{2} or photosynthetic Fe(II)-oxidizing bacteria in the oceans’ photic zone. However, prior to the rise of atmospheric oxygen and the development of a protective ozone layer, the Earth’s surface was subjected to high levels of ultraviolet radiation. Bulk ocean waters that were anoxic at this time could have supported high concentrations of dissolved Fe(II). Under such conditions, Fe(OH\textsuperscript{3})\textsuperscript{+} would have absorbed radiation in the 200-400 nm range, leading to the formation of dissolved ferric iron [Fe(III)], which in turn, would have hydrolyzed to form ferric hydroxide [Fe(OH\textsubscript{3})\textsuperscript{−}] at circumneutral pH. We evaluated the relative importance of photochemical oxidation using experiments that simulated the chemistry of ambient Precambrian seawater mixing with Fe(II)-rich hydrothermal fluids with, and without, UV irradiation. We found that if Fe(II) was effused from relatively shallow seamount-type vent systems directly into an anoxic photic zone, the photochemical contribution to solid-phase precipitation would have been negligible. Instead, most of the Fe(II) would have precipitated rapidly as an amorphous precursor phase to greenalite and/or siderite, depending on different simulated atmospheric pCO\textsubscript{2} levels. Conversely, in experiments where Fe(II) was exposed either to phototrophic Fe(II)-oxidizing bacteria or to O\textsubscript{2}, ferric hydroxide formed rapidly, and the precipitation of ferrous iron phases was not observed. If, as suggested on mass balance grounds, BIF deposition requires that Fe be sourced from shallow seamount-type systems, then we are driven to conclude that oxide-facies BIF are the product of a rapid, non-photochemical oxidative process, the most likely candidates being direct or indirect biogenic oxidation.
New insights into the geochemical behaviour of W by high precision isotope dilution measurements

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The geochemical behaviour of W during silicate Earth differentiation is only poorly constrained, largely due to its low abundance that makes high precision measurements difficult. Previous results (e.g., [1]) indicate a lower W/Th of the mantle (ca. 0.19) compared to the Earth’s crust, (ca. 0.26), suggesting that W appears to be more incompatible than Th. New data for MORB [2], however, demonstrate that W/Th is not significantly fractionated during dry peridotite melting, rather suggesting a fractionation of the two elements during crust formation by subduction related processes.

In order to assess the geochemical behaviour of W closer, we determined concentrations of W together with those of other high field strength elements by isotope dilution, using a mixed 183W-180Ta-242Zr-180Hf-176Lu tracer and multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS). In contrast to concentrations of other HFSE, which typically can be reproduced to within ±1%, W concentrations obtained for replicates display a larger scatter, ranging up to a few percent. The external reproducibility obtained for W concentrations (typically 3-4% 2σ) appears to depend on petrological properties, suggesting an influence of sample heterogeneity effects. For the BHVO-2 standard, significant variations in both Ta and W concentrations can be observed between multiple analyses. However, whereas measured W concentrations display large variations (200 – 350 ppb), Ta/W ratios (4.96-5.16) still yield an external reproducibility of ±4% (2σ). Altogether, our results confirm a similar compatibility of Th-W and Ta that is also reported for variably depleted MORBs [2], where measured Ta/W ratios only range from 4 – 6.

First Ta-W abundances determined in basaltic glasses and whole rock powders from various island arc settings display Ta/W ratios of 0.6 – 1.7, significantly lower than the values reported for MORB. These systematic differences indicate a higher mobility of W relative to Ta in subduction related processes, which possibly causes the selective W enrichment in the continental crust.

References
The speciation of carbon dioxide in silicate melts from in situ infrared measurements

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Carbon dioxide may dissolve in silicate melts either as molecular CO$_2$ or as carbonate. The ratio of the two species strongly depends on composition. While molecular CO$_2$ predominates in silica-rich, polymerized glasses, only carbonate can be detected in depolymerized basaltic glasses. However, the diffusion coefficient of CO$_2$ in rhyolitic and basaltic melts is nearly the same at identical temperatures, despite the fact that CO$_2$ speciation in the quenched glasses is very different. This suggests that the speciation observed in quenched glasses may not be representative for CO$_2$ speciation in silicate melts.

In order to determine CO$_2$ speciation directly in the silicate melt, we measured the infrared absorption spectra of silicate melts inside an externally heated diamond cell to more than 1000 °C. Samples include an alkali silicate melt with a degree of polymerization similar to a basalt and a dacite melt. Type II a diamonds of reduced thickness were used to minimize absorption due to the anvils. Measurements to about 700 °C were carried out using a globar source, experiments at higher temperature were carried out at the ANKA synchrotron source in Karlsruhe.

Only carbonate was observed in the alkali silicate melt to the highest temperatures studied. In the dacite melt, molecular CO$_2$ and carbonate were found to coexist in the melt. The quantification of speciation was complicated by the fact that the extinction coefficients of both molecular CO$_2$ and of carbonate were found to significantly decrease with temperature. This effect can be attributed to the changes in the population level of the vibrational states with temperature.

The high-PT stability of apatite: Constraints on transport and storage of phosphorus and halogens in the Earth’s upper mantle

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High-PT experiments were performed in a range 3-15 GPa and 850-1450°C in order to constrain the stability field of OH- and Cl-apatite and to study the partitioning of phosphorus between apatite or its high-P breakdown-product and the coexisting phases. The following starting materials were used: (1) an average MORB, (2) an Fe-free simplified MORB equivalent in the system SiO$_2$-Al$_2$O$_3$-MgO-CaO-Na$_2$O-TiO$_2$ and (3) a fertile lherzolite. The starting materials were doped with 3% synthetic OH-apatite or Cl-apatite and with a trace element mix. In the average MORB, OH-apatite is stable to 7 GPa/950°C coexisting with grt + cpx + SiO$_2$ + TiO$_2$. From 7.5-11 GPa and 950-1200°C, OH-apatite is replaced by tuite (γ-Ca$_3$(PO$_4$)$_2$ [1]) coexisting with the same assemblage. At higher P and T, no phosphate-phase was found due to increasing partitioning of phosphorus into coexisting grt or grt + melt. The P$_2$O$_5$-concentration in grt buffered by apatite, tuite or quenched melt is between 0.2-0.3 wt% but rises to 0.6-0.8 wt% in the absence of a phosphate-phase. Compared to MORB, the lherzolite system shows notable differences in the stability of phosphate-phases and in the P$_2$O$_5$-concentration of coexisting silicates. Apatite is stable to slightly higher pressures of ≥7.5 GPa/≥1000°C and was found to coexist with tuite at 8.5 GPa/1000°C in an assemblage ol + cpx + cpx + grt. In addition, apatite in the lherzolite incorporates significant amounts of Mg and Fe, reaching a total of 4.0 wt% at 8.5 GPa. This may be a reason for its increased P-stability in bulk (3). By comparison, (MgO+FeO) in eclogitic apatite does not exceed 1.0 wt% at 7.0 GPa. In coexisting apatite and tuite, the latter strongly partitions Sr and REE. The P$_2$O$_5$-concentration in lherzolitic grt is always higher than in MORB-grt, ranging from 0.7 wt% at 6 GPa/1100°C coexisting with apatite to 1.9 wt% at 13 GPa/1200°C in the absence of a phosphate-phase. The results of this study show that apatite in both MORB and lherzolitic bulks has a much smaller PT-stability field than previously assumed [1] and, consequently, that halogens cannot be transported and stored in apatite to depths > approx. 250 km.

References
Distribution of environmentally significant trace elements of the Tertiary bituminous shale deposits in NW Anatolia, Turkey

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There are 1.6 billion tones of bituminous shale reserve in 6 different fields in NW Anatolia, Turkey. In this study, environmental element concentrations (As, Cd, Cr, Cu, Hg, Mn, Pb and Zn) and enrichment factors of bituminous shales and element-organic matter relations were investigated and characteristics of fields were compared.

The maximum and minimum concentrations of environmental elements are As: 3.16-55.58 µg/g, Cd: 0.06-0.22 µg/g, Cr: 8.69-114.14 µg/g, Cu: 18.69-38.67 µg/g, Mn: 401.13-1451.50 µg/g, Pb: 4.62-16.32 µg/g, Zn: 23.93-50.02 µg/g and Hg: 17.33-77.07 ng/g. With enrichment factors (EF) less than one, Cr, Hg and Pb concentrations of the Bahçecik field and Hg contents of the Gölpazar field are depleted with respect to average shale values while other elements are enriched. In general, Hg shows the least enrichment and the highest enrichment was calculated for As. The highest and lowest enrichments for As were found in the Hatıldag (EF=35.28) and Bahçecik (EF=1.01) fields, respectively. In general, all elements are highly abundant in the Beypazar and Seyitömer fields and they have low concentrations in the Himmetoğlu, Bahçecik and Gölpazar (except for As) fields.

It was determined that the average Cd, Cu, Pb, Zn and Mn concentrations in all the fields are below the critical levels proposed for the soil (however, manganese concentration of the Bahçecik field is very close to the critical value). As concentrations in the Hatıldag and Gölpazar fields, Cr concentrations in the Hatıldag, Gölpazar and Seyitömer fields and Hg concentrations in the Himmetoğlu, Hatıldag and Seyitömer fields are higher than critical soil levels. A positive correlation between total organic carbon (TOC)-As and TOC-Pb at a significance of p≤0.01 and 0.05 was found in none of the fields. A positive correlation at significance of p≤0.05 was observed for TOC content with Cd in four of the fields, with Cu in two fields and with Cr, Mn and Zn in only one field.

40Ar-39Ar dating of mineral separates of shergottite Dhofar 019

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40Ar-39Ar thermochronology of SNC-meteorites yields insights into the thermal history, crystallization and cratering events of the martian lithosphere. We applied high-resolution 40Ar-39Ar dating to the olivine-phryic shergottite Dhofar 019 (whole rock, mineral separates). The intermediate/high temperature extractions of Dhofar 019 maskelynite, pyroxene and olivine separates suggest trapped argon with 40Ar/39Ar=300-400. Corrected age spectra show plateaus with similar ages of 642±72 Ma for maskelynite (~91% 39Ar release) and 603±96 Ma for pyroxene (~60% 39Ar release), the latter separate being dominated by maskelynite impurities. These ages are compatible with Sm-Nd and Rb-Sr ages [1]. In the olivine separate, the melt inclusions within olivine megacrysts [2] control the age spectrum. After correction for trapped argon, the extractions releasing 26-81% 39Ar display an age of 1086±252 Ma. This age could date the entrapment of a magmatic liquid during crystallization. On the other hand, the higher age of the olivine separate compared to maskelynite could be caused by incomplete degassing during shock metamorphism. 38Ar CRE ages determined from stepwise release age spectra of Dhofar 019 pyroxene and maskelynite are highly concordant with an average age of 15.7±1.1 Ma.

The young Rb-Sr/Sm-Nd and Ar-Ar ages of shergottites were usually regarded as crystallization ages [3]. Currently, there are strong debates about the interpretation of young Rb-Sr/Sm-Nd and Ar-Ar ages for shergottites, envisaging much older crystallization ages [e.g., 4, 5]. Although shergottites are severe shocked rocks, Rh-Sr, Sm-Nd and Ar-Ar chronometers cannot suffer a major reset by mere shock effects, e.g. conversion of feldspar to maskelynite causes only minor 40Ar loss [5]. Complete reset by 40Ar would require much stronger local shock wave effects (e.g., melt formation as observed for L chondrites [6]) or substantial accompanying heating effects (e.g., impact melt sheet covering, as could be the case for eucrites [7]).

References
High-temperature Raman spectroscopy and thermodynamic modelling of silicate melts, based on the problem-oriented database
“Thermo-melt”
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The work is devoted to theoretical and experimental researches of a structure of silicate melts M₂O-SiO₂, where M - Li, Na, K. The thermodynamic model of silicate melts, founded on spectroscopic data about their real structure was used. As a basis to construction of model the approach elaborated for oxide glasses in work [1] was applied. But as against the given approach the standard Gibb's free energy is expressed through the sum on Qₙ-structural units of a silicate melt. Search of a minimum of free energy of system is carried out by the decision of the system of equations of mass balance of the components and the law of mass action for all reactions proceeding in system.

For the definition of thermodynamic characteristics of these structural units data of silicones were used as initial parameters which have been received for the given systems at the project on creation of the database «Thermo-Melt». At the first stage, the collecting of bibliographic information for anhydrous crystal silicones and their glasses formed in systems O-Si-Me (where Me = Li, Na, K, Rb, Cs) is carried out and files of the literary data are created. The evaluation of the experimental thermodynamic information for the substances formed in considered chemical systems is carried out. Standard values of entropy, enthalpy and standard Gibb's free energy of silicates of alkaline metals are recommended. The new equations for the temperature dependences of the heat capacity of these substances are obtained.

For the testing the model and definition of Qⁿ-distribution of structural units experimental quantitative investigation of structure of lithium, sodium and potassium silicate melts were carried out by high-temperature Raman spectroscopy [2]. It is shown, that experimental values of concentration of structural units for these silicate melts and glasses are in a good agreement with the model. It is established that the temperature dependence of Qⁿ-distribution in the system Li₂O-SiO₂ differs from the dependence of Qⁿ-distribution in sodium and potassium silicate melts.

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Boron isotopes of K-tourmaline from the Kokchetav UHP massif
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Recently, high-K tourmaline (Tur; 2.76 wt% K₂O) co-existing with microdiamond was discovered in quartzofeldspathic rocks from Kumdyl-kol in the Kokchetav UHP massif, northern Kazakhstan [1]. The sample investigated in our study from the same locality is dominated by quartz, K-feldspar and Tur (~10 vol%), with minor titanite, phengite, chlorite, zircon, biotite, apatite, graphite and sulphide. Mineral assemblages preserved as inclusions in zircon consist of garnet, phengite and coesite. Despite an extensive search, no Tur inclusion was identified in ultrahigh-pressure (UHP) minerals (e.g. zircon, garnet, K₂O-bearing clinopyroxene). Furthermore, numerous quartz grains, but no coesite or microdiamond was identified as inclusions in Tur in our sample. We therefore interpret K-Tur in our sample to have formed under retrograde P conditions in the quartz stability field. The chemical compositions of Tur, however, is similar to the Tur for which [1] reported microdiamond inclusions.

Tur in the Kumdyl-kol sample is a K-analogue of dravite (0.35 Na pfu; Mg#: ~87) with remarkable contents of tetrahedral B (~3.3 B pfu) and Ca (~0.3 pfu), K₂O contents are as high as 1.57 wt % (~0.3 K pfu). The Tur displays a very low X-site vacancy (~0.05) and high OH (~3.4 pfu) and F (0.27 pfu) contents. At their rims and along cracks, all Tur grains show a strong decrease in K content to less than 0.05 wt%, accompanied by an increase in Na (~0.5 pfu), in X-site vacancies (0.2 to 0.3 pfu), and a slight increase in Al. All other elements are unzoned.

Tur cores are homogeneous in B isotopes (δ¹¹B = +10.6 ‰; analysed by SIMS in Heidelberg, Germany). Towards the rims, δ¹¹B values decrease to +5.5 ‰. These values are significantly higher than values reported previously for Tur from metasedimentary rocks or any (U)HP rocks (typically ~10 ‰). Heavy-B Tur (δ¹¹B > +5 ‰) has been described only from metapelitic-marble contacts [2,3], from partially melted granulites [2], from evaporites, and from hydrous reaction zones around HP metamorphic blocks formed by an influx of external hydrous fluids [4].

Hence, the high modal proportion of heavy-B Tur in the Kokchetav samples is best explained by a post-peak pressure influx of B-rich fluids or melts generated in biogenic-chemical sediments, i.e. carbonates or meta-evaporites.

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Historical carbonate mortar and plaster – Proxies for ancient environments

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Main focus of this study lays on mineralogical, chemical and isotopic composition of carbonate binders of historic roman, medieval and pre-industrial buildings as well as local limestone deposits (Styria, Austria). The respective mortars and plasters mostly consist of calcite as cement with aggregates of calcite, dolomite, quartz, and other silicates like clay minerals or mica.

E.g. 87Sr/86Sr, Sr/Ca, and Mg/Ca ratios of the cement may reflect the composition of the natural deposits used for manufacturing of lime mortar. Values depend on the geologic environment and mineralogical composition of the primary limestone.

δ13C/12C and δ18O/16O composition of the carbonate cement comprise a wide range and for an ideal case δ13C vs. δ18O shows an almost linear correlation. In general, calcite is isotopically lighter at the exterior versus the interior mortar layer. Range and systematic correlation of the data reflect isotopic fractionation effects upon setting of the cement and during the history (e.g. re-crystallization and weathering) of the cement. From another point of view isotope signatures can be used as a proxy for calcite formation conditions.

As one may use historical carbonate binder for 14C dating a promising pre-selection of suitable samples can be done by exclusively using carbonate cement or especially lime pops with specific δ13CCaCO3 and δ18OCaCO3 values.

Fe isotopic composition in sulphides from hydrothermal deposits at the Arctic mid-ocean ridge

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Hydrothermal vents represent an important source of iron for the deep ocean water. Their iron isotopic composition has been reported as constant relative to Fe residence time in the ocean but also as highly variable with respect to the sampling sites. It has been proposed that sedimentary record of Fe isotopic composition can be used locally to study the past fluxes of Fe but such study is limited by our poor understanding of Fe isotopic fractionation in the hydrothermal systems.

On average, the hydrothermal vent fluids have a slightly lighter (~ -0.5‰ δ56Fe; Sharma et al., 2001) iron isotopic composition compared to the oceanic crust (~ 0‰ δ56Fe; Rouxel et al., 2003), suggesting that seafloor hydrothermal systems fractionate iron isotopes. The isotopically light hydrothermal emanations of Fe2+ become progressively lighter through subsequent oxidation and precipitation processes within the water column (Severmann et al., 2004). The isotopic fractionation of Fe between the fluids and the precipitated sulphides is not yet fully understood but it varies with redox conditions, progress of the reaction and reaction rates.

We have studied isotopic composition of Fe in sulphides associated with newly-described hydrothermal systems along the Mohns Ridge in Norwegian-Greenland Sea. Pyrite from a tectonic breccia recovered from deep parts of the upflow zone is isotopically heavier compared to the pyrite from chimney fragments and sulphide precipitates on the sea floor. The studied pyrite precipitated at ca. 300-330 °C, i.e. at temperatures similar to many black smoker fluids, and higher than can be tolerated by thermophile bacteria. It also formed before the redox conditions were significantly changed by interaction of the Fe-bearing fluids with the deep sea water. The heavy iron isotopic composition in the pyrite from the tectonic breccia suggests that a significant fractionation may take place in the deeper parts of the upflow zone, and that this could explain the shift towards lighter iron seen in many vent fluids. The enrichment of heavy iron in pyrite from the deeper part of the upflow zone is probably related to factors other than the fluid temperature.

References
Electrokinetic potentials of metal oxides in highly concentrated electrolyte solutions

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The sign and the magnitude of the surface charge at the solid/liquid interface define the adsorption behavior of ionic species. The surface charge and the point of zero charge derived from potentiometric titrations are frequently used in adsorption modeling, while the electrokinetic potential is used chiefly in assessment of colloid stability, and very seldom in adsorption modeling. Limited usefulness of electrokinetic data was partially due to the fact that older-generation zetameters produced reliable results only at low electrolyte concentrations. This situation has changed over the recent decade, namely the new-generation instruments are able to measure the zeta potentials at electrolyte concentrations in excess of 1 M. The instruments based on electroacoustic method (electric sonic amplitude ESA or colloid vibration current CVI) are especially useful for this purpose. The problem with electroacoustic method is that electrolyte solutions also produce ESA and CVI signals, which is roughly proportional to salt concentration. At high electrolyte concentrations the ESA and CVI signal of salt is higher than the signal produced by a colloid. This problem is solved by electrolyte background subtraction procedure, which is a standard feature in commercial instruments. Thus, the zeta potentials are obtained as a result of subtraction of two large and almost equal numbers, and the value of the difference is very uncertain.

We suggest an alternative method to solve the problem of electrolyte background correction in electroacoustic measurements. By mixing two salts with common ion (e.g., LiNO₃ and LiCl), which give electroacoustic signals of opposite signs we prepared electrolytes, which give negligibly weak electroacoustic signal. Electroacoustic measurements in such electrolytes do not require electrolyte background correction, even at very high electrolyte concentrations, when the proportions of the components of mixed electrolyte solution are properly adjusted.

The electrokinetic potential of anatase (pristine isoelectric point IEP at pH 6.8) was studied as a function of pH in 1.73 m Li(NO₃,Cl) solution. The zeta potential at high ionic strength was positive at pH up to 10.5. This result confirms the phenomenon reported by several research groups, namely, Li salts at high concentrations induce a shift in the IEP of anatase and of other metal oxides to high pH. Such a shift is due to preferential adsorption of Li, which is observed at high salt concentrations, and which is absent at low concentrations. This preferential adsorption is cation-specific, and the role of the anion is less significant. Very likely, in the studied system there is no IEP at all, and the zeta potential of anatase is positive also beyond the data range.

Aspects of deep biosphere in intertidal sediments from the Wadden Sea (southern North Sea, Germany)

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Holocene intertidal sediments deposited in the backbarrier tidal system south of Spiekeroog Island (Northwest Germany) show similarities to those of the deep biosphere in various aspects. The research group on “BioGeoChemistry of Tidal Flats” sampled sediment cores down to a depth of about six metres by means of a vibration corer and studied them with microbiological and geochemical methods.

Sediment sequences and pore water profiles differ between the study sites. The sediments become anoxic at a few centimetres depth. Sulphate concentrations decrease within the upper several decimetres, but zones with a maximum of pore water sulphate were observed at greater depth. Methane concentrations mirror those of sulphate. Molecular biological analyses and the presence of intact phospholipids containing archaeol and hydroxyarchaeol show the presence of ANME-2 consortia and suggest that anaerobic methane oxidation occurs in the sulphate-methane-transition zones.

Organic matter is present throughout the core, but the content strongly varies with grain size. Mud-rich sediments contain up to 2% total organic carbon. With increasing depth organic matter shows a more terrestrial geochemical signature, becomes more recalcitrant and thus is harder to degrade. Molecular biological analyses of the microbial community composition shows clear depth zonations which reflect the pore water chemistry and organic matter quality and availability. Bacteria in the upper parts of the sediment sequences are dominated by Proteobacteria. In deeper layers, Chloroflexi and other groups of non-cultivated bacteria often found in the deep biosphere prevail indicating that subsurface tidal flat sediments harbour similar prokaryotic populations as those found in the deeper sub-seafloor biosphere.

Resting, inactive cells present as bacterial endospores represent up to 10% of total bacterial cells. The spore numbers, estimated from the content of dipicolinic acid as a spore-specific biomarker, strongly depend on the type of sediment. Pure cultures obtained from deeper samples were dominated by the spore forming Firmicutes.

The results show that various aspects of the deep biosphere can be studied in a relatively easily accessible but complex environment.
Identifying environmental sources of mercury using stable mercury isotopes

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There are many anthropogenic and natural sources of toxic mercury in the environment. As analytical methods for mercury isotopes improve, there is increasing interest in using stable isotopes of mercury to identify sources. San Francisco Bay is significantly impacted by nearby mercury mines, where anthropogenic activities have drastically influenced both the distribution and speciation of mercury. These mines have multiple sources of mercury, including unprocessed and processed wastes, as well as liquid elemental mercury. To determine whether mercury isotope composition can be used to distinguish mercury sources at these mining sites, we modeled mercury ore roasting and subsequent condensation processes used to recover liquid elemental mercury. Using simple Rayleigh fractionation models and estimates of mass-dependent fractionation factors, 202Hg/198Hg ratios in processed waste tailing piles are projected to be 3-4‰ larger than unprocessed mercury ores, whereas 206Hg/198Hg ratios in the liquid elemental mercury product are projected to be 0.5-0.9‰ smaller than unprocessed ores. These projected changes in mercury isotope composition appear to be large enough to distinguish between different anthropogenic sources, and can potentially be used to direct remediation efforts by quantifying relative source contributions to receiving waters.

An analytical method utilizing liquid sample introduction, rather than cold vapor generation, with sample reproducibility approaching 0.1% for 206Hg/208Hg ratios, will be presented. When applied to samples from locations downstream of mercury mines, this analytical method will help distinguish anthropogenic source contributions. Additionally, observations of isotope fractionation under laboratory conditions will be described.

Acknowledgement

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Hf-W and U-Pb ages of the Earth core formation: A solution of the paradox

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In most mantle processes involving only silicate phases Hf, W, U, and Pb behave like lithophile elements, however if a metal phase is present W and Pb demonstrate moderately siderophile properties. Radioactive decay of 182Hf to 182W, 238U to 206Pb and 235U to 207Pb make it possible to use these elements to study processes of silicate/metal differentiation. If Hf/W and U/Pb ratios of the Earth mantle had been changed by the core formation before 182Hf extinction, then mantle derived rocks should bring us consistent information about timing of the process in both isotopic systems.

Assessments of the core formation time based on Hf-W isotopic system vary from 45±5 My (Wood, Halliday, 2005) to about 30 My (Jacobsen, 2005) depending of the assumption about initial 182Hf/180Hf and some features of the accretion and core segregation styles. The time here is given relative to the Sun System Start (SSS).

Effective core segregation time as assessed from U/Pb delayed fractionation was rather more prolonged. Our best assessment based on 1150 MORB analyses is 120 My. We show that a solution of this discrepancy lies in an assumption of a gradual batch-by-batch differentiation of the proto-mantle material. Observed long-term Pb-Sr-Nd-Os isotopic heterogeneity of mantle rocks suggests impossibility of fast W isotopic equilibration as well between undifferentiated and metal-silicate differentiated portions of the young Earth mantle. In such an assumption different scenarios of one and two-stage core evolution were tested by numerical modeling. In two-stage core formation models the first stage is related with primary metal segregation and the second one – with Fe2+ disproportionation on silicate Fe3+ and metallic Fe0 (Galimov, 2005; Wood, Halliday, 2005).

One-stage linear (lasting ~130 My) and exponentially damped (<~ ~117 My) core growth models bring almost good agreement for Pb and W isotopic theoretical results with available data. Two-stage models involving the fist stage of fast and linear core growth (80-90% of the today core mass for 100-120 My) and the second one of slower linear or exponentially damped growth give exact solution for both isotopic systems.

In general, we show that in case of relatively fast Earth accretion and prolonged core growth, both Pb and W isotopic data could bring concerted model ages for Earth mantle rocks.

References

Environment of diamond formation in UHPM rocks from the Greek Rhodope: A Raman study of inclusions in zircon

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The Rhodope Massif in northern Greece is a newly established ultrahigh-pressure metamorphic (UHPM) province in the world (Mposkos and Kostopoulos, 2001).

Microscopic observations on zircons separated from a garnet gneiss revealed a simple zoned structure consisting of a somewhat rounded detrital core and a metamorphic overgrowth rim. Numerous mineral and fluid inclusions were found in the metamorphic rim especially near the interface of the two domains.

We carried out a detailed laser µ-Raman spectroscopic study of the inclusions and their zircon host in both domains. Quartz and monazite were identified in the detrital core whereas diamond, albite, phengite, hematite, rutile and CO2 gas were identified in the rim. Interestingly, albite occurs always in pockets with phengite and diamond whereas the latter two phases can occur independently. We interpret these pockets as precipitates from a melt phase at high pressures.

The microdiamonds were probably formed by dissociation of CO2; the thus liberated oxygen was combined with iron available from the fluid/melt phase to precipitate hematite. Importantly, there is clear-cut distinction in the Raman spectra of detrital and rim zircon, with the latter being additionally characterised by a broad band at Å1332 cm-1. What is more significant is that by approaching the included diamonds the above band in zircon increases dramatically in intensity. This can either be assigned to carbon occupying interstitial sites in zircon and in all probability reflects a luminescence band or to enhanced carbon solubility in zircon (Shcheka et al., 2006), with the diamonds reflecting sites locally supersaturated in carbon.

We favour the former explanation since similar bands, often associated with CO2 peaks, were also observed in inclusions in garnet for which C solubility is negligible.

References

An experimental basis for eco-safe geoconservation of radioactive nuclides in aluminosilicate matrixes based on fusible bentonites

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The most important requirements to matrixes for burring of radioactive wastes are recognized characteristics of absorption of radiation by substance with its warming up and tension relaxations, and also admissible levels of saturation by radioactive nuclides of bonding skeletons.

The authors suggest the creation of cheap silica-alumina matrixes based on fusible bentonitic cation-exchange clays. Using these clays it is possible to develop almost “pure” technologies for production of silica-alumina matrixes separately for products of nuclear fission (PNF) and separately for transuranium elements (TUE). At a “wet” (exchange) stage of charge preparation it is possible to separate radioisotope cations from anions of strong inorganic acids at once. As the exchange capacity of clays is insignificant, the demanded level of saturation of an initial material can be reached by addition of absorbing radioactive nuclides of humus substances. At the subsequent thermal treatment the organic compounds will burn out completely with formation of dense glass ceramic shard of lithoidal structure. The nearest natural analogues of such silica-alumina matrixes are high-temperature metamorphic rocks and volcanic glasses, which have been stable in watered systems for millions years.

Experiments at different temperature modes with modeling nitrate raffinates of PNF containing stable Cs, Ce and Sr have confirmed that they active replace exchange cations of clays - Ca, Na and K. Moreover, the cation exchange capacity achieves 190 mg/100g. Fast saturation of clays by PNF simulators within the first hour was established. This gives necessary information for a substantiation of wet technology processes at low temperatures. During sorption from modelling solution within 6-7 hours up to 80 mass. % of Ce, up to 50 mass. % of Cs and up to 30 mass. % of Sr pass into clays. Mechanisms of the thermal sintering of silica alumina matrixes were determined. With the purpose of definition of the maximal concentration of organic substances (peats), which possible to enter into bentonite matrix with preservation of its integrity after baking and without critical increase in porosity, a 40 experiments series was carried out. The results show that bentonites are perspective materials for production of glasses and ceramics, which strongly immobilize not only highly radioactive isotopes of alkaline, alkaline-earth elements and lanthanoids but also actinoids and other metals forming at nuclear fission and neutron activation.

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The effect of $[\text{Ba}^{2+}] / [\text{SO}_4^{2-}]$ ratio on the mechanism of barite growth at constant supersaturation

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We investigated the mechanism of barite growth in a fluid cell of an Atomic Force Microscope by passing solutions of constant supersaturation ($\Omega$) but variable $[\text{Ba}^{2+}]$ to $[\text{SO}_4^{2-}]$ ratio over a barite substrate. We observed that the potential for two-dimensional nucleation increases with increasing $[\text{Ba}^{2+}] / [\text{SO}_4^{2-}]$ ratio and the mechanism of crystal growth changes from advancement of pre-existing steps to massive island spreading as the cation:anion ratio increases.

Experiments were carried out at two different degrees of supersaturation (7.2 and 12.6) with $[\text{Ba}^{2+}] / [\text{SO}_4^{2-}]$ ratios varying over several orders of magnitude. We observed advancement of pre-existing cleavage steps to be responsible for crystal growth for $[\text{Ba}^{2+}] / [\text{SO}_4^{2-}]$ ratios up to 0.25, while two-dimensional nucleation was not observed. At higher cation:anion ratio two-dimensional nucleation occurs with the island density generally increasing with increasing cation concentration in solution.

The results suggest that the rate limiting factor for two-dimensional nucleation to occur is the frequency of cation attachment, which is determined by the barrier for cations to approach the surface. We carried out further experiments using water-methanol mixtures for the growth solution to corroborate the hypothesis that the solvation water of the crystal surface and of the cation effectively hinders the ability of the cation to reach the surface and that desolvation is the rate-limiting kinetic process in crystal growth. Massive island nucleation was observed on the barite surface in contact with water/methanol solutions with $[\text{Ba}^{2+}] / [\text{SO}_4^{2-}]$ ratio two orders of magnitude lower than 0.25 (while adjusting the ion concentration to the desired $\Omega$ in the solvent mixture). Step advancement and island-spreading velocity also changes with varying cation to anion ratio with the tendency to reduce growth velocity while moving towards extreme values of ion ratio.

Our findings show that barite crystal growth under the same supersaturation conditions occurs by different mechanisms with the cation adsorption on the surface being the rate limiting factor for two-dimensional nucleation. This conclusion is relevant in considering natural systems where crystals grow from solutions of highly variable stoichiometry.

Distribution of Platinum-group element and minerals within the chromitites of Tauride Ophiolite Belt (Pozanti-Karsanți, Pınarbaşı, Mersin), Southern Turkey

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The Tauride Ophiolite Belt was emplaced in southern Turkey. Total bulk platinum group element (PGE) concentrations of chromitites from the Pınarbaşı area range from 67.5 to 253 ppb. The total bulk PGE values of Pozanti-Karsanți chromitites are between 38.2-2730 ppb. The PGE distribution of Tauride chromitites exhibits a negative slope in chondrite normalised diagram. Their Pd/Ir ratio is between 0.01-0.95 which may reflect a magma source which has a severely depleted character. Although most of the chromitite samples from the Tauride Ophiolite Belt have negative slopes in chondrite normalised diagrams, one of the samples from the Pozanti-Karsanți ophiolite is unexpectedly PPGE-enriched (Rh: 150; Pt: 1390 ve Pd: 832 ppb) and has a positive slope in the normalised chondrite diagram. The PPGE values of the chromitites from Pozanti-Karsanți are recorded in the literature as one of highest determined PGE values of chromitites in Turkey (Kozlu-Erdal and Melcher, 2006). The primary PGM inclusions (Pınarbaşı) are laurite, Ir-sulphide, cuproiridsite, Ru-Os (Pozanti-Karsanți) alloys and Os-Ir alloys (Mersin) (Kozlu-Erdal and Melcher, 2007).

Conclusions

The geochemical character of chromitites from Tauride ophiolites and their PGE and PGM composition reflect crystallization from severely depleted boninitic magmas in the supra-subduction zone.

References


Basalt weathering at high-latitude regions on Mars

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Thermal-infrared (TIR) spectroscopic analyses of Mars indicate that, although bulk regolith SiO₂ contents are globally constant (Karunatillake et al., 2006), high-silica mineral(oid)s are common in dark regions at middle-to-high latitudes (Bandfield et al., 2000; Michalski et al., 2005). Near-infrared (NIR) data from northern-hemisphere regions rich in high-silica materials are consistent with ferric oxide coatings on basaltic substrates (Mustard et al., 2005). Yet, the NIR data lack hydration features, indicating that coating formation may have been anhydrous (Bibring et al., 2006; Poulet et al., 2007). From laboratory experiments, however, we have determined that NIR hydration features of hydrous, amorphous silica are absent from spectra of rocks with thin coatings of silica. The same coatings significantly affect TIR spectra. Such coatings could explain why there are high-silica materials at higher latitudes on Mars despite globally similar bulk SiO₂ contents. Formation of silica coatings by the materials at higher latitudes on Mars despite globally similar spectra. Such coatings could explain why there are high-silica coatings of silica. The same coatings significantly affect TIR determined that NIR hydration features of hydrous, amorphous silica are consistent with ferric oxide coatings on basaltic substrates (Mustard et al., 2005). Yet, the NIR data lack hydration features, indicating that coating formation may have been anhydrous (Bibring et al., 2006; Poulet et al., 2007). From laboratory experiments, however, we have determined that NIR hydration features of hydrous, amorphous silica are absent from spectra of rocks with thin coatings of silica. The same coatings significantly affect TIR spectra.

We suggest that low-temperature, aqueous weathering of basaltic materials has occurred at Martian middle-to-high latitudes, in agreement with Wyatt et al. (2004). We further suggest that the weathering under these conditions has occurred in soils, where liquid water formed periodically as a result of percolation of melt water from surface ice or snow, or when soil ice melts at grain interfaces. Because dissolution and precipitation likely occurred in small, transient pockets or films of liquid water, weathering products would be poorly crystalline and metastable, while thermodynamically favored phases would be kinetically inhibited from forming. It is further likely that weathering would favor dissolution of high-surface-area aeolian dust, which could supply SiO₂ to form rock and particle coatings like those found in some icy soils on Earth (e.g. Dixon et al., 2002). Authigenic minerals in icy Martian soils may be dominated by amorphous silica, formed as coatings on coarser particles of basalt, contributing the spectral signals detected from orbit.

References


Adsorption of As in rice paddy soils of West Bengal

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Worldwide in large areas groundwater is naturally polluted by As. Millions of people are drinking this water without any treatment. In many areas large portions of the groundwater is even used for irrigation purposes (Sanyal and Naras, 2002).

The groundwater investigated in the area near Kaliachak, West Bengal can be ranked as highly polluted (to 817 µg/L As, WHO recommends 10 µg/L). In groundwater, the more toxic As(III) species dominates. After flooding the rice fields with this highly contaminated water, more than 90% of the As is retarded in the soil within 24 h resulting in an increasing accumulation of As in paddy fields.

The spatial distribution of As and other major and trace elements in soil particles from different soil depths was mapped by using µ-SXRF. Iron and As- speciation was determined by µ-XANES (FLUO-Beamline, ANKA/ Karlsruhe; Beamline L, HASYLAB/ Hamburg).

Statistical evaluation of the µ-SXRF data and extended µ-XANES suggest that mica (biotite or illite) and chloride host the minor concentrations of As. Tiny goethite grains embedded in the clay matrix seem to be a major phase for As immobilisation of irrigation water.

Redox conditions in soils control the abundances of the redox sensitive species of Fe and As immitted by irrigation water. The decrease in the relative small As(III) proportions with depth give strong hints for changing redox conditions.

Arsenic is mainly co-precipitated with Fe-oxides forming directly after irrigation. A considerable portion of As in rice paddies is adsorbed to Fe rich coatings which have been formed by O₂ release of rice roots. Highest total As concentrations (up to 1600 mg/kg As) as well as the highest As(III)/As(V) ratios have been observed at the innermost side of the coatings (Kiczka, 2005). In Fe- rich coatings considerable amounts of limonite, a mixture of Fe(OH)₃ and FeO(OH) are observed additionally to mica and goethite in soil matrix. These coatings are an important sink for As in rice paddies acting as barrier for the soil plant transfer of As.

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References


A ~4.3 Ga U-Pb age from lunar meteorite SaU169 and the chondritic Sm/Nd of the Moon

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A remarkably consistent set of $^{142}$Nd/$^{144}$Nd and $^{146}$Nd/$^{144}$Nd data of lunar rocks reported by Rankenburg et al. (2006) provides evidence for a chondritic Sm/Nd ratio of the Moon. An apparent minor inconsistency is present for the most fractionated lunar rock in their data set, the Imbrian high-KREEP lunar meteorite SaU169, which yielded a subchondritic initial $\varepsilon_{142}$Nd value if this parameter was calculated for its reported SIMS zircon date of 3909 ± 13 Ma (Gnos et al., 2004). The zircons dated were skeletal grains that crystallized from the impact melt.

We have carried out a leaching experiment on a 2 mg heavy mineral concentrate from the same impact melt, containing zircon and some merrillite, as follows. Step 1: 4N HNO$_3$, 25°C, 15 min. Step 2: 4N HNO$_3$, 100°C, 8 hrs. Step 3: Inverse aqua regia, 100°C, 16 hrs. Step 4: HF + 4N HNO$_3$, 150°C, 3 days. Isotope ratios of the $^{235}$U + $^{208}$Pb spiked leaches were measured on a Nu Instruments® MC-ICP-MS.

The final HF+HNO$_3$ step has $^{208}$Pb/$^{206}$Pb = 0.37 and $^{206}$Pb/$^{204}$Pb = 440 and dominantly reflects zircon. It yields a near-concordant U-Pb date of 4290 ± 30 Ma. This is robust, but significantly older than the SIMS dates of 3909 ± 13 Ma reported by Gnos et al. (2004), which give the age of the Imbrium impact melt. We suggest that our older age reflects a mixture of zircons crystallized from the impact melt, such as dated by Gnos et al. (2004), and much smaller, but collectively dominant crystals that might have survived impact melting and had a lunar crustal or KREEP source origin, with ages of 4300 Ma or older (Papike et al., 1998).

If the $^{142}$Nd/$^{144}$Nd ratio of Rankenburg et al. (2006) for SaU169 is extrapolated back to the age of 4.3 Ga suggested by our result, the initial $\varepsilon_{142}$Nd value plots precisely on the chondritic evolution curve, consistent with their models. This further strengthens the case for a chondritic Sm/Nd ratio of the Moon and therefore, terrestrial fractionation after the Giant Impact.

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Sr-isotopes and trace elements in feldspar and clinopyroxene: Tracer of magma mixing in gabbros from Uralian-Alaskan-type complexes in the Ural Mountains, Russia

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We applied LA-ICPMS techniques to determine Sr isotopes and trace element concentrations of rock forming minerals in gabbroic rocks from zoned mafic-ultramafic complexes (Nizhnii Tagil and Kytlym) in the Ural Mountains in Russia.

These gabbros have porphyritic textures with clinopyroxene phenocrysts in a matrix of olivine, clinopyroxene and spinel ± plagioclase. Based on the composition of additional matrix minerals two types of gabbro can be distinguished. One is silica saturated, contains plagioclase (An56-97) and in places orthopyroxene as matrix phases (bytownite gabbro). The second gabbro type is silica undersaturated and contains in the matrix plagioclase (An26-41) and pseudoleucite, an intergrowth of nepheline and K-feldspar (Or53-93).

Clinopyroxene of gabbros from Nizhnii Tagil and the western part of the Kytlym Complex is enriched in LREE (87Sr/86Sr 0.70384-0.70405 ±0.00004). These features imply that silica undersaturated gabbros are derived from thin section scale.

References
**Direct analysis of various geological materials using 213 nm and 193 nm laser ablation systems and ICP-MS**

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Laser Ablation ICP-MS has come a long way since its introduction in the mid-eighties. Most common commercial systems are using 266 nm, 213 nm or 193 nm. Laser energy in the deeper UV range is more efficient at delivering the laser energy to a wider variety of samples, allowing uniform sampling of even transparent materials. This is of special importance when analysing a variety of geological samples.

The CETAC LSX-213 Laser Ablation system is operating at a wavelength of 213 nm and is optimised to deliver homogenized “flat-top” energy profile with > 4mJ, 5 ns laser pulses with repetition rates of 1-20 Hz. The use of Helium as a carrier gas improves sample transport efficiency and reduces fractionation. It finds its application in the analysis of several types of geological samples, such as soils and sediments, Otoliths, gemstones, quartz samples, and other materials. Various applications are discussed.

For the most challenging and highly transparent samples the best suitable wavelength is 193 nm. Due to the use of a very stable Excimer Laser, its high energy density of up to 45J/cm² at 193 nm, and a highly homogenized beam profile, the GeoLas Pro has advantages for very precise geochronology and fluid inclusion analysis, especially for very small craters down to 4 µm in diameter. The use of a powerful petrographic microscope enables the identification of even very small features of a few micrometers. Features and Applications for this 193 nm Excimer Laser system are discussed.

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**Petrology of shoshonitic lamprophyres and related carbonatites in the Svecofennian Domain**

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The latest stage of magmatism related to the Svecofennian Orogen involved numerous, low-volume bimodal shoshonitic granitoid intrusions. Several contemporaneous shoshonitic lamprophyre dyke swarms are found throughout the Svecofennian Domain, as well as three small calciocarbonatite dyke swarms. We present petrological data on these dyke rocks and consider their genetic relationships.

The shoshonitic lamprophyres in the Lake Syväri area of eastern Finland occur as a swarm of narrow dykes. Additional lamprophyre dykes are found in the west Lake Ladoga region, Russian Karelia. Age determinations (SIMS U-Pb, zircon) from both areas give concordant intrusion ages of 1.78-1.77 Ga. Petrographically, these lamprophyres are characterized with aggregates of biotite in a fine-grained matrix of K-feldspar, plagioclase, calcite and apatite. Typical accessory minerals are titanite, magnetite, baryte, pyrite, ilmenite, diopside and allanite. Blebs or vesicles of carbonate minerals have been found in samples from both areas. They are strongly enriched in LREE, P, Sr and Ba. Similar enrichment is seen in shoshonitic lamprophyres in the west Lake Ladoga region, Russia, and their plutonic equivalents in the easternmost part of the Svecofennian Domain.

The three calciocarbonatite intrusions occur at Halpanen in southeast Finland as a single, relatively large dyke as well as at Naantali, southwest Finland and Panjavaara, east-central Finland as swarms of small dykes. In addition to calcite, the dykes contain 5-10% modal fluorapatite. Typical accessory minerals include magnetite, bastnäsite, monazite, titanite, allanite and baryte. The carbonatite intrusions also show strong enrichment in LREE, P, F, Sr and Ba, along with depletion in Nb and Ta. Preliminary age determinations from monazite suggest an intrusion ages between 1.78-1.76 Ga. \(\varepsilon_{Nd}(1800)\) was found to be near zero, indicative of metasomatic mantle enrichment from ca. 1.9 Ga subduction. \(\delta^{13}C\) ratios fall between ~8 and ~15‰ for all carbonatite intrusions as well as the carbonate vesicles in the Lake Ladoga region lamprophyres. Intensity of enrichment as well as the \(CO_2/H_2O\) ratio increases from west to east, a trend parallel to that described by Andersson \textit{et al.} (2006).

Despite the wide geographic distribution of these intrusions, the combined petrological and geochemical evidence suggest a genetic relationship between the lamprophyre and carbonatite dykes, as well as the shoshonitic granitoid intrusions.

**References**

Age of HP metamorphism from the Escambray Massif, Cuba

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The geochronology of HP/LT metamorphism constitutes a major challenge in the reconstruction of subduction zones. In Cuba, the Escambray metamorphic complex comprises a nappe stack involving both HP/LT subduction-related metamorphic rocks as well as island-arc-related LP/HT units [1]. A Mesozoic age has been suggested for the protoliths of these rocks based on poorly preserved fossils [2]; final exhumation is indicated by the appearance of pebbles of metamorphic rocks in conglomerates at about 45 Ma.

Although the timing of the rapid exhumation of the Escambray nappe stack is well constrained between 75 and 65 Ma [1, 3], available age data on earlier stages of subduction history are in conflict. A concordant U/Pb age of 102±2 Ma for zircons has been reported for an eclogite [4]; however, other eclogites yield discordant populations with a lower intercept at 148 Ma [3]. SHRIMP analyses of single-grain zircon show a broad spectrum of ages between 105 and 176 Ma. Only metamorphic sphene provides a U/Pb age of about 71 Ma interpretable as a “metamorphic age”.

New results from Lu–Hf dating on eclogites and garnet amphibolite from subduction-related nappes help to shed light on this discrepancy. The eclogites and garnet amphibolite yielded ages of 72-67 Ma and 80 Ma, respectively. If garnet nucleated before peak P, eclogite ages may even predate attainment of maximum subduction depth. This new result will have to be integrated into models of the geodynamic development of Central Cuba.

References

Speciation of organometal(lloid) compounds in landfill gas and landfill leachate by hyphenation of GC with ICP-MS

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Organometal(lloid) compounds, metal(lloid) species bearing at least one metal-carbon bond, are usually more toxic than their inorganic representatives. These compounds can be formed in wet environments and occur as methyl or hydride derivates in the gas phase, while ionic species stay in the liquid phase. Organometal(loids) are also present in landfill gas and landfill leachate. Amongst them toxic compounds like Tetramethyltin, Tetraethyltin, Tributyltin or Dimethylmercury. The total amount of metal(loids) being alkylized in landfill sites still remains unknown. Organotins are the most abundant metal(loid) species in landfill gas and landfill leachate. Determination of these metal species in landfill samples turns out to be difficult, as they occur in ultratrace levels which requires a good trace-matrix separation and a powerful detection technique. Coupling of capillary gas chromatography (GC) with inductively coupled plasma - mass spectrometry (ICP-MS) provides a very sensitive analytical tool for organometal(loid) speciation.

A self-made cryotrapping (CT) - cryofocussing (CF)-GC-ICP-MS system was used for the analysis of landfill gas. We found more than 15 volatile organotins, with a concentration range from 11 pg/L to 31ng/L. But also Dimethylmercury, Dimethylselenide and Dimethyltelluride were found in landfill gas.

Landfill leachate is analysed using GC-ICP-MS for liquid injections of organic solvent extracts. Water soluble organotins were transferred into peralkylated compounds by derivatization with sodium tetra-(n-propyl)-borate and extracted with n-hexane. By using propylation instead of ethylation we were able to find ethylated organotin species in leachate. For the first time we found more than 10 organotins with concentrations from 0.1 to 7.9 ng/L. But we could not find any Hg, Se or Te species in the leachate yet.

This indicates that organometal(lloid)s are produced within a landfill site in large number and can be carried out of the system via gas and leachate.
Radiohaloes in cordierite: Radiochemical transformation of channel constituents

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Yellow pleochroic radiohaloes are frequently observed in cordierite. Their formation is caused by the impact of alpha particles originating from actinoid-bearing inclusions, which create scattered point defects in the cordierite structure. This process may result in a significant disturbance of the short-range order of this mineral (Nasdala et al., 2006).

Cordierite is well known to contain hydrous species and CO2 in structural channels that are oriented parallel to the c axis (Aines and Rossman, 1984). Our micro-spectroscopic investigations yield evidence for radiochemical changes of such molecules. Raman and infrared (IR) spectra of radiohaloes are characterized by less intense OH stretching and CO2 bands when compared to the host cordierite, whilst concurrently an extra band appears at \( \sim 2135\text{cm}^{-1} \) (Fig. 1). This band is assigned to CO stretching vibrations (Khomenko and Langer, 2005). Our observations suggest that carbon monoxide (observed only in radiohaloes) must have formed from CO2 caused by the impact of alpha radiation.

Figure 1: Polarised IR absorption (left) and Raman spectra (right) taken inside a radiohalo and in the unaltered host cordierite, indicating irradiation-induced CO2 → CO transformation.

References

Boron isotopic compositions of tourmaline from a hydrothermal gold deposit – Constraints on fluid sources

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The ultimate sources of ore forming fluids still remain a key question in orogenic gold research. In this regard the boron isotope and chemical compositions of tourmaline provide important constraints on the source compositions of the mineralizing fluids because tourmaline (a) is a common gangue mineral in many Archaean lode gold deposits and is often closely associated with gold mineralization, (b) is stable over a wide p/T range and is resistant to alteration and weathering, (c) is indicative of source lithology as reflected by its compositional variability, and (d) is the main host for boron in most rocks, where the boron isotopic composition in tourmaline is controlled by the composition of boron in the source, the p/T conditions of crystallization, and by fractionation effects related to phase changes.

We investigated tourmalines from the Hira Buddini Gold Deposit within the Archaean Hutti-Maski Greenstone Belt in southern India. The tourmalines belong to the dravite-schorl series with major element variations being related to their host lithology. SIMS determined \( \delta^{11}\text{B} \) values vary in a wide range from -13‰ to +9‰ with 95% of the values are between -4‰ and +9‰. The bimodal distribution with peak \( \delta^{11}\text{B} \) values at about -2‰ and +6‰ is consistent with the presence of at least two isotopically distinct fluids which penetrated the hydrothermal system along different access-pathways and were subsequently mixed. The calculated \( \delta^{11}\text{B} \) values of the fluids being about 0‰ and +10‰, respectively, rule out a crustal origin for the source fluids, suggesting an involvement of metamorphic and/or magmatic sources. The isotopically lighter fluid may have been generated during metamorphic devolatilization reactions, whereas the heavier fluid is attributed to degassing of I-type granitic magmas that provided heat and fluids to the hydrothermal system.
SEM-CL analysis of quartz gangue in the Big Creek Mining District, Idaho, USA indicate that CL textures predate quartz crystal formation and final optical orientation

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SEM-CL textures uniquely identify quartz in veins and alteration assemblages with various stages of hydrothermal deposition in the Big Creek Mining District of central Idaho. These mesothermal veins and disseminated mineralization associated with hydrothermal alteration are related to the Idaho batholith, and are located within a large structural zone that is enriched in gold and silver locally.

In a number of slides CL textures do not correspond to grain contacts identified using polarized light microscopy with crossed nicols (PLM). This indicates that the CL patterns formed prior to crystallization and associated optical characteristics. In several slides, grain boundaries do correspond to CL patterns and in others the relationship between specific grains and CL texture is vague. SEM-CL reveals textural evidence of deposition and brecciation events in quartz prior to crystal formation with associated grain boundaries and the establishment of optical properties. Later recrystallization may change original optical properties in specific grains but not the original CL texture.

Hydrogen isotope ratio of Acid Volatile Sulfur in saltmarsh sediments

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Reported what probably are the first δD measurements of Acid Volatile Sulfur (AVS) extracted from sediments. The samples represent the upper 50 cm of a salt marsh from Sapelo Island, GA, USA. The site is sparsely vegetated by Spartina alterniflora. Sediment core and pore water samples were collected, the core samples being taken within few centimetres from the pore water sampling sites. The sampling devices, pore water diffusion equilibrators (“peepers”), were covered using 0.2 µm pore sized dialysis membrane. Sampling of the pore waters was done anaerobically at 1-2 cm intervals from the sediment water interface. The AVS from the sediment samples was released using a novel method, which involved treatment of pre-weighed, dry samples (5 cm interval) with 100% phosphoric acid under vacuum conditions. The gases produced by this reaction included CO2, SO2 and H2S. The H2S was converted to hydrogen by reacting with hot cupric oxide and then passing the resulting water over hot uranium. δD of this hydrogen was measured and the values ranged from -500 to -615 ‰. The δD of the 100% phosphoric acid used was -140‰. The SO2: H2S ratio was ~2 for all samples. The δD values strongly point to organically bound sulfur as the source of H2S. This organically bound sulfur in turn can be considered to have resulted from methane oxidation in the presence of sulfate via the pathway:

\[
\begin{align*}
\text{CH}_4 + \text{SO}_4^{2-} & \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O} \\
\downarrow & \downarrow \\
\text{AVS} & \rightarrow \text{CaCO}_3
\end{align*}
\]

This argument is supported by the down core variation in pore water SO4 and Dissolved Inorganic Carbon (DIC) concentrations and the relatively low δ13C values (-19.5±5‰) for the carbonate fraction ‰.
New data concerning the high-Mg rocks of the Siberian trap formation in the Noril’sk region

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The problem

The huge Siberian trap province consists of the tholeitic basalts in general. High-Mg rocks are very rare, especially in its Western part. Meanwhile their composition and origin are very important to the reconstruction of the evolution of the whole magmatic system and the ore-forming processes.

There were described two main horizons of the picritic basalts in the Noril’sk region: inside the Gudchikhinsky and the Tyklonsky Formations (Godlevsky, 1959; Dodin, 1964; Fedorenko et al., 1996 etc.). Numerous basic-ultrabasic intrusions located here contain the picritic gabro-dolerites as well, sometimes with Pt-Cu-Ni deposits. It is believed that they are the result of the interaction between the Tuklonsky magma and the surrounding rocks, and thus they belong to the Nadezhdinsky Formation (Naldrett, 1992; 1996; Lighthfoot et al., 1997). But the relationships between intrusive and effusive rocks are not recognized enough.

The main goal of this study was to understand the origin of high-Mg intrusive rocks in terms of their connection with the effusive rocks. To solve this problem we have investigated the complete section of the Nadezhdinsky Formation in the Mikhangda river basin. It consists of two different units: the lower part is represented by layered flow (about 70 m thickness) and the upper part consists of 7-10 massive flows (140-150 m thickness). The lower part is the most interesting because it contains the interlayers of picritic basalts (17-19 mas.% MgO, the summary thickness is about 15 m) among the tholeiitic basalts. All rocks of the layered flow are characterized by very similar features: they have high LIL concentrations, Ta-Nb negative and Pb positive anomalous, very low Cu, Ni, Co contents. Olivine composition not vary significantly: Fo content changes from 76 up to 78 mol.%, NiO = 0.09-0.11 mas.%, HREE =0.1-0.3 ppm. In contrary, picritic gabro-dolerites of the ore-bearing intrusions possess another behaviour of these elements – average LILE, high metal contents and another typomorphical features of olivines (Fo₇₈₋₈₃, NiO = 0.2-0.3 mas.%, HREE=3 ppm).

Conclusions

For the first time the high-Mg rocks were established in the Nadezhdinsky Formation. This is the third level of the tholeiitic basalts in the vertical sector of effusive rocks in the Noril’sk region. They can be formed from the tholeiitic basalts to adding 32 % olivine crystals (Krivolutskaya et al., 2005). These picritic basalts are not comagmatic rocks for the picritic gabbro-dolerites from intrusions with unique Pt-Cu-Ni ores. The latters were formed from another magmas.

This study was supported by Russian Foundation for Basic Researches (project № 07-05-01007).

Age distribution and geochemistry of cinder cones in the Bandas del Sur, South Tenerife (Canary Islands)

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The three shield massifs of Anaga, Roque del Conde and Teno (constructed between 11.9 and 3.9 Ma, Guillou et al. 2004) are the oldest volcanic units exposed on Tenerife island. In the central part of the island, the prominent Las Cañadas volcano formed between ~3 and 2 Ma. Three caldera-forming eruptions occurred between 1.59 and 0.17 Ma (Marti et al. 1994; Bryan et al. 1998) and are collectively responsible for the development of the Las Cañadas Caldera (Marti et al. 1994, 1997). The Bandas del Sur Formation, in the south of Tenerife, records two explosive volcanic cycles of basaltic to phonolitic eruptions with more than seven ignimbrite sheets, erupted from the Las Cañadas edifice. These cycles correlate with the caldera-forming eruptions. Each cycle started with flank eruptions of the Las Cañadas volcano associated with alkali basaltic lavas and the formation of cinder cones within the Bandas del Sur (Bryan et al. 1998).

The cinder cones within the Bandas del Sur are important volcanic units for understanding the explosive volcanic cycles on Tenerife during the Pleistocene. Palaeomagnetic studies, major and trace element geochemistry, as well as Y/Nb ratios, Zr/Nb plots, and radioisotopic dating (K-Ar) have been carried out on prominent cinder cones to discover their stratigraphic position. Combining our results with previous K-Ar data, the cinder cones and lavas can be subdivided into three stratigraphic units. Each unit shows specific Y/Nb ratios and distinctive remanent magnetization. Multielement plots, as well as variation diagrams depicted for each unit yield further information with respect to mantle source and degree of partial melting. The first two units were constructed between 0.948-0.779 Ma and 0.323-0.300 Ma. These units define volcanic cycles ending in violent plinian eruptions. The third and youngest unit possibly marks the beginning of a further volcanic cycle 0.095 Ma ago.

References

On the basis of geophysical constraints (P- and S- wave velocities, moment of inertia and mass of the Moon) and method of mathematical modeling of phase relation and physical properties in the system CaO-FeO-MgO-Al$_2$O$_3$-SiO$_2$, we examine the hypothesis of chemical differentiation of the Moon as a result of partial melting of initially homogeneous material (hypothetical magma ocean). We consider models of internal structure of the Moon with five layers including a crust, a three-layer silicate mantle, and a Fe–10 wt.% S-core ($\rho = 5.7$ g cm$^{-3}$). The general methodology is to combine geophysical and geochemical constraints and thermodynamic approach, and to develop, on this joint basis, the self-consistent model of Moon, accounting for its chemical composition and internal structure. The Al$_2$O$_3$ content in the lunar crust ($\rho = 2.9-3.0$ g cm$^{-3}$) varied between 25 and 30 wt%. The concentrations of major oxides for the entire mantle varied in the ranges $2 \leq$ CaO and Al$_2$O$_3 \leq 8\%$, $25 \leq$ MgO $\leq 45\%$, $40 \leq$ SiO$_2 \leq 54\%$, $6 \leq$ FeO $\leq 20\%$. The technique of Gibbs free energy minimization was used, and equations of state of minerals and solid solutions were included in the database. The solution of the inverse problem is based on the Monte Carlo method. We determine the ranges of chemical composition, mineralogy, velocities and density in the upper, middle and lower mantle as well as core sizes. The results of our inversion procedure generate velocity and composition distributions in the lunar mantle. The bulk composition of the silicate portion of the Moon (mantle+crust) is estimated (wt. %): 3.8< CaO<3.8%, 3.7< Al$_2$O$_3$<4.7%, 11< FeO<12.5%, 28< MgO<30%, 49< SiO$_2$<51%, MG# ~81. The chemical composition of the Moon bears no genetic relationship to the terrestrial material as well as to any of the known chondrites. This research was supported by RA S under Programs 9 and 18, and by RFBR grant (06-05-64308).

We used EMPA to measure sodium in olivine and glass in type I and II chondrules of UOC Semarkona (LL3.0). Goal of our study is to show whether alkalis were present in the liquid during olivine crystallization. Na in olivine was analyzed with a beam current of 300 nA for 600 s on the peak and 2 x 300 s on the background. The detection limit was determined to be $\sim 10$ µg/g.

Na$_2$O-concentrations in mesostasis vary in the range of 0-12 wt%. Na$_2$O in olivine in chondrules varies in the range of 0-68 µg/g (type I) and 40-110 µg/g (type II).

Our data show that Na was present in chondrules during olivine crystallization. The apparent $D_{Na}$ (ol/mesostasis) is 0.0005 for type I and 0.001 for type II chondrules, respectively. Calculating the $D_{Na}$ between olivine and bulk gives a $D_{Na}$ of 0.005 for type I and II. Borisov et al. (in prep.) give a $D_{Na}$ (ol/melt) of $\sim 0.003$. This value is in agreement with our data. Absence of loss of alkalis requires either high alkali partial pressures and/or a very rapid heating and cooling of chondrules. Our interpretation of the presence of Na in chondrule olivine explains the absence of K-isotope fractionation in chondrules in the way that evaporation did not take place during chondrule melting.

Reference
Relict refractory inclusions in chondrules from the metal-rich carbonateous chondrites

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We have recently concluded that the CH/CL-like chondrite Isheyevo and other CH chondrites contain multiple generations of chondrules (Krot et al. 2007a): (i) magnesian chondrules with cryptocrystalline and skeletal textures, similar to those in CB3 chondrites, which may have formed from a gas-melt plume resulted from a large-scale asteroidal collision (Krot et al., 2005); (ii) ferromagnesium and Al-rich chondrules with porphyritic textures which appear to have formed by melting of solid precursors. Here, we report the discovery of abundant Ca,Al-rich inclusions (CAIs) inside porphyritic chondrules from Isheyevo and CH chondrites Acfer 182/214 and PAT 91546. These, now relict CAIs formed before the host chondrules, were subsequently mixed with the chondrule precursor materials and melted to various degrees during chondrule formation. About half of the relict CAIs belong to a population of 26Al-poor, very refractory inclusions dominated by grossite and hibonite; other relict CAIs consist mainly of spinel. Grossite and hibonite of the relict CAIs and anorthetic plagioclase of the host chondrules show no evidence for 26Mg excesses related to decay of the short-lived 26Al radionuclide. The only two exceptions are grossite-rich CAIs having small 26Mg/28Mg ratios corresponding to an initial 26Al/27Al ratios of (1.7±1.3)×10^-6 and (3.3±3.0)×10^-7. The 26Al-poor grossite-rich and hibonite-rich igneous CAIs comprise about 50% of all refractory inclusions in the metal-rich chondrites studied (Krot et al. 2007b,c). Such CAIs, however, are virtually absent in ordinary, enstatite and other carbonaceous chondrite groups. We infer that this isochronally and mineralogically unique population of CAIs was present in the region where ferromagnesian porphyritic chondrules of CH and CH/CL-like chondrites formed, suggesting that these chondrules formed at a different time or in a different nebular region than chondrules from other chondrite groups. Since most CAIs outside chondrules in Isheyevo and CH chondrites show no clear evidence for being affected by the chondrule-forming processes, we infer that either the scale of chondrule-forming event(s) was relatively small and a number of chondrule-forming events in a localized nebular region where these chondrules formed was limited, or chondrule-forming event(s) had little effect on compact objects, like CAIs.

References

Pine Point, Canada Pb-Zn deposits: Better resolved S-isotope study

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Introduction
Insight on the formation of the Pine Point (NWT, Canada, 60°41'N, 114°30'W) Pb-Zn deposits was acquired four decades ago using traditional stable isotope methodology (Sasaki and Krouse, 1969; Fritz 1969; Fritz and Jackson, 1972). This presentation summarizes δ34S data from better resolved sampling techniques. (1) Trace sulfate and sulfide in carbonate (Ueda and Sakai, 1983), (2) different organic components (Krouse et al., 1987), and (3) laser probe produced SO2 from mineral surfaces (Kelley and Fallick, 1990).

Results and Discussion
Fritz (1969) and Fritz and Jackson (1972) identified at least three dolomitization events in the deposits. In the current study, trace sulfide and sulfate from an early dolomite had δ34S values of +18.5% (the mean value of the ore) and +25.7%, consistent with partially reduced Devonian seawater sulfate. The δ34S values of sulfate and sulfide in a vug were +28.0 and +57.7% respectively, consistent with low temperature bacterial sulfate reduction and sulfide loss.

Powell and Macqueen (1984) found unaltered bitumens to have lower S-content and bulk δ34S values than altered bitumens. Below 300°C, H2S evolved during pyrolysis had low δ34S values consistent with post ore deposition low temperature sulfate reduction. Most H2S was evolved between 300°C and 500°C with δ34S in the range associated with the ore. H2S released at higher temperatures had δ34S values found for unaltered bitumens. Altered bitumens released more H2S in the 300°C to 500°C range than unaltered bitumens.

Laser probe produced SO2 revealed systematic δ34S variations in a single PbS crystal of the order of 2‰ which is comparable to data for hand specimens throughout the deposits (Sasaki and Krouse, 1969). This supports low temperature (<100°C) estimates for ore deposition.

Conclusions
Better chemically and spatially resolved sampling provided δ34S data which complement those of traditional stable isotope methodology at the Pine Point Pb-Zn deposits. Overall, the newer techniques better describe processes involved during and post ore deposition.

References
The role of mantle fluid in formation of modern oceanic sulfide ore: Os isotope evidences

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Great potential of Re-Os isotope system as a tool for hydrothermal sulfide ore study and searching of the metal sources has already been demonstrated (Ravizza et al., 1996; Brügmann et al., 1998; Gannoun et al., 2003; Sharma et al., 2000; Cave et al., 2003). It was shown that the main sources for Os and Re in submarine hydrothermal systems are seawater, rocks of hosted oceanic crust (sediments, basalts, ultramafics), hydrothermal fluid and extraterrestrial dust. But, the data about pristine plume component with prominent mantle-like signatures are very limited (Cave et al., 2003; Sharma et al., 2000) and lacks further investigation in order to find out the true significance of this source in the process of oceanic ore formation. The main goal of the present investigation was to study behavior of Re-Os isotope system in the process of modern hydrothermal sulfide formation and to determine the role and share of mantle substance in this process. To solve these problems we choose modern (active from 7 thousand years ago till nowadays) Ashadze hydrothermal field developed over ultramafic basement and represented by different types of sulfide formations – from massive sulfides and smokers (up to 7-10 m high) to secondary Fe-Mn and hydrogenic crusts. The Ashadze hydrothermal field as a whole is located on the western slope of the MAR rift valley at 13°N, 44°50’W. Re and Os concentration and Os isotope composition of 15 hydrothermal sulfide samples and 14 host rocks were determined by NTIMS methods for detecting synthetic chalcogenide (MeX, X = S,Se,Te) nanoparticles at trace levels in the environment are of interest in view of possible large-scale commercialization of nanotechnology (1). Natural aquatic metal sulfide nanoparticles already have been observed (2). Nanoparticles composed of several metal sulfides sorb strongly at Hg⁰ electrodes (2-4), where cumulative deposits can be quantified by cathodic scans (MeSÆMe⁰ amalgam). Thus Hg⁰ electrodes can serve both for preconcentration and for determination of chalcogenide nanoparticles. Detection at <10⁻⁶ M (as Me⁰) has been demonstrated and lower limits are probably feasible.

Understanding the preconcentration mechanism is the key to optimizing detection of chalcogenide nanoparticles. In a detailed study of semi-spherical, copper sulfide (Cu,S) aggregate particles having mean diameters of 5-20 nm, a three-step mechanism is required to explain preconcentration. The first step involves Brownian diffusion of particles to the Hg⁰ surface. When both the electrode and particles have negative surface potentials, this process resembles charge-impeded coagulation, obeying the Schulze-Hardy rule in various electrolytes. The second step involves atomic reordering of Cu,S, probably to Cu₅S₆ adlayers. A very significant (~0.3 V) negative shift in the Cu,S reduction potential results, owing to a free energy decrease from release of the nanoparticles’ surface energy and from favorable chemical interactions between Cu₅S₆ adlayers and Hg⁰. The third step, which competes with the second, involves size-dependent, reductive loss of electroactive Cu₅S₆ prior to the cathodic scan. This loss is greatest for the smallest particles with greatest surface free energy.

Methods for detecting synthetic chalcogenide (MeX, X = S,Se,Te) nanoparticles at trace levels in the environment are of interest in view of possible large-scale commercialization of nanotechnology (1). Natural aquatic metal sulfide nanoparticles already have been observed (2). Nanoparticles composed of several metal sulfides sorb strongly at Hg⁰ electrodes (2-4), where cumulative deposits can be quantified by cathodic scans (MeSÆMe⁰ amalgam). Thus Hg⁰ electrodes can serve both for preconcentration and for determination of chalcogenide nanoparticles. Detection at <10⁻⁶ M (as Me⁰) has been demonstrated and lower limits are probably feasible.

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References

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Comparison of TiO2 and SnO2 (100)
and (110) hydrated surfaces via
molecular modeling

Reactive transport simulation of
mineral trapping of CO2 in operated
geothermal aquifers

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Periodic density functional theory (DFT) calculations
using the programs CASTEP and VASP were carried out to
model the H2O-TiO2 and the H2O-SnO2 (100) and (110)
interfaces. These two minerals have the same crystal structures
but different unit cell dimensions and dielectric constants.
Comparisons of the behavior of H2O at each surface can be
used to test the effects of these two parameters on H2O
dissociation and interfacial structure. Energy minimization
and molecular dynamics (MD) simulations were conducted
with periodic DFT methods to examine the relative energetic
stability of a variety of configurations. In order to more
completely sample configuration space, interatomic force
fields were developed for the H2O-TiO2 and H2O-SnO2
interfaces using the program GULP. Thus, classical MD
simulations could be carried out over longer time periods than
practical with the DFT method. The force field reproduces
structures calculated with DFT reasonably well and the
relative energies of configurations are similar between the two
methods. In addition, the effects of deprotonating the surfaces
to mimic the negative surface charge on real surfaces are
examined. Differences in H2O adsorption mechanisms are
attributable to unit cell parameters and basicities of surface
oxygen atoms. Starting with the associated H2O molecules we
have obtained the mixed associative-dissociated structure in
the case of SnO2. The most interesting observation is that
dissociation of H2O occurred indirectly. In the first stage, the
H+ bonds to a bridging oxygen from one of nearest H2O,
forming the intermediate OH– state. In the second stage, the
terminal H2O H+ transfers to the OH– ion forming the new
H2O molecule and terminal OH–. No such process was
observed for TiO2 surface. A stable mixed adsorption structure
was obtained by optimization after manual H+ transfer on the
same path as was spontaneously passed in the case of SnO2.
Analogously, starting with the broken H2O molecules in the
first layer, we have obtained the stable dissociated structures
both for TiO2 and SnO2 where hydroxyls were attached to
5-fold Me and H+ were bonded to the bridging oxygens.

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Innovative technology
Costs for carbon dioxide (CO2) sequestration into deep
saline aquifers can be transformed into a benefit in
combination with ecologically desirable geothermal heat or
power production. The current “CO2Trap” project aims to
develop a scientifically and technically feasible new
technology to achieve a safe and economically attractive longterm storage of CO2 trapped in minerals. Numerical models
are applied to study injection of aqueous CO2 into the
subsurface and to quantify subsequent precipitation of calcite
(CaCO3) in potential geothermal reservoirs.

Geothermics and CO2 storage
Exploitation of geothermal energy in Germany is mainly
provided from deep sandstone aquifers. The common
arrangement of boreholes is the well doublet, consisting of one
well for hot water production and one well for cooled water
re-injection. The cooled water is loaded with dissolved CO2
generating carbonic acid. After re-injection into the reservoir
this cold water becomes enriched in calcium e.g. due to
dissolution of anhydrite (CaSO4). Because the solubility of
anhydrite increases with decreasing temperature, injecting
cold water dissolves anhydrite in a growing region around the
well. The favored reaction path, the transfer of anhydrite into
calcite, leads to a surplus of acid. Alkalinity to buffer the
reaction can be provided from rock forming minerals (e.g.
oligoclase). Subsequently CO2 will react with the calcium ions
to form and precipitate calcium carbonate.

Conclusion
We demonstrate the feasibility of transforming anhydrite
into calcite by reactive transport modeling. Buffering capacity
(alkalinity) from the reservoir rock is necessary for the
transformation of anhydrite into calcite. Although it turns out
that anhydrite is not the major player from the chemical point
of view, its dissolution with concurrent pore space increase is
important to balance the pore space reduction by precipitation
of calcite and secondary silicates in the geothermal reservoir.


Aqueous-solid solution model of strontium uptake in C-S-H phases  
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Cement wasteforms are composed mainly of calcium silicate hydrate (C-S-H) phases which can incorporate divalent cations such as Sr (including the fission product ⁹⁰Sr relevant in nuclear waste disposal). In this context, our C-S-H Aq-SS model was extended with Sr, Na, and K end members. We used our Sr uptake data in pure water and in artificial cement water (ACW); Nagra-PSI chemical thermodynamic database; and the GEMS code (http://les.web.psi.ch/Software/GEMS-PSI) in forward chemical modeling and inverse dual-thermodynamic calculations (DTC).  

DTC can retrieve unknown stoichiometry and standard molar Gibbs energy G° of an ideal solid solution end member from several experimental bulk compositions of co-existing aqueous solution and solid solution phases. Using DTC with 13 end member candidates, the following “optimal” stoichiometries were found: Sr(OH)$_2$SiO$_2$H$_2$O (SrSH); [(NaOH)$_{2.5}$ SiO$_2$H$_2$O]$_{0.2}$ (NaSH); [(KOH)$_{2.5}$ SiO$_2$H$_2$O]$_{0.2}$ (KSH), with the associated mean G°$_{298}$ values and 2σ uncertainty intervals.  

Two extended C-S-H quinary ideal solid solutions were used in forward modeling of our Sr uptake data (ca. 90 experiments at ambient T,P). Two modeled cement degradation scenarios show that Sr is retained much stronger in the “carbonation” than in the “dilution” (CO$_2$-free leaching) process.  

The Aq-SS approach requires somewhat different G°$_{298}$(SrSH) value for modeling Sr uptake in C-S-H (Ca:Si ~ 1.1±0.1) prepared in water than that prepared in the alkaline ACW. The difference (ca. 3.4 kJ mol$^{-1}$) could be explained by a weaker silicon tetrahedra polymerization in C-S-H during synthesis with alkali cations. Preliminary studies also indicate that the Ca-Na-K-Sr ion-exchange model on “tobermorite” sorbent may be more precise in predicting Sr uptake by C-S-H in ACW than the ideal solid solution model.  

References  

Binding of metal ions by natural organic matter (NOM) – Investigated by lanthanide ion probe spectroscopy (LIPS)  
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The binding to natural organic matter (NOM) determines transport, bioavailability, and toxicity of metal ions in water and soil environments. The understanding of the underlying interaction mechanisms between NOM and metal ions is therefore indispensable for the development of reliable models for the prediction of mobility and fate of metal ions in the environment. Because of their outstanding spectroscopic properties lanthanide ions (Ln$^{3+}$) are excellent probes for the direct investigation of metal binding to NOM. Especially, the spectral sensitivity to changes in the close coordination sphere of the Ln$^{3+}$ ion as well as the dependence of the luminescence decay time on the type of ligand coordinated can yield valuable information on the stoichiometry and symmetry of metals bound to NOM.  

In our experiments Eu$^{3+}$ and Tb$^{3+}$ ions were used as luminescence probes to investigate the binding of metal ions to humic acids (HA) and fulvic acids (FA), which represent a major part of NOM. The Ln$^{3+}$ luminescence was excited either directly or via sensitization by radiationless energy transfer from HA or FA ligands. The intra- and intermolecular energy transfer processes were investigated in detail using H$_2$O and D$_2$O as solvents.  

Because of the high complexity of NOM simpler organic model ligands such as aromatic and aliphatic hydroxy carboxylic acids were investigated as well. In ultra-low temperature measurements at 4 K the non-degenerated $^5D_0$-$^7F_0$ transition of Eu$^{3+}$ and the Stark splitting of the $^7F_1$ and $^7F_2$ levels were used to evaluated the stoichiometry and the symmetry of the complexes formed. Furthermore, time-resolved luminescence spectra of Ln$^{3+}$-L (L = NOM or model ligand) measured in H$_2$O and D$_2$O were analyzed and the number of coordinated water molecules was determined.  

References  
A comet nucleus sample return (CNSR) mission in ESA’s Cosmic Vision program

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Rationale
We propose a comet nucleus sample return (CNSR) mission in the context of ESA’s Cosmic Vision plan. After the detailed investigation of comet 67P/Churyumov-Gerasimenko by the Rosetta orbiter and lander, a sample return mission is the logical next step in cometary exploration.

Scientific background
In comets we find a mixture of original interstellar grains with material that was re-processed in the solar nebula. That mixture is of particular interest for the study of the formation of the solar system. Laboratory investigation of samples brought back from different (active and inactive) regions of a comet allows to reveal this mixture of low and high temperature compounds. The Stardust mission has shown that those compounds are intimately mixed on small scales (Brownlee et al. 2006, Mc Keegan et al. 2006). The analysis of the returned sample from a cometary nucleus will determine the processes of the formation of the planetary system and their chronology (the amount of material collected by Stardust was too small to achieve that goal). It will be possible to determine how far out and in which proportion material processed near the Sun during the formation of our planetary system was transported out into the Kuiper belt where it was mixed with pristine interstellar material. A stratigraphic sample from a cometary nucleus will reveal the structure of the intricate porous mixture of ice-dust grains that make up a comet nucleus and provide for its unique activity.

The mission
A relatively small spacecraft will be launched into its interplanetary trajectory to a short period comet. After a short monitoring period near the cometary nucleus, needed to find suitable sampling spots, the spacecraft will touch down on the surface of the nucleus to collect samples. The sampling depth will be several decimeters. Finally the cooled samples will be returned to Earth. The mission is proposed to ESA’s Cosmic Vision and exploration programs, in co-operation with the Russian space agency.

References

Modeling study on glacial-interglacial variations of atmospheric CO2 concentration: The effect of Southern Ocean

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Ancient air trapped in Antarctic ice cores shows that the atmospheric CO2 concentration, pCO2, was lower during the ice ages than it is today. For example, at the Last Glacial Maximum (LGM), pCO2 was 180-200 ppm which is roughly 80-100 lower than the pre-anthropogenic value. Although many hypotheses have been proposed to explain the pCO2 variations for two decades, there is no widely accepted explanation for the variations.

Geological records suggest that, during the LGM, the extent of sea ice in the Southern Ocean was greater than that at present. In this study, we used an ocean general circulation model (COCO3.4, an ocean component of our atmosphere-ocean coupled general circulation model, MIROC3.2 (K-1 Model Developers, 2004)) coupled with a simple biogeochemical model (Yamanaka and Tajika, 1996). We examined the model sensitivities to changes in sea ice extent in the Southern Ocean on pCO2 and discussed the effect of the Southern Ocean on the low pCO2. We obtained the following two results. First, the reduced ventilation due to the sea-ice expansion would have had only a small effect on the reduction of atmospheric CO2 concentration. The effect of reduced ventilation is much weaker than that predicted by a box model in a previous study. The difference resulted from the different efficiencies of water exchange between the surface water and the deep water in southern high-latitude regions. Second, sea-ice cover may have had the additional effect. If biological activity was reduced below the sea ice, the effect of decrease in consumption of CO2 through biological activity might exceed that of decrease in the supply of CO2 from the atmosphere. We propose that this effect was opposite and possibly stronger than the reduced-ventilation effect. These results suggest that sea-ice expansion was far from the principal mechanism for low CO2 concentration during the LGM.

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Composition, temperature, and thickness of the lithosphere of the Kaapvaal craton

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A new model is proposed for the structure of the Kaapvaal craton lithosphere. Based on self-consistent thermodynamic approach, profiles of the chemical composition, temperature, density, and S-wave velocities are constructed for depths of 100–300 km. For the computation of the phase diagram for a given chemical composition (garnet-bearing lherzolite xenoliths and primitive mantle composition, we have used a method of minimization of the total Gibbs free energy combined with the Mie-Grüneisen equation of state. Our forward calculation of phase diagram, seismic velocities and density and inverse calculation of temperature includes anharmonic and anelastic parameters as well as mineral reaction effects, including modes and chemical compositions of coexisting phases. The estimated temperatures depend rather strongly on bulk composition and proportion of phases stable at various depths of the upper mantle. We find that the upper mantle (normal and cratonic) cannot be treated as uniform in terms of bulk composition because a fixed uniform composition leads to a non-physical behaviour of geotherms. The mantle beneath the Kaapvaal craton is chemically stratified: an upper layer at depths between 100 and ~200 km consisting of depleted garnet peridotite and a lower layer (below ~200-220 km) made of a more fertile material [1]. The material composing the cratonic root at a depth of ~275 km does not differ in its physical and chemical characteristics from the composition of the normal mantle, and this allows one to estimate the thickness of the lithosphere at 275 km. The results of this work are compared with data of seismology, thermal investigations, and thermobarometry.

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Reference

Radiocesium distribution in North-West coast of the Kola Bay

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Introduction
The migration of $^{137}$Cs in North territories was investigated to better identify specieshes of its prevalence in tundra landscapes. The territory of interest is located from north-west coast of Kolskiy bay to Norway border.

Methods
Our method is based on landscape approach developed by A. I. Perelman. Depending on the relief character, the territory was subdivided into four geochemical landscapes. The eluvial landscape is located at the top of nipples, the transit landscape – on the slopes, accumulative and aqual (water) landscapes – on the bottom lands. According to this approach the geochemical map (scale 1:50 000) was created. During the investigation, about 500 samples of soils and lichens (cladonia, cetraria) from 154 points was taken.

Results and Discussion
Data of radiocesium distribution in soil genetic layers and plants were obtained. Areal with maximum $^{137}$Cs concentrations in soils and plants were determined. The highest $^{137}$Cs content in soil is 332 Bk/kg, in plant is 194 Bk/kg. The regularities of $^{137}$Cs distribution on the territory studied depending on location of supposed sourses is revealed.

The results of investigation of $^{137}$Cs vertical in the soil profile are obtained. It was defined that the most polluted components of landscapes are plants and top soil layer. The latter consists of indecomposable organic relics more than one half. This layer sustainibly retains $^{137}$Cs.

Conclusion
The detected levels of radiocesium pollution are much less than 1 ku/km², thus it is not dangerous to the people living on territory investigated.

Reference
Fluid inclusions of metamorphic rocks and a late-orogenic granitic intrusion

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The Ladoga region is considered a typical example of andalusite-sillimanite type of metamorphic zoning in the southern part of the Baltic shield. On the basis of mineral assemblages and compositions, as well as the amount of leucosome in metapelitic rocks, the Ladoga region is divided into five metamorphic zones. The PT-estimates of the Early Proterozoic Ladoga metamorphic complex range from 3–4 kbar and 400–500°C to 5–6 kbar and 800–900°C.

The Tervu granite massif (intrusion) is one of the late-collision granites that intruded a high-grade core of the Early Proterozoic Ladoga metamorphic complex. The Tervu massif consists mainly of two feldspar mica granites with rare veins of aplite and pegmatite. The U-Pb age of zircon of the Tervu massif is 1.86 Ga. The age of monazite from the latest veins of the Tervu massif is 1.85 Ga. Minerals of the Tervu granite massif consist of different types of fluid inclusions such as H2O, H2O–salt (up to 1–3 % NaCl, KCl, CaCl2, MgCl2), CO2, CH4, N2. Original homogeneous allocation of a fluid phase is expected at the moment of crystallization of the massif. This is supported by the monotonic mineral composition of rocks of the massif, absence of significant bulks of facies and phase varieties. Fluid inclusions of the massif have more or less the same compositions, but there are also specific features of their allocation: 1) CO2 inclusions occur only in the northern and central parts of the massif, 2) aqueous, mineralized by salts Ca, Mg (Cl2) occur in the northern peripheral part, 3) methane - nitrogenous inclusions occur in the northern and central areas, 4) only aqueous occur in the south-east and northern areas of the massif, 5) aqueous inclusions with NaCl and KCl mineralization occur in the southern, central and northern parts, 6) aqueous inclusions with a low mineralization occur everywhere within the intrusion. Such variability of compositions of fluid implies that most likely the total contents of fluid in samples varied from the moment of crystallization because of new volatile phases, which have caused variations in composition of fluid inclusions in the most fluid-enriched rocks.

Comparison of compositions of fluid of the Tervu massif with composition of fluid of metamorphic rocks demonstrates mostly their similarity. However, the fluid inclusions enriched with salts CaCl2 and MgCl2 are not characteristic for the metamorphic rocks. It is possible to consider that genesis is primary magmatic for such fluid inclusions.

CO2 inclusions are unusual for the Tervu intrusion but the surrounding migmatitic leucosomes have a lot carbonic inclusions. Thus, the Tervu massif is characterized by unequal fluid compositions, and strong variations in density and salt contents in different parts of the massif. The specified features of allocation of fluid may be a consequence of redistribution of the fluid phases within the massif during post-crystallization tectonic and thermal processes.

30Si isotopic signature of major terrestrial and aquatic pools

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Silica is the second most important element in the Earth crust. Weathering of minerals in soils as well as global Si fluxes have strong effects on the global cycling of many other elements including carbon. Despite the important role of Si in terrestrial and marine ecosystems and for living organisms, the knowledge about Si fluxes in biogeosystems is strongly limited. An important gap in the knowledge on global Si cycling is the absence of a clear explanation of the enrichment of marine ecosystems with 30Si – the heavy stable Si isotope. Therefore, we aimed this review on 1) critical evaluation of the 30Si data existing for various pools of terrestrial and marine ecosystems, and 2) linking 30Si signatures in terrestrial and marine pools by considering isotopic fractionation of 30Si by biological processes.

Table 1. Overview about published δ30Si values for various pools in global biogeosystems (standard: NBS28)

<table>
<thead>
<tr>
<th>Si pools</th>
<th>Δ30Si, ‰</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Rivers</td>
<td>+0.4…+1.2</td>
<td>De La Rocha et al. 2000</td>
</tr>
<tr>
<td>Seas</td>
<td>+0.6…+1.7</td>
<td>De La Rocha et al. 2000</td>
</tr>
<tr>
<td>Rocks</td>
<td>-1.0…+0.3</td>
<td>Douthitt 1982; Ding et al. 1996</td>
</tr>
<tr>
<td>Primary quartz</td>
<td>-0.1…+0.7</td>
<td>Basile-Doelsch et al. 2005</td>
</tr>
<tr>
<td>Secondary quartz</td>
<td>-5.7…-1.6</td>
<td>Basile-Doelsch et al. 2005</td>
</tr>
<tr>
<td>Pedogenic kaolinite</td>
<td>-1.9…-1.0</td>
<td>Ding et al. 1996</td>
</tr>
<tr>
<td>Phytolites</td>
<td>-1.7…+2.8</td>
<td>Douthitt 1982</td>
</tr>
<tr>
<td>Phytolites of maize</td>
<td>-1.8…-0.8</td>
<td>Ziegler et al. 2000</td>
</tr>
<tr>
<td>Soils from basalt</td>
<td>-2.5…-0.5</td>
<td>Ziegler et al. 2005</td>
</tr>
<tr>
<td>Soil extracts</td>
<td>more posit. than soils</td>
<td>Ziegler et al. 2005</td>
</tr>
</tbody>
</table>

Based on the δ30Si values, the following processes can be reconstructed: Si dissolved by weathering of primary minerals becomes a component of soil solution. The elements in the soil solution, including Si, are mainly subject of two mass flows: upward uptake by plants and downward transport by leaching. As light isotopes are preferred for uptake in biological processes, δ30Si values in plants are negative: -1 to -2.5‰. The remaining soil solution will be enriched by 30Si. The 30Si depleted phytoenic Si remains in terrestrial biogeosystems, mainly in the upper soil horizons and will be reused by plants and microorganisms in further cycles. Therefore, at least a part of secondary minerals is 30Si depleted, which was biologically recycled at least once. The 30Si enriched soil solution discharge into rivers, seas and oceans. Further biological depletion by continental transport (limnic and fluvial systems) leads to additional accumulation of 30Si up to +0.5…+1.4‰ in discharge systems and seas.


O isotope exchange during the breakdown of dolomite: An experimental study

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Dolomite commonly breaks down to periclase + calcite in the presence of an H2O-rich fluid in contact-metamorphic environments. We investigated the kinetics of the reaction in dolomite rock samples experimentally to determine whether 18O from the external fluid exchanged only with the neomorphic calcite and periclase or whether exchange between the fluid and preexisting dolomite occurred as well. We sealed 4×6 mm cylinders of rock in gold capsules with an aliquot of 18O enriched H2O and heated the capsule to 700 °C at 100 MPa for a period of up to 8 weeks. Samples were examined after experimentation by electron and ion probe techniques. The x-ray images indicated that some reaction took place along grain boundaries, even in the interiors of the sample. Ion images of the reacted sample were obtained from Cameca 4f, 7f, and 1280 ion probes to determine the distribution of 18O. Calcite produced during reaction showed an enrichment in 18O wherever the breakdown reaction had occurred. In addition, the dolomite shows a distinct 5–10µm-wide zone adjacent to the grain boundary that is also enriched in 18O (figure right). Point analyses across the exchanged zone at a scale of 1 µm indicate that the boundary between the exchanged and unexchanged dolomite is a step, although there is some indication of a diffusion profile at the boundary. That step suggests that the exchange occurred by solution-reprecipitation, but there is no secondary porosity or optical misorientation found. It appears that H2O does it again, greatly facilitating isotope exchange between a fluid and a preexisting mineral grain.

Evolution of the basal dense magma ocean: The ultimate deep mantle rug!

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Since the discovery of the ultralow velocity zones in the lowermost mantle, evidences for the presence of partial melt at the bottom of the mantle have continually accumulated. The maintenance of the magnetic field for at least 3.2 Gyr requires cooling of the core over that period and implies an even larger quantity of melt in the lowermost mantle in the past than at present. We investigated the implications of such an hypothesis in terms of thermal and chemical evolution of the mantle and found that it can offer an explanation for several different observations. The crystallization of melt, controlled by the energy balance, is exponential to first order, with a time scale of about 1 Gyr. The melt is denser than the overlying solid that crystallizes from it, due to a larger Fe content. In addition, the huge viscosity contrast renders entrainment of melt by convection in the mantle negligible, preventing any sampling through surface magmatism. The melt is then the ideal hidden reservoir and can contain about 20% of the Earth’s budget in incompatible elements. Moreover, because of the difference between the partitioning coefficients of Sm and Nd at high pressure, the evolution of the deep magma ocean-mantle system naturally generates the observed ε143Nd in mantle derived rocks and explains the systematic of chondrites with all terrestrial samples in ε142Nd. The existence of melt in the lowermost mantle for most of Earth’s history, deduced from geophysical arguments offers a solution for some of the long-standing geochemical paradoxes of the Earth’s mantle.

SIMS ion image showing 16O/(16O + 18O) in dolomite near grain boundary (black).
Mercury stable isotope variations in a Bolivian watershed: Evidence for mass-independent fractionation

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Mercury contamination is an environmental problem of increasing concern in the Amazon basin. In Bolivia, indigenous people have elevated methylmercury hair concentrations. This highly toxic molecule originates in the release of inorganic Hg from chemical and physical weathering and from human activities. The aim of our study is to trace the sources and the processes involved in the cycle of Hg, in the Beni River watershed, through variations in Hg isotopic compositions. Three types of samples are studied: sediments, liquid Hg0 from gold mining and hair from gold miner and indigenous populations. Hg isotopic compositions were analyzed on a Thermo-Finnigan Neptune MC-ICP-MS at Trent Univ. and at the LMTG after sample digestion by aqua regia at 120°C (Foucher and Hintelmann, 2006).

The δ202/198Hg values (relative to NIST 3133) are significantly different with respect to the external precision of 0.05-0.2 ‰ (2σ): -0.34 ± 0.02 ‰ for liquid mercury, -1.05 ± 0.14 ‰ for sediments, -0.44 ± 0.20 ‰ for miner hair (n=9), +1.18 ± 0.10 ‰ for indigenous people hair (n=12). Mass-independent isotope fractionation was observed for odd isotope ratios in all hair samples (Figure 1): ∆199Hg and ∆201Hg anomalies of up to 1.16 and 0.98 ‰ respectively were observed, and were more pronounced for miners than indigenous communities. Preliminary data on fresh and oxidized black shale samples show up to 2 ‰ variation.

Figure 1: Mass-independent fractionation observed for δ199/198Hg for gold-miner and indigenous people hair samples. Lines represent mass dependent fractionation.

Reference
Foucher D. and Hintelmann H. (2006), ABC, 384 1470-1478

First steps in the feasibility study of CO2 geological storages monitoring through noble gas geochemistry

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Since noble gases are relatively inert, and for some of them lighter than CO2, they migrate faster. Thus they are potential precursors to survey the integrity of CO2 storages. By monitoring the surrounding aquifers, it could be possible to detect these precursors (e.g.: Helium (He) or Argon form spikes or air-pollution), and then to properly survey the trapping efficiency of a storage. In order to study the noble gases dissolved in brines, we have developed a new fully automated line, linked to a quadrupole mass spectrometer QMS200 by Balzers. We extract our water samples in gas phase, trap the water vapor on cold traps, and then purify the residual gas phase to analyze noble gases with our QMS. Gas aliquots can be sampled in order to analyze isotopic ratios using our glass-made mass spectrometers Aresibo.

As preliminary step, we chose to validate our new line with a simple analogue of CO2 storages: the Pavin lake, in the French Massif Central. Pavin lake is a crater lake (max. depth 90 m), aged of about 6 000 years and resulting from a magmato-phreatic eruption. The water column of this lake is stratified in two major layers, isolating the lower one which accumulates biogenic or magmatic gases like CO2 or He.

We collected water samples in mechanically sealed copper tubes, and analyzed them using our system. Our results enable to plot dissolved 4He concentration profiles. Whereas the upper layer presents 4He concentrations around 7.81e-6 cm3STP/g of water at -40 m, the lower layer presents higher 4He concentrations with 5.64e-5 cm3STP/g at -80 m.

We focused our study on the water layer with the highest 4He concentration gradient (between -60 m to -70 m) to compare our results with those obtained by Aeschbach-Hertig et al. (1999). Our results between 2.49e-7 cm3STP/g at -60 m and 1.77e-6 cm3STP/g at -70 m are in accordance with those published in 1999. Helium isotopic ratios are also similar to the value obtained by Aeschbach-Hertig et al. (1999), i.e. the subcontinental mantle ratio (6.5 Ra).

The accordance of our results with those published by Aeschbach-Hertig et al (1999) validates our new extracting-purifying-analyzing line and completes the preliminary step of our work. Our aim is now to test on a CO2 natural accumulation in France, the feasibility of the monitoring methodology we suggest.

Reference
The geochemical behaviour of Pb during core formation and accretion

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The lead isotope signature of the Bulk Silicate Earth (BSE) is not consistent with a simple single stage evolution model but requires an early process that has fractionated U from Pb. Core formation might be such a process, as previous studies suggested that significant amounts of Pb are sequestered in the Earth’s core. To examine the role of metal segregation, we have determined sulfide-silicate and metal-silicate partition coefficients (D) of Pb at upper mantle PT conditions. Our results indicate that Pb is incompatible in Fe melts but compatible in Fe-S melts at O2-fugacities representative for terrestrial core formation. Uranium on the other hand is incompatible in both iron melt and sulfide melt [1]. Modelling shows that Fe-dominated melts do not sufficiently fractionate U/Pb ratios whereas pure sulfide melt segregation could have formed a δBSE~8, assuming that the bulk Earth started with low initial μ~0.7 [2]. However, segregation of a pure sulfide melt is probably not consistent with mantle abundances of chalcophile elements.

It has been also assumed that U-Pb chronometry might date a late stage of core formation with a small amount of sulfide-dominated melt sequestered to the Earth’s core [3]. The late addition of oxidized impact material (~ 10 %) with a maximum CI-chondritic sulfur content after segregation of a Fe-rich melt would limit the amount of segregated sulfide melt to 2-3 %. Such a small amount of sulfide melt would require a D_{Pb}^{(sulf姊al)}~1000 assuming complete sulfide-silicate equilibration, much higher than measured. This indicates that Pb-model ages probably do not date a late stage of sulfide segregation to the Earth’s core but rather reflect a volatile depletion process.

References
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A light lithium source for komatiites

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Komatiites provide key information on melting processes and the geochemical composition of the Archean mantle. To gain more insight we have analysed the Li isotopic composition of komatiites of various ages and from different localities. Li was chosen because it has been shown that its isotopes can be used to study melting processes within the mantle and characterise mantle sources [1].

Care was taken to analyse only the least altered whole rock samples and, in addition, separates of olivine phenocrysts. The olivines from the Phanerozoic komatiites of Gorgona range in δLi from +6.9 to -7.5‰ (5 samples). Exceptionally well-preserved late Archean komatiites from the Abitibi greenstone belt have δLi from +1.9 to +6.0‰ (4 bulk rocks). Their primary olivines (3 samples) yield much lighter compositions from -0.8 to -4.3‰. Samples from several localities within the early Archean Barberton Greenstone belt yield δLi between +0.2 to +7.1‰. Although no primary minerals are available, it is noticeable that the best-preserved sample has the lightest δLi.

Li-isotopes of bulk rock komatiites roughly coincide with the value for Bulk Silicate Earth of δLi = 3.3 to 4.0‰ [1, 4], while fresh olivine phenocrysts give varying and strongly deviating negative values. Even the freshest komatiites have suffered some degree of low temperature alteration and metamorphism so that the olivines should reflect the original isotopic signature of the magma. However, such negative values have not been observed in any modern type basaltic magma. Komatiites must tap a source not accessible to present day magma genesis. We speculate, in conjunction with the high Helium isotopic ratios in these olivines [2, 3], that the source material once resided in the lower mantle.

Reference
Tracing of industrial emissions in an urban environment using Pb, Sr, Nd, and C isotopes (tree bark biomonitoring and aerosol sampling)

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The chemical composition of the atmosphere is affected especially in the northern hemisphere by increasing concentrations of heavy metals due to both natural and anthropogenic emissions. These pollutants are concentrated in submicrometer aerosols, which can be transported through the atmosphere over long distances before their deposition. Grousset and Biscaye (2005) showed in their review paper that combined Sr, Nd and Pb isotope ratios are most powerful tracers to identify natural dust sources and to identify their transport patterns. It has also been shown in many studies that Pb isotope ratios provide a very effective method of tracing anthropogenic atmospheric pollution. However Sr and Nd isotopes have very seldom been used for environmental studies. Only recently a first comprehensive study of trace metal pollution by a steel plant has successfully been performed using tree barks as biomonitors and Pb, Sr and Nd isotope ratios as environmental tracers and shows that the combination of the three isotope systems is extremely powerful for tracing of an anthropogenic pollution (Lahd Geagea et al. 2007).

In the present study we can show that the combination of the three isotopic systems is also extremely powerful for the distinction of different industrial atmospheric emissions sources in the same urban environment. This is of importance because Pb isotope ratios alone do not allow such distinction since industrial emissions like domestic waste incinerators, chemical waste incinerators or steel plant have very similar Pb isotopic compositions (206Pb/207Pb, 87Sr/86Sr, 143Nd/144Nd) as environmental tracers and shows that the combination of the three systems is extremely powerful for tracing of an anthropogenic pollution.

Re-Os systematics of Svecofennian Ni-Cu deposits in Finland

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Svecofennian magmatic Ni-Cu deposits are hosted by mafic-ultramafic intrusions that emplaced close to the peak of the Svecofennian orogeny (~1.89 Ga). These orogenic intrusions have a high potential for magmatic Ni-Cu sulphides and have been the main source of nickel in Finland. One mine – Hitura – is in current production. The studied intrusions are located in different areas of the Svecofennian domain: Vammala and Hyvelä are a part of the Vammala nickel province in SW Finland, while Kotalalhti, Rytykyl and Hitura belong to the Kotalalhti Ni-belt close to the craton margin in eastern Finland. Previous studies have emphasized the significant role of crustal contamination, but the nature of the assimilant and timing of the magma-country rock interaction has remained controversial.

We report Re-Os results from these five deposits in order to constrain the origin of the ores in more detail. Eighteen whole-rock samples and five sulphide fractions were analyzed, all but one from the mineralized parts of the intrusions. Os and Re contents in the whole-rock samples range from 0.012 to 57 ppb and 0.24 to 654 ppb respectively, and in the sulphide fractions from 14.6 to 5580 ppb and 92.1 to 1187 ppb respectively. The Re/Os-ratio ranges between 1.4 and 37.3 with an average of 13.9. The Re-Os variation shows very little secondary disturbance and the samples from all intrusions define a Re-Os isochron giving an age of 1993± 29 Ma and an initial 187Os/188Os value of 0.32± 0.10. The radiogenic composition of the ores indicate crustal contamination, which is supported by low εNd (1900 Ma) values (-1.4 – 0.4) process, but occurred at deeper crustal levels. Sulphides have probably been transported in suspension to their present location.

Our results imply that crustal contamination led to the sulphide saturation in these Svecofennian orogenic magmas, and that this was not an in situ process, but occurred at deeper crustal levels. Sulphides have probably been transported in suspension to their present location.

References

Different sources of bacterial methane revealed by radiocarbon dating – Example from glacially deformed sediments, Denmark

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Methane is widespread in the Quaternary deposits, up to 200 m thick, of northern Denmark. Seabed sediments of the coastal seas are also rich in gas. Moreover, seeps and authigenic methane-derived carbonates are observed along the coast. Stable isotope data show that all of the methane is bacterial in origin, although radiocarbon datings of methane from different areas show a large variation, Fig. 1.

![Figure 1. Methane radiocarbon ages. Circles = Skagen-3 well; solid squares = shallow wells; open squares = submarine seeps; crosses = seabed sediments.](image)

In areas characterized by continuous deposition, the age of methane increases with the depth and age of the sediment: Skagen-3 well and piston cores [1]. However, methane from seeps [2] and some shallow wells is much older than would have been expected from its depth of occurrence. The shallow high-age methane is most likely derived from organic-rich interglacial marine deposits which were deformed and brought to shallower depths during the last ice-age, as is nicely illustrated in nearby coastal cliff exposures.

References

Nickel immobilization by coprecipitation with calcite

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Nickel contamination from industrial and mining activities can pose a serious risk to groundwater. Because Ni is toxic to plants and animals, data describing its behaviour and fate are required for valid assessment of risk and designing effective remediation strategies. Because the interaction of calcite with Ni controls its distribution in calcareous environments, better understanding of the mechanisms responsible for nickel uptake would improve modelling capabilities.

This work investigated calcite’s affinity for Ni and extent of partitioning into calcite precipitated from electrolyte solutions under strictly controlled conditions. Experimental conditions and all solution variables were held constant for each run and varied systematically in separate experiments.

Ni was moderately partitioned from solution into calcite. For dilute solid solutions (X_Ni < 0.001), $\lambda_{Ni}$ was estimated to be $\sim 1$ at $pCO_2 \sim 1$ atm and $10^{-3.5}$ atm and was weakly dependent on calcite precipitation rate in the range of 3-230 nmoles m$^{-2}$ s$^{-1}$. Changing $pCO_2$ does not imply any change in Ni incorporation mechanism, in spite of the significant impact of $pCO_2$ on calcite surface speciation. Ni molar fraction in the solid is directly proportional to Ni concentration in the solution. The fit of the data to such a model is good evidence that Ni is incorporated as a true solid solution, not simply by physical trapping.

Extrapolation of our experimental results to lower recrystallization rates ($\sim 10^{-2}$ nmoles m$^{-2}$ s$^{-1}$) gives $\lambda_{Ni} \sim 1.5$. It may be that this value is never exceeded in any natural or laboratory calcite (re)crystallization process so $\lambda_{Ni}$ may always lie within the limits of 1 – 1.5. Ni follows the behaviour of other elements with $\lambda > 1$ (Cd, Mn, Co) for which equilibrium $\lambda$ values are never achieved.

The effect of coprecipitation on nickel retardation in natural systems depends on $\lambda_{Ni}$ and on the thickness of a surface layer of solid solution equilibrated with the aqueous phase within a given period of interest. Coprecipitation will be important if large enough amounts of secondary calcite precipitate and if precipitation / recrystallization rates are high compared with transport rates in the solution. Considering a flow rate of $\sim 10$ m/year and Ni concentration $1\mu$M, Ni flux would be $0.3$ nmoles m$^{-2}$ s$^{-1}$, which is compatible with calcite recrystallization rates. With $\lambda_{Ni}$ obtained in this work, the mass distribution coefficient of Ni$^{2+}$ to calcite was calculated to be $K_d = 4$ at pH=8 and $K_d = 0.5$ at pH=6.5 for one (re)crystallized monolayer of calcite. This results in corresponding retardation factors R = 37 and 6. This means that solid solution partitioning to calcite can lead to a significant reduction in Ni mobility over a wide pH range.
**Genetic considerations in microbial silicification**

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The encrustation and entrapment of microbes in silica sinter is an inevitable outcome of life in some hydrothermal systems, where disequilibrium conditions lead to the spontaneous precipitation of amorphous silica. As some of the oldest evidence for life on Earth is found in >3.5 Gyr cherts, understanding factors that control the silicification process is critical to the study of life’s antiquity. Research to date has largely focused on the relative rates at which different microbes become encrusted with silica. These studies have generally demonstrated that microbes play a largely passive role in the silicification process, where their surface layers, or any other exposed surfaces for that matter, become encrusted with silica simply as a consequence of living in systems where its precipitation is inevitable. The influence of silica on the life of the microbe, however, has been given much less attention. In both the field and the laboratory, bacteria grow under conditions that are highly supersaturated with respect to amorphous silica, and in some cases, biological responses, such as sheath thickening for cyanobacteria, or increased EPS production in biofilms, have been noted. In order to better understand the dynamic interplay between microbe and mineral in these systems, we examined several relevant bacteria (i.e., a sheathed and unsheathed cyanobacteria, and a biofilm-forming thermophile) for biological responses to the silicification process that are manifest at the proteome level. Polyacrylamide gel electrophoresis was used to separate proteins that were regulated in response to the silicification process for identification via mass spectroscopy. Our results indicate that microbes are genetically equipped to respond to the silicification process, and although at present there is insufficient data to make any phylogenetic inferences, this study raises interesting questions regarding the role of silica in the survival of Earth’s earliest life forms.

**Lithogeochemical identification of Ni-Cu mineralised intrusions using fertility analysis**

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**Nickel and cobalt numbers**

A novel lithogeochemical exploration methodology for nickel sulphide and PGE deposits utilising lithogeochemistry of barren cumulates was developed. The essential part of the fertility analysis is to identify whether target has experienced sulphide saturation and segregation. For that purpose two parameters, nickel and cobalt numbers, were introduced:

\[
\text{Ni#} = 100 \times \frac{\text{Ni}}{\text{Ni} + \text{Cu}} \\
\text{Co#} = 100 \times \frac{\text{Co}}{\text{Ni} + \text{Cu} + \text{Co}}
\]

Fractionation of olivine from ultrabasic-basic magma brings the Ni# down but Co# remains at the same level, whereas segregation of sulphides increases the Co# significantly in the residual melt and in sulphides equilibrium with it. Therefore the Ni# describes the primitiveness of the magma from which sulphides have segregated and the Co# indicates the nickel depletion. In primitive komatiitic and picritic systems the Ni# is greater than 75, in basaltic 50-75 and in more evolved flood basalts <50. The calculation is reliable if sulphides are a cumulus phase, i.e. >0.3 wt%.

In studied Ni-Cu ores Co# was low, at 1-5, but it increased in the stratigraphic units above the ore. In the ultramafic intrusions the range was quite narrow, at 2.9-15, but in differentiated mafic intrusions the range was as wide as 3-60. In depleted intrusions Co# was uniformly high, >10.

**Fertility analysis**

The parameters of the fertility analysis quantifying the requirements of the Ni-Cu sulphide ore formation are: 1) primitive character of the magma, 2) extent of sulphide saturation, 3) Ni-rich, chalcophile undepleted magma, 4) magmatic sulphides that are in equilibrated with a large amount of magma, 5) coeval primitiveness and sulphide segregation, 6) sulphide accumulation and 7) fractionation or mobilisation of sulphides. The values of the parameters and value of the overall discrimination index, OD, are calculated from the whole-rock analyses of the rock samples (Lamberg 2005). Mineralised samples are excluded from the analysis.

In the test with extensive lithogeochemical datasets of the Svecofennian intrusions of Finland (7517 samples / from 353 targets), Thompson Ni belt, Canada (287/27) and Cape Smith belt, Canada (287/27), the fertility analysis successfully discriminated between fertile and barren targets.

In low grade PGE deposits, Kevitsa and Duluth, Co# was found to correlate negatively with total PGE grades indicating that Co# may be a potential tool for identifying PGE potential intrusions and their parts and localising mineralised reefs.

**References**

Investigation of biominerals in the human knee of advanced osteoarthritis

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Motivation

Osteoarthritis (OA) is a painful joint degeneration disease and in most cases leading to a complete surgical knee replacement. There is evidence that pathologic mineralisation contributes to OA (Swan et al., Pritzer et al.), but an actual distribution and composition of involved minerals, as well as the mechanisms of their generation still remain poorly understood.

Our intention was to find an effective and implementable way to analyse methodically the presence, nature and composition of minerals in the knee, to find out more about the physiological processes which lead to this special mineralisation.

Methods

Our studies were carried out on pieces of cartilage of medial femur condyle gained from over 30 different patients undergoing total knee replacement surgery. Additionally, chondrocytes obtained from these cartilage-specimens were cultured and investigated. We used several analytical methods in conjunction, including radiography, optical polarised light microscopy (LM), SEM, TEM, X-ray microdiffraction and Raman spectroscopy.

Results

Mineralisation was discovered in all specimens and analysed with the mentioned methods. Almost amorphous or polycrystalline hydroxyl-apatite was detected in huge amounts. In some cases idiomorphic calcium pyrophosphate was detected, but mostly associated with hydroxyl-apatite.

Discussion

Our data imply that mineralisation of articular cartilage seems to be a common event in end-stage OA. However, calcium pyrophosphate appears not to be the initiator of this disease. Instead, the mineralisation of apatite is a more likely cause, considering it was identified in all specimens. The production of pyrophosphate inside the cells perhaps functions as an inhibitor to reduce further mineralisation of apatite in cartilage.

References

Swan, A.J., et al. (1992), J. Rheumatol. 19, 1764-73
**Geochemical constraints on Shaxi porphyry Cu-Au deposit: A possible link to adakitic genesis?**

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**Introduction**

The Shaxi porphyry Cu-Au deposit is located in the northwestern part of the Luzong volcanic basin, as one of important metallogenic belt in Yangtze valley. Tectonically, the Tan-Lu and Tongcheng-Fanshan faults cut and passes through the ore district. Former studies show that this deposit has a genetic link to the Yansha nian intrusive (c.a.130 Ma), consisting of quartz diorite porphyrite.

**Experiment and Results**

The total REE content of the Shaxi porphyry Cu-Au deposit ranges from 69.31×10\(^{-6}\) to 123.7×10\(^{-6}\), the ratio of \(\sum \text{Ce} / \sum \text{Y}\) is relatively high, ranging from 7.55 to 11.53, and the ratios of (Ce/Yb)\(_N\) and (La/Yb)\(_N\) range from 18 to 38, much higher than those of Shaxi, the ratios of (La/Sm)\(_N\) and (Gd/Lu)\(_N\) are all around 2 or so. The relative low \(\delta\text{Eu}\) anomaly was determined ranging from 0.8 to 0.95. The REE distribution pattern exhibits relatively large fractionation between LREE and HREE. The spider diagrams of trace elements such as Sc, Cr, Co and Ni and some transitional compatible elements such as Ti, V, Mn, Fe and Cu in the Shaxi Cu-Au porphyry deposit have have experienced strong fractionation as compared to the trace elements of crust rocks. The igeous rocks related to Cu-Au mineralization in this area have high concentrations of Al\(_2\)O\(_3\) and Sr, low contents of Y, with very high ratios of Sr/Y and La/Yb. All these geochemical characteristics resemble the distinct adakitic genesis. This study presents the fact that the Shaxi porphry Cu-Au deposits have possible link to the subduction of the Pacific Ocean to the east China continent edge from southeast to northwest in Mesozoic. This processing brought a large mount of oceanic crust to produce the adakitic rocks in Yangtze megalogenic region. During this oceanic-crustal collision and later magmatism, the Cu and Au and other uncompatiable elements enriched.

**Acknowledgment**

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**Determination of SO\(_4^{2-}\) sources using stable S isotope for two karstic ground water systems, Guizhou Province, Southwest China**

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The objects of this study were to understand the sources of sulphate ion and its geochemical cycling in the karstic surface and ground water of the two largest cities, Guiyang and Zunyi, in Guizhou Province, China. The sulphur isotopic compositions of sulphate ions in different water samples largely vary, with a large variation of \(\delta^{34}\text{S}_{\text{SO}_4}\) values from -20‰ to +30.5‰, as shown the table blow.

<table>
<thead>
<tr>
<th>Study area</th>
<th>Ground water</th>
<th>Surface water</th>
<th>Sewage</th>
<th>Rain water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guiyang</td>
<td>-20.4 – +20.9</td>
<td>-9.6 – +1.9</td>
<td>-8.0 – -4.3</td>
<td>-5.1 – -4.9</td>
</tr>
<tr>
<td>Zunyi</td>
<td>-12.9 – +30.5</td>
<td>-2.7 – +22.6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The sulphate ions in the studied surface and ground water are of multiple sources, mainly derived from the dissolution of mineral and rocks, from rain water and anthropogenic inputs. Combined use of sulphur, carbon and strontium isotopes as tracers of sources and geochemical processes leads to a better understanding of water/rock interaction, oxidation of sulfide minerals and sulphur-containing organic matter. Sulphate ions of anthropogenic and natural sources show different isotopic composition, which allows identification of different contributions of various sources. Ground water of from city zone has much higher concentrations of sulphate ion as compared to that from outskirts of the city, suggesting that karstic ground water system is subject to pollution by human activities. Sulphur isotopic signatures and chemical composition of water show that carbonate rock was dissolved by both of sulphuric and carbonic acid, which needs further studies considering global carbon cycling.

**Acknowledgement**

This work was supported by the National Natural Science Foundation of China (Grant Nos. 40603004 and 40603005) and the Ministry of Science and Technology of China (Grant No. 2006CB403205).
ATEM-EELS study of diamond-like phases in the B-C-N system

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Diamond is the hardest known material but its technical use as abrasive tool is limited by the finite thermal stability. On the other hand, cubic BN is thermally more stable and resistant to oxidation but is less hard than diamond. It is thus desirable to synthesize ternary diamond-like B-C-N phases that may combine the best properties of both materials.

To synthesize such B-C-N phases we have used static (multi-anvil, diamond anvil cell) and dynamic (shock) high-pressure techniques pressurizing nano-powdered graphite-like (BN)0.5C0.5 to 30 GPa at temperatures up to 3500 K [2]. The structures, compositions and properties were subsequently studied by analytical transmission electron microscopy, electron energy loss spectroscopy, and X-ray powder diffraction.

Analyses of recovered materials reveal the formation of nanocrystalline diamond-like B-C-N compounds of variable composition ranging from BC2N to BC8N. B, C and N are homogeneously distributed in nanocrystals; superstructures with ordered arrays of C and BN have not been observed. The lattice constant $a$ is a linear function of the composition. The variation in chemical compositions indicates however that there is no complete solid solution between diamond and cubic BN. Due to supersaturation of diamond in the BN component all ternary diamond-like B-C-N phases tend to decompose at high temperature into an diamond + cubic BC assemblage.

References

Ordering of the Al cation distribution in the octahedral sheets related to the ordering of Al in the tetrahedral sheets of phlogopite studied by $^1$H $^{29}$Si CPMAS NMR spectroscopy

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Our research project is part of the ORION-project (Ordering of Ions in Minerals) in the EuroMinSci programme of the ESF which aims the elucidation of ionic ordering in three exemplary systems by combining experimental investigations and theoretical calculations. One of the systems to be investigated is phlogopite, a trioctahedral 2:1 layer silicate.

Previous NMR solid state experiments of phlogopites indicated a non-statistical distribution of cations and anions in the octahedral sheets: F prefers sites coordinated by three Mg, whereas OH prefers sites with Al as next-nearest-neighbors (Fechtelkord et al. 2003). Further investigations will be carried out on phlogopites with various Al-contents and synthesized at different temperatures. In addition to that, cross-polarization (CP) experiments will be performed to clarify, whether the degree of ordering in the octahedral sheets is related to that in the tetrahedral layers.

The CP experiment is a double resonance experiment which allows the transfer of magnetization from a nucleus with a strong magnetic polarization due to its high natural abundance and high magnetogyric ratio, such as $^1$H, on a nucleus with a low spectral resolution such as $^{29}$Si via heteronuclear dipolar interaction. The increase of magnetization is a function of the cross polarization time, the number of proton spins, and the distance of these spins, $r_{ij}$, to the $^{29}$Si nucleus. Thus, direct neighborhoods of protons in the octahedral sheets to Si environments in the tetrahedral sheets can be correlated in one- and two dimensional CPMAS NMR experiments. Moreover, information on the position of Al in both sheets can be achieved indirectly.

Our first experiments clearly indicate a direct neighborhood of aluminum in the tetrahedral sheets to aluminum in the octahedral sheets and, thus, a relationship between the ordering of ions in both sheets.

References
Earthworm calcite production rates

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It is a little known fact that many species of earthworm excrete calcite granules. These comprise either individual or aggregates of calcite crystals that can reach up to 2.5 mm in diameter. Despite being described by Darwin (1881) relatively little work has been carried out on these granules. It is known that the granules form by the coalescence of CaCO3 spherulites in the calciferous glands but the function of the granules is unclear – possibilities include, Ca, CO2 and pH regulation though significant problems exist with each of these hypotheses.

Preliminary work by Canti indicated granule production rates by the earthworm *Lumbricus terrestris* of up to 76 mg calcite in 35 days (2.2 mg per day). Assuming an average earthworm density of 300 m^-2, this corresponds to a rate of production of 2.4 moles of calcite m^-2 year^-1. Calculated another way earthworm calcite granule production potentially retains c. 60 kgC ha^-1 yr^-1 in the soil. Typical CO2 soil fluxes are 5 – 315 mol CO2 m^-2 yr^-1 and typical soil C sequestration measures would remove 300 to 800 kgC ha^-1 yr^-1. Thus earthworm calcite granules are potentially highly significant in the terrestrial C cycle.

In this presentation we consider the influence of soil chemistry on granule production rates. *L. terrestris* were cultured in high Ca - high pH, high Ca – low pH, low Ca – high pH and low Ca – low pH soils for 70 days. After 35 and 70 days calcite granules were extracted from the soils and production rates were determined. The impact of soil chemistry on production rates and also the impact of the calcite granules on the final soil pH will be discussed.

Reference

Darwin, C. (1881) *The formation of vegetable mould through the action of worms with observations of their habits.*

Residence time of suspended particles in the Dordogne River: Indications derived from ^7^Be and ^210^Pb

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Particulates that enter the ocean from rivers are the products of integrated basin-wide processes (soil erosion, sediment transport and deposition in watersheds). The fate of sediments in river is therefore challenging and generally analysed using hydrodynamics models. An alternative method relies on the use of fallout radioactive tracers, such as ^7^Be, ^210^Pb and ^137^Cs, to identify sediment source regions and/or to estimate suspended sediment age or the fraction of the suspended sediment recently eroded from the landscape (Dominik et al, 1987; Matisoff et al, 2005 and references herein).

This work presents the application of the two naturally occurring radionuclides ^7^Be (T1/2 = 53 days) and ^210^Pb (T1/2 = 22.3 years) to investigate residence times of particles in the Dordogne River (South-West France). The Dordogne River has a watershed of 24 500 km² with a mean discharge of 320 m³ s⁻¹ (max 12500 m³ s⁻¹). It flows westward about 500 km from the mountains of Auvergne, ending into the Gironde, its common estuary with the Garonne River, in the north of the city of Bordeaux. To characterize the suspended sediments of the Dordogne River, repeated samplings were performed from January through August 2007 at selected sites along this river system. Particulate and dissolved activities of radionuclides were determined using a low-background, well-shaped γ spectrometer. Additional examinations of river discharge, rain rate and particulate organic carbon were done to better interpret radioanuclide data. Particulate ^7^Be and ^210^Pb activities present marked spatio-temporal variations; dissolved fractions are always low. To derive sediment ages from the present dataset, two distinct modellings have been used: 1/ based on radionuclide budget (Dominik et al, 1987), and 2/ using ^7^Be/^210^Pb activity ratio (Matisoff et al, 2005). The age estimates will be compared in order to discuss the interest of each model in a large river system.

References

Lu-Hf age and isotope systematics of the Dora Maira nappe, western Alps

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Lu-Hf garnet-whole rock geochronology applied to metamorphic rocks that contain old and unequilibrated zircon can effect both the isochron age and calculated initial Hf isotope composition. In order to better constrain the magnitude of these effects, we have performed Lu-Hf isotope analyses of the Dora Maira nappe because it contains zircons that are ~230 Ma older than the age of metamorphism.

The sample locality within the Dora Maira contains pyrope megacrysts within a matrix of mostly quartz and white mica. Evenly distributed throughout the major phases are zircon grains that contain ~275 Ma cores and ~35 Ma rims; locally, the 35 Ma zircons are unzoned (Gebauer et al., 1997; Lithos, 41:5-24). Preservation of old U-Pb zircon ages suggests that Hf within the zircons may have only partially equilibrated with the UHP metamorphic assemblage, producing two reservoirs of Hf: one in old zircon and another in UHP-equilibrated phases that crystallized at ~35 Ma. We have conducted Lu-Hf isotope analyses of garnet and matrix phases such that the entire sample was digested, including unequilibrated zircon. This approach contrasts with the digestion methods used by Duchêne et al. (1997; Nature, 387:586-589), which were designed to avoid dissolution of zircon. The Lu-Hf age and initial ¹⁷⁶Hf/¹⁷⁷Hf ratio determined using the complete dissolution method is 35.74±0.71 Ma (2σ) and 0.282580±7, respectively; this compares with 34.1±1.2 Ma and 0.282661±16 obtained by Duchêne et al.

The difference in age and initial Hf isotope compositions between our isochron and that of Duchêne et al. reflects a rotation of the isochron due to inherited zircon. The atypically high ‘whole rock’ ¹⁷⁶Lu/¹⁷⁷Hf ratio of 0.263 (Duchêne et al., 1997) is much higher than would be expected for any reasonable protolith and highlights the strong leverage that zircon has on the effective Lu/Hf ratio and Hf evolution of the zircon-free matrix reservoir between the time of protolith crystallization and Alpine meta-morphism. Based on the present data, we calculate that roughly 30-40% of the protolith zircon (by volume) equilibrated during metamorphism. This partial equilibration preserves significant differences in Hf isotope compositions between the two reservoirs and is coupled with a systematic, but subtle difference in the measured Lu-Hf ages which are within error of one another. Because some zircon will be dissolved during sample digestion regardless of technique employed, any liberated Hf that did not isotopically equilibrate during metamorphism will result in the rotation of an isochron. In order to obtain accurate Lu-Hf ages of rocks such as the Dora Maira, the difference in age between protolith zircon and metamorphism must be less than a few 10s of Ma or nearly all of the zircon must have equilibrated with its co-existing phases during metamorphism.

Geochemical characteristics of eclogites from the Eastern part of the Kokchetav complex (N. Kazakhstan)

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Amphibolised eclogites were studied in the eastern part of the Kokchetav complex (Borovoe region). They consist mainly of garnet, omphacite, quartz, and rutile. During the retrogression, eclogites assemblages became unstable: omphacite was substituted by clinopyroxene-plagioclase symplectites. Garnet grains were surrounded by two coronas: an inner (adjoining to garnet) made of plagioclase (sometimes - of symplectites of Pl and Cpx), an outer – of hornblende. Rutile is surrounded by ilmenite, and by titanite rims. Borovoe eclogites show a P-T peak conditions (at T=670-690 C, P=16-19 kbar) of the metamorphism, its decompression stage with Cpx-Pl symplectite development at 9-12 kbar, and final transformation to garnet amphibolites. Host quartz-phengite schists show similar P-T parameters (up to 20 kbar).

Major and trace element study of the Borovoe eclogites provides an insight into their magmatic petrology, and also to the later metamorphic transformations: dehydration processes during the subduction of the basalts, and to the amphibolisation of the eclogites at the exhumation stage.

Geochemistry of the eclogites shows that their protolith composition probably corresponds to the MORB and/or island-arc basalts. Depletion in the light REE, that is observed in some samples, might be related to these elements loss during dehydration of the subducted oceanic crust.

Strong enrichment in large-ion-lithophile-elements (LILE) and U may be due to the amphibolisation of the eclogites during their exhumation stage. Moreover trace elements concentrations probably vary slightly depending on the extent of the retrograde changes of the eclogites.

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Thermodynamic potential for the 
abiatic synthesis of nucleobases, 
ribose, and deoxyribose under 
submarine hydrothermal conditions

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Common to all organisms, ribose, deoxyribose, and the 
five common nucleobases (or, nucleic-acid bases) are 
constituent molecules of nucleotides, which are involved in 
the storage (DNA) and transmission (RNA) of genetic 
information. They serve as bioenergetic intermediates (ATP, 
GTP), oxidation-reduction couples (NAD and NADP) and are 
central to poly saccharide synthesis (UDP). Because these 
molecules are essential to so many basic metabolic functions, 
documenting the range of fluid compositions and chemical 
potentials required to generate and stabilize nucleobases and 
(deoxy)ribose is crucial to better understanding conditions that 
were conducive for the emergence and early evolution of life.

Due to the high chemosynthetic potential created by fluid 
mixing in extant hydrothermal systems and the relatively close 
phylogenetic relationship that many thermophilic organisms 
might have with the last common ancestor, numerous 
experimental and theoretical studies have explored the role 
that submarine hydrothermal environments may have had in 
hosting the origin of life. In this study, we have quantified the 
thermodynamic potential for the abiotic synthesis of 
nucleobases (adenine, cytosine, guanine, thymine, and uracil), 
ribose, and deoxyribose as a function of temperature, pressure, 
and bulk fluid composition using formaldehyde and HCN as 
precursor building-block molecules. Under low concentrations 
of these precursors and for a wide range of temperature and 
pressure conditions, favorable thermodynamic conditions are 
established for the abiotic synthesis of ribose, deoxyribose and 
all of the common nucleobases except thymine. A 
thermodynamic description and interpretation of the 
biogeochemical reactions involved in these pre-biotic 
processes can be used to design experimental investigation of 
the abiotic synthesis nucleic-acids and related biomolecules.

The Paleocene volcanic succession in 
West Greenland: Compositions, 
volumes, and mantle sources

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The Paleocene volcanic succession on Disko and 
Nuussuaq in West Greenland consists of up to 2 km of of 
mainly picrites with on average 15.7 wt% MgO (the Vaigat 
Formation, VF) overlain by up to 2 km of tholeiitic flood 
basalts with on average 6.5 wt% MgO (the Maligât Formation, 
MF) (MgO in uncontaminated rocks). The whole succession 
has been dated at 62–60 Ma, with no measurable time lapse 
between the two formations.

The picrites of the VF represent unfractionated or slightly 
fractionated primary magmas, whereas the basalts of the MF 
are three-phase cotectic and distinctly fractionated. About 5% 
of the VF and 40% of the MF lavas are contaminated by 
sediments in high-level crustal magma chambers. Contamina-
ted rocks usually form separate volcanic units, and except for 
the upper part of the MF, uncontaminated rocks abound.

REE patterns for uncontaminated rocks of both formations 
are consistently convex-up with LaN/NdN= 0.6–1.1 and 
GdN/LuN = 1.3–2.7. Simple REE melting modelling suggests 
similar to slightly lower degrees of melting for the MF basalts 
compared to the VF picrites.

The magmas of both formations were derived from a 
uniform asthenospheric mantle source which was 
geochimically and isotopically depleted. Uncontaminated 
magmas have ⁸⁷Sr/⁸⁶Sr(i)= 0.70294–0.70344, ¹⁴³Nd/¹⁴⁴Nd(i)= 
0.51291–0.51308, and ²⁰⁶Pb/²⁰⁴Pb(i)= 17.51–17.99. Two units 
in the VF and some scattered lavas in both formations show 
various ‘enriched’ geochemical signatures and are considered 
to be contaminated during their passage through the 
lithospheric mantle with metasomatized areas there.

Based on the measured lava volumes on Disko and 
Nuussuaq, extrapolation to the whole region, and 
consideration of the amount of fractionation and estimated 
degrees of melting, the total volume of mantle involved in the 
generation of the Paleocene volcanic succession in West 
Greenland is 550,000 km³. With a ‘rift’ length of 300 km and 
a width of the productive areas of max. 50 km, the involved 
mandle prism was min. 37 km deep. This volume of uniform 
and hot mantle is best envisaged as part of a mantle plume.

Convex-up REE patterns are uncommon in LIPs. They 
would be produced by melting of a depleted mantle in garnet 
facies under a thick lithospheric lid and would occur on the 
broken-up margins of thick cratons such as Precambrian ones.
In the North Atlantic region they occur along the periphery of the 
suggested mantle plume but not in the centre.
H/D isotopic interpretation of hydration isotherms

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Various methods have been developed since years for describing the poral distribution of porous materials from hydration isotherms measurements. The most well known is the BJH method, which relies on a model of cylindric pores. More recently, methods (e.g. Or and Tuller, 1999) consider pores with various geometries (slit pores, pores with polygonal section), providing great improvements in the description of hydration isothers and/or retention curves.

However, these approaches are based on a series of assumptions (constant molar volume of hydration water, a priori geometrical characteristics of pores, no contact angle between adsorption film and capillary meniscus, etc). As a result, determination of the amount of water available for chemical reactions remains qualitative in such systems.

Richard et al. (2007) have measured the H/D isotopic fractionation factor (α) between hydration water and water vapor as a function of relative humidity (RH). Two main types of water were identified and interpreted as 2D (low RH) and 3D (high RH) water networks. The 3D-water is considered as the location where aqueous reactions occur.

Based on this work and without any a priori assumption on the pore space geometry, we propose a new approach aiming at quantifying the amount of "reactive" (capillary) water in a porous medium as a function of water saturation.

We have developed a new approach for the determination of hydration isotherms and the amount of "reactive" water (capillary water). This approach is based on the measurement of the H/D isotopic fractionation factor (α) between hydration water and water vapor as a function of relative humidity (RH). Two main types of water were identified and interpreted as 2D (low RH) and 3D (high RH) water networks. The 3D-water is considered as the location where aqueous reactions occur.

Figure 1: schematic representations of a) H/D fractionation factors and b) amounts of film and capillary water along a hydration isotherm, as a function of RH.

A new version of the Fe-Ti-oxide thermo-oxybarometer relevant to basic magmatic rocks

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The Fe-Ti-oxide thermo-oxybarometer, which is based on equilibrium between coexisting Ilm (ilmenite-hematite solid solution) and Tmt (magnetite-ulvöspinel solid solution) has been widely used to retrieval information on temperature and oxygen fugacity (O2) during magmatic and metamorphic processes. However, the two available formulations (Andersen & Lindsley, 1988; Ghiorso & Sack, 1991) yield unsatisfactory results at high temperature and low to moderate O2, i.e. in conditions relevant to crystallisation in basic rocks.

To contribute to a re-calibration of the Fe-Ti oxide thermo-oxybarometer, we have carried out synthesis and re-equilibration experiments in the systems Fe-Ti-O (Lattard et al. 2005) and Fe-Ti-Mg-Al-O at 1000 to 1300°C and a large variety of O2. The compositions of coexisting Tmt and Ilm were derived by EMP analysis.

Our results show that the addition of Mg and/or Al in the concentration ranges that are usual in Fe-Ti oxides from basic magmatic rocks can be accommodated by simple projections in the range 800-1300°C under low to moderate O2 conditions. To generate an empirical formulation of the Tmt-Ilm thermometer-oxybarometer for this T-O2 range we have performed numerical fits on an experimental data set comprising our results and those of selected literature studies (e.g. Evans et al. 2006). With the resulting expressions we can retrieve temperature values from X'usp and X'ilm (projected mole fractions) of Tmt-Ilm pairs and O2 values from X'usp and T.

We have tested our numerical formulations by using the compositions of Tmt-Ilm pairs in products of liquidus experiments conducted at known T- O2 conditions in the frame of several literature studies (e.g. Toplis & Carroll, 1995). In most cases, the calculated values reproduce the experimental ones within ± 50°C and ± 0.4 log O2. This is a significant improvement compared to the previous models.

References
Time span of Malani Igneous Suite, NW India: Constraints from mineral and wholerock Sm-Nd isotope studies

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Malani is an important Neoproterozoic igneous suite, covering an area of approximately 51,000 sq km in Northwestern Indian shield which shows Bimodal volcanism. The Malani consists mainly of volcanic, granite and dyke phases. Crawford and Compston (1970) determined Rb-Sr age of ~ 745 Ma for the volcanics and granites. Rathore et al. (1996, 1999) on the basis of whole-rock Rb-Sr and Ar-Ar studies suggested that Jalore and Siwana granites, which are part of Malani Igneous Suite, were emplaced at 727 ± 8 Ma and 698 ± 10 Ma, respectively and affected by later thermal event ~ 550 Ma ago.

In order to reliably determine age of magmatism of Malani suite of rocks we have initiated Rb-Sr and Sm-Nd isotope studies on mineral separates and wholerock. Amphibole and K-feldspar were separated from a sample of Siwana granite, a major granite phase of the Malani suite. These minerals along with the whole-rock define a collinear array in Sm-Nd isotope evolution diagram (Figure 1) whose age corresponds to 813 ± 13 Ma (MSWD = 0.57). We interpret that this as the age of crystallization of the Siwana granite, near Mokalsar, Rajasthan, India.

Figure 1: Sm-Nd Mineral isochron on a sample of Siwana granite, near Mokalsar, Rajasthan, India

References


Experimental determination of the Iridium solubility in silicate melts

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To understand the fractionation of Os, Ir, and Ru during partial anatexis in the Earth's mantle, we investigate experimentally the solubility of Ir in silicate melt and the partitioning of Ir between chromite and melt at high pressure as a function of oxygen fugacity (fO2). Starting material is a natural picrite doped with 15 wt.% FeCr2O4 component and 5 wt.% Ir as Ir2O3. Run conditions are 1700°C and 2.5 GPa. Liquidus phases are silicate melt, chromite, and (Ir,Fe) alloy. To promote chromite grain sizes sufficiently large for LA-ICPMS analysis we add several percent Li teraborate. fO2 at run conditions are derived from Fe activities in the alloys. fO2 is varied between FMQ-4 and FMQ+3 using different capsule materials and pressure assemblies. Reduced conditions are imposed with talc-pyrex assemblies and graphite capsules, oxidized conditions are generated with anhydrous materials and olivine capsules embedded in hematite.

It is found that Cr2+ is about ten times more soluble in silicate melts than Cr3+. Based on Cr concentration in silicate glasses, the switch from predominantly trivalent to predominantly divalent chromium is observed at an fO2 of around FMQ-2.5. Chromite compositions appear to be less sensitive to the valence state of Cr, in that Cr/(Cr+Al) ratios show little variation with fO2. Apparently, Cr2+ is rather incompatible with the chromite lattice.

The combination of high temperature, chromite oversaturation, and Li tetraborate flux in the silicate melt allows to grow chromite up to 200 µm in diameter, appropriate in size for quantitative LA-ICPMS analysis. Iridium analyses of glasses and chromites are carried out with an ArF excimer laser coupled to a single-collector magnetic sector ICPMS. Isotopes recorded in addition to 191Ir and 193Ir are 58,59,60Cr, 57Fe, and 57Fe. Count rates are normalized to the isotope 57Fe and the FeO content of each phase.

Preliminary results of two charges synthesized at FMQ-2 show that under reduced conditions, Ir concentrations in the chromites and the picritic melts are below detection of the laser probe, i.e. around 15 ppb. Hence, it is not possible to calculate partitioning coefficients for Ir between chromite and melt. The low Ir solubility, even at 1700°C, in the picrite melt suggests that sulfide-undersaturated primitive basalts are generally saturated with the refractory PGE (Os, Ir, Ru), hence capable of crystallizing discrete PGE-Fe alloys. It is expected though that, as more oxidized experiments become available, Ir solubilities will turn out higher in silicate melts more oxidized than FMQ-2. Refractory Os-Ir-Ru-alloys exhibit strong epitactic preferences to chromite surfaces. Hence, the refractory PGE may be fractionated relative to Pt and Pd whenever a silicate melt is saturated with chromite.
Yellow Mn-rich elbaite from the Canary mining area, Zambia

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The only commercial source of yellow gem tourmaline is the Canary mining area, located 32 km west-southwest of Lundazi in eastern Zambia. Since 1983, tourmaline has been mined in colors typically ranging from yellow-green to yellow to orange and brown; much of the orange-to-brown material is heated to attain a “golden” or “canary” yellow color. Significant production has come from eluvial and alluvial deposits, but the largest find (~3 tonnes) occurred at a nearby granitic pegmatite, in a large cavity that also contained abundant quartz crystals and “cleavelandite” feldspar. The pegmatite is lens-shaped and discordantly intrudes biotite schist; it strikes east-west (~100°) and dips moderately south.

By the time of the authors’ visit in 2004, most of the pegmatite had been removed via a large open pit that was partially filled with water. Visible portions of the footwall showed a medium-grained border zone (~15 cm thick) and in places a discontinuous aplitic zone that abruptly transitioned into a coarse-grained intermediate zone consisting mainly of K-feldspar and subordinate sodic plagioclase. Quartz was leached from the rock, resulting in vugs containing black tourmaline and local albite (An0-1.5, as clear overgrowths on K-feldspar). Conspicuous veins (up to 10 cm thick) of black tourmaline ± K-feldspar + albite cross-cut the pegmatite.

Electron-microprobe analysis of 23 samples of yellow-to-brown and yellow-green tourmaline from the associated secondary deposits showed they were elbaite with 1.14-7.59 wt.% MnO and 0.04-0.54 wt.% TiO2; iron was typically absent but exceptionally ranged up to only 0.21 wt.% FeO. Previous studies have recorded up to 9.18 wt.% MnO in this elbaite (e.g., J. E. Shigley et al., Am. Min., 71, 1986, pp. 1214-1216), approaching the tsilaisite end member.

Gem tourmaline typically consists of pink, green, or blue elbaite that is mined from the lepidolite-bearing inner zones of complex LCT pegmatites. In contrast, Mn-rich (and Ti-bearing) yellow-to-brown elbaite from the Canary mining area appears to have formed in a relatively simple pegmatite that was enriched in B and H2O, but not Li. Early crystallization of abundant schorl consumed the available Fe, inhibiting subsequent crystallization of garnet and biotite; this allowed Mn to be conserved until the late-stage formation of gem tourmaline. Following pegmatite crystallization, the influx of an unusual B-, Fe-, K-and Na-rich fluid (apparently from an external source) resulted in local tourmaline ± K-feldspar + albite veining and quartz dissolution; the same event also brecciated some of the yellow elbaite with black tourmaline ± K-feldspar + albite assemblages.

Bixbyite in bixbyite – Precipitates as indication for fast diffusion pathways

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Large Bixbyite crystals (Mn,Fe)2O3, space group Ia3, occur only at one location in the Thomas Range (Utah), where crystals up to 4 cm have been discovered.

In contrast to the commonly small isomorphic crystals, most of the larger Bixbyite crystals show distinct re-entrant facets at halfway of every edge of the cube, linked by a band of parallel linear features. The structure of these linear features was studied using high-resolution transmission electron microscopy (HRTEM). HRTEM revealed atomically sharp interfaces between lamellae running along {100} of the Bixbyite structure and the matrix.

Regular formed precipitates aligned parallel to these lamellae show the same chemical composition by EDS as the host crystal and electron diffraction indicates that the precipitates have the same crystal structure as the host crystal.

We present a model explaining the formation of small ‘child crystals’ with identical structure and composition in the host Bixbyite matrix, which makes use of the assumption that the observed lamellae act as fast diffusion highways.
Chemistry of a Swedish groundwater affected by oxidising alum shale

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Background
Alum shale (black shale) is a rock rich in sulphides as well as in many trace elements. The shale is readily weathered when exposed to air and water and since many of its elements have toxic properties such weathering can constitute a contamination source for soils and waters, a process analogous to metal leaching from acid sulphate soils and acid mine drainage. This study aims at assessing the mobilisation of a number of elements to the groundwater phase in an old mining area with outcropping alum shale and deposits of burnt shale. The chemistry of the local groundwater, both originating from the mining deposits and the natural bedrock, was monitored for a period of eight months.

Results
The variations existing in groundwater chemistry between nearby sampling points were large, while the temporal variations generally were marginal. At some sampling points the groundwater was acidic (pH 4), while at others it was circumneutral (pH 6-8). All the groundwater samples were, however, clearly affected by the shale material, as shown by elevated metal concentrations.

The acidic groundwater was found in an area covered by extensive deposits of burnt shale where the conditions for sulphide oxidation were especially favourable, and the water was strongly elevated in the metals Al, Cd, Co, Cu, Ni, U and Zn. Uranium and Cd were, however, also abundant in many of the circumneutral water samples only affected by the natural bedrock. Another metal that was enriched in the circumneutral waters was Mo, which appears to be particularly easy mobilised from this type of shale.

Conclusion
The mobilisation of metals from the alum shale in the investigated area has clearly been enhanced by the historical mining activities, but also weathering of the natural alum shale bedrock is a considerable source for groundwater metal contamination.

Ra and Rn enrichment in the water column of the Gulf of Aqaba (Northern Red Sea)

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The Gulf of Aqaba is a pull-apart basin along the Dead-Sea-Red-Sea Transform (RST). It is about 180 km long, 20 km wide and on the average 800 m deep (maximum depth reaches ~1800 m). The gulf is bordered by active faults on which numerous earthquakes (magnitude up to 7.4) occur. The gulf is connected to the main Red Sea via the narrow Straits of Tiran. Due to large excess of evaporation, its average salinity is high (40.7 ‰) and larger than that of the northern Red Sea. Residence time of water in the gulf is about 1.5 y. The water column fluctuates seasonally between deep mixing in the winter and intensive summer stratification.

The activities of $^{226}$Ra and $^{222}$Rn were measured in several transects, a depth profile and a well dug on the beach. The gulf's water column contains exceptionally high levels of $^{226}$Ra (up to 60 dpm·100 L$^{-1}$) and unsupported $^{222}$Rn (up to 700 dpm·100 L$^{-1}$). The temporal fluctuations of both nuclides are very high even in the center of this deep-water gulf. The activity of the long lived $^{226}$Ra in the gulf is about twice as high as that in the northern Red Sea. Considering the short residence time of water in the gulf, this indicates an intra-gulf source of the Ra, which supplies Ra (and Rn) rather rapidly. The depth profiles show that the high values are near the bottom (flux from the sediments) and in the upper 200 m (Fig. 1).

We propose that both the temporal and spatial variability of Ra and Rn in the gulf are related to their release from the major faults that border the RST, especially during and following earthquakes. For example, after the Nov. 19, 1998 earthquake (Mag. 4.4) we observed a sharp peak in both Ra and Rn in the open water column.

Figure 1: Depth profiles of $^{222}$Rn and $^{226}$Ra (dpm·100 L$^{-1}$) at stations A1 (ca. 4 km off shore), R2 (ca. 1.5 km), R3 (ca. 0.7 km) and R4 (ca. 0.2 km).
Ra and Th adsorption coefficients in lakes – Estimate based on a whole ecosystem study in Lake Kinneret (Sea of Galilee)

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A whole ecosystem balance of Ra isotopes that enter with saline springs into the freshwater Lake Kinneret provided a unique opportunity to constrain the Ra and Th adsorption characteristics in the lake. We suggest that preferential adsorption of Ra on particles in the lake is responsible for the decrease of 226Ra activity from a range of 7·103 - 250·103 dpm·m-3 in the springs to about 5·102 dpm·m-3 in the lake. Similarly, the adsorption of 228Th results in the reduction of the 224Ra/228Ra and 224Ra/223Ra activity ratios correspondingly from 1.5 and 8 in the springs to about 0.1 and 4 in the lake. Solving simultaneously the mass balance equations for 223Ra, 224Ra, 226Ra, 228Ra and 228Th in Lake Kinneret (using the accepted water exchange constants for the lake) yield the time scales required to reach steady state, the residence time and the steady state values for each nuclide as a function of the adsorption coefficients for Ra and Th. The model predicted very well the steady state values of 226Ra and the 224Ra/228Ra and 224Ra/223Ra ratios in the lake (the solid circles in Fig. 1). The estimated adsorption rate constants in the lake are: 0.005 to 0.02 d-1 and 0.5 to 1 d-1 for Ra and Th, respectively. The Ra desorption rate coefficient was estimated to be about 100 times larger than its adsorption rate constant. The observed activity ratios of the Ra nuclides in the lake are all steady state ratios that are achieved after a rather short time. They depend only on the rate constants and the activity ratios in the saline springs, and are independent of the flow rate of the saline springs. Thus, the estimated constants should apply for any productive, meromictic lake.

Leaching bench – scale experiments to model aquifer storage and recovery (ASR) operations in laboratory conditions: Central Florida case studies

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Arsenic (As) is found in the Floridan Aquifer mostly associated with pyrite. Pyrite is thought to dissolve and release As during aquifer storage and recovery (ASR) due to the injection of ozone-treated surface waters. As a result concentrations of As of up to 100 µg/L were observed in recovered water. To simulate the release of As during ASR in the laboratory we conducted a series of leaching experiments using different water compositions and aquifer matrices. These experiments were performed in standing PVC columns of 0.019 m in diameter in different lengths using native ground water from the Floridan Aquifer and drinking water from the City of Tampa, Florida. Water was pumped from the bottom through the columns by peristaltic pump to ensure complete saturation of the sediment. Leachate samples were taken at certain intervals, monitored for T, pH, ORP, S2-, and Fe2+, and analyzed for major anions, major cations, and total As. Our study showed: (1) Low As concentrations (<6 µg/L) and negative ORP values for leaching test using the native ground water from the deep Floridan well; (2) Mobilization of As during injection of drinking water with concentrations up to 42 µg/L; (4) Consecutive injection tests for a period of four months at two weeks interval indicated the decrease of As concentrations from 42 µg/L to <10 µg/L; (5) Distributions of As from leaching experiments were comparable to those of sulfate concentrations, confirming the dissolution of pyrite.

Reference
Timing of mantle depletion and enrichment from single subcalcic garnet grains (Finsch mine, SA)

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Subcalcic garnets are characteristic for the peridotitic inclusion suite in diamonds and constituents of clinopyroxene free harzburgites and dunites. The latter rock types are rare among the xenolith suite in kimberlites. The subcalcic garnets, however, are index minerals for diamonds in heavy mineral concentrates. In the absence of clinopyroxene, garnet is the main carrier of many trace elements and thus reflect the bulk composition. With this assumption we have identified and selected 21 subcalcic garnets out of 700 garnets from a heavy mineral concentrate from the Finsch Mine in South Africa (Kaapvaal craton). The grains were 3-5 mm sized. We have analysed major and trace elements by EPMA and LA ICP MS and Lu-Hf and Sm-Nd isotopes on the single grains by MC-ICP-MS.

The garnets have low CaO (1-6 wt\%) compared to their respective Cr\textsubscript{2}O\textsubscript{3} of 2-12 wt\% and high Mg-values (Mg\textsuperscript{#}=85-90). Their depleted nature is also shown by low Zr, Ti and LILE. The REE mostly show the sigmoidal pattern commonly observed in subarthonic peridotite mantle lithologies. The HREE have a positive slope reflecting the original depletion event which must have occurred in the uppermost mantle \cite{1}. Light to middle REE are bow shaped and enriched relative to primitive mantle. The range of Hf and Nd isotope signature is large in these low-Ca garnets. They have mostly radiogenic Hf isotope compositions with $\varepsilon$Hf up to 640. Nd displays mainly unradiogenic $\varepsilon$Nd down to -36 and only few have radiogenic $\varepsilon$Nd up to +25.

The results for the Lu-Hf isotopic system yield an isochron age of 2.529 ± 130 Ga. Since garnet is the major host for Lu and Hf in the clinopyroxene free harzburgites this garnet isochron should provide a similar age to that of a whole rock isochron. A minor correction for Lu-Hf in opx would slightly increase the whole rock age. We thus consider our Lu-Hf results on garnets as a minimum age for the timing of the final depletion of the subcratonic mantle which coincides with the final cratonization of the Kaapvaal craton.

The Sm-Nd system displays a large range of isotopic compositions with only weak correlations of $\varepsilon$Nd with Sm/Nd. However, corresponding ages are always younger than Lu-Hf ages, which may indicate various enrichment events during orogenic cycles within the Kaapvaal craton.

Reference


Reduction of hematite nanoparticles by \textit{Shewanella oneidensis} MR-1

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The ability of \textit{Shewanella oneidensis} MR-1 to reduce hematite (α-Fe\textsubscript{2}O\textsubscript{3}) nanoparticles of different sizes was examined under anaerobic conditions. Hematite nanoparticles used in these experiments had a size range between approximately 11 nm and 99 nm. Particle surface area was determined by BET and size distribution, aggregation, and morphology was determined by TEM. \textit{S. oneidensis} was grown in a defined anaerobic media and the different sized nanoparticles were added as the sole electron acceptor. Reduction of the nanoparticles was verified by analyzing the cell supernatant for Fe\textsuperscript{2+}. Experiments have shown that the reduction rates of the larger 99 nm particles are faster than the smaller particles when normalized to surface area. The greatest difference in surface area normalized reduction rates (one order of magnitude) were seen between the 11 and 99 nm particles. The two particles have similar morphologies (pseudo-hexagonal to irregular shaped) and they aggregate very similarly when suspended in the media. The variation in reduction rates are likely caused by differences either in size-specific particle properties or the bacteria’s cellular response to the two particle sizes. Internal and surface structural differences, exposed crystal faces, Fe\textsuperscript{2+} surface passivation, or decreased solubility of the smaller nanoparticles are potential size-dependent properties that could influence reduction rates, but evidence for the influence of these properties on nanomaterials in this system remains elusive. Testing whether actual cellular differences are evident between cells grown on the two particle sizes, however, can be done within the framework of a detailed knowledge of the genome of \textit{S. oneidensis}. Ongoing work focuses on examining the genetic and proteomic response of \textit{S. oneidensis} to the different sized hematite nanoparticles in hopes of elucidating the primary factors that influence size-dependent reduction rates.
**Experimental kinetic study of carbonaceous material maturation: An appraisal of pressure and time effects on vitrinite reflectance at 400°C**

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Vitrinite reflectance ($R_0$) measurement in organic carbonaceous material-bearing rocks is of great interest in metamorphic petrology. This stems from the ability of $R_0$ to constrain paleotemperature conditions and maturity degree of organic matter in very low- to low-grade metamorphic terranes where recrystallization is not obvious. However, considerable discrepancy still exists concerning the role of pressure and time on $R_0$ evolution.

Consequently, the goal of this laboratory rate study is to understand and estimate the effects of pressure and time on the development and kinetic evolution of $R_0$. We conducted a series of maturation experiments at 400°C in a closed system at pressures of 2, 10 and 20 kbar employing a high-pressure piston-cylinder apparatus and cold-seal pressure vessels. Experiments were performed on dry (no water added) xylite of swamp cypress and involved run lengths from 0 second to 80 days.

The experimental results demonstrate for the first time that a kinetic equation of the form

$$R_0(P, t) = R_0(P, 0) + k(P) t^n(P)$$

where, in contrast to the initial $R_0$ at $t = 0$ [$R_0(P, 0)$], the rate constant $k(P)$ is found to decrease with $P$. This kinetic equation supports all our qualitative observations. With the exponent $n(P)$ increasing regularly with $P$ and $0 < n(P) < 1$, our parabolic equation calls for a larger increase in $R_0$ and a lesser deceleration with $t$ of the $R_0$ isothermal kinetic evolution with increasing $P$. We regard our kinetic formulation as providing a step toward a general equation describing the $R_0$ evolution as a function of pressure, time and temperature.

**Directed proteomics applied to the detection and characterization of arsenic-transforming enzymes in complex communities from the Alvord Basin hydrothermal system**

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Microorganisms have the ability to transform over forty elements on the periodic table including major, minor, and trace elements. Microbial enzymes carry out a wide variety of these transformation reactions, any of which can potentially be measured. The primary goal of this research was to apply directed proteomics to the detection and characterization of arsenic-transforming enzymes in multi-species microbial systems inhabiting a hydrothermal environment.

Microbial mat samples were collected from the Alvord Basin in southeast Oregon, USA. One laboratory isolate (Thermus Strain A03C), cultivated from the Alvord Basin, was used as a positive control as it is has been shown to oxidize arsenite and respire on arsenate. Proteins were sequentially extracted using detergent-aided lysis of biomass and then mechanically extracted using a vigorous glass bead-beating procedure. Microbial arsenite oxidase and arsenate reductase activities were successfully detected and resolved using zymography, an approach that allows the detection of enzyme activities among proteins and enzymes resolved by electrophoretic methods. Activity stains specific for arsenite oxidase and arsenate reductase activities were used to visualize enzymes involved in arsenic transformation. Several activity bands were effectively resolved in individual mat samples and suggest distinctive isoforms of the enzymes. Activity bands were excised from the gel, processed, and analyzed using Liquid Chromatography-Mass Spectrometry (LC/MS). The majority of peptides obtained from the LC/MS analysis had corresponding database matches for the enzyme of interest, and functional gene analysis confirmed the presence of corresponding genes. However, some samples had no peptides related to the specific activity. These sequences could signify new unidentified enzymes involved in the transformation of arsenic and can be compared to sequences in the metagenome to potentially assign a defined biological function to ‘hypothetical’ or unidentified proteins and their associated genes.

By combining tools commonly used in the study of microbial ecology with the most contemporary proteomic separation and analysis techniques, great strides can be made in achieving a greater understanding of microbial enzymes and their ecophysiological roles.
**Effect of carbonates on the sorption of U(VI) onto granite: Correlation with aqueous speciation**

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The mobilization of metal contaminants through geological media is strongly influenced by the reaction between metals and the surrounding rocks and mineral phases. In this study, the effect of carbonates on the sorption of U(VI) onto a Korean crushed granite was investigated by performing batch sorption experiments. A correlation between the uranium sorption behavior and the aqueous speciation of U(VI) in the solution was also analyzed. The chemical speciation of uranium was calculated by MINTEQA2 at different geochemical conditions.

**Figure 1:** The Carbonate effect on U(VI) sorption onto granite

The distribution coefficients ($K_d$) of U(VI) onto granite were found to be highly dependent on the solution pH and the aqueous carbonate concentration. As shown in Figure 1, the maximum $K_d$ was significantly decreased and the peak was shifted to a lower pH side as the carbonate concentration increased. Thus the concentration of carbonate can be directly related to the distribution of the aqueous U(VI) speciation. The $K_d$ values were decreased even in the absence of carbonate which was correspondent with the formation of anionic uranyl hydroxo complexes.

Based upon the calculations at $10^{-6}$ M of U(VI) and acidic pH, free uranyl ion $(\text{UO}_2^{2+})$ was the dominant species sorbed onto crushed granite in the absence of carbonate. However, the uranyl carbonates such as $\text{UO}_2\text{CO}_3(\text{aq})$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$ were dominant in $10^{-4}$ and $10^{-2}$ M of carbonate concentrations, respectively. This reveals that U(VI) sorption on granite is inhibited by forming uranyl carbonate complexes, resulting in a lower sorption affinity to the granite at a neutral pH region. Thus the formation of uranyl carbonates is one of the most important factors in the prediction of the uranium migration in natural environments.

**References**


Analysis of water movement through an unsaturated soil zone in a volcanic island using oxygen and hydrogen isotopes

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In order to analyze water movement through an unsaturated soil zone in Jeju Island, soil waters were collected biweekly at three different soil depths using suction lysimeters. For comparison, precipitation was collected monthly using a plastic bottle. Temporal variations in the oxygen-18 and deuterium isotopes of the precipitation and soil waters were then monitored for about one year. The stable oxygen and hydrogen isotopic compositions of the soil waters are plotted between or near the two local meteoric water lines for summer and winter precipitation indicating that the soil waters were recharged from the year-around precipitation, and evaporation was negligible even during hot summer season in the study area. Finally, mean residence times of the soil waters were estimated from the δ¹⁸O, δD, and deuterium excess or d-values of the precipitation and soil waters using two well-mixed or exponential models (EM) and one exponential piston-flow model (EPM). The regression results show that the combination of the exponential piston-flow model and the d-values of the precipitation and soil waters gives the most reasonable estimation of the mean residence times of the soil waters in the study area: 74 days (2.5 months) and 198 days (6.6 months) to depths of 30 cm and 60–80 cm, respectively, in the unsaturated soil zone from the ground surface. The estimated low moisture contents and hydraulic diffusivities of the soils at the three different depths also suggest that the boundary between the upper fine-grained soil and the lower coarse-grained soil may act as a capillary barrier, and the soil waters probably flow slowly through micropores rather than rapidly through macropores in the unsaturated soil zone.

Revealing the composition and crystallinity of weathered alkali feldspar surfaces by XPS, FIB and TEM techniques

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How does the composition and structure of silicate mineral surfaces change during their reaction with acidic solutions in the field? Recently, Zhu et al. 2006 (Geochimica et Cosmochimica Acta 70, 4600-4616) have described ~10 nm thick amorphous layers on naturally weathered alkali feldspars, which supports the experimentally derived ‘leached layer’ model for silicate dissolution. We have tested this model further by comparing the chemical composition and crystallinity of the near-surface regions of alkali feldspars used in pH1 laboratory dissolution experiments with minerals from the same parent rock that had been naturally weathered. Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) provided the compositional data whereas information on crystallinity and structure was obtained by cutting cross-sections of grain surfaces using the focused ion beam (FIB) instrument for high-resolution TEM imaging.

AR-XPS data confirm that the outermost ~9 nm of alkali feldspars reacted with pH 1 HCl are non-stoichiometric (i.e. enriched in Si and O relative to Al and alkalis). Analyses acquired at the shallowest take-off angle are most Si-rich, indicating that the ‘layer’ is likely to be considerably thinner than the maximum ~9 nm XPS sampling depth. TEM images of FIB-produced cross-sections of the etched grain surfaces show that they are crystalline throughout; if the non-stoichiometric layer is amorphous it must be thinner than can be resolved by the FIB-TEM technique (i.e. <~2.5 nm), or if thicker than 2.5 nm it must be very irregularly distributed over the grain surface and so has not been sampled.

AR-XPS data from naturally weathered grain surfaces are more difficult to interpret. Most analyses show enrichment in Al and depletion in Si relative to the unweathered grain interior, with data for the alkalis showing no clear trend. These data are inconsistent with the presence of a silica-rich layer equivalent to that formed experimentally but may indicate that aluminosilicate weathering products have been produced. However, secondary minerals could not be found by SEM, and FIB-TEM work has again demonstrated that the feldspars are crystalline to within <~2.5 nm of their outer surface. These results indicate that any chemical and structural modification is restricted to the outermost <2 nm of these alkali feldspars and so thick ‘leached layers’ are absent.
Use of CaCO$_3$ as an amendment to immobilize heavy metals from the contaminated farmland soil around abandoned mines

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Experimental method
This research focused on the soil stabilization process by using limestone (CaCO$_3$) to decrease the leaching of arsenic and other heavy metals from contaminated farmland soils around abandoned mines, Korea. Pilot scale column experiments were performed to investigate the efficiency of limestone as the immobilizing amendment to reduce the heavy metal leaching from the contaminated soil. A physical model for the genuine contaminated soil environment was designed and heavy metal leaching rates by artificial rainfall were measured in diverse treatment conditions.

An acrylic column (19cm in diameter and 30cm in height), which of the upper and lower part consist of dense lattice screen plates and the drain system for injection and extraction of artificial rainfall, was used for the column experiments. As the amendment, granulated limestone (4 ~ 6mm in diameter) was used for the “mixing treatment” experiment. Two or 5 w.t.% of granulated limestone was well mixed with the farmland soil. At every 12 hr, 817 ml of artificial rain (33% of average monthly rainfall) was uniformly sprayed on the top of the column at the constant rate of 200 ml/min for thirty days, representing 5 year of soil leaching in the real farmland field. Discharged water was sampled from the bottom of the column at different time interval. The pH of discharged water was measured and its heavy metal leaching concentrations were analyzed on ICP/OES to calculate the accumulative mass of each heavy metal leached from the soil for 5 year.

Results and discussion
With only 2% of granulated limestone, As, Cd, and Zn leaching concentrations decreased by 53%, 97%, and 98%, respectively, compared to that without the amendment mixing and they maintained much below Korean Drinking Water Limit (KDWL) for 5 year leaching. Although 5 w.t.% of limestone was added as an amendment in the column experiments, the pH of the leaching solution slightly increased and maintained lower than 9 (mostly lower than 8), but its efficiency immobilizing heavy metals in the soil was potent. Because of low pH change, less adverse effects, and economical consideration, limestone could be more available to immobilize heavy metals from the farmland soil than lime(CaO) in the real contaminated site.

Conclusion
From the pilot scale continuous column experiments, it was investigated that the “mixing treatment” using limestone will become one of major processes to immobilize heavy metals from the contaminated soils around abandoned mines.

Influence of organics on microbial reductive dissolution of synthetic Fe-Cr oxides

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Cr speciation either as Cr(III) or Cr(VI) in subsurface environment is corresponding to its chemical state; reducing or oxidising, which is again controlled by microbial activities. Cr speciation is of environmental concern due to their different behaviour in mobility and toxicity. Amorphous and crystalline Fe-Cr oxides were synthesized using the method of Sugimoto (1992). Firstly, three different experimental settings were established using the Fe-Cr oxides under anaerobic condition; 1) Oxides + 2,6-anthrahydroquinone disulphonate (AQDS) + Iron reducing bacteria (Shewanella sp.). 2) Oxides + Iron reducing bacteria and 3) without the microbe and AQDS. The Shewanella sp. used in the experiment has been isolated and cultured from the sea clay collected in western coast in Korea. The mixture was placed in vials and were run for up to 40 days. In the experimental set mixing the synthetic oxides and the microbe, more Cr was been released from amorphous Fe-Cr oxides, compared to crystalline oxides (45.4 and 30.8mg/Kg). Addition of AQDS enhanced the mobility of Cr to 57.6 mg/kg (amorphous oxides) and 35.4 mg/kg (crystalline iron oxides), respectively. Cr concentrations increase with days but reached rather constant values in 10 (crystalline) to 20 (amorphous) days, whereas the Cr in the samples without bacteria and AQDS increase to a certain level (10 and 5 mg/Kg for amorphous and crystalline) and then decrease to 0 in 40 days. Fe(II) and Fe$_{total}$ concentrations are corresponding to the changes in Cr released from the synthetic oxides, as well as Eh. Little Cr(VI) has been detected in all samples and the Cr speciation in the experiment is believed to exist nealy as Cr(III). Both Fe(II) and Fe$_{total}$ were more released from amorphous oxides, compared to crystallin oxides. Humic acids are utilised as an electron shuttle in the metal-microbe-organic system. Namely, the Fe-Cr oxides are dissolved under reducing condition through interactive chains of electron shutting involving iron reducing bacteria, AQDS and metals (Fe, Cr) in subsurface environment. This geochemical process is instrumental in remediating metal contaminated soils.

Reference
Geochemical implications of Sr isotopic compositions in hot springs, Korea

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Though, at present, there is no volcanic activity, high temperature hot springs with more than 40°C water temperature occur near to Jurassic and Cretaceous granite area in South Korea. In order to clarify the heat source of the hot springs in the South Korea, we carried out a geochemical study using Sr isotope compositions of the hot spring water being collected from the fourteen area for 5 years. In this report, we discuss some relationship between the distribution of granites and geochemical characteristics of Sr isotope ratios from the high temperature hot springs.

The hot springs in the Jurassic granite area are mainly of Na-HCO₃ type, whereas those of the Cretaceous granite area are Na-Cl(-SO₄) type. In Sr isotope ratios, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the hot springs in the Jurassic granite area range in 0.710 to 0.730, whereas those in the Cretaceous granite area range 0.700 to 0.710. In addition, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from each hot spring is constant for five years, respectively. Another interesting characteristic of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the hot springs from the South Korea is that each $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from the hot springs corresponds well to the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the granite itself at the area that the hot spring occurs. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the hot springs is divided into also three groups according to geographical classification of South Korea such as eastern, western and southern part.

The correspondence between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the hot springs and the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the hot spring-bearing granite indicates that the high temperature hot springs in South Korea may be derived from the heat source related with the Mesozoic granite though it is difficult to think that the Mesozoic granite itself is the heat source of the hot spring.

Mineralogical study on the uranium sorbed biotite

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Experimental

Large books of biotite were cushed to less than 3 mm. Some biotite samples were oxidized with $\text{H}_2\text{O}_2$ solution (34%) for 2 weeks. The biotite was characterized by a series of techniques, including XRD, SEM, TEM, and chemical analysis. A range of experimental reactions with biotite were conducted at a solid to solution ratio of 1:100 in 50 mL centrifuge tubes. $\text{U}^{\text{VI}}$ solutions were prepared by adding $\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}$ (Reagent grade) to deionized water (electrical resistivity at 25°C $> 16.6 \text{ mol/Ωcm}$). Solution compositions covered pH 3.0-9.0, and $\text{U}^{\text{VI}} = 0.2 \text{ mM}$.

Results and interpretation

The XRD patterns of biotite changed by the effect of oxidation treatment: a lowering of peak height, a broadening of peak width, a low-angle shift of the (001) peak, and a high-angle shift of the (060) peak. Iron oxidation and cation loss from the biotite were occurred and caused a decrease in the $b$-dimension with the formation of discontinuities, resulting in partial hydrous interlayers (<10%).

U sorption was higher on the fresh biotite rather than on the one treated with $\text{H}_2\text{O}_2$. At low pH (pH 3), U was mainly sorbed onto the biotite interlayer, replacing K elements from the interlayer sites. In addition, U sorption was affected by the surficial condition of the biotite such as its morphology and edge types.

TEM recorded nano-scale U-rich zones in the interlayer region for those samples with relatively high uranium sorption.

References

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Reduction of Chromium(VI) by *Cellulomonas* sp. and *Propionibacterium* sp. in anaerobic soil microcosms

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**Introduction**

Chromium is considered as one of the priority pollutants in the USA and elsewhere (Hedgecott, 1994). A number of biological treatment methods which use microorganisms for the chromium(VI) removal have been investigated and developed to remediate chromium contaminated soil. While the chromium(VI) reduction in aerobic soil microcosms has been extensively studied, there is little information in anaerobic soil community (Turick and Apel, 1997; Kourtev et al., 2006).

In this study, we used *Cellulomonas* sp. and *Propionibacterium* sp. to study the effect of various initial concentrations of Cr(VI) on chromium reduction rate in anaerobic soil microcosms and to examine the effect of various oxygen concentrations on Cr(VI) reduction rate.

**Results and Discussion**

The reduction rates of Cr(VI) decreased with an increase of Cr(VI) concentrations. When the second dose of Cr(VI) added after the onset of Cr(VI) reduction, the reduction rate of Cr(VI) decreased, indicating that the developing Cr-resistant communities had a relatively low tolerance threshold.

The oxygen was added from 2 % to 20 %, with 2 % interval, in anaerobic enrichment culture mediums. The reduction rates of Cr(VI) by *Cellulomonas* sp. decreased with an increase of oxygen concentrations. When the 20 % of oxygen added, which is the oxygen concentration in the atmosphere, the Cr(VI) did not reduce. The addition of oxygen can inhibit the reduction of Cr(VI). However, the concentrations of Cr(VI) was reduced by *Propionibacterium* sp. with the additions of oxygen continuously. Therefore, the reduction of Cr(VI) by *Propionibacterium* sp. was not affected by the presence of oxygen.

**References**

U-series comminution ages: Depositional age and transport times for non-marine sediments

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An important timescale in sedimentary cycling is the elapsed time between formation and deposition of sediment grains. This timescale is critical for assessing sediment residence and transport times, and may equate with depositional age in some environments. U-series isotopes may provide a way to determine this timescale, referred to as the “comminution age” (DePaolo et al. 2006). The approach is based on the decrease in the $^{234}\text{U}/^{238}\text{U}$ activity ratio resulting from alpha-recoil loss of the $^{234}\text{U}$ isotope from a grain once it is reduced below a threshold grain size.

We have investigated the relationships between the $^{234}\text{U}/^{238}\text{U}$ activity ratio and sediment characteristics for a core from the Kings River alluvial fan to determine if this method can be applied to non-marine deposits. This fan is a large Pleistocene-age feature whose deposits originate from a glacially-influenced drainage basin on the western side of the Sierra Nevada, California (Weissmann et al. 2002). We confirm a decreasing $^{234}\text{U}/^{238}\text{U}$ ratio with decreasing grain size and with increasing sediment age, consistent with a model where recoil loss of $^{234}\text{U}$ is the dominant process controlling the $^{234}\text{U}/^{238}\text{U}$ ratio in the detrital fraction. Various leaching procedures to remove non-detrital phases were investigated; the U isotope signature of the residue can be sensitive to this leaching. Parallel studies of sediments from Owens Lake, CA (USGS core OL-92) do not show a strong correlation between grain size and $^{234}\text{U}/^{238}\text{U}$ activity ratio, likely due to relatively high concentrations of U in non-detrital components that are not easily removed by leaching.

These initial results indicate that the $^{234}\text{U}/^{238}\text{U}$ comminution age method may indeed be a valuable tool for understanding sedimentary timescales, but methods for sampling and treating the sediments need refinement. Combining this approach with Nd and Sr isotopes to assess provenance, studies of sediment composition and physical characteristics, and modeling of recoil effects will also be discussed.

References

Integrated air quality assessment – Accumulation, transport, and source recognition of PAH

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In a multidisciplinary approach atmospheric quality in the Greater Cologne Area (GCA) was studied using pine needles as bioreceptors. Here we report accumulation behaviour, transport fractionation, source allocation and the spatial distribution of polycyclic aromatic hydrocarbons (PAH). The organic pollutant load is compared and interpreted in concert with major and trace elements, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopes, and environmental magnetic data.

The GCA comprises a complex mixture of various PAH emission sources, mainly lignite fueled power plants, highly trafficked regions, domestic heating and large industrial complexes along the Rhine Valley. Our previous studies demonstrated a systematic accumulation of PAH in/on pine needles and a statistically significant variability in the PAH concentrations between different sampling locations. In this study we focus on the discussion of PAH distribution maps based on data from 71 locations that are equally distributed on 3000 km² in the GCA.

In addition to the parent PAH listed in the EPA priority list we analyzed the dispersal of alkylated 3/4-ring PAH, increasing the number of PAH to >50 and thus improving their source diagnostic potential. In the GCA the dominant emitters of PAH are lignite-fueled power plants, followed by traffic in urban regions, and petrochemical plants along the river Rhine. Power plant emissions are characterized by elevated concentrations of phenanthrene, dibenzoanthracene and benzo[a]pyrene and reduced amounts of methyl- and dimethylphenanthrenes (MP, DMP). Traffic derived combustion PAH are recognized by high abundances of anthracene, 9-MP, 1,7-DMP and cyclopenta[def]-phenanthrene (CPP). Emissions of thioaromatics from vehicular engines are small due to the recent introduction of low-sulfur diesel. Release of uncombusted PAH from refineries and petrochemical industry is indicated by a high level of alkylated PAH and specific alkylation patterns. The ratio of 2/1-MP or 1,3+2,10+3,9+3,10-DMP/CPP are particularly high in refinery areas. Wood combustion is recognized by specific distribution patterns of 1,7-DMP (gymnosperms), 1,8-DMP (angiosperms) and retene.

Transportation distance and fractionation are assessed by investigating the relative proportions of 4-, 5-, and 6-ring PAH. Concentrations of particle phase bound PAH correlate well with those of magnetic combustion particles and are dominated by short transportation distance. Traffic indicator PAH show a perfect spatial distribution match to trace element indicators like Sb, Fe and Cu. Multiproxy air quality analyses allow for very reliable and independent source allocation especially in areas with multiple emission sources.
EarthChem – A geochemistry data network

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EarthChem is a collaborative effort to create an advanced and integrated network of geochemical data collections, to make a greatly expanded range and number of data collections discoverable and accessible for the broad Earth Science community through a single portal (‘One-stop-Shop for Geochemical Data’), and facilitate the analysis and integration of geochemical data with other geological, geochronological, geophysical, and geodetic information, and incorporate new legacy and future data. Current partners of the EarthChem project include SedDB, PaleoStrat, EarthRef, MetPetDB, CZEN (Critical Zone Experiment Network), MexDB (Mexican Volcanic database), the IODP US, the USGS, and GEON. EarthChem focuses on three areas:

1. Operation of a data portal (‘One-stop-shop for geochemical data’) that provides search capabilities across federated databases and tools for data quality assessment, data analysis, and visualization including plotting methods and an information-rich map interface. As part of the portal development, EarthChem has created an XML schema for geochemical data that allows all partner databases to communicate their data in a common format.

2. Expansion of available digital data collections for geochemistry. EarthChem is building tools to facilitate data submission from users, and contribution of focused projects, and compiles new critical datasets as identified by the community. Over the past year, a new data collection for the Petrology of the Deep Lithosphere has been created. A new geochronological data collection is being developed to provide a home for EarthTime and GeoEarthScope geochronology data.

3. EarthChem addresses user concerns, and responds to broad scientific and educational needs. EarthChem hosts workshops, holds exhibits, and works with scientific societies to address community issues related to data management and data use such as citation of original data contributors/authors versus citation of databases or standards for reporting data and analytical metadata in publications. Examples include: (a) Implementation of a ‘Data Usage Index’ on the EarthChem portal to track the number of times that data from a specific publication has been downloaded by users of the EarthChem portal. Ensuring credit to the author(s) of original data publications is fundamental for the broad geochemical community to support digital data collections. (b) Through several community workshops, EarthChem has defined recommendations for the reporting of analytical and sample information in geochemistry data publications.

Lithium isotope systematics in the Strengbach catchment (Vosges, France)

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Lithium isotopic compositions of rocks, soils and continental waters are proposed to be proxies of continental weathering processes, but the reason of isotopic fractionation is not entirely known. The aim of this study is to better constrain Li isotope fractionation processes during weathering by studying variations of Li concentrations and isotopic compositions at the scale of a small granitic watershed (Strengbach catchment, Vosges, France, http://ohge.unistra.fr). Samples of precipitations, spring and stream waters and soil solutions have been collected during 2 years for Li concentration and isotopic measurements. Some of the principal results are compiled below:

- Based on the Li concentrations and isotopic compositions of rainwaters, soil solutions, spring and stream waters, it can be shown that the Li isotopic composition of the waters collected at the outlet of the Strengbach catchment results from mixing between two different fluxes: a “deep” one corresponding to rock weathering and a surface one, more significant at high discharge, corresponding to waters that interacted with soils. Due to solid/solution interactions, the δ7Li of these two fluxes are significantly variable.

- At low discharge, δ7Li of spring and stream waters increases with decreasing altitude. This should signify that waters sampled at the bottom of the catchment drained less weathered rocks than at the top. Isotopic signatures of the weathering flux seem to depend of the weathering degree of the drained rocks.

- Isotopic ratios (δ7Li) display also a great range of variations in soil solutions. In the first horizons of soil, [Li] and δ7Li in solution results from the combination of vegetation recycling and Li release from mineral. At the opposite, in deeper horizons, Li concentration and isotopic composition of soil solutions are driven by adsorption and/or coprecipitation processes.

This study particularly shows the interest of lithium isotopes to trace water circulations at the scale of a little catchment.
Solvation processes in steam: *Ab initio* calculations of ion-solvent structures and clustering equilibria

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Reports of the high ion content of steam and low-density supercritical fluids date back to the work of Carlon [1], who invoked ion and neutral water clustering as a mechanism to explain why ions partition into the low-density aqueous phase. Mass spectrometric, vibrational spectroscopic measurements and quantum chemical calculations have refined this concept by proposing strongly bound ion-solvent aggregates and water clusters, e.g. Eigen and Zundel-type proton clusters \(H_2O^+\) and the more weakly bound water oligomers \(H_2O_m\). The extent to which these clusters affect fluid chemistry is determined by their abundance, however, little is known regarding the stability of such moieties in natural low-density high temperature fluids. Here we report, building on our recent report of the structures and energetics of protonated water clusters [2], results from quantum chemical calculations using high-accuracy multi-level G3 [2], and CBS-Q [4] theory to address this question. In particular, we have investigated the cluster structures and clustering equilibria for the ions \(H_2O^+\)(\(H_2O\))\(_m\)(\(H_2S\))\(_n\), \(NH_4^+\)(\(H_2O\))\(_m\)(\(H_2S\))\(_n\), and \(H_3S^+\)(\(H_2O\))\(_m\)(\(H_2S\))\(_n\), where \(m\leq6\) and \(n\leq4\), at 300 to 1000K and 1bar as well as under vapour-liquid equilibrium conditions between 300 and 646K. We find that incremental hydration enthalpies and entropies derived from van’t Hoff analyses for the attachment of \(H_2O\) and \(H_2S\) onto \(H_2O^+\), \(NH_4^+\) and \(H_3S^+\) are in excellent agreement with experimental values and that the addition of water to all three ions is energetically more favourable than solvation by \(H_2S\). As clusters grow in size, the energetic trends of cluster hydration begin to reflect those for bulk \(H_2O\) liquids, i.e. calculated hydration enthalpies and entropies approach values characteristic of the condensation of bulk water (\(\Delta H=44.0\ \text{kJ mol}^{-1}\), \(\Delta S=-118.8\ \text{J K}^{-1}\text{mol}^{-1}\)). Water and hydrogen sulphide cluster calculations at higher temperatures indicate that a significant fraction of \(H_2O^+, NH_4^+\) and \(H_3S^+\) ions exists as solvated moieties.

References


Constraints on the Earth’s mantle heat budget from mantle plumes

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Mantle plumes may be derived from thermal boundary instabilities in the bottom thermal boundary layer (e.g., the core-mantle boundary) of the convective mantle and may contain important information on the heat transfer across the bottom thermal boundary layer. Plume heat flux and plume excess temperature for the upper mantle can be used to constrain the heat flux from the core to be ~35%-40% of the total surface convective heat flux and internal heating rate for the mantle to be ~60%-65%, depending on whether mantle convection is layered or whole-mantle convection. Here, we extended this study by computing models for a large parameter space (particularly different mantle rheology) and a much improved resolution and also by considering different criteria for detecting plumes. The new results confirmed that ~30-35% of the surface convective heat flux or ~10-12 TW needs to be derived from the core. We demonstrated that plume heat flux may account for ~90% of the core heat flux when plumes are generated above the CMB but plume heat flux decreases significantly as plumes ascend from the lower mantle to the upper mantle by a factor of ~2. More importantly, we demonstrated that the reduction of plume heat flux as plumes ascend is mainly caused by the large adiabatic cooling of plumes due to their excess temperature, while subadiabatic temperature only contributes less than 30% towards the plume heat flux reduction. We also showed that the plume temperature follows the adiabat for the plumes, and this provides a new approach to constrain the CMB temperature or the averaged dissipation number for the mantle from plume temperature in the upper mantle. Our results again suggest that for cooling rates less than 70K/Ga, the radiogenic heat generation rate for the MORB source regions needs to be more than 4 times higher than that for the depleted mantle.
Iron oxyhydroxide nanomaterials play important roles in the mobility of aqueous metal species through sorption and desorption processes. The growth of such nanophases leads to changes in their structure and reactivity and may additionally modify the mechanisms by which metal ions are adsorbed and retained. In this study, macroscopic and microscopic techniques were used to elucidate the sorption, desorption and incorporation mechanism of metals onto and within nanoscale iron oxyhydroxides during their aging and growth.

The retention of Zn(II) and Cu(II) to iron oxyhydroxide nanoparticles aged at 25 – 75°C for 0 – 96 hours was demonstrated through macroscopic uptake and desorption experiments. While uptake of Zn(II) (Fig. a) and Cu(II) (data not shown) was rapid and complete within an hour, desorption was found to be partially irreversible (Fig. b) and showed a clear relationship with both nanoparticle aging time and temperature. Less Zn was desorbed from material aged at either higher temperature or for longer time periods, indicating stronger adsorption or the role of physical incorporation mechanisms in these cases. X-ray absorption spectroscopy (XAS) of selected sorption and desorption samples supports the hypothesis that the retained metals are present as structurally incorporated sorption complexes. This is evident by the higher metal-Fe coordination observed in samples from which the readily desorbed material has been removed.

Used together such techniques provide information about how these and possibly other metals are 1) complexed on the surface of iron oxyhydroxides or 2) are incorporated into the iron oxyhydroxide structure. These findings have implications for the long-term removal of hazardous metals from the aqueous phase and the development of possible remediation strategies targeting contaminated environments.

References
Nano-carbonate clustering in organic globules supports a biogenic origin of 2.7 Gyr old stomatolites

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The macroscale morphology of Archean stromatolites has been used as evidence of early microbial ecosystems. But as Archean stromatolites only rarely contain fossil microbes, their biogenicity is tacitly assumed on the basis of macroscopic morphological comparisons with modern structures. Biogenetic definitions, however, require microscopic examination of suspected stromatolites.

We obtained an unique collection of pristine samples from a diamond drillhole that intersected the 2.7 Ga Tumbiana Formation, Australia (Pilbara Drilling Project, Van Kranendonk et al., 2006). We report the occurrence of micron-sized globules of organic carbon intimately associated with the host micritic carbonate. Scanning Transmission X-ray Microscopy (STXM) analysis revealed that these organic globules are composed of organic carbon with aromatic, aliphatic and carboxyl functional groups. High Resolution Transmission Electron Microscopy (HRTEM) analysis revealed that the organic material occurs in intimate association with clustered, 50-200nm rounded bodies of aragonite. These nano-aragonite aggregates show striking similarities with nano-carbonate spheroids associated with microbial cells and polymers in modern microbialites.

Our results indicate that Tumbiana stromatolites were likely formed via in-situ microbial lithification. They also extend the geologic record of aragonite back more than 2,300 million years, with profound implications on the environmental conditions prevailing on Early Earth.

Reference

⁷Be, excess ²¹⁰Pb and artificial radionuclides as tracers of orographic deposition of aerosols

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Aerosols play a significant role in global biogeochemical cycles and climate system. In mountainous sites, atmospheric deposition of pollutants and nutrients is enhanced by different mechanisms including feeder-seeder effect or cloud-interception. Understanding these mechanisms is necessary to improve deposition models and evaluate the sensitivity of these fragile ecosystems.

We use inventories of ²¹⁰Pb, ⁷Be, both natural aerosol-bound radionuclides and artificial radionuclides (¹³⁷Cs and Pu) in undisturbed soils to quantify mechanisms influencing aerosol deposition along the different slopes of the Puy de Dôme (1465m asl), an unactive volcano in Massif Central. We combine these results with 2-years measurements of aerosols and atmospheric deposition at the top and the base of Puy de Dôme.

The figure 1 shows that ²¹⁰Pb inventories are increasing with altitude. Using also ⁷Be and ¹³⁷Cs inventories, we are able to demonstrate that this increase of ²¹⁰Pb and therefore aerosol deposition is due to orographic effects. It seems that NO and NE slopes are more affected by orographic deposition. Other mechanisms increasing the deposition of "surface air" enriched in ²¹⁰Pb like the feeder-seeder mechanism can also explain these results. ⁷Be gives us insights of aerosol origin from the free troposphere and the stratosphere. Despite shorter representativity of ⁷Be values (¹/₂life: 50d), measured flux ratios of ²¹⁰Pb/⁷Be (0.04-0.016) in soils are in good agreement with ²¹⁰Pb/⁷Be ratio measured in aerosol and precipitations (0.1-0.16).

It will be discussed how the use of both radionuclides can offer a way to quantify wet deposition mechanisms and validate 3-D conceptual models of atmospheric deposition.

![Figure 1: ²¹⁰Pb inventories in soils vs. altitude along different slopes of the Puy de Dôme](image-url)
Insights into refertilization processes in lithospheric mantle from integrated isotopic studies in the Lherz Massif

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Differentiation of the Earth’s mantle occurs principally through partial melting and extraction of basaltic melt. Among the mantle rocks occurring at the Earth’s surface, harzburgites are widely considered as refractory mantle residues left after extraction of a basaltic component. In contrast, fertile lherzolites are generally regarded as pristine mantle, only weakly affected by partial melting. However in the Lherz Massif (France), structural mapping shows that the lherzolites are secondary rocks formed at the expense of the harzburgites. Variations of major, minor and trace elements across the harzburgite-lherzolite contacts indicate that the lherzolites were formed through a refertilization process involving interaction of refractory, lithospheric mantle with upwelling asthenospheric partial melts. Rare-earth elements (REE) in clinopyroxenes display variable chondrite-normalized REE patterns. Massive harzburgite bodies show U-shaped REE patterns whereas lherzolites have classic N-MORB REE patterns as observed in orogenic lherzolites worldwide. However at the contact, both lherzolite and harzburgite show more LREE-enriched clinopyroxenes than their distal counterparts. These REE enrichments also cannot be explained by partial melting model and provide further evidence for refertilization.

In order to further constrain the mechanisms involved in the refertilization process, we investigated Sr, Nd and Hf isotopic compositions of over 15 samples across a harzburgite-lherzolite contact, as well as “distal” samples. Sr isotopes were measured in whole-rocks and clinopyroxene separates (TIMS and MC-ICP-MS), combined with the Sr in-situ method on clinopyroxenes (LA-MC-ICP-MS). Al2O3 is negatively correlated with 87Sr/86Sr and positively correlated with 143Nd/144Nd. These correlations are consistent with REE patterns. Distal harzburgites have 87Sr/86Sr = 0.703638(6), while distal lherzolites have 87Sr/86Sr between 0.7020 and 0.7025. Towards the contact, the lherzolites show a steady increase in 87Sr/86Sr up to 0.7032. The harzburgites within the contact radiogenic compositions up to 0.7055. The highly radiogenic composition of the contact zone is not compatible with melting models. Further investigations are in progress to characterise the scale and range of isotopic variations across the transition from harzburgite and lherzolite.

P-V-T equation of state of glasses and melts by X-ray microtomography and absorption

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The new high-pressure X-ray tomographic microscope installed on 13-BM-D at GSECARS-APS/ANL is being refined to measure the volumetric properties of glasses and melts. Bulk moduli are constrained through direct measurements of volume changes by X-ray computed tomography and density is determined from X-ray absorption. The tomographic microscope consists of two opposing anvils compressed within an X-ray-transparent containment ring supported by thrust bearings driven by a 250-ton hydraulic press. This system permits the pressure cell to rotate under a load, while collecting radiographs through 180 degrees of rotation. Individual radiographs are recorded by a CCD camera after conversion to visible light by a YAG scintillator and are combined to render the volume using a back-projection algorithm and standard flat/dark field corrections with minimal filtering, following by image processing. The 13-BM-D beamline configuration permits switching between a monochromatic beam to produce high-quality radiographs and a white beam to measure pressure through energy dispersive diffraction of a standard. Density is recovered from the linear attenuation coefficient calibrated against internal pressure standarts. Preliminary results are reported for refractory magnesium silicate glasses compressed to ~11 GPa and heated to glass transition temperatures using a modified toroidal anvil cell. Strategies to reach the melting interval for in situ studies of compositions relevant to the Earth’s mantle and core will be discussed.
Tectonothermal evolution of Helanshan Complex, westernmost part of the Khondalite belt in the Western Block of North China Craton

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New data show that the Western Block of the North China Craton formed by the amalgamation of the Yinshan Terrane in the north and the Ordos Terrane in the south along a Paleoproterozoic collisional belt, named the Khondalite Belt [1-6]. However, the timing and tectonic nature of this collisional event remains unclear. More and more studies show that the metamorphic P-T evolution can be successfully used to constrain the tectonic nature and processes of orogenic belts. In this study, we present petrological and thermobarometric data for the Helanshan Complex at the westernmost segment of the Khondalite Belt, which provide important insights into the tectonic history of the belt.

The Helanshan Complex consists mainly of Al-rich gneisses, quartzites, marbles and calc-silicate rocks, called khondalite series in the Chinese literature, and S-type granites. Microstructural analysis and metamorphic reaction relations show that the Al-rich gneisses underwent four major metamorphic stages. The M1 assemblage is represented by inclusions found in the garnet poikiloblast, which includes quartz, plagioclase, biotite and kyanite. The M2 stage is defined by growths of matrix minerals quartz, plagioclase, K-feldspar, biotite, cordierite and sillimanite and garnet porphyroblasts. M3 is represented by the reaction rim of cordierite formed around the garnet porphyroblast. The final stage, M4, is represented by muscovite and sericite, and occasionally, andalusite, overprinting the major foliation in the rock.

These mineral assemblages and their P-T estimates define a clockwise P-T path involving decompression, which indicates that the Helanshan Complex underwent initial crustal thickening and subsequent exhumation, accommodating a collisional environment, supporting the recently-proposed model that the Khondalite Belt represents a collisional belt along which the Yinshan and Ordos Terranes amalgamated to form the Western Block in the Paleoproterozoic.

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References

Role of natural nanoparticles (imogolite and allophane) on the mobility of trace metals in soils from La Reunion island

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This research adresses the sensitive field of waste management in an insular context. The case of the Reunion Island bears some aggravating factors making the waste management an even more sensitive subject: 1) it is a small island with a fast growing population and associated activities 2) the agricultural soils (mostly andosols) have an elevated natural concentration of trace metals. An inexpensive form of waste management is to reuse agricultural- waste (especially pig manure) as fertilizer. However, reuse of waste, may modify physico-chemical conditions and trace elements can be released from the soils. The accuracy of the prediction of metal fluxes in soils will be greatly enhanced by a detailed knowledge of the pollutants' speciation, which controls their mobility, toxicity and ultimately their bioavailability. Although the trace metals Cu, Ni, Zn selected for this study because of their occurrence in the soils and wastes, may bind to numerous components of the soils (clays, Fe and Al oxides, organics), we chose to focus on 2 types of nanosized aluminosilicates: the tubular imogolites (2nm diameter) and the spherical allophane (3-5nm). The choice of these phases is justified by their high abundance in the andosols of the Reunion, and their suspected high reactivity arising from the presence of -SiOH and -AlOH at the surface of structures whose specific surface area can reach 700m²/g. Here we detail using a molecular approach the types of the binding mechanisms between pollutants and natural occurring nanoparticles.
Unveiling the origin and evolution of dust in comets

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Investigating the properties of dust released by comets is of major interest to constrain their formation models. Instruments flying-by comet Halley had discovered the presence of organics, and pointed out the low albedo and extremely low density of the dust. Analyses of IDPs and remote spectroscopic observations have indicated that cometary dust consists of an un-equilibrated heterogeneous mixture of organic refractory materials and of amorphous and crystalline silicate minerals, as recently confirmed by Stardust. Observations of the solar scattered light, together with elaborate simulations, have revealed physical properties of the dust. For a well-documented comet, the mass ratio between silicates and absorbing organics, the size distribution and the structure of the dust particles, can be estimated, suggesting that a fair amount consists in fluffy aggregates built up from submicronic grains [1,2], as recently confirmed by Stardust. A detailed analysis of the waves passing through the nucleus of the propagation delay of long wavelength radio waves [3]. On board the Rosetta probe, MIDAS experiment will provide unique information on the dust texture, shape, size and flux, during the rendezvous with comet Churyumov-Gerasimenko. Moreover, the CONSERT experiment will investigate the deep interior of the nucleus from measurements of the propagation delay of long wavelength radio waves [3]. A detailed analysis of the waves passing through the nucleus will put constraints on the materials and on the heterogeneities within the nucleus. While it is now established that nuclei have low densities and are significantly fragile, it will then be possible to better constrain their formation process and their origin.

References

Partial melting of eclogite to form high-pressure granitic rock: A case from the Erzgebirge, Southeast Germany

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We describe an eclogite body from the shore of the Saidenbach reservoir in the Erzgebirge, Germany, that appears to have partially melted to produce a high-pressure granite. The primary eclogite assemblage is omphacite (commonly altered to jd-poor cpx + plag (An10 – An17) symplectites) + garnet + quartz + phengite + rutile. Within these rocks are numerous veins (1 mm to 5 cm wide) and pockets of potassium feldspar + quartz + plagioclase (An11) + phengite + garnet + rutile. This coarse-grained leucocratic material also occurs somewhat diffusely throughout portions of the eclogite matrix, in direct contact with unaltered omphacite.

Textural evidence leads us to believe that the leucocratic material is derived from fluid-fluxed partial melting of the host eclogite. Anatectic of metabasalt compositions typically leads to the formation of tonalites and trondhjemites, but at high pressures partial melting of potassium-enriched eclogites can produce granite over a significant range of melt fractions (Schmidt et al., 2004). The major element composition of the granitic veins in the Saidenbach eclogites is very similar to experimentally generated, basalt-derived granitic melt compositions, with K:Na ratios of ~1.4 (Schmidt et al., 2004). The granitic melt generated by partial melting of the Saidenbach eclogite may also be related to diamoniferous quartzofeldspathic rocks outcropping on the shore of the same reservoir. These kyanite-bearing rocks have been interpreted as high-pressure metasediment melts due to their high aluminum content (Massonne, 2003). However, experiments have shown that high-pressure eclogite melts can also be aluminous (Schmidt et al., 2004). Mineral assemblages of the eclogite leucosomes and the nearby quartzofeldspathic rocks are extremely similar, except for occurrence of kyanite and a higher abundance of carbon (in form of graphite and/or diamond) in the latter. By comparing the geochemistry of the two rock types, we have the rare opportunity to work out the similarities and differences of possibly sediment-derived and clearly eclogite-derived melts, allowing more precise statements about the metasomatic capacity of high pressure melts.

References
Water delivery from the outer planetary system: The role of dynamical instabilities

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Water abounds in the outer regions of planetary systems. Indeed, comets, which are the leftover building blocks of the giant planets, are roughly 40% water by mass. Thus, these regions can furnish a significant amount of water to terrestrial planets provided a dynamical mechanism exists that can transport enough material inward.

In recent years it has become recognized that planetary systems can become dynamically unstable, leading to a violent redistribution of the planetary orbits. Indeed, we see evidence of such instabilities in some of the extra-solar planetary systems thus far discovered (Rasio & Ford 1996). These events, which can occur quite late in the history of a planetary system, can liberate a large amount of water rich objects and deliver them to the inner planetary system where they can strike the terrestrial planets.

Such an event may have occurred in our own Solar System. Many of the large basins on the Moon formed ~700Myr after the beginning of the Solar System – much too late for the impactors to be the leftovers of terrestrial planet formation (Bottke et al. 2007). The model that has been the most successful at reproducing the characteristics of these basins is one where the orbits of Uranus and Neptune became unstable, sending a large amount of icy material into the inner Solar System (Gomes et al. 2005). Such an event would have contributed roughly 5% of Earth oceans. Also, it would have contributed enough icy material to Mars to explain its putative early massive atmosphere (Levison et al. 2001).

More details on this talk can be found at www.boulder.swri.edu/~hal/talks.html

References

Volatiles and Boron isotopes analysis in olivine-hosted melt inclusions from Vulcano (Italy) and Pichincha (Ecuador) lavas

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We have analysed in-situ major and trace elements (electron probe, LMV, Clermont Ferrand, France), as well as volatiles and boron isotopic compositions (ion probe, 1280 WHOI, MA, USA) in olivine-hosted primitive melt inclusions (MI) in basic lavas of two volcanoes from two different subduction settings:

1- The Ecuadorian subduction zone is controlled by the subduction of the Nazca plate beneath South America. The collision of the Carnegie aseismic ridge disturbs the subduction, flattens the slab (small dip from 20 to 30°) and controls the surface expression of active volcanism. Slab melt takes part in the formation of these lavas and some adakite occurrences have been described.

2- The Aeolian arc lavas are thought to represent typical examples of island-arc calc-alkaline magmatism. The tectonic setting of the Tyrrenhian Sea is dominated by the convergence between the European and African plates. The Aeolian arc is related to the subduction of the oceanic Ionian plate beneath the Tyrrenhian Sea (strong dip around 50 and 60°), actually in eastward migration.

Primary MI are at equilibrium with their host minerals, so they preserve information on the composition of intermediate steps in the formation of magmas. In particular, MI in the early-formed olivine phenocrysts have been proposed to be pristine samples of mantle-derived melts that were trapped prior to mixing at shallower levels. Moreover, unlike lavas, MI keep their primitive volatile content.

The MI from these two different settings are CaO-rich and nepheline-normative. These compositions have been interpreted as the result of melting of a lower crust clinopyroxene-rich lithology (Schiano et al., 2000)

$^{11}$B in MI range from –5.0±1.0‰ to +3.0±1.0‰ for Vulcano, and from –18.8±1.0‰ to +9.5±1.0‰ for Pichincha) which suggest heterogeneous sources for the two volcanoes. MI from Vulcano are enriched in H2O and Cl, and those from Pichincha are enriched in CO2, F and S (Vulcano: 0.95 to 3.50% H2O, 80 to 170 ppm CO2, 805 to 910 ppm F, 3000 to 3500 ppm Cl and 2000 to 2400 ppm S; Pichincha: 0.1 to 1.5 % H2O, 130 to 800 ppm CO2, 100 to 400 ppm F, 200 to 700 ppm Cl, 500 to 2500 ppm S; relative errors are equal to or less than 5%). We will discuss the results in terms of source variation and input from the slab.

Reference
Low temperature nucleation of ferric arsenate using microorganisms

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Introduction
The safe disposal of arsenic is important for the metal extraction industry worldwide. Previous work has shown that crystalline ferric arsenate (FeAsO$_4$·2H$_2$O), which is a synthetic version of the natural mineral scorodite, fulfils most of the criteria for safe disposal. Presently, this requires the use of expensive pressurised equipment in industrial applications. There is increasing evidence that microorganisms play an important part in the geochemical cycle of As. In environmental samples, bacteria are often closely associated with mineral precipitates, as well as in bioleaching samples.

Method
Strains of acidophillic bacteria (Acidithiobacillus spp., Sulfobacillus spp. and Thiomonas spp.) have been enriched and isolated in liquid and on solid media from rock samples from former mine sites in the Czech Republic and the UK, and experiments carried out to determine whether the bacteria can catalyse the formation of ferric arsenate.

Results
No distinct mineral phases have been identified by XRD, and there is no variation in crystallinity with varying concentrations or valences of arsenic species. FTIR analyses of precipitates have identified no crystalline mineral phases, and there is no increase in crystallinity with age over the months during which the precipitates have been studied.

Conclusions
To date we have no evidence that the selected bacteria can precipitate ferric arsenate on solid media, despite varying concentrations of As added as As$^{3+}$ or As$^{5+}$. Material formed has been x-ray amorphous due to rapid formation, and FTIR analyses have shown no increase in crystallinity with age over the months in which the precipitates have been studied.

References

FT-IR investigation of the uranium S-layer interaction in aqueous solutions

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Many bacteria possess so-called surface layer (S-layer) proteins, forming paracrystalline lattice structures on the cell wall [1]. Beside its ecological relevance for the retention of toxic metals, they are a good model system for investigations of the interaction of bio-ligands, e.g. proteins, with uranium in aqueous solutions. Several S-layers from different Bacillus strains were proved to have high binding capacity to uranium. But there is still little knowledge of the interactions between the functional groups of the protein with the actinyl ions at a molecular level [2].

In this work we present results of batch experiments where the uranium binding capacities of different S-layer protein from different Bacilllus strains were determined. The experiments were carried out at different pH values (pH 4, 6, and 8) for each isolated S-layer protein. It was found that the uranium binding capacities of each gram S-layer range from 5.0 mg and 63.9 mg, from 11.1 mg and 561.1 mg, and from 14.2 mg and 33.5 mg at pH 4, 6, and 8, respectively, depending on the respective S-layer.

For a deeper understanding of the molecular binding of the uranyl ion to the protein we used Attenuated Total Reflectance Fourier-transform Infrared spectroscopy (ATR-FTIR) which allows vibrational spectroscopic investigations of aqueous solutions containing actinide ions and dissolved proteins as well [3, 4]. The spectra clearly demonstrate carboxyl groups are the major functional groups which interact with the uranyl ions at pH 4. Additionally, the infrared spectra suggest the formation of different uraniu m-protein complexes depending on the incubation period (1 h vs. 48 h) which can be observed by a peak shift of the absorption band representing the antisymetric uranyl stretch to lower wavenumbers.

This spectroscopic approach constitutes the foundation of more detailed investigations on the impact of the pH value and of other functional groups (e.g. phosphate or amino groups) on the uranium complexation by bio-systems.

References
Experimental study on liquid immiscibility of lamprophyre – Sulfide melt at high temperature and high pressure

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The liquid immiscibility of silicate-sulfide melt is a common geological phenomenon in magmatic processes (Naldrett, 1989; Roedder, 1992). This phenomenon is often used to explain the zonal distribution of ore layers in basic-ultrabasic rocks and the formation of magmatic Cu-Ni sulfide deposits (Naldrett, 1989, 2005). At present, the experimental investigation of liquid immiscibility of the silicate-sulfide melt in synthetic FeO-SiO₂-FeS system has accumulated a lot of data (Fleet and Pan, 1994). But the investigation in the system of natural rocks is hardly conducted.

By taking lamprophyres and pyrites from the Laowangzhai orefield, Yunnan Province, China as starting materials, at 1.5 GPa to 3.0 GPa and 1160 °C to 1560 °C, this paper carry out experimental study on liquid immiscibility of lamprophyre-sulfide melt at high temperature and high pressure in the DS-29A cubic 3600t/6 type high pressure apparatus.

The results show that the liquid immiscibility of silicate-sulfide melt is a common geological phenomenon in magmatic processes (Naldrett, 1989; Roedder, 1992). This phenomenon is often used to explain the zonal distribution of ore layers in basic-ultrabasic rocks and the formation of magmatic Cu-Ni sulfide deposits (Naldrett, 1989, 2005). At present, the experimental investigation of liquid immiscibility of the silicate-sulfide melt in synthetic FeO-SiO₂-FeS system has accumulated a lot of data (Fleet and Pan, 1994). But the investigation in the system of natural rocks is hardly conducted.

By taking lamprophyres and pyrites from the Laowangzhai orefield, Yunnan Province, China as starting materials, at 1.5 GPa to 3.0 GPa and 1160 °C to 1560 °C, this paper carry out experimental study on liquid immiscibility of lamprophyre-sulfide melt at high temperature and high pressure in the DS-29A cubic 3600t/6 type high pressure apparatus.

The results show that the liquid immiscibility of lamprophyre-sulfide melt in magmatic processes will happen during the early magmatic evolution (high-pressure condition), and this process should also occur in every stage of the magmatic evolution (from high-pressure to low-pressure condition) if sulfur exists. The sulfide melt which separated from the silicate melt will make directional movement in temperature and pressure field and assemble in the low-temperature and low-pressure region. Because the density of sulfide melt is higher than that of silicate melt, the former would gather together in the bottom of magma chamber and there would exist a striking boundary between the two melts.

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References

A new genetic model for the Noril’sk-Talnakh Ni-Cu-PGE sulphide deposits

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A popular genetic model for the Ni-Cu-PGE sulphide ores in the Noril’sk-Talnakh intrusions in Siberia which emphasizes a direct link between the sulphide-bearing intrusions and the overlying PGE-depleted basaltic lavas has been criticized because of differences between the intrusions and lavas such as trace element ratios and S-Sr-Nd isotope compositions. In addition, the unusual combination of high PGE concentrations and high δ³⁴S values (~11‰) in the sulphide ores has not been explained adequately. Based on our new S isotopic data and mass balance calculations, we suggest that such an unusual combination resulted from anhydrite dissolution in sulphide under-saturated, PGE-enriched magma. We propose that the PGE-enriched magma was generated by complete resorption of early immiscible sulphide liquids in new pulses of mantle-derived, sulphide under-saturated magma in a deep staging chamber. The magma became sulphide saturation again after subsequent assimilation of anhydrite country rocks at shallower levels. Abundant anhydrite xenoliths with δ³⁴S values of ~16‰ in the intrusions provide direct evidence for anhydrite-magma interaction during magma ascent and final emplacement. The PGE-depleted lavas which may have contributed chalcophile elements to the early sulphide liquids in the deep staging chamber directly erupted to the surface without interacting with anhydrite-bearing country rocks; thereby they did not acquire anhydrite S isotopic signatures.
New carbon isotope stratigraphy of an old section in southwest China: Implications for placement of PC-C boundary on Yangtze Platform

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We report a high-resolution carbon isotope profile from Laolin section on Yangtze Platform, in northeastern Yunnan Province, southwest of China. The Laolin section, located east to the Dianchi Fault, has more continuous strata around the Precambrian-Cambrian (hereafter PC-C) boundary than the Meishucun section located west to the Dianchi Fault, where exist depositional hiatuses between Batianshao member (including the Xiaowaitoushan member) and Zhongyicun member, and between Dahai member and Qiongzhusi Formation (Qian et al., 1996). Thus the Laolin succession has great value for placement of PC-C boundary on the Yangtze Platform and global correlations. Shen & Schidlowski (2000) studied the carbon isotope chemostratigraphy for the Laolin section, though their strata frame was doubted by Zhu et al. in 2001. Our study on carbon isotope stratigraphy of the Laolin succession based on careful stratum frame work yielded two negative excursions (L1´ and L3´) and a positive excursion (L4). The first negative δ¹³C excursion (L1´) in upward order around the PC-C boundary occurs just below the first appearance data (FAD) of small shelly fossil (SSF) which was found at the base of the Zhongyicun member (Luo et al., 1991). Such combination of negative δ¹³C and FAD of SSF is the same as the situation of eastern Siberia PC-C boundary. We correlate the Laolin succession with those in Mongolia, eastern Siberia, northern Siberia, Iran and Canada, where similar situations that the first negative δ¹³C excursion occurs closely beneath or over the FAD of SSF, and provide a better PC-C boundary on the Yangtze Platform than the Meishucun succession. This study is supported by NSFC grant 40572017.

References

ISODUST: A Nd-Sr isotopic database to trace the source regions of Asian dust

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Mineral dust emitted from Asian Interior has broadly environmental impacts as it is spreading in the atmosphere. The knowledge on the source regions of Asian dust and their temporal variations is critical for predicting the overall dust impacts and understanding the paleo-environmental proxies in the dust deposits. Radiogenic Nd-Sr isotopes have been proven to been reliable source tracers, but this method needs long-term accumulation of data. This database is designed to solve this problem. It contains more than 400 pairs of Nd-Sr isotopic data which belong to the following three sub-databases mainly based on our own measurements.

ISODUST1: Potential Source Regions
It covers all of the potential source regions in North China and Mongolia, including the deserts, sandy lands, Gobi, fluvial fans, dry riverbeds and dry lake basins. Most of the data are based on the fine (< 75 µm and < 5 µm) silicate fractions of the samples, which enable the direct comparison between the dust and their potential sources without the influences of weathering and transportation. It is shown that different source regions have distinct Nd-Sr isotopic compositions controlled by their tectonic settings. The tectonic control suggests that the Nd-Sr isotopic signatures of these sources could be quite stable on the sub-tectonic time scales, which enable the use of this database to trace the provenances of the ancient dust.

ISODUST 2: Ancient Dust Deposits
Silicate Nd-Sr isotopes of ancient dust deposited in North China, North Pacific and Greenland are collected. It shows that the vast distributed loess in North China is transported from their adjacent regions by the prevailing near-surface wind. The provenance of the eolian deposits in Chinese Loess Plateau is quite stable in the most times of past 7 Myrs. However, rapid changes in source regions have been detected, probably reflects some abnormal monsoon conditions. The Asian end members of the ancient dust in North Pacific and Greenland are mainly the deserts on the margin of Tibetan Plateau, where the westerly jet passes by.

ISODUST 3: Modern Dust
It consists of the silicate Nd-Sr isotopic data of the atmospheric particles collected in the past years. The Nd-Sr isotopes provide a method to trace the sources of modern dust in addition to other observational techniques. Anthropogenic influence on the dust sources in Beijing has been detected by comparing the Nd-Sr isotopic compositions of the modern dust to those of the ancient dust deposits (loess) in this region. Dust emitted from the locally dry riverbeds caused by water management can explain the observed anthropogenic influence.
Microbial uranium mineralization and hydrocarbon oxidation in the Qianjia-dian deposit, NE China

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Braided rive facies sandstone - hosted tabular uranium deposit has recently been found in the Lower Cretaceous Yaqia Formation in the Qianjadian deposit, the Kailu basin, NE China. The mineralization consists mainly of pitchblende (UO₂, x=2.16 to 2.7) and small amount of brannerite (UTi₂O₆). U-Pb dating shows the main U-mineralization took place at about 53±3Ma during the early Himalayan orogeny, when the basin was uplifted and petroleum was up-migrated from the Upper Jurassic lacustrine source rock through faults. Subsequently, part of the U ore was re-mobilized and re-precipitated at about 7±0 Ma during the late Himalayan orogeny. Uranium ore occurs as cement or adsorbed on plant debris, but no correlation occurs between TOC and U content. Some of the pitchblende is intimately intergrown with ore-stage pyrite, Fe dolomite and calcite, indicating part of carbon was derived from petroleum oxidation. The host sandstone contains adsorbed petroleum and oil inclusions with adsorbed methane up to 5530µl/kg. GC data from oil inclusions and adsorbed oils show the existence of unresolved complex mixtures, and significant amounts of demethylated hopanes and tricyclic terpanes. These lines of evidence indicate petroleum was likely oxidized by sulfate reducing bacteria (SRB) simultaneously with reduction of U(VI) to U(IV) and thus supplying some of the carbon in the carbonates. This suggestion is partially supported by the low-temperature diagenetic environment (<50°C). However, U(VI) pre-concentration by adsorption and subsequent inorganic reduction is likely to be less significant than direct reduction of U(VI) by SRB in the Qianjadian deposit. This is because ore-stage solution is non-acidic, as indicated by digenetic mineral assemblage pyrite, Fe-dolomite, calcite and pitchblende and lack of marcasite precipitation and carbonate dissolution in the host sandstone. The proposal that direct reduction of U(VI) to U(IV) by SRB is supported by recent finding of mineralized microorganisms in the Dongsheng deposit, NW China (Cai et al., 2007).

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References

Sm-Nd and Rb-Sr isotopic ages of adamellite body from the Longquan in the south of Zhejiang, China

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The adamellite body lies in the south of Zhejiang Province, China. The sampling location lie at Badou Group of Lower Proterozoic of Longquan area.

Analytical Method
Analysis of Rb-Sr abundances and their isotope compositions were performed on an automated multi-channel mass spectrometer VG 354 at Center of Modern Analysis, Nanjing University. $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.710224±6 (2σ) for NBS987 standard. $^{43}\text{Nd}/^{144}\text{Nd}$ = 0.512465±6 (2σ) for BCR-1 standard.

Discussion of Results
The age of Rb-Sr isochron for the adamellite body from Badou Group area. is 665.5±21Ma and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.74175±92. Sm-Nd isotope age of the whole rock-mineral internal for the adamellite body rock is 2059± 52Ma. The isotopic age of the whole rock-mineral internal Sm-Nd isochron for the adamellite body from Badou Group of Lower Proterozoic of Longquan area is 2059±52Ma and initial εNd(t) is -1.97~2.46.

Conclusion
Rb-Sr age of the the adamellite body whole-rock and mineral samples reflects the age of this intrusion after the disturbance of the subsequent geological processes. Sm-Nd age of the the adamellite body whole-rock and mineral samples is consided as the emplacement age of the adamellite body and indicates that the earliest activity of granitic-magma in Zhejiang. In combination with the geological evidence and geochemical date,it is believed that the adamellite body belong to a S-type [1] or transformation-type granite. It was formed by partial melting of the crustal materials mainly of sedimentary constituents. $^{187}\text{Os}/^{187}\text{Os}$ of 5 whole rock-mineral samples is about 2600-2700Ma.

Reference
Analysis of Rb-Sr isotopic mass spectrometer and dating for bauxite deposits in Shanxi Province

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Introduction
The Carboniferous bauxite deposits are diasporic bauxite deposits in Shanxi, China. Carboniferous bauxite in Shanxi massif is considered the combination of BED G bauxite and Shanxi-type iron deposit, which joint together and are called Ferrallite Formation (Wang Y. et al., 2000).

Analytical Method
Analysis of Rb-Sr abundances and their isotope compositions were performed on an automated multi-channel mass spectrometer VG 354 at Center of Modern Analysis, Nanjing University. Isotope dilution method was used for determination of the abundances. All Sr isotopic data are corrected for mass fractionation to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and reported relative to a value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.710224 \pm 6 (2\sigma)$ for NBS987 standard.

Discussion of Results
Isotopic age of the whole rock-mineral internal Rb-Sr isochron for Bauxite Clayrock from Wu Tai In Shanxi is $316.9 \pm 1.2 \text{ Ma}$ and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is $0.71054 \pm 14$; Isotope age of the whole rock-mineral internal Rb-Sr isochron for Bauxite Clayrock from Linxian In Shanxi is $315.5 \pm 1.3 \text{ Ma}$ and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is $0.71086 \pm 18$; Isotope age of the whole rock-mineral internal Rb-Sr isochron for Bauxite Clayrock from Xiaoyi In Shanxi is $317.3 \pm 1.1 \text{ Ma}$ and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is $0.71050 \pm 14$.

Conclusion
We have been obtained for the bauxite whole-rock and clay mineral samples from Wu Tai (RS01), Linxian. We have been obtained for the bauxite whole-rock and clay mineral samples from Wu Tai (RS01), Linxian (RS02) and Xiaoyi (RS03), Shanxi Province respectively. These ages indicate that bauxite and the ore-hosting sedimentary sequence in Shanxi were deposited in the time interval between 315-317 Ma, corresponding to the Late Carboniferous Epoch.

Reference

Chemical weathering in Yangtze River: Evidence from water chemistry and $\delta^{13}C$ of dissolved inorganic carbon

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Dissolved inorganic carbon (DIC) of river water from the mainstream and major tributaries of Yangtze River were measured with a main purpose to understand the chemical weathering. The equivalent ratios of $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^- + \text{SO}_4^{2-}]$ of most samples are around unit, indicating a relatively large part of Ca$^{2+}$ and Mg$^{2+}$ need to be balanced by SO$_4^{2-}$, which may be from the gypsum dissolution and/or dissolution of carbonate minerals by H$_2$SO$_4$. Based on chemical budget and stoichiometry analyses, the estimation resulted in that carbonate weathering, on average, accounts for ~67%, and silicate weathering and evaporite dissolution for ~22% and ~11%, respectively.

The $\delta^{13}\text{C}_{\text{DIC}}$ values range from -8.9‰ to -3.4‰, which represents a mixture of DIC produced by the following weathering pathways: (i) carbonate weathering by carbonic acid (-8.5‰); (ii) silicate weathering by carbonic acid (-17‰); (iii) carbonate weathering by H$_2$SO$_4$ (0‰) derived from the oxidation of sulfide and/or anthropogenic SO$_2$ emission. A positive relationship exists between the SO$_4^{2-}$ and the $\delta^{13}\text{C}_{\text{DIC}}$, which further supports the hypothesis that H$_2$SO$_4$ is primarily neutralized by carbonates.

Acknowledgement
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Fe isotope fractionation during Fe(III) hydrolysis in Cl\textsuperscript{-} medium at low temperatures

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Realisation of the potential offered by stable isotope systems requires an adequate understanding of the factors controlling their isotope fractionation. Various processes such as reduction-oxidation, dissolution-precipitation, and biological utilisation, have been documented to be important controlling factors for Fe isotope fractionation. Here we extend this kind of study to Fe(III) hydrolysis in Cl\textsuperscript{-} medium at low temperature conditions.

A solution of 1mg/mL Fe(III) in milli-Q water was prepared from ferric chloride, and 9 mL- aliquots of the solution were loaded into 9 microcentrifuge tubes that were tightly stopped. 5 centrifugal tubes were put in water-bath solution were loaded into 9 microcentrifuge tubes that were prepared from ferric chloride, and 9 mL-aliquots of the low temperature conditions.

Duration of the experiments was 95 days. Ferric oxyhydroxide precipitation began after about a day for the experiments at 46\degree C, whereas it only started after about a month for those at room-temperature. After 95 days, the precipitates and residual solution were separated by centrifuging, and the precipitates were washed with Milli-Q water twice. Both supernates and precipitates were purified through anion exchange chromatography, before Fe isotope measurement using a Nu Plasma HR MC-ICPMS at high-resolution mode. The results are expressed in \(\varepsilon\) unit which is deviations in parts per 10\(^4\) from the same isotope ratios of the original FeCl\(_3\) used in the experiments. It is observed that the Fe isotope compositions in precipitates are systematically lighter than those of the corresponding supernates, which is consistent with a previous study (Skulan et al., 2002). The differences between precipitates and supernates in \(\varepsilon\)\(^{57}/54\)Fe are 17.0 \(\pm\) 0.8 and 20.2 \(\pm\) 1.8 for experiments performed at 20\degree C and 46\degree C, respectively.

It has been noticed that the measured Fe concentrations in the supernates are three orders of magnitude higher than those predicted from the solubility constant product for experiments performed at room temperature, whereas the measured and predicted Fe concentrations are similar in the residual solutions for those conducted at 46\degree C. This suggests that significant amount of ferric oxyhydroxide colloid has not flocculated, but remained in those supernates. Assuming isotopic equilibrium has been reached between the solid and liquid phases for experiments conducted at both temperatures, the Fe isotope composition of the ferric oxyhydroxide colloid must be lighter than that of the solution by at least 3 \(\varepsilon\) units in \(^{57}/54\)Fe ratio.

Reference

Origin of ore-forming fluids of the Dajiangping pyrite deposit, South China: Evidence from He-Ar isotopes

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The ore genesis model for the Dajiangping ultra-large pyrite deposit in the South China has long been in dispute, and the major debate focuses on whether the pyrite orebodies were formed by a vapour-liquid superimposition event during hydrothermal alteration, or whether formation of ores was the products of hot-water sedimentation. He and Ar isotopes have been widely applied in tracing the origins and water-rock interactions of contemporary crustal fluids. Recently, these isotope systematics have also been successfully applied to the study of the origin of ancient ore-forming fluids and mineralization. In this work, we report He and Ar isotopic data for the Dajiangping ore deposit for the first time, and discuss the origin and evolution of the hydrothermal fluid.

He and Ar isotope were measured in fluid inclusions from six pyrites in the Dajiangping Deposit. These pyrite samples were collected from different ore types or places: orebody III (banded ores), orebody IV (massive ores), CK36 drill core and wall rocks. The results of helium and argon isotope data are shown that the fluid inclusions from pyrite have \(^{3}He/^{4}He\) ratios of 0.18~3.55\(\times\)10\(^{-6}\)(0.13~2.55Ra). The values of \(^{40}Ar/^{36}Ar\) ratios show slight variation between 348~443, which is higher than air-saturated water’s \(^{40}Ar/^{36}Ar\) ratios of 295.5(ASW). As shown in the plot of \(^{3}He/^{4}He\) vs. \(^{40}Ar/^{36}Ar\) ratios, the data fall among three sources district, which indicates that the hydrothermal fluid did not originate from the single source, and instead may be a product of crust-mantle mixture. The six pyrite samples come from two orebody IV, two orebody III, one CK36 drill core (depth 133 m), and one wall-rock in study area. We find that the data of fluid inclusion of two pyrites from orebody IV fall in between mantle-derived fluids and ASW. In contrast, the others lie lower on the graph; the CK-36 and DP-11 even lie between ASW and crust fluids.

These data indicate that mantle-derived fluids contributed to the ore-forming fluids. This study suggests that the hot fluids from the mantle intruded into the places of orebody along the thrust faults, and hydrothermed the orebody. This caused differentiation of the two typies orebody to result in the formation of the banded orebody III and the massive orebody IV.

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Nitrogen and oxygen isotopes in phengite from UHP metamorphic rocks in the Sulu orogen, China

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Ultrahigh-pressure (UHP) metamorphic rocks in the Dabie-Sulu orogenic belt of east-central China are documented to be remnant of the Neoproterozoic supercrustal materials that were subducted into the upper mantle in the Triassic. Previous studies of O, H and Ar isotopes show that these UHP rocks experienced limited fluid-rock interaction during subduction and exhumation, and thus have preserved the stable isotope features of their protoliths that underwent extensive meteoric-hydrothermal alteration during magma emplacement. Here, ammonium-N contents and isotopes, combined with oxygen isotopes, of phengites in UHP eclogite and gneiss from the Donghai area in the Sulu orogen were investigated in an attempt to understand the behavior of this volatile element during continental subduction-zone metamorphism and the potential effect of the recycling of the continental crust on the mantle N reservoir.

The phengites show low δ18O values of –11.9 to +3.3‰ as a result of different degrees of Neoproterozoic meteoric-hydrothermal alteration. The phengites also contain very low N from 6.5 to 34.4 ppm with a wide range of δ15N from –4.5 to +8.9‰. Samples from Qinglongshan show a negative relationship between N concentrations and δ15N values but no clear relationship between δ15N and δ18O. However, a positively correlated trend between δ15N and δ18O was observed at a larger spatial scale. The low N concentrations of phengites in these rocks might be inherited from their igneous protoliths. However, the negative δ15N are not consistent with an igneous origin, but indicate a significant negative shift by a 15N-depleted N source or N-isotope fractionation during the Neoproterozoic water-rock interaction. The negative relationship between N concentration and δ15N for the Qinglongshan samples could be caused by either Triassic subduction devolatilization or Neoproterozoic alteration. Further study of trace elements (Rb, Cs, etc.) may better constrain these possibilities. In either case, the presence of unnegligible amounts of N in phengites, which together with other K-rich minerals (e.g., muscovite, K-feldspar) may constitute of as much as 20 vol.% of the eclogites and 60 vol.% of the gneiss/schist, implies that considerable amounts of N could have been conveyed into the mantle due to breakoff of the subducted continental slab. Because the continental material is more 15N-enriched than the mantle, this deeply subducted N may have potential to increase mantle δ15N at a certain scale.

Two Mesozoic volcanic activities in Fujian Province, China: constraints on the transformation of tectonic domain in Southeastern China

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Two representative geologic sections of the late Mesozoic “Nanyuan Formation” volcanic rocks in eastern Fujian Province have been dated by zircon SHRIMP U-Pb technique. Two volcanic activities have been identified, i.e. the earlier at 162-150 Ma and the latter at 142-130 Ma. Basaltic rocks of the earlier period have geochemical features similar to those of OIB with significant crustal contamination and fractional crystallization of olivine and clinopyroxene, while the counterpart of the latter period are rich in Al, Fe, LILE and LREE and depleted in HFSE. It seems that the two volcanic activities should not be grouped into the same Formation and the magmas may have been generated in different tectonic settings. The above data may indicate a transfromation of Mesozoic tectonic domain in Southeastern China in a period of 150-142 Ma.

It is suggested that the earlier volcanic activity was generated by local extension resulted from the combining action of Tethyan tectonic dynamic system and Paleo-Pacific tectonic system whereas the latter was attributed to the regional extension induced by high-angle subduction of the Paleo-Pacific plate.

KEY WORDS   transformation of tectonic domain, U-Pb age, Nanyuan Formation, southeastern China.
Evolution of carbon in the karst groundwater, Zunyi, China


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The carbonate system evolves with weathering reactions driven by CO₂ dissolved from the soil and subsequent organic/inorganic reactions in soils and aquifers. This study focuses on the carbon evolution of karst groundwater, Zunyi, China.

The studied area is mainly characterized by karst landforms in Southwest China. The mean values of DIC in winter and summer are 4.54 and 3.82 mmol C/L respectively, reflecting the dilution effects of the heavy monsoon rains; The average δ¹³C_DIC values of ground water are -10.3‰ in winter and -11.1‰ in summer, which suggests that soil CO₂ makes a larger contribution to the DIC in summer than in winter. The concentration of DOC and POC in most of ground water samples are lower than 2.00 mg C/L and 0.50 mg C/L but some contaminated waters, respectively. There is a larger range of δ¹³C_POC in summer than that in winter. P₇_CO₂ of the waters generally is higher than 10⁻³.₅, and P₇_CO₂ in ground water is generally higher than that in surface water, showing deep soil CO₂ makes a greater contribution to ground water. The seasonal difference of contents and isotopic composition of carbon species reflect that the carbon evolution of karst groundwater is easily affected by the monsoon rains.

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Cu isotope signature of granites

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The Cu isotope signature of bulk earth is proposed to be homogeneous (δ⁶⁵Cu=0) based on measurements of sulphides from mafic intrusions (e.g. Larson et al., 2003) and a limited numbers of mantle-driven rocks (e.g. Archer and Vance, 2004). However, it has been reported that highly evolved granite can have a Fe isotope signature remarkably different (about 0.5‰ δ⁵⁷Fe) from bulk earth values (Poitrasson and Freydier, 2005). As Cu is a trace element in most common rocks, and is also multivalent, its isotopes are more likely to be fractionated by Rayleigh (magma evolution) and redox (weathering / sedimentation) processes than Fe isotopes. Here we report our preliminary work to determine baseline values of δ⁶⁵Cu for various granite rocks and examine the Cu isotope homogeneity of crust.

A chemical procedure, modified from Maréchal (1999), was used to separate Cu from rock matrix. Quantitative recovery (100.9±1.2%) with a low total procedural background (2.65±0.66ng) for Cu has been achieved, allowing Cu isotopic measurements on samples with as little as 10 ppm Cu. Elution curves for peridotite, basalt and granodiorite indicate that elution of Cu is not affected by the bulk composition of rocks. Cu isotope ratios were measured with a Nu Plasma MC-ICP-MS using solution nebulisation sample introduction. Mass bias was corrected by both the sample-standard bracketing and the Ni-doping methods. The long-term external reproducibility of the measurements was 0.09‰ (2 sigma).

S-type and I-type granites from southeastern Australia have been analysed. The S-type granites have a large range of δ⁶⁵Cu, varying from -0.40‰ to 0.37‰, while the δ⁶⁵Cu values of I type granites are less variable (from -0.05‰ to 0.26‰), generally overlapping each other within error around zero (the bulk earth value). However, samples of the mafic end member (SiO₂<55wt%) of an I-type granite suite show remarkable heavy Cu isotope signatures (δ⁶⁵Cu up to 1.56‰).

The distinguishable variation in Cu isotopic composition of the S-type granite may reflect isotopic heterogeneity in the sedimentary source region as a result of redox processes. However, the possibility of Cu isotope fractionation during magmatic and magmatic-hydrothermal processes cannot be ruled out.

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Zircon ages and Hf isotopic composition of gneisses from the Sulu UHP terrain, China

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Identification of coesite and micro-diamond inclusions in eclogites of the Dabie-Sulu terranes in east-central China [1-2] demonstrates that supracrustal material was subducted to mantle depth of >120 km and underwent UHP metamorphism. Time of this collision was constrained at ca. 230-220 Ma by radiometric studies [3-4]. UHP eclogites occur as lenses in dominant gneisses of different types.

This study presents zircon U-Pb ages and Hf isotopic composition of gneisses in the Sulu UHP terrain for origin and provenance of the protoliths. Zircon grains from three samples of gneiss yield SHRIMP U-Pb ages of 710-770 Ma, consistent with protolith ages of eclogites and orthogneisses in other regions of the Dabie-Sulu orogen, interpreted as formation time of magmatic protoliths of the gneisses, which were contemporaneous with the magmatism during the breakup of the supercontinent Rodinia. Initial εHf values at (750 Ma) and Hf modal ages of zircon grains from the fourteen gneiss samples are variable. Zircon grains from two gneiss samples commonly give very low initial εHf values (average -16.4) and a mean Hf modal age of about 2.70 Ga. Seven gneiss samples contian zircon grains that yield a mean initial εHf value of -7.7 and Hf modal age of 2.15 Ga. These results suggest that part of protoliths were formed in Neoproterozoic by remelting Archean to Paleoproterozoic crustal material and further indicate existence of Archean crustal section probably of the Yangtze affinity beneath the Sulu UHP terrain. Other six gneiss samples mostly contain young zircon grains, having mean initial εHf values of -56 to 6.6. Part of them give Hf modal ages of 0.81 to 0.94 Ga. This suggests magmatic activity of mantle origin, new crustal formation and coeval crust-mantle interaction probably during breakup of supercontinent Rodinia in Neoproterozoic. Underplating of magmas of mantle origin caused remelting of the overlying Archean - Paleoproterozoic crustal section to form granitic magma along rift zones or marginal regimes of the Yangtze block.

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References

Ca. 850 Ma intraplate magmatism in South China: implications for onset of the breakup of Rodinia

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Early to middle Neoproterozoic igneous rocks are widespread throughout South China, and their genesis and tectonic affilliations are important for understanding the geological evolution of South China with direct bearing on the Rodinia reconstruction. There are two main competitive models regarding their genesis. One is that the ≥900 Ma rocks were formed prior to or during the Sibao Orogeny related to the Rodinia assembly, whereas the 830-740 Ma rocks were anogenic products related to mantle plume activities during the breakup of Rodinia. An alternative model is that all these rocks were formed in active continental margins and/or during the amalgamation between the Yangtze and Cathaysia Blocks, and the coherent South China could not have formed until ca. 800 Ma.

We report here geochronological and geochemical data for the Shenwu dolerite dykes and Gangbian syenite intrusion from SE Yangtze Block. These rocks were dated at ca. 850 Ma by SHRIMP U-Pb zircon method. The Shenwu dolerites are tholeiitic in compositions, and exhibit overall moderate enrichment in most incompatible trace elements resembling intraplate basaltic rocks. They have relatively restricted range of εNd(T) value between 0.4 and 2.1, suggesting derivation from a metasomatized lithosphere mantle. The Gangbian syenites show a wide range of SiO2 = 46-67% and Mg# = 4.8% and K2O/Na2O = 0.4-1.2. They are enriched in LIL and depleited in Nb and Ta with εNd(T) = 0 to -6. The syenites were likely derived from the common metasomatized mantle source by small degrees of partial melting followed by varying degrees of crystal fractionation associated with minor crustal contamination. These ca. 850 Ma dolerites and syenites share close affinities with the intraplate basaltic and alkaline rocks, indicative of an intraplate origin, rather than products of arc magmatism.

The studied dolerites and syenites postdate the ca. 1.1-0.9 Ga Sibao Orogeny, and predate the formation of ca. 820-650 Ma Nanhu rift basin, providing an important petrological constraint on the tectonic transformation from ca. 1.1-0.9 Ga orogenesis to ca. 850 Ma intraplate rifting in South China. These rocks are synchronous with some reported ca. 850 Ma anogenic igneous rocks in other Rodinian contonents, possibly pointing to ontset of the breakup of Rodinia supercontinent.
An ecological explanation for high resolution stable carbon isotope stratigraphy approaching the Permian/Triassic boundary in Meishan area, South China

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High resolution carbon isotope stratigraphy has been generated from marine carbonate and organic carbon during the Changhsingian at the end of Permian and earliest Triassic from Meishan in south China. The result reproduces a gradual decline in δ13C_carb during the Changhsingian, but this decrease trends is superimposed by three large positive excursions in δ13C_carb at lower, middle and upper interval. This observation maybe reflect changes in the rate of organic matter burial during the late Permian. The large positive δ13C_carb excursions would present the enhanced organic carbon burial, presumably in response to episodic transgression-associated anoxia.

The δ13C_carb values indicate much more variable compared to the δ13C_carb, however the values of ∆13C (δ13C_carb - δ13C_org) have fallen in only two groups: (1) between 28~30.3‰ and indicative of maximal fractionation of carbon isotopes by phytoplanktonic producers; (2) greater than 30.5‰ (< 33.3‰), and apparently indicative of significant input from bacterial biomass in bottom water. The δ13C_org of each of these groups parallels (separately) the more detailed profile of δ13C_carb, strongly suggesting that differences in δ13C of both inorganic and organic carbon related to difference in δ13C of CO2(aq) in photic zone. The multiple coeval negative excursions in δ13C of both carbonate and organic carbon occurred before extinction intervals, suggesting that isotopically CO2 was recycled into the photic zone from stagnant water below. The pattern and magnitude of change in both δ13C_carb and δ13C_org are easy to reconcile with the gas hydrate hypothesis as the explanation for abrupt negative δ13C anomalies at extinction interval. The methane−consuming associations of sulfate−reducing bacteria may have contributed to this dramatic negative shift.

References
Geochemistry, Sm-Nd and Rb-Sr isotopic compositions of eclogite in the Lasha terrane, Tibet, and their geological significance

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Eclogite was first discovered in the Lasha terrane, northeast to the Lasha city, Tibet, China. It is located in the north of the Gangdese island arc belt. The eclogite occurs as a 500-600 m thick belt, extending in EW for over 10 km. Most eclogites are massive, coarse-grained and fresh. Three types of eclogite have been recognized, which are rutile eclogite, quartz eclogite and phengite eclogite.

The major elements, trace elements, rare earth elements, Sr-Nd isotopic compositions and Sm-Nd isotopic chronology of some eclogites were obtained in this study. The major elemental compositions and relatively high \(\varepsilon_{\text{Nd}}\) (t) of about +7.9 for the eclogites suggest that the protoliths of eclogites were ancient basaltic rocks developed in ocean crust, similar with the typical N-MORB, and derived from the depleted mantle. The \(87\text{Sr}/86\text{Sr}\) of the eclogites vary over a wide range, from 0.70335~0.70457, which is not closely relevant with the \(\varepsilon_{\text{Nd}}\) (305 Ma) and trace elements. We favor that this irrelevant may be due to the ocean environment of these eclogites developed and the later aqueous alteration after its formation. The Sm-Nd age of 305.5±50 Ma defined by the whole rock is interpreted to represent a developed age, indicating that there was ancient Tethys and its deep subduction in northern Gangdese at early Carboniferous-lately Permian.

Fe isotopes of banded iron formation from Anshan, northeast China

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Fe is the most abundant element engaging in redox chemistry, and is one of the element has been used biologically at very early stage. Thus understand the geochemical cycling of Fe has great implications for the development of an oxygenated atmosphere and the origin of life. Banded iron formations (BIFs) are chemical deposits from oceans. They have potential to preserve paleoceanographic signatures. Here we report the results of an iron isotope study on BIFs from North China Craton.

The BIFs studied were formed at the Archean–Proterozoic transition period (2.5 Ga), and subjected to amphibolite-facies metamorphism. They consist of finely layered alternating beds dominated by magnetite and quartz respectively, with minor amounts of pyrite and hematite. The minerals of magnetite, hematite and pyrite were separated. After purification using anion exchange chromatography, Fe isotope ratios of the mineral separates were measured using a Nu Plasma HR MC-ICPMS in conjunction with a DSN 100 desolvating nebuliser. The results are expressed in \(\varepsilon\) units which are deviations in parts per 10\(^4\) from the same isotope ratios of the reference material IRMM-14. Fe isotope compositions of the mineral separates range in \(\varepsilon_{\text{57Fe/54Fe}}\) units from 1.1 to 20.9, 8.6 to 12.5, and 1.3 to 18.5, for pyrite, hematite and magnetite respectively. Another observation is that the Fe isotope compositions of pyrites are systematically heavier than corresponding magnetites in each samples.

The average Fe isotope compositions obtained from BIFs in this study for pyrite and magnetite are unusually high relative to the bulk silicate Earth, other BIFs in Transvall and Greenland, and MOR hydrothermal fluids. This suggests that only a small fraction of Fe(II) in sea water has been oxidised to Fe(III) to form the BIFs in Anshan area, which implies an atmosphere with low \(O_2\) contents at the time. Alternatively, this may imply that some fraction of Fe(II) has been precipitated as iron sulfide or carbonate, resulting relative enrichment of heavy isotopes in seawater, prior to the precipitation of BIF. Indeed, some archean pyrite deposits in North China exhibit very light Fe isotope signature.

As the contents of pyrite in the BIFs studied are <1%, the Fe isotope compositions of bulk rocks are predominated by magnetite. The fact that the Fe isotope compositions of pyrites are systematically heavier than corresponding magnetites in each samples suggests that these mineral pairs were re-equillibrated in terms of Fe isotopes during metamorphism.
Effects of source heterogeneity and upwelling rate on trace element distribution during mantle melting

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Several lines of evidence suggest that the melt generation and segregation regions of the mantle are heterogeneous consisting of chemically (enrich vs. depleted) and lithologically (peridotite vs. pyroxenite) distinct domains of variable size and dimension. Partial melting of such heterogeneous mantle source regions give rise to a divers range of basaltic magmas erupted on the sea floor. Although significant progresses have been made in understanding the processes of mantle melting using simple (e.g., batch, fractional, dynamic, and fluxed) melting models, none of the models identified can be readily used to study the effects of source heterogeneity and melt and solid flows on the distribution and evolution of trace elements and isotopes in the melt and residual solid during partial melting in an upwelling mantle column.

In order to better assess the role of source heterogeneity during mantle melting, we have undertaken a theoretical study of trace element and isotop distribution during partial melting in an upwelling mantle column. The 1-D version of the advection-diffusion-melting equation of McKenzie (1984, his Eq. A42) was solved analytically for both uniform and distributed melting rates and under the assumption of constant and uniform partition coefficient, porosity, melt and solid velocities. For simplicity, we neglected diffusion in the melt. Source heterogeneities of various forms (e.g., pyroxenite vein) were introduced into the melting column through initial and boundary conditions. Main results of our analyses to date can be summarized as follows. (1) Since melt flows faster than the solid, heterogeneities introduced at the base of the melting column are decoupled during melting and upwelling: while being diluted during melting, the incompatible element signatures of the source travel with effective velocities that largely follow the flow of the melt, whereas heterogeneities recorded by compatible elements follow mostly the solid matrix. Hence the overlaying mantle (above the pyroxenite vein, say) is cryptically metasomatized by the percolating melt derived from the pyroxenite. (2) When melting happens only in the lower part of the column (distributed melting), significant extent of metasomatism occurs in the upper mantle column. A lack of chromatographic separation among trace elements in lavas may indicate additional means of melt migration: i.e., flow through porous channels or open fractures. (3) The simple analytical solutions obtained in this study make it possible to invert for mantle source compositions through systemat studies in the future.

Examples illustrating the distribution and evolution of selected trace elements and isotopic ratios during partial melting of a pyroxenite-veind lherzolitic mantle will be discussed.

Deciphering the time of igneous activity in the Lavrion ore province, Attica, Greece: Manifestation of Late Miocene and Triassic magmatism

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The Lavrion area, known as a 3000 years old mining district, is part of the Attico-Cycladic Belt (ACB). A detachment fault separates the Lower Mesozoic metamorphic Basal Unit from the overlying Cycladic Blueschist Unit (Skarpelis, 2007). 9.4±0.3 Ma old granodiorite dykes and a Late Miocene granodiorite stock intruded the footwall of the detachment in a roughly N-S directed regional extensional stress field. With the aim of assessing the Miocene metallogenic evolution in Lavrion area, in conjunction with the igneous activity in the ACB, we dated by U-Pb of zircon (SHRIMP; GSC Ottawa) slightly deformed, hydrothermally altered porphyritic S-type granitoids occurring as sills along or within the hangingwall, close to the detachment fault. The zircon in cathodoluminescence (CL) displays euhedral long-prismatic crystals consisting either of a single oscillatory zoned, igneous domain or of a round (resorbed) inner core with relatively homogeneous CL and an oscillatory zoned, igneous rim. The resorbed character of the core, in combination with its homogeneous CL, are typical for zircons recrystallized under granulate-facies conditions. The cores and the igneous domains yielded (Tera-Wasserburg) lower intercept 206Pb/238U ages of 11.93±0.41 Ma and 8.34±0.20 Ma, respectively (error: 95% c.l.), interpreted as the time of a granulate-facies metamorphism (for the first time reported in ACB) and the time of magmatic crystallization, respectively. Emplacement was facilitated by the detachment fault. The dated S-type rocks of Lavrion, interpreted as partial melts of lower crustal granulites, are ca. 7-1 Ma younger than S-type granitoids in the ACB, also associated with an extensional tectonic regime. Above zircon ages constrain the time interval of active ductile to ductile-brittle deformation of the detachment fault.

Orthogneiss lenses within the metaclastic part of the Basal Unit in Lavrion (Kaesarian schists), previously considered of Tertiary age, yielded a lower intercept 206Pb/238U zircon age of 240±4 Ma interpreted as the time of crystallisation of the magmatic protolith. Opposite to earlier ideas about only Tertiary felsic magmatic rocks in Lavrion, our data show that there is an age diversity of the magmatic activity. The resulting age is consistent with the regional pattern of Triassic magmatism in the Hellenides.

Reference

Methane fluxes and turnover in permanent anoxia: In situ studies of the Dvurechenskii mud volcano (Black Sea)

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Cold seeps are often called oases of life in the deep sea for their rich chemosynthetic communities populating the seafloor. Many typical seep organisms like the giant tubeworms, diverse bivalves and mats of giant sulfide oxidizing bacteria have a considerable influence on the biogeochemistry of methane-laden seafloor e.g. by bioturbation, bioirrigation and by replenishing sulfate to the electronacceptor-limited sediments. Here we investigated the biogeochemistry of a gas-emitting cold seep system in permanently anoxic waters, where animal life is completely absent. At most cold seeps the methane rising from subsurface reservoirs is oxidized anaerobically with sulfate diffusing into the seafloor from the overlying bottom water. Normally the produced sulfide is further oxidized by chemical and microbiological processes with either Fe(III), nitrate or oxygen as terminal electron acceptor. In the Black Sea these electron acceptors are absent below the chemocline, thus the sulfide may be largely exported to the water column.

This study was carried out at the Dvurechenskii mud volcano (DMV, Sorokin Trough) during expedition M72/2 with RV METEOR and ROV QUEST (MARUM, Bremen) in the framework of the EU FP6 integrated project HERMES and the DFG/BMFB GEOTECHNOLOGIEN program MUMM.

The main questions of our investigation were 1) Where are the hotspots of methane emission and turnover at the DMV?, 2) How does the absence of bioturbation affect rates and distribution of anaerobic oxidation of methane?, 3) How does the absence of oxygen and nitrate in the bottom water affect pH gradients and sulfide fluxes?

To answer these questions, we carried out in situ microprofiler measurements of H2S, pH, redox, and temperature along a transect from the center of the mud volcano northwards to the outer rim. Methane-fueled sulfate reduction was measured in situ by using the INSINC incubator and methane fluxes were determined with a benthic chamber as well as by concentration measurements in gravity cores and bottom water. Our results show that fluid flow velocity strongly controls methane turnover and export at these anoxic cold seeps, suggesting that the absence of seep fauna reduces the efficiency of the benthic methane filter.

Stable Strontium (δ88/86 Sr) and U-Th systematics of cold-water corals as new proxy for Holocene changes of the Mediterranean outflow

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This study combines the stable strontium isotope method (δ88/86 Sr) after Fietzke and Eisenhauer (2006) as a potential paleotemperature proxy with MIC-ICP-MS (multi ion counting – inductively coupled plasma – mass spectrometry) U-Th geochronology on cold-water corals from the central Gulf of Cadiz. The sampled reef structure in 1325 m depth on top of the Captain Arutyunov Mud Volcano (MV) consists predominantly of dead Lophelia pertusa, accompanied rarely by living solitary corals (Flabellum sp., Dendrophyllium sp.). Potentially recorded environmental influences on these archives are significant water mass changes, e.g. variation of depth and intensity of the Mediterranean Outflow Water (MOW) due to climate changes, time intervals of marine methane emanation (surface-near gas-hydrate occurrence close to the coral site) and the mud volcano activity itself.

Assuming a temperature dependent strontium isotope fractionation during calcium carbonate precipitation temperatures were determined for the living solitary corals, ranging from 9 to 11.5 °C (typical error: ± 1°C). For comparison, during sampling the bottom water temperature was 8.96 °C and the lower MOW reached from 1075 to 1188 m depth with 10 to 10.5 °C. First U-Th age data reflect slow growth rates of 0.13 to 0.25 mm/year for the solitary corals.

However, the temperature correlation implies the stable strontium approach, which was originally deduced from reef building corals, as suitable for solitary species as well.

For the fossil Lophelia pertusa colonies the actual δ88/86 Sr data set indicates a range from 7.5 to 13 °C with a distinct U-Th age distribution over the last 10 ka, closely correlating with the water depth specific record of lower MOW published by Schönfeld and Zahn (2000). The implication of a lower MOW control on reef formation is supported by coincidence of its actual elevated position with the lack of living Lophelia pertusa at the sampling site.

The stable strontium isotope ratio δ88/86 Sr of biogenic carbonates may serve as a new paleo-temperature proxy for reef-building and solitary deep-sea corals and thus introduce new perspectives in paleoceanography, such as changes in intermediate and deep-sea temperature and ocean circulation.

References


Vapor-liquid fractionation of B, Li, and Cl stable isotopes: Experimental constraints at 400 and 450°C, 20 to 42 MPa

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We experimentally determined the vapor-liquid fractionation of the B, Li, and Cl stable isotopes in the systems H\(_2\)O-NaCl-B\(_2\)O\(_3\) and H\(_2\)O-LiCl. Experiments were performed at 400 and 450°C / 20 to 42 MPa. Vapor and liquid samples were analyzed for Na, B, and Li by inductively coupled plasma emission spectrometry. Isotopic ratios were determined by positive thermal ionization mass spectrometry. 

No coherent vapor-liquid fractionation of the different stable isotope systems is apparent. \(^{11}\)B has a preference for the vapor and fractionation increases along the individual isotherms towards lower pressure. The data have been fitted with a logarithmic function of the form \(1000 \ln \alpha_{v,l} = a + b \ln[(P - P_{sat}) + e^{c+\text{cutoff}}]\) and extrapolated to salt saturated conditions: maximum stable isotope fractionation is 1000 \(\ln \alpha_{v,l}(^{11}\text{B}) = 0.94 \text{ ‰ at } 400\text{°C and } = 1.43 \text{ ‰ at } 450\text{°C. Mass balance calculations show that for high degrees of fractionation fluid phase separation in an open system significantly alters the boron isotope signature of low-salinity fluids in hydrothermal systems. Comparing the results with natural oceanic hydrothermal fluids, however, indicates that other processes than fluid phase separation dominate the boron geochemistry in oceanic hydrothermal fluids.}

Contrary to the boron system, the lithium system indicates a slight preference of the heavy \(^{7}\)Li for the liquid. Measured fractionation is, however, very small and the data do not allow extrapolation of 1000 \(\ln \alpha_{v,l}(^{7}\text{Li})\) to salt saturated conditions. The data nevertheless suggest 1000 \(\ln \alpha_{v,l}(^{7}\text{Li}) \leq -0.5 \text{ ‰ at all studied conditions. The very small isotope fractionation indicates that even for fractionation in an open system the Li isotopic signature of vapor, liquid, and bulk system will not be altered by more than 1 ‰. The lithium stable isotopes are conservative tracer during aqueous fluid phase separation and any lithium stable isotope fractionation in natural hydrothermal systems reflect the combined effects of source reservoir and fluid-mineral interactions.}

For the chlorine system, no trend is apparent: At all studied conditions 1000 \(\ln \alpha_{v,l}(^{37}\text{Cl})\) is < 0.2 ‰ and switch between positive and negative values. Our data suggest a lack of notable stable isotope fractionation between vapor and liquid in the H\(_2\)O-NaCl system. This is at variance to the H\(_2\)O-HCl system, where recent data indicate significant vapor-liquid fractionation of up to 9 ‰.

Can millennial-scale geomagnetic field models improve time-integrated predictions of cosmogenic nucleic production rate scaling models?

Preliminary results using \textit{in situ} cosmogenic \(^{14}\text{C}\)

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\textit{In situ} cosmogenic nuclide (CN) production rates are typically determined by measuring CN concentrations in surficial rocks with well-constrained exposure histories. Scaling these time-integrated production rates to other locations with different exposure durations, though, requires knowledge or assumptions of how temporal and spatial geomagnetic field variations have affected instantaneous production rates. Previous attempts to quantify geomagnetic effects on CN production rate scaling have relied on various geocentric dipolar approximations to the effective vertical cutoff rigidity (\(R_C\)), driven by separate records of geomagnetic pole position and paleointensity (e.g., Lifton et al., 2005). However, the CN production rate scaling models in those studies are parameterized using detailed modern geomagnetic field representations. Applying dipolar paleomagnetic records spanning millennial time scales to scaling models derived using the modern geomagnetic field may lead to systematic errors in any calculated results.

A new continuous geomagnetic model covering the last 7 kyr (CALS7K.2) (Korte and Constable, 2005) may allow reduction of such errors by bridging the gap between detailed modern geomagnetic and simplified paleomagnetic models. I have developed a new model describing temporal and spatial variation in \(R_C\) for 0-7 ka and earlier, based on CALS7K.2, which explicitly accounts for non-dipole field effects while attempting to mitigate systematic scaling biases.

Scaling factors derived using the new \(R_C\) model predict significant longitudinal variability in time-integrated CN production, while predictions using dipolar geomagnetic approximations do not. One can test these predictions using \textit{in situ} cosmogenic \(^{14}\text{C}\) (in \textit{in situ} \(^{13}\text{C}\)) in quartz. Due to its short half-life, \(^{14}\text{C}\) attains secular equilibrium between production and decay after approximately 25 ky of exposure, at which point its measured concentration is only a function of its integrated average production rate. Preliminary \textit{in situ} \(^{14}\text{C}\) results from samples at secular equilibrium from 38°N and 3.5 km in Tibet and eastern California are consistent with the longitudinal variability predicted by the new model.

References


The influence of a method of sample preparation on element content in pore waters of sediments of Lake Baikal

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Pore waters always contain a certain quantity of suspensions which cannot be removed by means of usual centrifugation and filtrations. The content of some elements, partially or completely being in colloidal state in pore waters, will depend on quantity of fine dispersed matter. Our purpose was to find what elements are connected with colloidal particles in pore waters of the sediments of Lake Baikal and to estimate what effect will give ultracentrifugation in comparison with filtration. A core (20 cm, depth 1300 m) of Baikal bottom sediments was collected in Southern part of the Lake. Pore waters were separated from six horizons of sediments by centrifugation, filtered through 0.2 µm filters and subjected to ultracentrifugation (70000 rpm, 2h). Experiments were carried out in argon atmosphere to prevent change Red/Ox conditions. The solutions were analyzed by ICP-MS method. The content of Al, a measure of terrigenic matter, in filtered pore waters is significantly higher (in 7-140 times), than in solutions after ultracentrifugation. The content of other terrigenic elements (Be, Ti, Y, Zr, Nb, Pd, REE, Hf, Ta, Th, and Fe, Ga, Ge, Ag, Pb, Bi, U) in filtrates are also increased (2-1200 times). V, Cr, Cu, Se, Ba are less subjected to concentration on the particles – a degree of their enrichment is <2 times. The content of Li, B, C, Na, Mg, Si, P, S, Cl, K, Ca, Sc, Mn, Co, As, Br, Rb, Sr, Mo, Sn, Sb, I, Cs, W, Re, Ti does not change after ultracentrifugation.

Magmatic evolution and crustal accretion in the Northern Oman-U.A.E Ophiolite: New insights from LA-ICP-MS analysis of clinopyroxene

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The exceptionally well preserved Cretaceous Oman-United Arab Emirates (U.A.E.) ophiolite offers an ideal opportunity to study the original structure and composition of oceanic crust constructed by MORB magmas that show an increased role for water in their evolution, more akin to magmas from island arc or back arc basins.

Fieldwork has been conducted in co-operation with the British Geological Survey on the ophiolite sections in the U.A.E. This has led to the generation of geochemical data on basalts, dolerites and gabbros from the crustal section. These data record a complex history for the northernmost sections of the ophiolite. Initial magmatic events exhibit a MORB-like composition, indicating that the early crust formed at a ‘normal’ mid-ocean ridge. These primary events were followed by successive periods of magmatic activity, localised predominantly along major extensional faults, with each subsequent event exhibiting an increase in the subduction-related component. The northern Oman-U.A.E. ophiolite thus provides geochemical evidence for the transition from spreading- to subduction-related volcanism.

The use of a new LA-ICP-MS analytical technique has enabled trace element analysis of clinopyroxene crystals from individual gabbro units. With these data it has been possible to unlock the signatures of crustal gabbros and match plutonic units to their extrusive counterparts, providing a detailed chronology of crustal accretion events. Specifically two intrusive gabbro units are described, which represent discrete off-axis magma chambers that fractionated to feed upper extrusive units after ‘normal’ mid-ocean ridge processes had ceased. Geochemical and field characteristics of these units provide important constraints on the influence subduction-related fluids have on the amount of melting, mechanisms of magma fractionation and methods of crustal accretion at a fast-spreading ridge.

With the growing database of clinopyroxene trace element data this new LA-ICP-MS technique also offers significant potential for the identification of the tectonic environment of formation for cumulate rocks.
Analysis of aqueous Sr concentration in groundwater of carbon aquifer of Moscow artesian basin

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Underground waters of Carbon of Moscow artesian basin are enriched in Sr due to high Sr content in carbonate rocks of the area. The certain part Sr is from clays of confining layers contiguous to carbonate rocks.

The limiting factor of aqueous Sr enrichment is the solubility of Sr minerals. The aqueous Sr concentration curve (Sr=3.607-lnS+5.828, where S is salinity; R^2=0.508) is shown in fig below. Two reactions (dissolution of Celestite and deposition of Strontianite) occur simultaneously. It results in usually up to 8 - 10 mg Sr/l. In two samples the Sr concentration is even more: 13.8 mg Sr/l (DUBNA borehole, g2 layer of Upper Carbon) and 27.7 mg Sr/l (KLEPIKI, pd-ks layer of Middle Carbon).

The process of Sr accumulation is influenced by two major factors: the hydrogeochemical type of groundwater alteration along groundwater flow and delay of a groundwater filtration into direction of plunge the water-bearing layers.

Using thermodynamic approach the process of accumulation Sr looks as follows:

- Gypsum and Celestite dissolution brings SO_4 and Sr.
- Strontianite formation limits the aqueous Sr concentration, thus it is the regulating factor of accumulation Sr in ground waters Moscow artesian basin.

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Formosa Ridge, A cold seep with densely populated chemosynthetic community in the passive margin, southwest of Taiwan

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Chemosynthetic community and massive hydrate are two typical features appeared at cold seep environment. Mussel, clams, bacterial mats, and tubeworms also frequently found in the cold seep environments. In order to understand mechanism driving the chemosynthetic community found in the study area, ROV and Towcam surveys as well as core sampling were conducted on board the r/v Natsushima and r/v OR-I at the Formosa Ridge.

ROV Hyperdolphin survey showed that unusually densely populated chemosynthetic community appeared at water depth of about 1200 m in the passive margin southwest of Taiwan. Bathymodiolus Platifrons and Shinkai cronieri are two predominant macro fauna, patchy distributed on top of a stratigraphy high with clear Bottom Simulating Reflector (BSR) at depth. Mussel attached on porous carbonate with partially cemented mudstone tubes and laminate acting as gas and fluid conduit. Vent fluids are high in dissolved sulfide and methane. Δ13C of the authigenic carbonate lamina and vent tubes are as low as -56. Mussel shells, however, showed typical sea water carbon composition. Lower concentrations of pore water chloride indicate hydrate dissociation near surface.

Unlike other cold seep environment, no massive hydrate and tubeworms were found on the sea floor. The chemosynthetic community of the study Formosa Ride is supported by unusually high concentrations of dissolved sulfide and methane seeping through sea floor.
Competitive adsorption between tricarboxylic acids and phosphate

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The mobility and bioavailability of organic and inorganic ligands in soils and aquifers are dependent on interactions with mineral surfaces. Carboxylic acids are a group of organic ligands that have been noticed to be excreted by roots as a response to several stressful conditions, i.e. phosphorus depletion, iron deficiency and toxic aluminium conditions.

Citrate, a hydroxyl-tri-carboxylic acid, is known to be excreted by various plant species under all of the above mentioned conditions. The phosphate acquisition is thought to take place through dissolution of phosphate-rich minerals and/or through competitive adsorption between the organic acid and the nutrient on mineral surfaces. The present work focuses on the comparison of the competitive adsorption between citrate and phosphate on goethite (α-FeOOH) with that of two other tricarboxylic acids; tricarballylic acid and 1,2,4-butanetricarboxylic acid. Tricarballylic acid is identical to citrate without the hydroxyl group and 1,2,4-butanetricarboxylic acid has the same molecular structure as tricarballylic acid with one extra CH₂-group between two of the carboxylic groups. The aim of this work is to elucidate what effect small differences in structure and composition of otherwise similar organic ligands has on the ability to compete with phosphate for mineral sites.

In order to meet the research objectives, a combination of quantitative adsorption data and molecular spectroscopic data were collected. The work was made in series of batch experiments, measuring ligand adsorption as a function of pH. In-situ ATR-FTIR spectroscopy was extensively used to evaluate the speciation and adsorption mechanisms of phosphate and the carboxylic acids. In addition, ionic chromatography and atomic absorption spectroscopy were used to gain quantitative adsorption and dissolution data. Adsorption data of the three organic acids and of phosphate will be presented to illustrate the competitive adsorption in these systems and ATR-FTIR spectra will be used to explain the mechanisms behind the competition.

Laser Raman-spectroscopy study on fluid inclusions of sandstone-type uranium deposits in the Ordos basin, Northwest China

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Introduction

The Ordos basin is the second largest sedimentary basin in China. With the deep-going ore exploration, in-situ leachable sandstone-type uranium deposits have been discovered in several localities in different parts of the basin (Liu, 2005; Ling et al., 2006). This study focus on the compositions of fluid inclusions bearing in sandstones of these uranium deposits as well as their genesis.

Experiment and Results

The chemical compositions of fluid inclusions are determined with RM-1000 laser Raman spectroscopy produced by Renishaw Company, at the State Key Lab of Geol. Proc. & Mineral Res., China University of Geosciences. The results show that most of the fluid inclusions are mainly composed of H₂O, CO₂ and CH₄. The fluid compositions existing in different phase manifest their distinct original fluid genesis. The relative high concentration CH₄ captured in fluid inclusions indicates that original fluids might come from the natural gases widely spreading in the Ordos basin. The fluid inclusions formed and their components accumulated in the reduced condition, whereas uranium minerals deposited later when the oxygenation was dominated caused by uplifting of the Ordos basin during Mesozoic-Cenozoic. This study is of significance for understanding the uranium formation with multi-energy resources and mineral deposits coexisting in the Ordos basin.

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Characterization of hydrous species in hydrous and nominally anhydrous minerals by $^1$H solid state NMR spectroscopy

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Nominally H$_2$O-free minerals (NAMs) like olivine and pyroxenes are considered to be significant reservoirs for H$_2$O in the upper mantle (e.g., Bai and Kohlstedt), which would drastically influence a number of physical properties of the mantle and processes related to these. The presence of H in small amounts may dominate the point defect chemistry of these minerals. Thus, depending on the exact incorporation mechanism and structural environment, physical properties like electrical conductivity and strain rates change compared to the completely dry mineral. The coordination of H in NAMs has been inferred so far either indirectly from the measurement of transport properties (e.g., Kohlstedt and Mackwell, 1998) or by interpretation of IR spectra.

Here we present $^1$H-solid state NMR spectroscopy as an alternative way to study the structural arrangement of H in nominally anhydrous minerals. A number of gem quality single crystals of NAMs like diopside and olivine as well as hydrous minerals like hydrogроссular and analcime were selected and prepared for both IR and $^1$H-NMR spectroscopy. The NMR spectra of hydrous minerals, where the coordination of H is well known, are used as a reference for comparison with the NAMs (Yesinowski et al. 1988). The pure $^1$H NMR signals in NAMs were derived by suppressing the probehead proton and background signal with a special DEPTH pulse sequence (Corey and Ritchie 1988). It was possible to identify clear $^1$H-signals using this technique, despite the significant Fe-content and the small amounts of H (< 1000 ppm) of the samples.

Preliminary results show that protons in diopsides are located in the structure as isolated (no neighboring H present) hydroxyl groups of a single coordination type. The chemical shift of the very narrow single $^1$H-signal is at approximately 1.8 ppm, which excludes the formation of silanol groups, but implies an association with Al$^{12+}$ on a Si site, as was suggested by e.g., Stalder (2004).

References


The Deep Biosphere: Quantitative and taxonomic constraints through microbial lipids

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The deep biosphere contains up to one third of the total carbon in live cells of our planet (Parkes et al., 2000; Whitman et al., 1998). Recent studies have provided information on metabolic activities and quantities of deeply buried prokaryotic cells, while fundamental questions remain regarding the taxonomic composition (e.g. Biddle et al., 2006; Inagaki et al., 2006). For example, various techniques appear to disagree already at the domain level on who actually dominates this vast ecosystem.

We analyzed intact polar lipids (IPLs), a marker for live prokaryotic cells in a set of sediment samples from a depth range of 0.01 to 367 mbsf from sites at Peru margin, Cascadia Margin, Demerara Rise, and Equatorial Pacific (RV Sonne SO147, ODP Legs 201, 204, 207, and IODP Expeditions 301 and 311). The observed IPL concentrations range from 4 to 16,000 ng mL$^{-1}$ sediment and display a similar concentration-depth relationship as observed in a global compilation of direct counts of active cells (cf. Parkes et al., 2000). Surface sediments are clearly dominated by bacterial IPLs with possible admixtures of eukaryotic lipids. Concentrations of bacterial lipids decline rapidly within the first 10 cmbsf to levels significantly lower than those of their archaeal counterparts. The analysis of ODP/IODP samples from deeply-buried horizons shows evidence for bacterial lipids in about 20% of samples analyzed to date. On the basis of these observations in combination with results of degradation experiments of archaeal and bacterial IPLs under typical anaerobic sedimentary conditions (Pamela Rossel et al., unpubl. data), we interpret the predominance of archaeal IPLs as evidence for a far more important role than suggested by other techniques.

References

Anomalously low δ^{18}O values of oxygen dissolved in groundwaters at a uranium mine

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Atmospheric oxygen with a constant δ^{18}O value of +23.5‰ is the dominant source for molecular O₂ present in subsurface environments. In the subsurface, O₂ may be consumed by various processes including organic matter decay, respiration, and oxidation of reduced metals. Biogeochemical O₂ consumption reactions preferentially consume the ^{16}O over ^{18}O. As a result, isotopic composition of O₂ in the subsurface becomes ^{18}O enriched and the resulting δ^{18}O values are greater than the initial +23.5‰.

The isotopic composition of dissolved oxygen in groundwater samples collected at a uranium mine in northern Saskatchewan, Canada were characterized by anomalous ^{18}O depletion with associated δ^{18}O values as low as +4.4‰. Subsequent to these observations, air saturated water samples were irradiated at the nuclear reactor facility for 0.5, 1, 2 and 5 h. The isotopic composition of O₂ present in headspace yielded a trend of increasing ^{18}O depletion with increasing irradiation time (Fig. 1). These observations suggest that water radiolysis may be responsible for the anomalous ^{18}O depletion observed in northern Saskatchewan groundwaters in proximity of uranium bodies. Further testing is being conducted; however if the ^{18}O depletion observed in the groundwater is attributed to radiolysis, oxygen isotopic anomalies may prove to be an exploration tool for the uranium mining industry.

Figure 1: Isotopic composition of water dissolved oxygen showing a trend of increasing ^{18}O depletion with irradiation time.

Technology of accounting of water exchange parameters at prospecting and exploration of carbon dioxide-bearing mineral waters

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The developed technology is assumptive to partial automate evaluative of stage of investigation for carbon dioxide mineral waters to use informational analysis in the combination with the elements of the theory of “discerning forms” (Lisenkov A.B., Goppa V.D.) This is essentially heuristic approach, because it allows combining the apparatus of the theory “discerning forms” and the experience of experts, working in the regime of dialogue with computer technology. The new technology realizing in four stages:

1. The selection of initial exponents for the informational research models. The circle of the exponents is expedient to limit to the list a-priory influential or changing the composition of carbon dioxide mineral waters. In our opinion for these purposes could be allotting next groups of the exponents: landscape, geologic, hydro geologic, tectonic and man-caused load, as well as three groups of the exponents (landscape, tectonic, man-caused load) might be obtaining with consume of the result of encode the SFP. The remained exponents might be received from the results of preliminary and particulars research, experience of exploitation, so as with consume GIS-technology.

2. The formation informative search models are emanating in two stages: on first stage it has to estimate information of the initial exponent’s correlate with function of purpose and selection informative. On second stage, from single indications we composing complex by the method of sorting and calculating the information likewise correlate with function of purpose. From the most informational compound indications is composing train matrix, which presents it the image of learned region and circulation carbonaceous mineral waters (informational search model).

3. Testing informative model accomplishing by the way juxtaposition the test part with form. In case if the model is effective, so on it basis realizing resolution conjectural problem (search sections are suitable for putting-up explorative works), i.e. accomplishing next fourth stage. In the other case is realizing return to the first and second stages. The experience of structure similar models for Kislovodsk territory group of entrails the carbon dioxide mineral water has shown it adequate efficiency and combination the informative indications is stressing the role of thickness water reservoir breed in forming chemical composition of mineral water, the role of tectonic certain configuration and extension in orientation fluid’s streams and also the influence of natural or man-caused border of pressure on mass carrying carbonic acid.

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Is mid-ocean ridge basalt chemistry a function of melt-rock reaction in the lower oceanic crust?

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Gabbroic rocks recovered from the Kane Core Complex (23°N, Mid-Atlantic Ridge), contain evidence for reactions between preexisting cumulates and melts migrating in diffuse, cm-wide channels. Evidence for melt-rock reaction includes disequilibrium compositions (anomalous Ti-Cr relationships in clinopyroxene, anomalous plagioclase-clinopyroxene equilibria) and textures indicative of mineral dissolution. The reaction that formed the reaction channels was: Melt 1 + olivine + high-An plagioclase = Melt 2 + high-Mg clinopyroxene + low-An plagioclase.

Modeling of this reaction as an assimilation-fractional crystallization process revealed that melts undergoing this reaction are enriched in MgO and Al₂O₃, and depleted in CaO. As such, this melt-rock reaction process can account for the global MgO-Al₂O₃-CaO systematics of mid-ocean ridge basalts (MORB). Previously, these systematics, as well as the occurrence of high-Mg clinopyroxene, were attributed to fractionation of mid-ocean ridge basalts in the upper mantle at elevated pressures. However, our modeling shows that the melt involved in the reaction yields increasingly higher pressures as the reaction proceeds, suggesting that such pressures may be artifacts of melt-rock reaction. In addition, our model produces high-Mg clinopyroxene. We suggest that lower crustal melt-rock reaction may significantly influence MORB chemistry, and that calculated pressures are overestimated as a result.

Transcription of E. coli on stringent promoter enhanced by nickel stress

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Nickel is proved to be utilized by a variety of bacteria for function and survival, however, high concentration of nickel is toxic to cells. Therefore, regulation of nickel import and export is critical process for bacteria to allow for optimal growth and resist to nickel stress.

In bacteria, control of transcription initiation of RNA polymerase on different promoters is the key step for directing the appropriate cellular response to environmental changes. Generally, bacterial promoters could be divided into two classes: stringent promoter (e.g. rrnB P1, pyrBI) and non-stringent promoter (e.g. lacUV). In this study, two strains RLG1319 and RLG1350 containing lacUV5-lacZ and rrnB P1-lacZ respectively were constructed from wild type MG1655 of E. coli. Compared with RLG1319 and MG1655, which were rarely affected at the given concentrations of nickel, the growth of RLG1350 was inhibited by the nickel (doubling time was 55, 60, 80 and 125 min at the concentrations of 0, 0.2, 0.5 and 0.8mM) but the relative β-galactosidase activity of the growing cells was augmented with the increase of nickel concentrations. Moreover, the transcriptional activity of RNA polymerase on stringent promoter was significantly higher than that on the non-stringent promoters at both log phase (OD600=0.4) and stationary phase (OD600=0.8). The mechanism of bacterial transcription on stringent promoters regulated by nickel is required to disclose in the future.
Highly siderophile element (HSE) compositions of Gakkel abyssal peridotites: Effects of serpentinization and constraints on accretion processes in early Earth

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Both fresh and typically serpentinized abyssal peridotites from the ultra-slow spreading Gakkel Ridge, Arctic Ocean, have been selected for HSE analysis (Os, Ir, Ru, Pt, Pd and Re). All but two harzburgites are fertile lherzolites with very low degree of partial melting. Previous Os isotopic studies indicate that the harzburgites have been subjected to low-degree partial melting in the early Proterozoic [1]. Comparison of HSE data between the altered rims and their corresponding fresh cores and between the fresh peridotites and serpentinites suggests that both Pd and Re are potentially affected by seawater alteration, whereas other HSE are not. The fractionation of PPGE (Pt, Pd) and Re from IPGE (Os, Ir, Ru) in Gakkel abyssal peridotites indicates that this is possible even at low degrees of partial melting (5-12%). Both Pd/Ir and Pt/Os show positive correlations with 187Os/188Os ratios, which cannot be explained by percolation of silicate/sulfide melts. We interpret these correlations to reflect the binary mixing of depleted and fertile components. The depleted component with low ratios of Pd/Ir (also Pt/Os) and 187Os/188Os represented by the harzburgites might be recycled ancient oceanic lithosphere or delaminated sub-continental lithospheric mantle (SCLM). The fertile component could have PUM-like HSE pattern and 187Os/188Os ratios in its history. The relationships of HSE/Ir ratios with both 187Os/188Os ratios and bulk Al2O3 contents in the fresh spinel lherzolites are used to estimate the HSE pattern of the PUM. We confirm the previously inferred non-chondritic HSE budget in the PUM [2], i.e., chondritic Os/Ir and Pt/Os ratios but supra-chondritic ratios of both Ru/Ir and Pd/Ir, which can neither be explained by secondary percolation of silicate/sulfide melts nor by addition of outer-core metals. It is also in conflict with the compositions of all known chondritic meteorite classes.

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[1] Liu et al., submitted.

Important roles of sulfur cycling in karstic catchment erosion, Southwest China

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In southwestern China, there is a large area (about 600,000 km2) of diverse karstic landscape, with well-known eco-environmental problems of land-degradation and rocky kastification. Sulfur isotopic compositions of sulfate from rain, river, ground water and soil leachate in karstic areas were determined to understand the linkage between sulfur cycling and catchment erosion.

The sulfur isotopic compositions of sulfate in the studied area show that a relative large part of sulfate ion comes from oxidation of sulfide mineral and organic sulfur. Combined with carbon isotope studies and water chemical composition, the sulfur isotope study suggests that carbonate rocks in the catchment were weathered by both sulfuric and carbonic acids. Meanwhile, the carbon isotopic compositions of dissolved inorganic carbon in the surface and ground water of the karstic catchment show a large contribution of carbon that was derived from oxidation soil organic matter. In conclusion, the karstic catchment in southwestern China has a high weathering rate and rapid loss of nutrients due to coupled sulfur and carbon biogeochemical cycling.

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Zoned zircon from eclogite lenses in marbles from the Dabie-Sulu UHP belt: A clear record of ultra-deep subduction and fast exhumation

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Eclogite lenses in marbles from the Dabie-Sulu ultrahigh-pressure (UHP) terrane are deeply subducted metasedimentary rocks. Zircons in these rocks have been used to constrain the ages of prograde and UHP metamorphism during subduction, and later retrograde metamorphism during exhumation. Inherited (detrital) and metamorphic zircons were distinguished on the basis of transmitted light microscopy, cathodoluminescence (CL) imaging, trace element contents and mineral inclusions. The distribution of mineral inclusions combined with CL imaging of the metamorphic zircon make it possible to relate zircon zones (domains) to different metamorphic stages. Domain 1 consists of rounded, oblong and spindly cores with dark-luminescent images, and contains quartz eclogite-facies mineral inclusion assemblages, indicating formation under high-pressure (HP) metamorphic conditions of T = 571-668 °C and P = 1.7-2.02 GPa. Domain 2 always surrounds domain 1 or occurs as rounded and spindly cores with white-luminescent images. It contains coesite eclogite-facies mineral inclusion assemblages, indicating formation under UHP metamorphic conditions of T = 782-849 °C and P = 5.5 GPa. Domain 3, with grey-luminescent images, always surrounds domain 2 and occurs as the outmost zircon rim. It is characterized by low-pressure mineral inclusion assemblages, which are related to regional amphibolite-facies retrograde metamorphism of T = 600-710 °C and P = 0.7-1.2 GPa. The three metamorphic zircon domains have distinct ages; sample H1 from the Dabie terrane yielded SHRIMP ages of 245 ± 4 Ma for domain 1, 235 ± 3 Ma for domain 2 and 215 ± 6 Ma for domain 3, whereas sample H2 from the Sulu terrane yielded similar ages of 244 ± 4 Ma, 233 ± 4 Ma and 214 ± 5 Ma for domain 1, 2 and 3, respectively. The mean ages of these zones suggest that subduction to UHP depths took place over 10-11 Ma and exhumation of the rocks occurred over a period of 19-20 Ma. Thus, subduction from about 55 km to more than 160 km deep mantle depth took place at rates of approximately 9.5-10.5 km/Myr and exhumation from depths about 160 km to base of the crust at about 30 km occurred at approximately 6.5 km/Myr. We propose a model for these rocks involving deep subduction of continental margin lithosphere followed by ultrafast exhumation driven by buoyancy forces after break-off of the UHP slab deep within the mantle.

Relationship between Hg and sulfur in coal from Huaibei coalfield, China

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Many authors have reported that Hg in coal can exist in solid solution within pyrite. Correlations between sulfur and Hg are often attributed to this mode of occurrence and are most common in coals that are extremely enriched in Hg.

The result of this study shows that coal samples from the Huaibei coalfield have relatively low sulfur values (average 0.59%). The correlation coefficient between ash and sulfur is -0.08, indicating that sulfur in the Huaibei coals has an intermediate (organic and inorganic) affinity. In a study of 29 coal samples from the Huaibei coalfield, we observed that organic sulfur is the dominant sulfur form when the total sulfur is near 0.5%. Some literatures report that organic sulfur compounds can capture Hg and result in the enrichment of Hg in coals.

The conclusion shows the relationship between Hg and sulfur in all 29 coal samples that we examined; note that the correlation coefficient is only 0.17 (n=29). Interestingly, and it shows a significant positive correlation between Hg and sulfur (n=21, R=0.64, p<0.05) is obtained by excluding the eight samples from the No. 5 and 7 coal seams, which were influenced by a magmatic intrusion. This suggests that the magmatic intrusion not only increased the concentration of Hg in seams 5 and 7, but also changed the mode of Hg occurrence in these seams. The significant, positive correlation between Hg and sulfur in coals from the No. 3, 4, and 10 seams suggests that Hg in these coal seams is bound to both organic sulfur moieties and within sulfide minerals.
Fluorine in Chinese coals and its health impact

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The health problems caused by fluorine released during coal combustion are more extensive than those caused by arsenic. More than 14 provinces and more than 30 million people in China suffer from various forms of fluorosis, and about 15 million people have been diagnosed as having fluorosis. More specifically, around 10 million people in Guizhou Province and surrounding areas suffer from various forms of fluorosis. In Beimen Zheng and Hua Chun in Guizhou, about 78% of the inhabitants are diagnosed as having skeletal fluorosis including osteosclerosis. Almost every family in this district has members suffering from skeletal fluorosis with limited movement of the joints, and outward manifestations such as knock-knees, bow legs, and spinal curvature. In Xiaotang Zheng, Pengshui, Sichuan province, among 5633 residents, there are about 98% of the residents suffering from tooth enamel mottling (dental fluorosis).

The authors carried out a series of fluorosis surveys in Guizhou. In a survey of one elementary school, among 57 students, only one student was found to be free of dental fluorosis, while 99% of the student population was diagnosed as having dental fluorosis. During these surveys, the authors also found that the youngest patient was about 1 year old. Typical signs of fluorosis include mottling of tooth enamel (dental fluorosis) and various forms of skeletal fluorosis.

TEM investigation of the non-oxidative dissolution of galena (PbS) nanoparticles in a hydrochloric acid solution

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Galena (PbS) is one of the most common base metal sulfide minerals in nature. The dissolution of galena in acid solution can be an important reaction controlling the transport and transformation of Pb in natural waters. Moreover, sulfide nanocrystals have been found in the natural environment as a result of bacterial metabolism (Labrenz et al., 2000) or the breakdown of sulfides and silicates (Hochella et al., 2005) which has sparked an intense interest in understanding the dissolution mechanism of sulfide nanocrystals. Chemical properties of crystalline materials are known to be dramatically influenced by crystal size, especially for dimensions of 100 nm or less (Alivisatos, 1996). Nevertheless, much is still unknown about the size-dependence of dissolution. As a result, we are studying the structure and dissolution of galena nanocrystals. This work not only is important for understanding the effects of mineral size on geochemical processes, it also has implications for environmental remediation and the impact of nanotechnology on the environment.

Bright-field TEM and HRTEM have been applied to investigate the morphology and structural characteristics of galena nanoparticles. Galena nanoparticles ~15 nm in diameter were synthesized via variations on a wet chemical method reported by Joo et al. (2003). HRTEM images of the galena nanoparticles exhibit lattice patterns, demonstrating their highly crystalline nature. The nanoparticles aligned along two principal lattice directions, [100] and [110], have been studied most carefully. {100}, {110}, and {111} faces are presented on nanoparticles and {100} faces are more developed than {110} faces, resulting in a truncated cubic shape. By comparing the bright-field TEM and HRTEM images of pre- and post-dissolution nanoparticles, the dissolution rate can be determined by calculating the size change versus time. Shape and structure evolution can also be observed, which will provide important information for understanding the dissolution mechanism.

References
Melt percolation in Songshugou ultramafic massif

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The Songshugou ultramafic massif is located to the north of the Shang-Dan fault, intruding into the Proterozoic Qinling Group in the eastern Qinling Mountains, central China. It is the largest Alpine-type ultramafic body in China, covering an area of ~20 km². Remarkably, this massif consists mainly of dunite (~80%) with minor harzburgite, and olivine diopsidite etc. Harzburgite occurred as lens in the dunite, while olivine diopsidite occurred as vein in the margin of the body.

The formation and tectonic affinity of the Songshugou ultramafic massif is very important for understanding the formation and evolution of the Qinling orogenic belt. Published results however, do not agree with each other [1-3], leading to different models for the early history of the Qinling orogenic belt and the interaction between the North and South China blocks.

Here we show LA-ICP-MS for olivine grains of a transition from dunite to harzburgite in the Songshugou ultramafic massif, show compositional variations. Ni and P are lower, whereas Sc, and incompatible elements, Ti, V, Cr, Rb, Sr, Y, Zr, Nb, Pb and REE, are higher in olivine grains in dunite than those in harzburgite. These observations can be plausibly interpreted by reaction of lherzolite and/or harzburgite with melt through porous percolation flow at high melt/rock ratios, similar to the melt percolation model proposed for dunite in other places [4,5].

The north Qinling orogenic belt is believed to be the result of backarc collision [6]. We propose that the Songshugou massif was part of the depleted mantle wedge peridotite during the early subduction along the Shan-Dan fault, which was intensively recasted through melt percolation. These results provide more constraints on the evolution of the Qinling orogenic belt.

References

The Paleoclimatic records of stalagmite traced by stable isotopes from Liangfeng cave in Southwest, China

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Speleothems especially stalagmite are important repositories of Paleoclimatic and Paleoeocological-Paleoenvironmental data. Based on the systematical studies of the sedimentary characteristics and the stable carbon (oxygen) isotopes, the Paleoclimatic Records of stalagmite from Liangfeng cave (E108°02′29″, N25°16′21″) in Southwest, China, have been made, which gives records from 14220 to 1570 aBP as follows: 14220-10500 aBP, Among Last Glaciation to Holocene, theδ13C values of stalagmite varies from –9.314‰ to –7.290‰, average –8.552‰. Theδ18O values of stalagmite varies from –5.651‰ to –6.942‰.

10500-9300 aBP, The temperature increased after the end of Younger Dryas, theδ13C values of stalagmite varies from –10.377‰ to –9.267‰, average –9.910‰, the vegetation above Liangfeng cave be dominated by C3 plants. Theδ18O values of stalagmite decreased obviously, varies from –7.420‰ to –6.077‰, average –6.854‰, rainwater increased and Southwest monsoon was strong.

9300-8300 aBP, The temperature fluctuates obviously along with the changes ofδ13C values (varies from –10.155‰ to –9.096‰, average –9.712‰) of stalagmite, and the proportion of C3 plants of vegetation above Liangfeng cave was unsteady. Theδ18O values of stalagmite varies from –6.796‰ to –6.260‰, average –6.490‰, the affect of East-Asian monsoon increased.

8300-3100 aBP, The temperature increased obviously, theδ13C values of stalagmite is much low (average –9.910‰), the vegetation above Liangfeng cave be dominated by C3 plants. Theδ18O values of stalagmite changes greatly, varies from –7.373‰ to –5.047‰, indicated that the climatic of monsoon is unsteady.

3100-1570 aBP, Theδ13C values andδ18O values of stalagmite increased greatly, theδ13C values varies from –12.097‰ to –6.495‰, average –10.275‰, theδ18O values varies from –8.650‰ to –4.677‰, average –6.854‰, the vegetation above Liangfeng cave be dominated by C3 plants mainly, the climatic of monsoon is unsteady.

Reference
The characteristics of tungsten mineralization in Nanling metallic province, South China

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Introduction

The Nanling metallic province is a famous tungsten metallic belt in South China. These tungsten deposits with close relation to the Yanshanian (J3) igneous activities have characteristics of multi-stages of mineralization (Xiao et al., 2006). This paper discusses factors controlled the tungsten formation in Nanling metallic province.

Experiment and Results

The chemical compositions of fluid inclusions are determined with RM-1000 laser Raman spectroscopy produced by Renishaw Company, at Institute of Geology & determined with RM-1000 laser Raman spectroscopy at Institute of Geology &

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Mesozoic magmatic activities of western Shandong (Luxi), China

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Mesozoic intrusions and volcanic rocks are widely distributed in the western Shandong Province (Luxi). Field relationships and available K-Ar, 40Ar-39Ar and U-Pb zircon ages (Tan and Lin, 1994; Xu et al., 1993; Xu et al., 2004a, b, c; Liu et al., 2004; Zhang and Sun, 2002; Qiu et al., 2001; Guo et al., 2003; Zhang et al., 2004, 2005) suggest that the magmatic activities mainly took place in Luxi during the late Mesozoic, and this area may underwent a quiet period in magmatic activity from 185Ma to ca.130Ma (Zhang et al., 2005). Mesozoic mafic dike swarms are widespread in Luxi. Comparatively few studies, especially precise dating, have been carried out on the voluminous mafic dikes in Luxi. Herein, we present the first precise U-Pb isotopic data on zircons obtained from two mafic dikes. Detailed SHRIMP zircon U-Pb dating yields emplacement ages of 144±2Ma and 143±2Ma for the two mafic dikes from Luxi (Mengyin and Zichuan). This study thus indicates that there did exist magmatic activities between 185 and 130Ma.

Acknowledgments

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References


Si and O isotopic evidence for the genesis of the secondary quartz in red weathering crusts of carbonate rocks in Guizhou Province

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In our previous study, the well-crystallized quartz had been founded in many in situ weathering crusts of carbonate rocks in Guizhou Province, which have been demonstrated the possibility of dating the weathering processed by the method of fission track dating. So, the genesis of the well-crystallized quartz is the key to date the weathering crusts of carbonate.

This paper focuses on the use of the ratio of $\delta^{18}O$ and $\delta^{30}Si$ of well-crystallized quartz, extracted from in soil layer of three weathering crusts. The ratios of $\delta^{18}O$ of well-crystallized quartz have a narrow range from 17.3-22.7‰ (SMOW), which were more positive than igneous rocks (8-10‰), metamorphic rock (10-16‰) and Hydrothermally modified rock (4-10‰), similar to the chert bearing in the low temperature-formed dolomite (14-24‰) and authigenic quartz (20-34‰) in sandstone in Mississippi river, implying the supergene genesis of well-crystallized quartz. Furthermore, the ratios of $\delta^{30}Si$, ranging from 0.8‰ to 1.7‰, were more positive than the crystalline rock, kaoline, diatomite and quartz veins, but overlap the shallow marine radiolarians-bearing siliceous rocks and siliceous dolomite, which implied the quartz were precipitated in low-temperature environment too. Based on the Si and O isotopic evidence, it is deduced that the well-crystallized quartz was secondarily precipitated from Si-rich weathering fluids during weathering processes of carbonate rocks.

According to the argillaceous soil layer lacking of enough space for the precipitation of quartz and well-crystallized quartz was found in small cave or cranny underlying parent rock in field, it can be confirmed that the quartz was precipitated in parent rock. That is to say, the age of secondary well-crystallized quartz in soil layer was the upper limit or oldest age of weathering processes of carbonate rock in Guizhou Province.

Acknowledgments

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Revised petroleum migration history in the Nanbaxian area of the northern Qaidam Basin (NW China): Constraints from oil-bearing fluid inclusion analyses

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The Nanbaxian area is the presently largest oil-gas producing provinces in the northern Qaidam Basin, NW China. Previous studies have suggested only the northern Middle Jurassic sources mainly feed the reservoir here, with little contribution from the southern Lower Jurassic mudstone. In this study, we obtained new insights on petroleum migration history based on analyses on hydrocarbon fluid inclusions.

Free oil in intergranular pores and petroleum in inclusions hosted by mineral grains of reservoir sandstone samples were analyzed by GC and GC-MS. Analytical results show that there is a distinctive difference of molecular geochemical signatures between the free and inclusion oils, including the peak carbon number present in GC chromatogram, the ratio of pristane relative to phytane, etc. Specifically, the value of tricyclic terpane C19/C20 was suggested as good oil-oil and oil-source correlation proxy by previous authors. Thus, as this value is greater than and lower than 1.0 for free and inclusion oils, respectively, we proposed that there were at least two oil charges ever happened, with the Middle Jurassic mudstone derived hydrocarbons charging firstly and the Lower Jurassic oils arriving later.

Petrography shows that there mainly exist three different fluorescence color hydrocarbons: yellow, yellow-green and brown orange. This indicates a complex petroleum charge history. The histogram of Th data shows three populations with modes at around 60°C, 70-80°C, and 100-110°C. Combined with the burial and paleotemperature history, this reveals that there include mainly two oil charge episodes in Early and Late Paleogene, respectively. In addition, the highest Th range (100-110°C) was indicative of gas charging during Neogene.

In summary, petrographic and geochemical investigations of oil-bearing fluid inclusions tend to suggest a revised petroleum migration history. The complexity here may be attributed to the two hydrocarbon source kitchens and the effect of fault-controlled petroleum migration.
Phases relationships in the actinide waste forms with a garnet structure

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Complex oxides with a garnet-type structure (sp. gr. Ia3d) are suggested for long-lived actinide waste immobilization (Yudintsev et al., 2007). Three cationic sites in the structure provide for simultaneous incorporation of actinides and other elements into lattice. The highest actinide content (30 wt.%) was found in the ferrate garnet, where the “B” and “X” sites are filled in Fe$^{3+}$. General formulae of the phases corresponds to $\text{VIII}_3\text{VIII}_2\text{VII}_3\text{VII}_2\text{X}_3\text{O}_{12}$, where “A” = Ca$^{2+}$, REE$^{3+/4+}$, An$^{3+/4+}$; “B” = An$^{4+}$, Zr$^{4+}$, Fe$^{3+}$; “X” = Fe$^{3+}$. We have summarized data on the phases relations and compositions in ceramics of the garnet stoichiometry doped with typical impurities of actinide waste (Na, Al, Cr, Mn, Ni, Si, Zr). 50 samples were produced by cold pressing and sintering method at 1300–1500°C and examined with XRD and SEM/EDS. Temperature in this range has a little effect on the phases composition. Addition of Al and especially Si reduced actinides solubility in the garnet structure resulting in appearance of actinide oxide (Fig. 1). Na and Si in precursor leads to decreasing of melting point and formation of glass. High corrosion products (Cr, Ni) content in the initial mixture resulted in appearance of spinel. This work was supported by the Russian Foundation for Basic Research (project 05-05-64005) and the U.S. DOE.

Figure 1: Formation of ThO$_2$ (white) in garnet-based (gray) sample as result of addition of silica into the initial batch.

Reference

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LAM ICP study of cloudy diamonds: Implications for diamond formation

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Cloudy centers of octahedral diamonds from the Internationalnaya and Yubileynaya Mines (Yakutia) have been studied by LAM ICP. They are abundant in nanometric melt-inclusions, consist of multi-phase assemblages (silicates, oxides, carbonates, sulfides, brine and fluid bubbles) (Logvinova et al., 2006). The centers (dark zone) of the cloudy area show the increase of TRE content of two orders of magnitude comparing to the clear periphery (Diamond 1). Abundance of TRE and La/Yb$_n$ ratios are close to those of kimberlite melts. Two-folded REE patterns are indicative of multistage melt percolations. The light matter often reveal Y dips common for diamonds. Diamond 2 shows Ta, Nb, Zr, Hf peaks typical of picroilmentines. Inclined REE for centers may suppose crystallization of protokimberlite melts. Multiplied zonation and polymict inclusions in many diamonds suggest a complex model for diamond growth near protokimberlite magmatic systems at which the evolved ultramafic melts splite to form sulfide, silicate and carbonate liquids during the cooling when they interact with surrounding peridotites and eclogites. The TRE patterns show mixed sulfide (Pb, Cu) and silicate melts signatures differing from spongier (Rege et al., 2003) and coated diamonds (Afanasiev et al., 2005). The abundance of Ba, U, Pb, high Cu/Ni ratio and Eu anomalies may suggest admixture of subduction components from the wall rock eclogites.

Figure 1. Trace element pattern for dark and light zones from cloudy diamonds.

Reference
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Rege S., Rondi M., Griffin W.L. *et al.* (2003) *8IKC Abs* FLA0087
Assessing the importance of ab- and adsorption to the gas-particle partitioning of different POPs

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The gas-particle partitioning of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) was examined (i) by re-interpreting results from controlled field experiments and (ii) in diurnal samples taken in the New Jersey - New York City (NJ) region. In the controlled field experiments, aerosol-laden filters were exposed to elevated concentrations of PCDD/Fs. Gas-particle partitioning coefficients, $K_{ps}$, were significantly correlated with octanol-air partitioning coefficients, $\log K_{oa}$. The regression of all individual datapoints resulted in the following best fit ($r^2 = 0.74$, $n= 87$):

$$\log K_{ps, \text{meas}} = 1.00 (\pm 0.13) \log (10^{-12} f_{om} K_{oa} / \rho_{oct}) - 0.15 (\pm 0.48).$$

We interpret this as showing that the ability of organic matter (OM) to absorb PCDD/Fs is generally well described by the octanol-air partitioning model ($f_{om} K_{oa}$).

Results will be compared to previous observations of the gas-particle partitioning of PAHs.

At the NJ land-based sites, samples were taken and analyzed for organic (OC) and elemental carbon (EC), gaseous and particulate PCDD/Fs. $K_{ps}$ were significantly correlated with the $f_{om} K_{oa}$ approach. Adsorption to the GFF and possibly to BC will have contributed to the observed $K_p$ values. Gas-particle predictions based on BC adsorption and OM absorption, with $K_p = f_{om} K_{oa} (10^{12} \rho_{oa}) + f_{BC} K_{BC, air} / (10^{12} \rho_{BC})$ resulted in $K_p$ predictions that were close to measured values.

In favour of adsorption to the GFF being the major reason is that NB displayed highest $K_p$ values, which was also most prone to this sampling artefact based on relatively low sampling volumes and TSP concentrations. In addition, while adsorption to BC would result in better prediction of $K_p$ values, no influence of $f_{BC}$ or $f_{BC}/f_{om}$ ratios was seen, suggesting that it was of lesser importance in our sample set.

Fe$^{3+}/\Sigma$Fe in lower mantle (Mg,Fe)O:
Calibration of the “flank method”

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The lower mantle, which represents more than half the Earth by volume, is dominated by (Mg,Fe)(Si,Al)O$_3$ perovskite and ferropericlase (Mg,Fe)O. Studying these phases are therefore critical to determining redox conditions and their consequences for mantle properties and dynamics. Studies have shown that the Fe$^{3+}$ concentration in (Mg,Fe)(Si,Al)O$_3$ perovskite is essentially insensitive to oxygen fugacity; hence our attention is turned to (Mg,Fe)O. Our goal is to calibrate the “flank method” [1] on synthetic (Mg,Fe)O using the electron microprobe, and then apply the method to determine Fe$^{3+}/\Sigma$Fe in ferropericlase inclusions from lower mantle diamonds.

Initial experiments focused on synthesis of polycrystalline (Mg,Fe)O with varying Fe/Mg and Fe$^{3+}$ concentrations with run product characterisation using transmission electron microscopy, X-ray diffraction and Mössbauer spectroscopy. However electron microprobe measurements of the X-ray emission $L\beta/L\alpha$ ratios showed up to 10% variation, likely due to the porous nature of the sample surfaces, so further synthesis was performed using a multianvil press to obtain single crystals. The reproducibility of $L\beta/L\alpha$ measurements showed dramatic improvement, and experiments are continuing in order to generate a suite of high quality crystals over a wide composition range. The use of enriched $^{57}$Fe enables Mössbauer measurements to be carried out on the same sample used for the electron microprobe measurements, and an ongoing parallel study on natural garnets shows promising results for this approach.

References
**Nd isotopes as tracers as crustal rejuvenation**

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Neoproterozoic rocks in SW Iberia are largely exposed in the Central Iberian and the Ossa Morena zones. Though different to each other, both areas witness for development within, or adjacent to, an active margin setting during the Late Neoproterozoic (Cadomian orogen). In the Palaeozoic, the following tectonic stages are recognised: 1) rifting event (Cambrian-Early Ordovician), 2) passive margin stage (Ordovician-Silurian-Early Devonian), and 3) Variscan Orogeny. Nd isotopic composition has been determined on fine grained, low-to very low-grade metasedimentary rocks, mainly shales. εNd(T) values range from +2.1 to -13.9. Significant excursions to less negative values between -3 to +2.1 are interpreted to record periods when the corresponding basins were significantly supplied of juvenile components from mantle sources. The εNd(t) values are negative in both areas and do not display any sharp changes during the Palaeozoic; a signature commonly found in recycled crustal-derived sediments. The isotopic data are consistent with the Ossa Morena and Central Iberian Palaeozoic successions being derived from a polycyclic mixture of old crust (≥ 2 Ga) and younger crustal components, coeval with the recorded orogenic and rifting phases. In summary, Nd isotope systematics points to clear differences between the two zones in Neoproterozoic times and significant similarities during the Palaeozoic.

**Do orogenic peridotites preserve platinum-group element systematics of mantle melting processes?**

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Most recent estimates of the Primitive Upper Mantle (PUM) composition allow significant deviation of Ru/Ir (2.03) and Pd/Ir (2.06) above chondritic values. The rationale behind PUM estimates is that fertile and refractory peridotites are products of a single episod of partial melting and melt extraction. The paradigm has now been questioned for a number of orogenic peridotite massifs such as Lanzo (Italy), Ronda (Spain), Beni Bousera (Morocco), Horoman (Japan) and Lherz (France), the type-locality of lherzolites. Harzburgites of residual origin (Ir N > 1.0; Re/OsN = 0.10-0.15; Pd/IrN = 0.1-0.4; N = PUM-normalized) have been identified in every massif. They contain little or no base-metal sulfide (BMS) : at Lherz, the PGE budget is accounted for by refractory discrete platinum-group minerals (laurite-erlichmanite; malanite-cuprorhodsite; Pt-(Ir)-rich alloys). Orogenic lherzolites display PGE concentrations and PGE patterns close to PUM estimate while showing many features of extensively percolated abyssal peridotites with regard to BMS. The BMS occur as ameboid, angular bodies (up to 500 μm) showing morphologies of blebs of metal-rich sulfide melts. These blebs (pentlandite + chalcopyrite ± bornite ± pyrrhotite) preferentially nucleated onto (or inside) the opx and Al-spinel (or on the cpx in the cpx-rich lherzolites). Extensive reactions between a S-saturated basaltic melt and olivine and Cr-spinel at 1-2 Gpa could produce such associations. Neither harzburgites nor lherzolites show mineralogical evidence of trapped Ms inside olivine, as one would expect from incongruent melting of BMS. Harzburgites, fertile lherzolites and websterites display broadly similar Cu/S ratios (1.5 x PUM estimates) while defining linear correlation trends in S vs. Al plots. Osmium, Ir, Ru and Rh (IPGE) negatively correlate with fertility indices, as predicted by D_mss/sulfide melt. However, harzburgites, lherzolites and websterites are aligned on the same regression lines which are therefore more likely mixing lines. Discrete laurite (less than 500 nm across) discovered in Lherz lherzolites (FEG-SEM data) may have been inherited from harzburgitic protoliths. Platinum concentrations do not correlate with fertility indices, nor with Pd, despite similar D_mss/sulfide melt, reflecting saturation in refractory Pt-rich alloys at mantle temperatures (FEG-SEM data). Palladium positively correlates with Cu, S, Ca and Al, in agreement with its almost exclusive partitioning in sulfide melt. The latter correlations are consistent with refertilisation reactions of refractory peridotites by variable amount of basaltic melts that precipitated Cu-rich sulfide melt, cpx, Al-spinel and opx.
The melting curve of Fe\textsubscript{3}C to 73 GPa

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Seismic data indicate the Earth’s outer core is about 10% less dense than pure Fe-Ni at the prevailing P-T conditions, whereas the inner core is some 4% less dense. Possible candidates for the light element component required to satisfy this discrepancy include H, C, O, S and Si. Constraints on core composition, phase relations and temperature are derived from knowledge of the melting relations in relevant iron-light element systems. In this study we have determined the melting curve of Fe\textsubscript{3}C up to 73 GPa using the Laser Heated Diamond Anvil Cell (LH-DAC).

Foils made from powdered Fe\textsubscript{3}C (synthesised by R. Dasgupta at LDGO) were loaded into ~100 µm holes in preindented Re gaskets. NaCl, ruby and sapphire were used as pressure media and thermal insulators. Samples were compressed to experimental pressure and then heated using a 60W Nd:YLF laser and a double sided heating geometry. Pressure was measured before and after each melting experiment by ruby fluorescence. Temperatures were determined by spectroradiometry. Congruent melting in a one-component system causes 1\textsuperscript{st} order discontinuities in physical properties. Here, melting is deduced primarily from discontinuities in the temperature and emissivity vs. laser power function, and in some cases by visual observation of melt convection. When these observations occur together they give a consistent melting temperature. The results of our data are shown in figure 1, the solid line being our preferred melting curve from a fit of the data to a Simon equation. An extrapolation of this curve predicts a melting temperature of ~3250±50 K at the core-mantle boundary and ~3800±100 K at the inner core boundary.

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Molecular scale study of the synergism between oxalate and desferrioxamine-B on goethite dissolution

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Oxalate significantly increases the rate of dissolution of goethite in the presence of siderophores. This is especially true if the goethite is preequilibrated with oxalate before siderophore exposure. It has been suggested that this phenomenon is due to an oxalate-goethite surface complex that is kinetically labile with respect to iron. In this way, oxalate acts as an efficient shuttle for Fe(III) from the goethite surface to the bulk solution. Once in solution, the strongly complexing siderophore seizes the Fe(III), and oxalate is free to go back to the surface for more iron [1-3].

In this study, we use quantitative \textit{in situ} infrared spectroscopy to further the mechanistic understanding of the role of oxalate in the dissolution of goethite in the presence of the siderophore, desferrioxamine-B (des-B). All experiments were performed at 25 °C in 0.1 M NaCl ionic medium and in the absence of light, and the pH was held at 6 using pH-Stat titration methods. The total concentration of oxalate was 1 µmol/m\textsuperscript{2}, and this concentration causes no significant dissolution of goethite in the absence of des-B. First, infrared spectra at the aqueous-goethite interface were collected as a function of time for one week to follow the adsorption and surface speciation of oxalate and des-B individually. Then, spectroscopic desorption experiments were performed in order to determine the relative stabilities of the ligands in the different types of surface complexes. Next, spectra were collected for several days after the simultaneous addition of 1 µmol/m\textsuperscript{2} concentrations of both oxalate and des-B. Finally, oxalate was reacted with goethite for one week, and then spectra were collected as a function of time after repeated 0.1 µmol/m\textsuperscript{2} additions of des-B every 24 hours. We identify an oxalate-goethite surface complex that increases the mobility of Fe(III) but is otherwise thermodynamically stable in the absence of des-B. These results are discussed with respect to their broader implications toward mechanisms for ligand-promoted mineral dissolution.

References
Oceanic basalts geochemical heterogeneities distribution in four large scale domains supporting a first order two large cells whole mantle convective structure

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The analysis of compositional heterogeneities displayed at a large scale by the oceanic basalts, using combined isotopic and incompatible trace element ratio diagrams, and in particular the $^{208}$Pb/$^{204}$Pb vs $^{206}$Pb/$^{204}$Pb, and Nb/La vs Th/La representations, leads to identification of four large scale domains. The mentioned representations display interesting properties for evidencing and quantifying intra mantle magmatic differentiation processes, as for estimating the residual characteristics of mantle sources according to the continental-mantle differentiation process. Two domains are identified within the Atlantic-Pacific realm, (specified as the Atlantic-East Pacific (AEP) and the South Central Pacific identified within the Atlantic-Pacific realm, (specified as the continental-mantle differentiation process. Two domains are residual characteristics of mantle sources according to the properties for evidencing and quantifying intra mantle domains. The mentioned representations display interesting representations, leads to identification of four large scale earth mantle flow models which take into account numerous structures issued from numerical modeling results as with domains. Such a structure looks consistent with convective mantle, and located inside the respective AEP and IO (specified as the Indian Ocean (IO), and Kerguelen - South Africa, is proposed for the enriched-type domain in the Pacific area, the enriched-type domain is related to the super-plume rising below the Pacific. A similar super-plume origin, but located below Africa, is proposed for the enriched-type domain in the Indian Ocean - South Atlantic area. A relationship can be drawn, in a more general way, between the geographical repartition of these domains and long wavelength geophysical features as seismic and gravity anomalies. The good advanced structure bears constrains on plumes as on plateau basalts origin.

Reference

MC-ICP-MS measurements with d-DIHEN direct injection nebulization

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Compared to the classical spray chamber nebulization, direct injection nebulization offers to increase the analyte transport efficiency and thus the sensitivity, to reduce the sample amount needed for one analysis and the memory effects, rendering bracketing isotopic measurements much more suitable and precise for elements such as boron.

The recently developed d-DIHEN (demountable Direct Injection High Efficiency Nebuliser, Westphal et al., 2004) has been tested for isotopic measurements on a Neptune (Thermo) MC-ICP-MS.

The spray is optimized by varying the capillary-nebuliser tip distance and observing the water meniscus formed at the end of the nebuliser tip, before the d-DIHEN is positioned into the torch (4mm before the intermediate tube tip) and the plasma lit up (1200W). Best sensitivities are obtained for sample gas flow between 0.15 and 0.20 l/min, and auxiliary gas flow around 1.5 l/min. A peristaltic pump allows uptake rates of 10 to 100 µl/min. Best performances were obtained for 20 to 50 µl/min.

The sensitivities with d-DIHEN are similar to those with APEX for elements such as Mg, Sr, Nd, and Pb (approx. 11, 12, 4.5 and 10 V on larger isotope for 100 ppb solutions at 25 µl/min), and are respectively 7, 2.5, 2 and 2 times higher than double Scott spray chamber ones. Sensitivity gains for B and Li are 4 and 6.

Signal stability is typically 0.07% (RSD for 5 minutes on B). Oxides and doubly charged are more abundant than with the previous introduction systems: typically NdO/Nd = 25%, Ba$^{2+}$/Ba = 2%.

Boron isotope measurements with d-DIHEN led to an external reproducibility of 0.4% (2σ) on purified 100 ppb B seawater samples. Internal reproducibility was 0.1%. 200 seconds of wash were sufficient to reach 1% of the sample signal (2V). Measurement accuracy was successfully tested with enriched standards for $^3^1$B between –50% and +40%.

Neodymium isotope measurements gave internal reproducibility similar to those obtained with a double Scott spray chamber for comparable signal intensity (2 ppm on $^{1^{4}}$Nd/$^{1^{4}}$Nd).

References

Isotopic and geochemical characteristics of late Neoproterozoic oceans from the Dalradian Supergroup of Scotland: Local basin infilling or global signatures?

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Recent studies have suggested that there are 3 glacial deposits in the Neoproterozoic succession of Scotland and Ireland and that the well-known Port Askaig tillite represents a Sturtian (720 Ma) glaciation. The identification of a boulder bed and overlying cap carbonate above an unconformity in the Easdale subgroup of Ireland suggest that it represents a Marinoan (640 Ma) glacial event (McCay et al., 2006).

New studies have focused on localised black shales and limestones from the middle Easdale subgroup of Western Argyll, Scotland, which are intermittently rich in sulphides. Unlike much of the Dalradian Supergroup, this area has been only subjected to chlorite-grade metamorphism and relatively low levels of deformation. While the organic carbon isotopes have been reset by metamorphism with an enrichment in 13C of around 15‰, the trend still parallels that of 13C carbonate. Geochemical data (K, Ba, Rb) indicate a period of high continental input to the ocean leading to high nutrient levels, elevated organic carbon contents (TOC) and 13C enrichment for the pre-glacial Islay and Tayvallich limestones at lower and higher levels respectively, in the Dalradian sequence (McCay et al., 2006).

Pyrite 34S cycles between +11 and +21‰ in the same sequence of black shales and overlying limestones and this can be correlated with continental inputs and basin infilling, resulting in probable restrictions to sulphate recharge.

The transition from limestone to overlying phyllites with minor limestones is associated with a sudden decrease to very low TOC and a negative carbon isotope excursion for carbonates, paralleled by the curve for organic carbon. δ34S continues to rise in the phyllites before falling to δ34S depleted values, the lowest stratigraphic level in the Dalradian for which δ34S depletion is recorded. Global Neoproterozoic δ34S records for pyrite show that the first depletion post-dates the Marinoan glacial period and is related to a significant increase in the oxygenation of the oceans and hence sulphate content (Hurtgen et al., 2005). This suggests that the Easdale subgroup in Scotland can be correlated with the Marinoan, despite there being no evidence so far for glacial deposits, and confirms the findings of McCay et al. (2006) for similar stratigraphic levels in Ireland.

References

Isotopic geochemistry of Dexing porphyry Cu-Au deposit of Jiangxi Province, China

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The Dexing porphyry Cu-Au deposit including Tongchang, Fujiawu and Zhushahong ore district is related to the Early Jurassic granodiorite porphyry stocks. The SHRIMP zircon U-Pb age of both the Fujiawu and the Tongchang porphyries are 171.4±3 Ma (Wang et al., 2004). The 187Re-187Os isochron age of molybdenite from Tongchang ore district is 170.4±1.8 Ma and is remarkably consistent with that of the porphyry stocks, suggesting that the formation of the Cu-Au ores was genetically related to the magmatism (Lu et al., 2005). The Cu isotope also indicates the copper was derived from the magmatic rocks (Lu et al., 2004).

The Si isotopic compositions of 17 quartz samples from the Dexing deposit were analyzed. The δ30Si values of two quartz samples from the Tongchang porphyry are 0.2‰ and 0.3‰ respectively. The δ30Si values of 11 quartz veinlet samples from the Tongchang deposit range from -0.2‰ to 0.5‰, most of which vary from 0.2‰ to 0.4‰. The Si isotopic compositions of the three quartz samples from the Fujiawu porphyry are -0.1‰, 0.0‰ and 0.4‰ respectively. One quartz sample from the Fujiawu ore has the δ30Si values of 0.0‰. The Si isotopic compositions of quartz from the ore-forming quartz veinlets are compatible with those of quartz from the related porphyries.

The characteristics of the isotopic geochemistry of the Dexing deposit show that the ore-forming materials might have been derived from the magmatic rocks.

References
Evidence and significance of water bridges in smectite of source rocks

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With the aim to examine the role of water in the organo-smectite interaction of source rocks, we study clay minerals from drill cores using situ DRIFT. DRIFT spectra, recorded at room temperature, are characterized by a C=O stretch of COOH at 1720 cm$^{-1}$ and a -OH stretch of H$_2$O at 3130 cm$^{-1}$. With heating further intensities of these bands decrease gradually, and frequencies are shifted towards lower wave numbers. After heating the samples at 400°C they almost disappear. The evolution of the interlayer water is accompanied by significant changes in the location and shape of the C=O. This observation indicates that COOH groups are bonded to water molecules by hydrogen bonds and water molecules are bridges between COOH groups and smectite. In subtracting spectra every 50°C (from 50 to 600°C), the ratio of H$_2$O Peak area to that of COOH tends to be a constant under temperature of 250°C to 400°C, while under 250°C it varies irregularly. It is well known that adsorption water on smectite surface and interlayer free water dehydrate under 250°C, and structure water dehydrate above 600°C, therefore water retained under temperature of 250°C -400°C in complexes is water bridge. The reasonable explain for the constant of $\Delta$H$_2$O/$\Delta$COOH ratio is that when water bridges are broken, water and acids associated with water molecules are expelled from smectite interlayer together. This validate the water bridge exists between acids and smectite further. Besides cationic polarization, water bridge form hydrogen bonds with acids, so it is higher in stability than surface adsorption water and interlayer free water, which leads to water bridge retaining in interlayer up to 400°C. As a result, the expelled temperature of interlayer acids delay, in other words, these acids are preserved well in <400°C temperature range. We suggest water bridges plays an important role in the organic matter preservation in source rocks, and have a great influence on hydrocarbon generation.

Acknowledgements

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References


Zn isotopes in chondritic components

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Zn isotopic compositions (expressed as $\delta^{66}$Zn in ‰ vs. JMC stdt) measured with high precision with MC-ICPMS have been reported in recent years that show variations of around 0.3‰ for whole rocks (WR) of Carbonaceous Chondrites (CC) and up to 2‰ for Ordinary Chondrites. The three isotopic ratios (66/64, 67/64, 68/64) vary linearly with mass difference, and define a common isotopic fractionation line with terrestrial samples. Zn was derived from an initially homogeneous reservoir. Although not the only answer, the common trend observed for CCs and UOCs in diagrams such as $\delta^{66}$Zn vs. elemental ratios (e.g. Cr/Zn; Luck et al. 2005) could be explained as a mixture between two major reservoirs: one represented by the "matrix" with heavy Zn (around 0.5‰), and another related to chondrules (or alternatively refractory material, in CVs) characterized by light Zn. Results are presented for constituents separated mechanically from Allende and Murchison (matrix, chondrules, aggregates), and sequential acid leachings from CIs. Preliminary data show chondrule (including rim) from Allende to be similar to WR. Sequential acid leachings were performed on IVuna, starting from dilute Acetic Acid to HCl to concentrated HNO3/HF following works on Cr (Rotaru et al. 1992) and Zr (Schönbächler et al. 2005) isotopes. Labile or easily-dissolved fractions seem to carry "normal" Zn (i.e. similar to WR; 0.4-0.5 ‰) while more acid-resistant material point to light Zn. It seems that for Zn – like for Cr and Zr isotopes – at least some isotopic heterogeneities have been retained in CIs.

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Genesis of low-mineralised groundwater in a fissured sandstone aquifer, Odenwald, Germany – Where has all the sulfate gone?

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Extensive hydrogeochemical data sampling has been carried out on groundwater in a fissured sandstone aquifer in the Buntsandstein formation of the Odenwald, Germany. The sediment rock sequence comprises quartz arenite and quartzitic sandstone with various content of biotite, K-feldspar, and clay minerals. The poorly-mineralised groundwater show conspicuous variation in ion concentrations and in groundwater composition in a range from Ca-HCO₃ to Ca-Mg-SO₄-HCO₃-type.

Groundwater pumped from wells in the sandstone aquifer shows a significant and marked decrease in sulfate concentration in comparison with spring water from the same area. A significant variation in Ca-Mg-ratio between spring- and well-groundwater samples is also indicated. Springs show low ratios of about 2, whereas wells are distinguished by higher ratios due to progressive calcite solution. The individual groundwater composition appears to be related to distinct mineral (rock) alteration mechanisms. It can be shown that alteration of silicate minerals in the aquifer is tied to the HCO₃-buffer system. Significant differences in water composition result from the presence of detrital feldspars in some sandstone units compared to strata that lack feldspar. Leaching experiments on representative sandstone samples produced leachates that were potassium dominated due to K-feldspar alteration. These findings are in sharp contrast to the very low potassium concentrations in the sampled waters. Fluid inclusions in the original detrital quartz grains contribute to the amount of dissolved chloride and sodium. Measured Cl/Br ratios of the leachates are low (50-100) and are diagnostic for saline fluid in basement complexes. Thus, chloride/bromide ratios reflect fluids from the crystalline basement that formed the pre-deposition source of the sandstone.

Ivory Coast tektites, microtektites, and glassy fallback particles of the Lake Bosumtwi impact crater, Ghana: Geochemical differences

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Lake Bosumtwi, a unique young impact structure

The ~ 10 km-sized 1.07 Ma old Lake Bosumtwi structure, Ghana, is the source crater of tektites (Ivory Coast [IVC] strewn field), microtektites (off-shore drill cores), and fallback particles (ICDP drill core LB-05B). These various glass types may have formed during different stages of cratering by different processes, whose mechanics are not known in detail.

Major element composition

Here we present electron microprobe data for the named glassy materials. Two IVC tektites show low SiO₂ (65.5 and 66.1 wt%) and medium to high CaO contents (4.2 and 3.3 wt%). Ten microtektites (drill hole K9-56) have SiO₂ contents between 63.3 and 67.3 wt%, the other major elements also compare well with published data (Glass, 1969, 2004; Koeberl, 1997), and the microtektites are homogenous in general. One, however, displays irregularly shaped domains of different chemical composition in which Mg, Al, K, and Fe contents increase with decreasing Si and Na contents. This microtektite shows low average concentrations of SiO₂ and Al₂O₃ (63.3 and 14.9 wt%, respectively), and high average FeO and MgO contents (7.6 and 6.7 wt%, respectively). Another microtektite (ODP hole 664) is characterized by remarkable low SiO₂ (55.8 wt%), Na₂O (0.7 wt%), and K₂O (0.5 wt%) and high FeO (8.5 wt%), MgO (13.6 wt%), and CaO (2.1 wt%) concentrations. Results of thirteen fallback particles are concordant to data of Luetke et al. (2007). In general, IVC tektites, microtektites and fallback particles are quite similar in composition, yet significant differences in Ca, and slight differences in Mg and Fe concentrations exist, probably caused by the particular mixture of precursor materials. Current LA-ICP-MS studies may help to understand the formation processes of the various glasses by detection of different trace element characteristics.

References
Petrochemical characterisation of natural stones from the Etruscan site of Marzabotto (Bologna-Italy): Preliminary results

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The tufa rocks used in sacral buildings in the Etruscan site of Marzabotto (Bologna, Italy) were characterised from a petrochemical point of view and compared with lithologies outcropping in the surrounding area in order to recognise the ancient quarries. These tufa, called “travertini” in the Italian literature, are very porous and are rich of macrophyte moulds revealing an origin by freshwater carbonate deposition (Ford-Pedley, 1996) Facies and thin section analyses show that these rocks were formed in cascade and paludal settings. Hypothesising that the possible quarry areas of travertine rocks were not far from the site and using the geological maps of the surrounding of the Etruscan site it was possible to identify few possible supply zones: 1) San Cristoforo di Labante (Castel D’Aiano, Bologna), 2) Rio Sponga (Marzabotto, Bologna) and 3) Rio Bucamante (Serramazzoni, Modena). Petrochemical characterisation were complemented with a statistical elaboration using the SPSS 14.0 (Copyright © 2006 SPSS Inc.) method and have highlighted that the San Cristoforo di Labante deposit could be the most suitable quarry area of the travertine used in Marzabotto.

The geomorphology of the area suggests that blocks were lowered from the San Cristoforo di Labante deposit through a “lizza” way (using rollers along a prepared slope) and then shipped along the Reno River to the Etruscan site of Marzabotto.

References

Change of iron redox state during terrestrial impact melts (glasses) formation

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Glasses of tektites and impact bombs are characterized by very low Fe$^{3+}$/ΣFe ratios in comparison with their source matter - Earth’s crust rocks. It is supposed that the main reason of reduced state of iron in impact melts (glasses) are redox reactions with the assistance of iron ions that exist during decompression of terrestrial matter exposed to powerful impact effect (Kadik et.al., 2003; Lukhanin and Kadik, 2007).

It is shown that redox reactions inevitably have to occur in oxide melts of Fe-O and SiO$_2$-FeO-Fe$_2$O$_3$ systems, containing various ions of iron, in consequence of incongruent evaporation of melts during pressure decrease under high temperature conditions. Reduction or oxidation of iron takes place during decompression evaporation of melt under both closed and open conditions depending on its initial oxidation degree. Fe$^{3+}$/ΣFe ratio in this process aspire to some extremely low value.

This property of Fe-bearing systems is important for understanding the redox state of melts forming in impact processes as a result of melting and evaporation of crust matter. Adibatical decompression of high temperature impactitic melts should be accompanied by their reduction (Fe$^{3+}$/Fe$^{2+}$ decrease) in comparison with relatively oxidized initial matter of the target. The main condition for reducing reactions to proceed is full melting and partial evaporation of matter, involved in the impact process, and the attainment of very high temperatures (>1800-2000°C) that are characteristic for impact bombs and tektites formation at certain stage of unloading. The higher is the temperature the stronger is the effect of decompression reduction. Extremely low Fe$^{3+}$/ΣFe ratios in tektites (≤ 0.1) are apparently the result of decompression reduction of the most high temperature impact melts.

References
Magma differentiation in a T gradient: Thermal migration and Soret effects are not dead!

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Most magma differentiation probably occurs within a body having significant temperature gradients. Compositional zoning tied to temperature differences in silicic ignimbrites were attributed to thermogravitational diffusion \cite{1}, catalyzing temperature gradient experiments by Walker and co-workers \cite{2}. Experiments showed, however, that compositional zoning in silicic rocks was opposite to Soret effects in a silicate melt \cite{3}. Our experiments/models suggest reassessment of temperature gradient effects.

We report on thermal migration experiments using wet andesite (AGV-1) or wet rhyolite (RGM-1). AGV-1 was run in 2 cm capsule with top at 950°C and bottom at 350°C in a piston cylinder apparatus for 66 days at 0.5 GPa. Bulk major-trace element compositions vary with position reflecting changing mineralogy with form and temperature in a linear “calc-alkaline trend” on an AFM diagram. Surprisingly, static trace element compositions vary with position reflecting in 2 cm capsule with top at 950°C and bottom at 350°C in an andesite (AGV-1) or wet rhyolite (RGM-1). AGV-1 was run temperature gradient effects.

We will also report compositional, isotopic and modelling results for a currently running cold seal experiment using RGM-1 in order to better compare to zoned silicic ignimbrite compositions and conditions.

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Changling inorganic carbon dioxide gas field in Songliao Basin, China

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Changling gas field is located in Chaganhua town in Qianguo county, Jilin province. Geotectonically, it is located in the uplift of volcanic belt in the central region of Changling fault depression, southwest Songliao Basin. Gas pays lie in the Lower Cretaceous Yingcheng Formation volcanic rocks. It is an important carbon dioxide gas filed with 4 drilled wells, being of controlled reserves of tens of billions cubic metres and controlled gas bearing areas of 8.39 km².

The main geochemistry characteristics of deep gases in the fault depression are listed as follows: (1) The gases are characterized by high CO₂ except Changshen 1 well (CO₂ accounts for 20.05%). Of the main components of gases in Changshen 1 well, CH₄ accounts for 71.99%, the hydrocarbon gases above C₂ account for 1.37%, He and N₂ account for 2.10, respectively. The δ¹³C values of CH₄ from Changling gas field are within the range of -22.26% to 29.71%, and the contents of hydrogen gases above C₂ are within the range of 0.20% - 0.26%. The contents of H₂, He, CO₂ and N₂ are within the ranges of 0.05% ~ 0.84%, 0.0076% ~ 0.012%, 71.64% ~ 67.46% and 4.24% ~ 1.53%, respectively. It was proposed that a gas field with CO₂ more than 60% could be called carbon dioxide gas filed (Dai et al., 2005), so the Changling gas field is a carbon dioxide gas filed. (2) The ranges for the δ¹³C₁, δ¹³C₂, δ¹³C₃ and δ¹³C₄ values of the gases from Changling gas field are -22.2% to -23.4%, -26.3% to -27.0%, -26.5% to -27.3% and -33.3% to -34.0%, respectively. It is a significant characteristic for inorganic hydrocarbon gas that the δ¹³C values are getting lighter with increasing molecular weight (Dai et al., 2005), so the hydrocarbon gases in this field are inorganic. The δ¹³C values of CO₂ from Changling gas field are within the range of -6.8% to -11.9%. It has been pointed out that CO₂ with δ¹³C₄>8‰ is inorganic (Dai et al., 2005). Most of the CO₂ from this field has δ¹³C₄ greater than -8‰, so it is inorganic. (3) In Changling gas field, the ranges of δ¹³C₄ in CO₂ and R/Ra values are 2.61×10⁻⁶ to 3.21×10⁻³ and 1.90 to 2.10, respectively. The He/⁴He values in the upper mantle and radioactive strata are within the range of 1.1×10⁻³ to 1.4×10⁻⁵ and 10⁻⁷ ~ 10⁻⁹, respectively (Wang, 1989). The δ¹³C values of He from this field are around 10⁻⁵, which indicates a large amount of He from the mantle. All these evidences demonstrate that the gases from Changling gas field are mainly inorganic.

References


Kink sites: A key to surface reactivity and dissolution kinetics

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Dissolution and corrosion of crystalline materials have been proven to be as complex as they are important. In recent years significant progress in our understanding of dissolution mechanisms and kinetics was based on experimental studies utilizing atomic force microscopy (AFM), interferometry (e.g., VSI and PSI) and other techniques. Building on the rapidly growing power of computers, these efforts have been complemented by computer models of rapidly increasing sophistication and complexity. Ab initio, DFT, Molecular Dynamics (MD), and lastly Monte Carlo (MC) calculations are contributing to an increasingly detailed picture of reaction kinetics in complex systems [1].

Here, we apply parameterized Monte Carlo simulations to explore dissolution kinetics at critical time and length scales, over which experimental and analytical tools have limited utility or feasibility as sources of precise information [2]. The system size that can be explored with MC simulations is now sufficiently large to permit realistic predictions of surface alteration and dissolution mechanisms that can then be verified experimentally. We use results from ab initio and DFT calculations to parameterize our calculations.

Lasaga [2] demonstrated that the arrival and departure rates (k) of atoms or molecules are equal at surface kink sites only when the crystal surface is at equilibrium, thus:

\[ k_{kink} = k_{kink} \]

The kink site is indeed the most important reactive site at a crystal surface, because a molecule in this position has precisely half the chemical bonds that it would have were it located in a bulk site. At the same time, a kink site is the only self-replicating site at a given crystal surface.

Our MC calculations use the ability to study kink site dynamics from a molecular (versus purely geometric) basis, and are case studies for crystal systems. When combined with a statistical treatment, our MC results demonstrate that the large amount of detailed information involved in the complex problem of surface reactivity, and its role in overall kinetics of dissolution can be significantly reduced by focusing primarily on the number, type, and density of kink sites and their development over time and space.

References

Geochemical trends in rutile forming reactions
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We are investigating the behavior of trace elements in prograde rutile growth reactions. Our aim is to understand how trace elements are behaving during metamorphic reactions, giving special attention to accessory minerals.

One rutile-forming reaction is observed in low- to medium grade (840°C / 0.6-0.9GPa) metapelitic rocks (Ms+Chl+Qtz+Ilm+Rt+Gra+Ap+Zrn+Mz; in order of abundance) from the Garnet-Phylite Unit of the Erzgebirge (Germany), where rutile starts to crystallize from Ilm according to the simplified reaction: Ilm+Silicate+H₂O ↔ Rt+Chl.

The other reaction, observed in the rocks from the Ivrea Zone (northern Italy), takes place in the transition between amphibolite and granulate facies, where rutile-free amphibolite facies (620°C, 0.4GPa) metapelites (Qtz+High-Ti amphibolite and granulite facies, where rutile-free amphibolite facies (620°C, 0.4GPa) metapelites (Qtz+High-Ti amphibolite and granulite facies) are replaced, with increasing metamorphic grade (480°C / 0.6-0.9GPa) metapelitic rocks (Grt+Sil+Qtz+Pl+Kfs+High-Ti Bt). The rutile formation is associated with high-Ti Bt breakdown and is coupled to melting reactions such as Bt+Sil ↔ Grt+Sil+melt.

Remarkably in the two areas, both the rutile-free precursor rock and the rutile-bearing “final product” are present, allowing comparison of the rutile trace element geochemistry in different stages of the reaction. In both cases, during the early stage of rutile formation, its Nb/Ti ratio is strongly controlled by the ratio of the precursor mineral (Ilm and Bt), being evidenced by a large inter-grain spread and Nb/Ti ratios different from those expected for rutiles occurring in equilibrium with the mineral assemblage in question. These features reflect the trace element partitioning between the minerals involved in the reaction and are in good agreement with the published partition coefficient between Ilm[1], Bt[2], Rt[3] and melt. In both examples, as the reactions evolve with increasing metamorphic conditions, the rutile Nb/Ti ratios change toward the value expected for a rutile occurring in equilibrium with the paragenesis in question. Furthermore, in order to equilibrate the rutile Nb/Ti ratio, Nb has to be mobilized, at least on a thin section scale.

References

Excess 17O – A new tracer in hydrology
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For more than four decades, water isotope ratios (18O/16O and 2H/1H) have played a key role in understanding the hydrologic cycle. For lack of analytical precision, it has been assumed that the 17O/16O ratio does not significantly deviate from a constant relation to 18O/16O and its measurement seemed redundant. Here we show that when all oxygen isotope ratios are measured with very high precision, they yield a wealth of valuable information.

We have designed and constructed an automatic fluorination system for producing pure O₂ from water samples. This allows isotope ratio measurements by dual inlet mass spectrometry with overall duplicate difference better than 0.06‰ for δ18O. The analytical errors in δ17O are mass dependent on the δ18O errors and therefore are less than 0.03‰. This allows determination of the relationships between 14O/16O and 17O/16O with extremely high precision.

Using this method together with experimental setups we determined the exponent (0; 17O = 16O a²) relating the fractionation factors in vapor-liquid equilibrium and vapor diffusion in air as 0.529±0.001 and 0.519±0.0006 respectively. The exponents do not depend on temperature. We also determined the global slope ln(17O +1)/ln(18O +1) for meteoric water as 0.528±0.001.

Our measurements show that meteoric water and atmospheric moisture samples fall above a line with a slope 0.528 that originates from VSMOW and thus have an excess of 17O with respect to seawater. This excess is defined as: 17O-excess = ln(δ17O +1) – 0.528·ln(δ18O +1)
The precision in measurements of the 17O-excess is 8 per meg (per meq = 0.001‰).

The magnitude of 17O-excess of meteoric water and atmospheric moisture is in the range of 10 to 70 per meg. It originates, similarly to deuterium excess, from evaporation that is affected by both isotope equilibrium and diffusion transport in air. Yet, in contrast to deuterium excess, 17O-excess is independent of temperature in liquid-vapor equilibrium and, therefore, it is a simpler indicator of hydrologic processes.

In general, 17O-excess in precipitation increases when the source vapor is derived from a region where there is large humidity contrast between the ocean surface and the overlying atmosphere. In contrast, its magnitude decreases in evaporating water bodies as well as in leaf water at low humidity. This behavior will be demonstrated in examples from meteoric waters and polar ice.

References
Is there a reversible step in $^{45}$Ca sorption onto pure calcite?

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Metal sorption onto carbonate minerals have been intensively interpreted in literature by two reaction steps: (1) a first one rapid and completed within few hours and (2) a second one slower, eventually irreversible and occurring at a constant rate (Davis et al., 1987; Zachara et al., 1991; Mevellec, 2000). The first step is often attributed to an ion exchange process, but its reversibility is rarely investigated. Consequently, discrimination of the global sorption phenomenon into two different mechanisms is not always justified.

Therefore, we have investigate both sorption and desorption of Ca, radiotraced with isotope $^{45}$Ca, onto synthetic pure calcite in aqueous solutions saturated with respect to calcite and in equilibrium with the atmospheric CO$_2$. Batch experiments were performed as a function of time and at different pH using anionic chemical buffers having no affinity towards calcite. The distribution coefficient of $^{45}$Ca was calculated from radiochemical measurements of the supernatants before and after sorption, and the total Ca aqueous concentration was measured by ion-chromatography.

As mentioned by previously cited authors, our results show that whatever the pH, Kd’s of $^{45}$Ca increase with time without reaching a stationary state within two weeks. Moreover, Kd’s calculated with desorption experimental data are systematically higher than those calculated with the sorption ones. In order to test the occurrence of a first reversible ion exchange step, we applied the approach of Badillo-Almaraz and Ly (2003) put forward for the interpretation of Ca sorption onto hydroxyapatite. More specifically, on the basis of isotopic equilibrium principle and from the knowledge of the isotopic ratios ($^{45}$Ca/Ca$_{total}$), it is possible to calculate “reversible” Kd’s of $^{45}$Ca for both sorption and desorption steps. Doing this, we observe that both calculated Kd’s values are similar, whatever the time and pH. In these conditions, we are able (1) to evidence the reversible step of retention of Ca and more, (2) to quantify the amount of Ca sorbed on the calcite surface, which can be compared to surface cristallochemical data.

P-T conditions and oxygen fugacity estimates suggest suprasubduction setting of Voykar ophiolites, Polar Urals

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Mantle section of Voykar ophiolites, Polar Urals, Russia contains exceptionally fresh harzburgites, dunites and pyroxenites. Dunites and pyroxenites indicate melt percolation event dated by Re-Os isotopes as 0.6 Ma old (Batanova et al., 2007). Host harzburgites yields much older ages (up to 2.5 Ga). Here we report estimations of P-T conditions and oxygen fugacity for harzburgites, dunites and pyroxenites based on mineral compositions.

P-T conditions of harzburgites correspond to T=950 C and P=1.2-1.4 GPa (Wells, 1977; Mercier, 1980). Oxygen fugacities -1.5-2.5 log units higher than QFM (Ballhaus, 1991). Pyroxenites yield T=950-1050 C and P around 1.4 GPa. The oxygen fugacity of pyroxenite and dunites still has to be evaluated.

The obtained high oxygen fugacities and low temperatures suggest suprasubduction settings for Voykar ophiolites.

References


References


Carbonate concretions as a window to the evolving chemistry of the early ocean and atmosphere

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Ellipsoidal calcium carbonate concretions with diameters ranging up to meter-scale are common in organic-rich shales throughout the Phanerozoic. These features arise through early (pre-compactional), highly localized cementation. This precipitation is catalyzed by enhanced alkalinity production (pre-compactional), highly localized cementation. Each of these conditions was likely well established by the late Neoproterozoic, when sulfate as an electron acceptor for BSR with concomitant anaerobic oxidation of organic matter (OM) and/or methane. Identical features are well expressed in the upper portions of the late Neoproterozoic Doushantuo Formation in south China, which shows trace metal enrichments consistent with increasing sulfate reduction (BSR) with concomitant anaerobic oxidation of organic matter (OM) and/or methane. Identical features are well expressed in the upper portions of the late Neoproterozoic Doushantuo Formation in south China, which shows trace metal enrichments consistent with increasing oxygenation of the ocean and atmosphere.

Several factors are important in the formation of large, distinct, shale-hosted concretions, including (1) availability of sulfate as an electron acceptor for BSR, (2) pore-water saturation states that are strongly elevated relative to ambient bottom water, and (3) sites of decaying OM that act to initiate localized cementation. Each of these conditions was likely well established by the late Neoproterozoic, when sulfate delivery to the ocean increased through greater oxidative continental weathering while pyrite burial decreased, and carbonate saturation decreased in the global ocean well below the hypersaturated conditions of the earlier Proterozoic. With decreasing ambient saturation, localized cementation became more likely and easier to sustain in response to sharp concentration gradients. Also, the Neoproterozoic advent of fecal pellet production enhanced the delivery of labile OM to the seafloor. This study seeks to explore the relationship of these late Neoproterozoic examples to carbonate concretions described from earlier Precambrian units. The paleoceanographic implications of older “concretions” can be obscured by the frequently generic use of the term to describe masses that differ in mineralogy, morphology, and likely mode of formation compared to those of the late Neoproterozoic/Phanerozoic. The suggestion is that the upper Doushantuo and equivalent strata may mark the beginning of Phanerozoic-style ocean chemistry as expressed in concretion formation, implied carbonate saturation, metal enrichments, and perhaps other tracers of the evolving biosphere.

Hydrochemistry of four tropical watersheds in central Panama

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Surface waters from 4 watersheds in central Panama that have similar pristine source regions in steep mountainous tropical rain forest, but are affected by different downstream land-use practices were sampled for major element chemistry during the dry season in 2005 and 2006. The bedrock geology of the region consists of Upper Cretaceous to Tertiary age basalts, basaltic andesites, gabbrons, and diorites plus less-abundant granodiorites, tonalites, and plagiogranites. The Rio Pacora (374 km2) watershed is developed on gabbro-diabase lithologies, whereas the Upper Rio Chagres (580 km2), Rio Pequini (281 km2), and Rio Cuango (175 km2) are formed on mixed terrains consisting of hydrothermally altered andesite, mafic-intermediate volcanic rocks, and minor felsic intrusive lithologies.

Overall, δD and δ18O values for the Chagres region waters fall on the Global Meteoric Water Line without systematic δ-excess change, suggesting that the H and O isotope variations are governed by air mass trajectories rather than altitude or topographic effects. There is a geospatial trend in Cl that mirrors the NE-SW precipitation gradient across the region. Low-order streams in the Pacora watershed have distinctly higher TDS values plus H4SiO4 and Ca2+ concentrations than those forming in the mixed lithology terrain. The gabbro terrane streams and rivers are also slightly more enriched in cations (TZ+) and HCO3-, relative to H4SiO4, than streams and rivers in the mixed lithology terrane, whereas K+ concentrations are uniformly low and, like Mg2+ and Na+, are similar in both terranes. Major rivers in both areas are similar in chemical character to their respective headwater streams, indicating that the most intense chemical weathering within the watersheds occurs in the headwater regions, and dilution of these solute-rich waters occurs at lower elevations downstream. Ca/Mg ratios for all watersheds are lower than the world river average, indicating the importance of the weathering of Mg-rich minerals. The Ca/Na, HCO3/Na and Mg/Na ratios for the Rio Pacora streams and rivers fall within the mid-range of what has been observed globally for other streams/rivers draining mafic rocks. Estimated TZ’ yields are very large, suggesting significant weathering rates in headwater watersheds of the Chagres region in central Panama.
Carbon isotopes of black shales in NW Hunan, China and the Early Cambrian atmospheric CO₂ level

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Total 82 Lower Cambrian black shale samples from the three sections in NW Hunan, China are analyzed for C isotopes of organic carbon (δ¹³Corg = −34.9 to −28.8 ‰ with average −31.9 ‰) and carbonate. Because of very low carbonate contents in the black shales, only 11 samples analyzed yielded credible δ¹³C_carb values from −4.0 to +1.7 ‰ with average −2.1 ‰. By which δA defined as the isotopic difference between the burial fluxes of sedimentary organic matter and carbonate is −30.5 ‰. Kump and Arthur (1999) developed a model, according to Henry’s Law at 25°C and assuming phosphorus as an ultimate bio-limiting nutrient, to obtain an expression relating δA to pCO₂:

\[ \Delta A = ((159.5 \times [PO₄] + 38.39)/0.034\text{pcO₂}) - 33 \]  

where [PO₄] (μmol/kg) proxies nutrient concentration in surface-ocean. Substituting the average carbon isotopic difference (−30.5 ‰) between the δ¹³C_carb and δ¹³Corg for δA in equation (1), rearrangement of the equation yield a linear expression for relationship between pCO₂ and [PO₄]:

\[ pCO₂ = 1881.2\text{[PO₄]} + 451.6 \]  

and thus would provide a means of estimating CO₂ concentration during sedimentation. Using our calculated average value for δA −30.5 ‰ and assuming that [PO₄] concentrations of the Early Cambrian ocean were similar to present (Holland, 1984) ranging roughly from 0.20 in oligotrophic surface-water to 3.5 μmol/kg in the nutrition-enriched deep water mass in modern ocean, the Early Cambrian atmospheric CO₂ concentration could range from 828 to 7036 ppmv. It should be 3 to 25 times pre-industrial revolution levels (ca. 280 ppmv). This is broadly consistent with predictions that the Early Cambrian atmospheric CO₂ level was as much as 20 times present day values (Kasting, 1993; Berner et al., 2001; Kaufman et al., 2003). If so, it would imply a high level of nutrient availability represented by phosphorus in the Early Cambrian. We relate the unusually low δ¹³Corg values of the black shales to an anoxic oceanic environment, high atmospheric CO₂ content and warm greenhouse climate. It should be propitious to trigger the “Cambrian explosion”.

References

The Paleozoic SSZ-type ophiolite and subduction rollback in the eastern Junggar, northwestern China

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There are two Paleozoic ophiolite belts, Karamaili and Aermantai, in the eastern Junggar orogene, northwestern China. The northerly Aermantai ophiolite, aged by 503 to 481Ma (Xiao et al., 2006; Jian et al., 2003), has been testified to forming in interarc basin setting (Jin et al., 2001) of supra-subduction zone (SSZ). Our data show that the southerly Karamaili ophiolite, generated in Silurian to early Devonian, contains some basaltic rocks with intermediate N-MORB/IAT composition (fig.1), in addition to E (N)-MORB and OIB reported by former investigators. We infer that the Karamaili ophiolite should have formed in a backarc basin of SSZ. The basalts with intermediate N-MORB/IAT composition formed in the early stage of the backarc basin, while the MORB-like and even OIB-type rocks formed in the “more expanding” stage of the backarc basin resulted from influx and upwelling of relatively enriched mantle driven by convective drag and succeedent rollback of the subducted oceanic slab. Thus the two ophiolite belts constituted the Paleozoic intraoceanic “dual arc-basin systems” in Eastern Junggar by subduction rollback of oceanic slab, similar to the multiple arc-basin systems of northwestern Pacific region. This dual arc-basin systems collapsed and closed at the early period of Later Paleozoic, and assembled in order to the southern margin of Siberian continent, on which the middle Cambrian (505Ma) active continental magmatic arc has been revealed by Windley et al. (2002).

Fig.1: N-MORB-normalized trace element patterns for basaltic rocks from the Karamaili ophiolite

References
Recycled oceanic crust as a possible source of kimberlites - Isotopic evidence from perovskite, Udachnaya-East pipe, Siberia

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In an effort to better understand the sources and petrogenesis of kimberlitic melts, we report new results from the ultrafresh Udachnaya-East kimberlite, Siberia. Earlier results [1,2] indicate that initial kimberlite magmas are H₂O-poor and rich in mantle-derived Cl and CO₂. Additional insights come from a recently identified inclusion from this pipe, which may represent a high-purity sample of the kimberlite melt component, uncontaminated by disaggregated xenoliths. Mineral compositions (fresh olivine, phlogopite, perovskite) in this inclusion are identical to those in the host kimberlite groundmass, but phlogopite and perovskite are unusually abundant (10 wt% perovskite). The bulk composition of the inclusion is ultramafic (32% MgO) and trace element concentrations are controlled by perovskite, with strong LREE enrichment and depletions at Sr and Zr; the latter are absent in the host kimberlite groundmass. Phlogopite Rb-Sr and Ar-Ar dating indicate a ≈370 Ma age, consistent with published pipe emplacement ages. The inclusion is thus best described as a late-stage cognate inclusion, or autolith. Initial Sr-Nd isotope ratios in inclusion perovskite (0.7030, εNd +5.5) differ from those of the (acid-leached) host kimberlite groundmass (0.7048, +4.0), possibly reflecting xenocrystic contamination in the latter. Alternatively, age corrections may be compromised, even in acid-leached groundmass, by the complex, polyphase nature of the kimberlite [2]. By contrast, the inclusion perovskite, with Rb/Sr =0, is a much simpler matrix and thus preserves a more straightforward isotopic record of the kimberlite melt component. The isotopic data, in particular the low ⁸⁶Sr/⁸⁸Sr, provides support for earlier suggestions [3], partly based on Hf-Nd isotope data [4], that recycled subducted MORB may form part of the kimberlite melt mantle source. Further isotopic data (Pb, Hf) will be reported.

References

Harnessing biomineralization: From cell factories to functional bionanomaterials

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Bacteria from the environment carry out many diverse processes which result in the production or transformation of minerals. This biomineralisation leads to the formation of mineral deposits which are retained on the bacterial cell surface or are scaffolded outside the cell or upon, or within, extracellular polymeric matrices. The cell therefore has a dual function in supporting the solid material, while providing the metabolic activity and localised chemical environment to promote biomineral growth.

Many of the biomaterials formed by bacterial action have potentially useful properties in various technological applications. Bio-growth is particularly useful because the scaffolding helps to prevent the agglomeration processes that beset the commercial production of nanoparticles, while the controlled growth can be steered towards the production of particular particle sizes. Both of these objectives are difficult to achieve by chemical production processes.

Nanoparticles are highly prized because they are very reactive and have properties which can be different from bulk materials. The ‘cell factory’ is a scalable approach to the bulk production of stable nanoparticles in a reproducible way.

Case histories will be presented to illustrate the production of bionanoparticles for applications in biomedicine, chemical industry, environmental remediation and clean energy, and the scope for using wastes as resources for nanomaterial production will also be discussed.
The rutile (110)-electrolyte solution interface to 250°C: A surface complexation synthesis of titration, ab initio, MD, and X-ray spectroscopic results

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We have been conducting potentiometric titrations of rutile powders dominated by the 110 crystal face to 250°C in several so-called “inert” electrolyte solutions (NaCl, NaTr (Tr=trifluromethanesulfonate), RbCl) over the past dozen years. More recently (since about 2000) these bulk, macroscopic measurements have been augmented by ab initio and molecular dynamics (MD) simulations, as well as synchrotron-based x-ray spectroscopic measurements, in order to obtain an unambiguous understanding of the rutile 110-electrolyte interface from the micro- to macroscopic scales.

The focus of this contribution will be our most recent attempts at incorporating the molecular information afforded by our ab initio, MD, and x-ray results into Surface Complexation Models (SCM’s) that accurately reflect both this microscopic reality and our bulk surface titration data. A MUSIC model description of surface protonation that utilizes this microscopic reality and our bulk surface titration data. A Complexation Models (SCM’s) that accurately reflect both complexation synthesis of titration, ab initio, MD, and X-ray spectroscopic results.

Planetary formation from icy planetesimals around 1 AU

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Formation and Evolution of Icy Planetesimals

Standard scenario of planet formation have been developed on the assumption that the primordial solar nebula was optically thin, so that H₂O ice condenses only outside 2.7 AU from the Sun. The solid material is composed of only rocks at the terrestrial planet formation region (Hayashi 1981).

However, it is widely accepted in the astronomical community that the protoplanetary disks are initially opaque owing to the floating small dust particles and become transparent at the late stage of planetary formation. In optically thick disks, the interior of the nebula is shadowed from direct exposure to sunlight, so that H₂O ice is prevented from sublimation outside about 0.7 AU (Chiang and Goldreich 1997).

As planetesimals are likely formed in such opaque protoplanetary disks, they should contain a large amount of H₂O ice. We call such planetesimals “icy planetesimals” hereafter. We perform numerical simulations of formation of protoplanets from icy planetesimals focusing on the competition between accretion and sublimation of H₂O.

![Figure 1: Water content in protoplanets.](image)

Results and Discussion

Fig. 1 shows the water content in the system when Mars-sized objects are formed after runaway accretion. It indicates that planets with diverse water contents (i.e., from dry planet to water-ball planet) can be formed. Water content is strongly dependent on the initial surface density of solid material and the time interval, t₀, between the icy planetesimal formation and the onset of icy planetesimal sublimation. We also find that final water content is dependent on object size. Most of water in the system is contained in largest protoplanets, while most of small planetesimals have lost their initial water.

References

Mineralogy of Zaroo ilvaite bearing skarns, Central Iran

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Zaroo Cu-skarns are located north-west of Yazd province and this region is included in Cenozoic magmatic belt of Central Iran. The widespread rocks in this region are Eocene age volcanic with granitoid intrusives. The Cretaceous limestones in western parts of Zarro are hosted by skarn-marble mineralization in parts. The skarns are distal type and characterized by following assemblages: clinopyroxene + magnetite + quartz + calcite. The paragenetic relationships of these minerals have revealed a polygenetic nature of skarn. Black crystals and masses of ilvaite have a close association with hedenbergite clinopyroxene and andradite garnet zone, likely as replacement bodies.

The formation of ilvaite is related to the following reactions:

andradite + Fe(OH)₂ + CO₂ = ilvaite + magnetite + quartz + calcite + H₂
hedenbergite + magnetite + Fe(OH)₂ = ilvaite

The early skarn minerals are formed at 550°C and the decomposition of early minerals to formation of final hydrous assemblages started below 470°C in high fO₂. The peak metamorphisms for marbels are about 540°C with mineral assemblage as follows:

Garnet + vesuvianite + termolite + epidote + calcite + quartz

Magmatic architecture and geochemical variability at the 9°N segment of the East Pacific Rise

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The 9°N region of the East Pacific Rise (EPR) has been densely sampled by submersible and wax-coring techniques, with over 1200 samples available from less than 100 km of ridge axis. Major and trace element and isotope data is available for many of the samples and can be used to quantify the role of source heterogeneity, mantle melting, fractional crystallisation and melt mixing in petrogenesis at a segment of fast-spreading mid-ocean ridge. The spatial control on the sampling locations and the growing catalogue of geophysical observations from the segment allow the geochemical variations to be understood in the context of the imaged distribution of melt at the ridge axis. The shallow axial melt lens plays an important role in the mixing of melts and destruction of mantle-derived compositional heterogeneity. Samples collected from the sea-floor lying above this melt lens show a narrow range of incompatible trace element ratios. In contrast, samples collected away from the ridges axis, or close to suspected ridge-parallel discontinuities in the melt lens, show much greater variation in their trace element composition. These samples appear to have bypassed mixing within the axial region. In addition, evolved compositions, with <7.3 wt% MgO, are rarely sampled above the imaged melt lens and may have been sourced from cooler regions containing low melt fractions. Along-axis major element compositional variations in samples collected <0.5 km from the axis show a strong correlation with variation in ridge bathymetry and depth to the axial magma chamber. However, trace element ratios show poor correlations with geophysical variation on the scale of the segment. It is therefore likely that variations in along-axis bathymetry reflect spatial focussing of melt in the crustal plumbing system rather than changes in mantle properties.

These results have important implications for the interpretation of downhole compositional variation in IODP core such as that from Hole 1256D. Systematic vertical variations in the composition of upper crustal rocks may result from steady-state crustal accretion at a typical fast-spreading ridge, rather than from large-scale variation in the temperature or composition of the mantle source regions.
Fast-spreading mid-ocean ridge magma chamber processes: Insights from the Oman ophiolite

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We investigate the physical and chemical processes in axial magma chambers and constrain the mechanisms of accretion of the lower crust at fast-spreading mid-ocean ridges by means of a combined structural, petrological and geochemical investigation of gabbroic lower crustal sections in the Oman ophiolite. Magmatically-deformed layered gabbros with fabrics parallel to the petrological Moho form the lower half of the plutonic sections. These normally pass upward via a transitional horizon a few hundred metres thick into massive, non-layered gabbros with vertical magmatic foliations and lineations, and thence into a thin (~200m) horizon of heterogeneous varitextured gabbros. We have previously suggested that the varitextured gabbros represent a fossil melt lens that was filled with variably fractionated, essentially basaltic liquids [1], overlying cumulates formed in the underlying crystal mush from which liquids were efficiently extracted. The vertical foliated gabbros we have interpreted as relict channelways of ascending melts that fed the melt lens. In this study we present major- and trace-element whole-rock and mineral chemical data together with quantitative textural and petrofabric information from complete lower crustal sections in Oman, with the aim of constraining the processes operating in the lower crustal crystal mush. Systematic changes in mineral trace element characteristics are observed. For example, La/Nd ratios in cpx in the layered gabbros increase progressively up section and show little intra-crystalline variability; however, at the transition into the foliated gabbros the extent of intra-crystal variability increases significantly. Whereas the variation in La/Nd between layered gabbro samples could, in isolation, be interpreted as being due to variations in parental melt composition, the same trends within individual crystals and the progressive change in ratio up-section are difficult to interpret in this way. Instead, they may be successfully reproduced using an assimilation–fractional crystallisation model of magmatic metasomatism: probably compaction-driven reactive porous flow of melt migrating upward through the crystal mush. Possible implications for magma chamber models will be discussed.

References

Differentiation of basaltic melt in the shallow mantle wedge: Implications for mass fluxes into the arc crust

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In general, magmatic differentiation is regarded as a process that affects primary basaltic melts after they have encountered a significant density interface. For this reason, many studies of differentiation in arc lithosphere focus on processes occurring at, or above, the Moho. However, there is ample evidence that subduction zone magmas can interact with the mantle wedge. Recent work in Surigao, eastern Mindanao, indicates that hydrous basaltic melt can also differentiate beneath the Moho [1].

The Surigao suite comprises a continuous spectrum of compositions from high-Mg andesite to adakitic rhyolite. Isotopic ratios and most incompatible trace element ratios are indistinguishable from contemporaneous calc-alkaline magmatism. These similarities point to derivation from similar sources i.e. metasomatised mantle wedge. Rare earth elements, notably Dy/Yb ratios, demonstrate that high-Mg andesitic and adakitic compositions developed through differentiation of hydrous basaltic magma at >30km depth, where garnet is stable. In the Philippines, where arc crust is thin, this represents sub-Moho depths.

The Philippine example suggests that both adakitic and high-Mg andesitic magmatism should be regarded as part of the natural range of magmatic compositions that might arise in any subduction zone. Their presence, or absence, reflects the suitability of a particular subduction zone to generate and then preserve these distinctive compositions. Crust-hosted differentiation could overprint or obscure the distinctive magma chemistry produced at deeper levels, which may be more widespread than is currently perceived.

Adakitic rocks, in particular, are often emplaced where subduction has unusual characteristics e.g. above young slabs or slab edges, and the majority of previous effort has been directed at linking the chemistry of magmatic products to features of the down-going plate. Specifically, both high-Mg andesitic and adakitic magmatism has been linked to melting of subducted oceanic crust. Data from the Philippines and several other locations challenge this finding and suggest that differentiation at more than 30km depth could generate adakitic magma from hydrous basaltic precursors. Differentiation at such levels will have important implications for mass fluxes from the mantle to the arc crust and, potentially, for the evolution of mantle wedge compositions.

Reference
Redox and solution behavior of c-type cytochromes from iron mineral-respiring bacteria

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Mono- and polyheme c-type cytochromes have been linked to ferruginous mineral respiration in a variety of bacteria, such as Acidithiobacillus, Geobacter, Shewanella, and Acidiphilium. While excellent genetic and genomic studies have been conducted, there is a paucity of information regarding the purification, manipulation, and redox behavior of these proteins in vitro. Many of these proteins are membrane or cell-surface associated, and preliminary evidence suggests that they can act as multiprotein electron transfer complexes. Our research goal was to identify methods for the effective purification and manipulation of these proteins, in order to facilitate subsequent study. Many redox active proteins are extractable by salt (NaCl, KCl) or mild detergent washing of cells, suggesting a cell surface location. Two examples are the polyheme cytochrome c OmcS from Geobacter sulfurreducens, and a 42 kDa cytochrome c from Acidiphilium cryptum. Sequential extraction of membrane fractions with incrementally stronger detergents yielded additional redox proteins, and this strategy is useful for targeted purification of particular proteins of interest. Since it is suspected that some of these redox proteins are embedded in a biofilm matrix, experiments were conducted to determine whether this material could be digested away to enable purification. Viscozyme, a mixture of polysaccharidases, was effective at depolymerizing the EPS and reducing problems associated with high levels of polysaccharide contamination. Once extracted out of the cellular and extracellular milieu, some of these proteins are extremely difficult to work with, due to hydrophobicity and subsequent aggregation. Some of these issues can be circumvented by use of non-denaturing detergents at low (sub-critical micellar concentrations) concentrations. Finally, our extraction and stabilization methods were applied to the directed proteomic detection of large-mass heme c-containing proteins directly from complex microbial communities, with the hypothesis that these proteins are similar in function to those found in pure cultures of iron reducing or iron oxidizing organisms. In all, our research efforts in protein purification of this interesting class of enzymes has revealed useful information regarding their behavior, which is critical for successful studies using voltammetry, Optical Waveguide Lightmode Spectroscopy, and other techniques used to characterize these proteins.

Variations in stable sulfur isotopes in acid sulfate soil materials

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This study represents the first comprehensive investigation into the use of stable sulfur isotopes in acid sulfate soil materials (ASS). The aim of this study was to: 1) examine the isotopic composition of a range of acid sulfate soils, 2) compare stable sulfur isotope ratios in terms of the ASS environmental setting and landuse history, and 3) examine the likely utility of using stable sulfur isotopes to identify the source(s) of sulfate (SO$_4^{2-}$) contributing to the formation of contemporary ASS materials. The sulfur isotopic composition of the acid volatile sulfur (AVS), chromium reducible sulfur (CRS) and soluble SO$_4^{2-}$ fractions were determined on sulfidic materials from coastal and inland floodplain landscapes.

In mangrove sediments the stable sulfur isotopic ratios of iron sulfides were strongly negative, indicating SO$_4^{2-}$ reduction from an open seawater SO$_4^{2-}$ source. In contrast, positive stable sulfur isotope ratios in other acid sulfate soil materials were indicative of a closed freshwater SO$_4^{2-}$ source. At one location, the Tuckean Swamp, both marine and freshwater sources of SO$_4^{2-}$ exert an influence, which may be related to changes in management practices such as opening flood gates to allow the ingress of tidal water. Stable sulfur isotope data for the inland sites suggest SO$_4^{2-}$ has been incorporated into sulfide precipitates from a range of potential sources. Similarities between the $\delta^{34}$S of the sulfide and soluble SO$_4^{2-}$ ratios at severely acidified sites indicate the oxidation of sulfides is contributing to the sulfur isotope signature of the SO$_4^{2-}$. This process may be responsible for supplying a source of SO$_4^{2-}$ which contributes to the seasonal formation of monosulfidic black ooze (MBO). The production of SO$_4^{2-}$ from sulfides also resulted in the freshwater overlying one study site having a sulfur isotope signature well outside the range previously given for freshwater SO$_4^{2-}$.

The results indicate the ‘open/closed’ concept as often used in stable sulfur isotope studies of sulfidic sediments is problematic in ASS landscapes in eastern Australia. The data also indicates that stable sulfur isotope ratios are a valuable tool to help understand environmental processes occurring in ASS landscapes. The application of stable sulfur isotopes in sediments and ground waters to help discriminate and quantify the contribution the oxidation of ASS is making to the SO$_4^{2-}$ concentration of surface and ground waters during different flow regimes is being examined.
Control of chemical weathering rates by secondary mineral precipitation: a reactive transport approach for understanding soil genesis

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The geochemical evolution of a soil chronosequence developed on progressively older marine terraces (65-226 ka) near Santa Cruz, CA is considered using a reactive transport approach. The model includes the aqueous concentrations, quantitative mineral abundances, and mineral-specific cation exchange. Using the reactive transport approach, we are able to quantify the rate of clay precipitation and directly assess the importance of clay precipitation in moderating chemical weathering rates. In the absence of clay precipitation, the model predicts that weathering fronts for plagioclase and K-feldspar would be restricted to the upper 0.5 meters of the profile, while in reality the weathering fronts extend to a depth of 3 meters for a 226 ka soil. This suggests that clay formation is required to generate the observed weathering profiles. Kaolinite precipitation facilitates primary mineral dissolution by removing aqueous Al and Si and therefore controlling the saturation state of the primary minerals, providing the driving force for dissolution. This effect is particularly important in natural systems where fluid residence times range from months to decades and the fluids would be saturated with respect to the primary minerals in the absence of secondary mineral precipitation.

Our analysis suggests that the "bulge" in clay abundance associated with an argillic horizon at about 1 meter depth can be explained by in situ clay precipitation and does not require or support significant translocation of clays. The incorporation of mineral-specific cation exchange did not affect the profile evolution. However, the addition of dust to the simulated profile effectively decreased the dissolution rate because of the increase in total mineral abundances. The weathering gradients and location of the reaction fronts were affected by differences in solubility of the primary minerals, the rate of kaolinite precipitation and fluid flow. The best fit to the data suggests kaolinite precipitation rates of $10^{12.4}$ mol/m²/sec, K-feldspar and plagioclase dissolution rates are $10^{14.6}$ and $10^{14.3}$ mol/m²/sec, respectively.

Successes and failures of garnet Lu-Hf and Sm-Nd geochronology: Examples in eclogites from the Western Alps

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The potentially high Lu/Hf and Sm/Nd ratios in garnet make these isotope systems attractive to geochronological applications in garnet-bearing rocks such as eclogites. Rayleigh fractionation modeling predicts that, due to the variation of Lu, Hf, Sm, and Nd distribution coefficients, Lu-Hf ages will tend to date early garnet growth due to high Lu/Hf ratios in the core, whereas Sm-Nd ages should reflect the average garnet growth age (Lapen et al., 2003, EPSL), assuming the blocking temperatures of these isotope systems were not exceeded. When Lu-Hf or Sm-Nd data fail to provide statistically meaningful garnet-whole rock and garnet isochrons, this is often ascribed to contamination of garnet by inclusions, and partial dissolution, annealing, and leaching strategies have been developed to address this.

The Zermatt-Saas ophiolite in the Western Alps is an example of a relatively cool (500-600 °C), dry eclogite terrane that was metamorphosed to HP and UHP conditions. Core-torim zoning of Lu, Hf, Sm, and Nd in garnet may be controlled by diffusion-limited uptake, deviating significantly from that predicted by Rayleigh fractionation. If their uptake is limited by diffusion, overall Lu/Hf ratios in garnet will sharply decrease from the garnet core resulting in a low bulk Lu/Hf ratio. Although low Lu/Hf ratios have been commonly ascribed to mineral inclusions such as zircon and rutile, this may not always be the case. For Sm-Nd geochronology, diffusion-limited uptake will produce low Sm/Nd ratios in garnet, reducing isochron precision. Such very low Sm/Nd ratios in garnet have been observed in a number of studies, and our element zoning studies indicate that low-Sm/Nd inclusions are not the sole explanation.

Partial dissolution tests demonstrate that "hot plate" dissolution, often thought to avoid dissolution of low-Lu/Hf phases, cannot always be relied upon to produce meaningful isochrons because the measured $^{176}$Hf/$^{177}$Hf ratios may be decoupled from the measured Lu/Hf ratio due to elemental fractionation associated with incomplete sample digestion. Distinction between Rayleigh fractionation and diffusion-limited uptake is critical for successful geochronology, and this requires detailed elemental traverses across central cuts of garnet, guided by 3D x-ray tomography. The likelihood of successful geochronology can be increased through consideration of 3D garnet distribution of specific samples, water contents, and peak metamorphic temperatures.
Calibration of the cosmogenic nuclide production rate of $^{36}$Cl on Fuerteventura, Canary Islands, Spain

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Cosmogenic nuclides are a promising tool of investigating the time span rocks have been exposed to cosmic radiation. Exposure dating has been applied in many geoscientific fields such as volcanology, (glacial) tectonics, structural geology and geomorphology. However, there is still major disagreement in determination of scaling factors and production rates for the cosmoneutrons.

Due to geographic position and presence of basaltic lava flows the island of Fuerteventura was chosen by CRONUS-EU to serve as a $^{36}$Cl calibration site. Young basalts from this island are analysed to better constrain scaling factors and production rate. Due to its relative short half-life $^{36}$Cl is well suited for age determination of rocks of relatively little exposure age.

The quality of the scaling factors that describe the influence of a number of parameters such as height, topographic shielding, and coverage is tested in terms of sensitivity to changes due to geologic/geophysical reasons and in terms of sensitivity for uncertainty in actual measurement and calculation of paleo-values. Special attention is focused on the effect of intensity and orientation variations of the Earth magnetic field throughout geologic time based on paleomagnetic data. The testing procedure is performed with different approaches of calculating scaling factors. Samples of varying ages provide essential information of changes of time-integrated production rates.

Results of AMS measurements in Utrecht as well as laboratory cross calibrations using other AMS facilities throughout CRONUS shed insight into site specific production rates of $^{36}$Cl at the island of Fuerteventura. This will help in future to better constrain scaling factors and production rates for other sampling sites.

Platinum-group elements in mantle xenoliths from the Kaapvaal craton

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We analysed 103 peridotite mantle xenoliths from 15 kimberlite pipes located on the Kaapvaal craton (Kimberley cluster, Jaagersfontein, Roberts Victor, Newlands, Frank Smith, Monastery, Lethlakane, Finsch, Venetia, Premier, Letseng la Terae, Liqhobong, Matsoku) and adjacent off-craton areas (Melon Wold, Markt, Gibeon) for their concentrations of platinum-group elements (PGE). The following results are highlighted: (i) We can model most of the observed PGE patterns by progressive partial melting of a primitive mantle source assuming PGE partitioning into mss, iss, and PGM/alloys. Refertilization by asthenospheric melts/fluids may locally cause elevated Pt and Pd contents, particularly in some LILE enriched MARIDs and PICs and in some high P-T samples derived from the base of the lithosphere. However, in most samples there is no correlation between the concentrations of incompatible trace elements and Pt or Pd, both at on-craton and off-craton localities. This suggests limited addition of Pt and Pd. (ii) Xenoliths from Group I kimberlite pipes tend to have higher IPGE/Pt+Pd and Pt/Pd ratios than those from Group II kimberlite pipes. This indicates that the mantle source represented by xenoliths in Group I kimberlites experienced more partial melting than the source represented by xenoliths in Group II kimberlites. (iii) Kaapvaal mantle xenoliths tend to have higher Pt/Pd ratios than primitive mantle, and relative to deep and shallow mantle samples from other areas. This suggests that Pt has been preferentially retained during evolution of the Kaapvaal mantle. The reason why Pt has been less effectively retained in other cratons is unclear. It could be a sampling problem, or the Kaapvaal craton could contain more refractory Pt alloys, or Pd could have been more effectively removed by metasomizing agents (melts and fluids).
Heat capacity and entropy of MgSiO$_3$ and Mg$_2$SiO$_4$ glasses

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Melting of the material in the crust and mantle of the Earth is one of the principal processes of this geologically living planet. The two most common rock types of the crust – granite and basalt – both originate from molten silicate liquids generated in depth.

In this work, we have measured the thermophysical (heat capacity, $C_p$, and entropy, $S^o$) properties of two glasses with composition relevant to basic and ultrabasic rocks. The glasses correspond in their composition to the minerals enstatite (MgSiO$_3$) and forsterite (Mg$_2$SiO$_4$). The thermophysical properties were measured with a commercial PPMS system in the temperature range 5 - 300 K on ~25 mg samples prepared by levitation and containerless quenching techniques. In combination with high-temperature DSC $C_p$ measurements, our data have the potential for constructing a complete thermodynamic dataset for glasses and liquids of enstatite- and forsterite-composition.

The entropy of the MgSiO$_3$ glass at 298.15 K was calculated as 73.0 J/(mol·K) and the heat capacity at this temperature is 80.2 J/(mol·K). The entropy of the Mg$_2$SiO$_4$ glass at 298.15 K is 105.6 J/(mol·K) and the heat capacity is 118.8 J/(mol·K). None of these entropy values includes the configurational contribution which cannot be estimated from our low-temperature calorimetry data alone.

The $C_p$ curves for both glasses display a pronounced “boson” peak at low temperatures (< 150 K), i.e., a pronounced positive difference of the $C_p$(glass) – $C_p$(crystal) value. Although this peak has been assigned simply to a variable coordination number of cations in glasses, it seems more likely that it is due to the presence of low-frequency modes in the relatively open framework of the glasses. The origin and cause of this difference will be discussed in further detail in a separate contribution.

Unusually high trace element abundances in residual peridotites: Implications for mantle-melt interactions at a Mid Oceanic Ridge

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We report unusually high trace element concentrations in clinopyroxene (CPX) and extremely high whole rock trace element abundances of a set of unmetasomatized peridotites from a ~2m high peridotite-gabbro section from the Horoman Peridotite Complex, Japan. Trace elements exceeding Primitive Mantle values suggest a fertilization event by addition of a melt producing a highly fertile peridotite suit. Gabbros represent added melts having higher Cr$_2$O$_3$ than both Type I [TiO$_2$ and rare earth elements (REE) rich] & II (Cr$_2$O$_3$ rich with distinct positive Sr & Eu anomalies) gabbros (Takazawa et al., 1999), whereas TiO$_2$ and REE contents are lower than Type I but greater than Type II. Mineral textures preserved in the peridotites support melt interaction and bulk rock trace elements can be successfully modelled by a gabbro-peridotite binary mixing process. Absence of metasomatic evidence and are signature in these samples clearly rules out the occurrence of melt interaction at a subduction zone. Highly depleted light REE patterns of both CPX and bulk peridotites and occurrence of two pyroxene spinel symplectites imply the peridotites are residues of polybaric melt extraction started from the garnet field. Thus, we propose these peridotites were intruded by magma and consequently melt-rock interaction occurred under mid ocean ridge tectonic setting. Intruded melts were then frozen as gabbros within the residual peridotites during decompression to the spinel facies conditions, eliminating any chance for melt-driven metasomatism. Subsequently, rocks were incorporated into a subduction zone setting and undergone deformation with extreme stretching and folding in H$_2$O bearing wedge-mantle forming millimetre to meter scale layering (Yoshikawa and Nakamura, 2000).

References


Zircons from ultramafic-mafic intrusions at Noril’sk area (Russia): A compositional and U-Pb study

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World-class platinum-group-element (PGE)-Cu-Ni deposits closely linked to intracontinental paleorift-related ultramafic-mafic intrusions are located in the northwestern corner of the Siberian craton, Russia. In spite of its significant metallogenic potential, age constraints for the ore-bearing intrusions are poorly defined. Similarly, timing and duration of the ore concentration responsible to form an economic deposit has been rarely evaluated quantitatively.

This study presents the results of trace element data and uranium-lead ages for about 550 grains of zircons, which were extracted using ppm-mineralogy technique (NATI Research JSC, St, Petersburg, http://www.natires.com) from drill core samples from the various types of igneous bodies. The latter include economic PGE-Cu-Ni deposits associated with the Noril’sk-1 (drill core MN-2), Talnakh (OUG-2) and Kharacelakh (KZ-844) intrusions, subeconomic deposits related to the Chernogorsk (MP-2), Zub-Marksheider (MP-27) and Vologochan (OV-29) intrusions and none economic the Chernogorsk (TG-31) intrusion. Isotope geochemical data (102 REE analyses and 616 U-Pb measurements) were determined with secondary ion mass spectrometer SHRIMP-II at All-Russia Geological Research Institute.

Zircons are characterized by a fuzzy (smoky) cathode luminescence, with a virtual total absence of zoning. Petrographic inspection, however, revealed at least two generations of zircon that show distinct solid inclusion discrimination diagrams (Sm/La) – La and Ce/Ce* - (Sm/La)zircons mainly plot in the field of “magmatic” zircon (after Hoskin, 2005), with a tale approaching the “hydrothermal” field.

Four age groups of zircon were determined, with concordant U-Pb ages that vary in the range 220-260 Ma. Polyphase grains also preserve domains with U-Pb ages that cluster around 300 and 340 Ma. Rare detrital grains (around 1900 Ma) have been observed. Our new findings are in a good agreement with assumption about the interaction of distinct magmas and a prolonged duration of component fractionation in the magmatic system. Consequently, these processes could lead to high degrees of separation and concentration of ore elements and formation of specific ore magma of unique scales and concentrations.

Linking between Mid Ocean Ridge basalts and Abyssal peridotites from Nd isotopes

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We have analyzed the trace element concentrations and Sr, Nd isotopic compositions of clinopyroxene (cpx) separates from abyssal peridotites (AP) from three different locations – South West Indian Ridge (SWIR), Mid Cayman Rise (MCR) and Mid Atlantic Ridge (MAR).

AP from all locations have trace element characteristics indicative of variable degrees of melt depletion. The SWIR peridotites from three different dredges show similar moderate to strong LREE (Light Rare Earth Elements) depletion, however the three dredges have distinct Nd isotopic composition. Nd-isotopic compositions of the cpx from the SWIR are on average higher than the ridge basalts. Cpxs from dredge VAN85 have some of the most depleted in REE abundances with CeN < 0.1 and YbN < 10. Cpxs from this dredge have high Nd-isotopes ratios (0.513086-0.513320) all higher than the Nd-isotopes ratios of the associated basalts. Dredge VAN78 is more homogeneous in Nd-isotope ratios (0.513003-0.513046) that fall within the range of Nd-isotope ratios of the associated basalts and display a less depleted REE pattern (CeN = 2-5) than dredge VAN85. In contrast cpxs from dredge VAN96 have elevated LREE abundances (CeN >0.4) and have most enriched Nd-isotope ratios (0.512885-0.512933) and are similar to the associated basalts. The cpxs from dredge VAN85 and VAN78 are not in equilibrium with the ridge basalts whereas the REE patterns from dredge VAN96 indicate that these cpxs could be in equilibrium with the associated MORB.

Cpxs from MCR peridotites all show extreme depletion in LREE abundances (CeN <0.4) and have variable HREE (YbN >4-17). The cpxs are too depleted in LREE to be in direct equilibrium with MORB. Nd-isotope ratios (0.513115-0.513425) of the cpxs overlap with the Nd-isotopes ratios of the associated basalts (0.512961-0.513190) and extend to higher ratios.

Cpxs from MAR show two orders of magnitude variation in Ce concentration (CeN =0.7-0.007) with YbN ~3. Nd-isotope ratios (0.513011-0.513190) of the cpxs are indistinguishable from the associated basalts.

The large variation in REE patterns at all locations indicates that there is significant heterogeneity in the sub-ridge mantle. The discrepancy in Nd-isotope ratios between basalts and AP at SWIR and MCR requires a low Nd-isotopic composition component not shown in the peridotites to contribute to the basalts. However, the fact that at some places basalts and peridotites overlap indicates that this low-Nd-isotopic composition component is not a ubiquitous component in the sub-ridge mantle.
**Geochemical hazard by coal-ash from a coal-based thermal power plant in Kolaghat, West Bengal, India**

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**Introduction**

Coal combustion of thermal power plants in India is a major source of environmental pollution due to the generation of huge amounts of ash rich in toxic and radioactive elements, which are disposed off in large ponds and on open grounds surrounding the power plant. Absence of an underground lining permits easy mixing of the ash with the top soil of the area. Geochemical and radionuclide study of coal, ash, water and soil was carried out around a major thermal power plant in India to assess the potential contamination of the soil and the groundwater system.

**Experimental methods**

Major, minor and trace elements in the ash, coal and soil samples around the ash ponds of the power plant by x-ray fluorescent spectrophotometer. ICP-MS was used to determine the concentration of the trace elements in the water samples collected from the wells located near the vicinity of the ash ponds and in the surrounding villages of the study area. NaI (Tl) induced gamma-ray spectrometer.

**Results and Discussions**

Major and minor oxide analyses of the coal and ash document predominance of silica and alumina. The coal-ash is significantly enriched in the trace elements Pb, Cu, Ni, As, Cd, Cr, V, Mo etc. Radiometric analysis of the ash shows that the radionuclides (\(^{238}\)U, \(^{232}\)Th) are enriched 3-5 times in the coal ash as compared to their crustal average. The average absorbed gamma dose rates at 1m above the ground from the ash as compared to their crustal average. The average which is ~4 times higher than the world average (43nGy h\(^{-1}\)).

Combustion of coal thus causes serious environmental concern due to the release of the toxic trace elements and the radionuclides in the ash, thus contaminating the top soil and the subsurface aquifer. People living near the ash ponds are subjected to a high radiation dose from the ash ponds and the soil cover, which is ~ 2.6 times higher than the world average.

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**Temperature-dependent molecular cell membrane adaptation of microbial populations in Siberian permafrost**

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Permafrost is a common feature in polar regions. The uppermost permafrost layer, thawed in summer, is characterized by an extreme temperature regime from about +15°C to −35°C. Even so a diverse range of microorganisms have been discovered in this so-called active layer.

The aim of the current study was to examine as to how the microbial populations within the different horizons of the active layer were adapted to the extreme variable temperature regime of the permafrost area. Thus, two soil samples were taken from the active layer on Samoylov Island in the central Lena Delta, Siberia: one surface-near sample (11-18 cm) and one permafrost-near sample (25-32 cm). Aliquots of each sample were incubated under 4 °C and 28 °C for about 4 weeks. Subsequently, the molecular cell membrane composition (phospholipids) was qualitatively and quantitatively evaluated using HPLC-ESI-MS/MS.

To maintain the membrane fluidity at low temperatures, microbial cells can decrease their solid-liquid phase transition temperatures below the ambient temperature. They change their phospholipid fatty acid composition to more bulky-shaped cis-unsaturated fatty acids and/or to more shorter-chain fatty acid, because of the lower melting temperatures of unsaturated and shorter-chain fatty acids.

The comparison of the phospholipid fatty acid (PLFA) distribution of the different horizons at 4 and 28 °C shows that the microbial population of both horizons does not incorporate significantly more unsaturated fatty acids under cooler conditions. In contrast to this the surface near as well as the permafrost near microbial communities reveal for both a distinct relative increase of short chain fatty acids of 7.3 and 10.3% in the 4 °C incubation experiment.

In addition to this distinct chain length adaptation, the PLFA proportions of the microbial population of the active layer differ with the different depth horizons. The permafrost near microbial community shows, in general, a higher relative proportion of unsaturated and shorter chain fatty acids. This indicates a stronger adaptation to cooler environmental conditions, whereas the surface near population reveals a higher flexibility towards warmer temperature conditions.
Mass-independant fractionation during TIMS measurements: Evidence of nuclear shift effect?

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“Abnormal fractionation” of the $^{207}\text{Pb}$ isotope relatively to the mass dependent fractionation between $^{206}\text{Pb}$, $^{206}\text{Pb}$ and $^{208}\text{Pb}$ has been detected during long high precision Pb isotope measurements by thermal ionization mass spectrometry (TIMS) of the standard SRM-981 (Thirwall, 2000; Doucelance and Manhès, 2001).

Zn, Cd and Pb isotope measurements with TIMS (Manhès and Göpel, 2003) revealed that the odd isotopes ($^{65}\text{Zn}$, $^{207}\text{Pb}$, $^{111}\text{Cd}$-$^{113}\text{Cd}$) were affected during extended runs by a mass-independent fractionation in addition to the purely mass-dependent fractionation shown by the even isotopes, leading to an accumulated depletion of the odd isotopes. TIMS Pb isotopic measurements of the standard SRM-981 spiked with $^{202}\text{Pb}$ and $^{207}\text{Pb}$ (Amelin, Davis and Davis, 2005) confirmed this effect. Both studies suggested the nuclear spin carried by the odd nuclides as responsible for these mass independent fractions.

Recently, Amelin, Davis and Davis (2006) suggested that these observed accumulated depletion of odd isotopes relatively to the even isotopes result from a larger volatility of odd isotopes due to the differences in the shape of the nuclei. This idea results from a new interpretation of mass independent isotope fractionationation observed in FUN inclusions of Allende meteorite (Fujii, Moinier and Albarède, 2006) implying the nuclear field shift (Bigeleisen, 1996). The nuclear field shift effect is evocated for the origin of mass-independent fractionation in chemical exchange reactions (Bigeleisen, 1996).

The aim of our study is to identify the process that induces the mass independant fractionation during the thermal ionization processes. Our experiments of the thermal ionization of Pb and Cd suggest that the evocated difference in volatility between odd and even isotopes is not the key process but the change in oxidation states of the elements inside the glass beads.

References


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Geochemical characteristics of adakites from different greenstone belts of Eastern Dharwar Craton, India – Implications on subducted slab-mantle wedge interaction

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The continental crust in the Dharwar Craton of Peninsular India has evolved through terrain accretion and amalgamation of oceanic plateaus and island arcs. The adakites identified from Sandur, Gadwal and Kushtagi greenstone belts exhibit geochemical variation reflecting on their petrogenesis. Adakites of Gadwal belt have SiO$_2$ = 56 – 72 wt.%, Al$_2$O$_3$ = 11 – 17 wt.%, high MgO (0.67 – 3.9 wt.%), Na$_2$O (2.2 – 4.9 wt.%), K$_2$O (0.57 – 1.9 wt.%), low Mg# (35 – 55), Ni (0.7 – 11 ppm), Cr (1.8 – 27 ppm), Sr (142 – 420 ppm), Y (10.3 – 19 ppm), Yb (0.79 – 1.5 ppm) whilst Sandur adakites have comparatively high SiO$_2$ (75 – 78 wt.%), low Al$_2$O$_3$ (12 – 13 wt.%), MgO (0.15 – 0.24 wt.%), high Mg# (58 – 85), Na$_2$O (4.7 – 7.2 wt.%), K$_2$O (1.01 – 2.05 wt.%), Ni (1.3 – 41 ppm), Cr (9.6 – 292 ppm), low Sr (175 – 237 ppm), Y (4.5 – 6.9 ppm), Yb (9.3 – 0.5 ppm). The Rare Earth Element (REE) patterns of Sandur adakites are highly fractionated compared to Gadwal (La/Yb = 43 – 71 and 9 – 29, respectively). Sr/Y ratio in Gadwal adakites is depleted (12 – 27) compared to Sandur adakites (26 – 46) whereas the Zr/Sm ratio of Gadwal adakites is 32 – 58, slightly higher than Sandur adakites. Phanerozoic adakites studied from different parts of the world along with Archaean adakites (from Abitibi) have been interpreted as melts derived from the subducted slab. The geochemical characteristics of slab melts is modified by their interaction with mantle wedge during its ascent and thereof the magmas derived from the partial melting of metasomatized wedge will reflect the composition of slab derived fluids/melts. The overall geochemical characteristics of these adakites and their occurrence with arc basalts, boninites, NEB and high Mg-andesites signify a transition from slab dehydration-wedge melting to slab melting-wedge hybridization and these new observations of adakite geochemistry in different greenstone belts endorse the emergence of complex are magmatism in Neoarchaean terranes.
Unequivocal evidence for a deep magma ocean from metal/silicate partitioning of Ta, V and Si during core formation  

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Heterogeneous core formation models propose a stepwise accretion process generally starting with metal-silicate equilibration in small bodies at relatively reducing conditions (Wänke, 1981; O'Neill, 1991). Initially reducing conditions are required in these models to explain why moderately siderophile elements such as Si, V, and Cr have been depleted from the Earth’s mantle. Studying the metal-silicate partitioning behaviour of refractory, undepleted elements such as Ta allows constraints to be placed on the lowest redox state under which significant terrestrial core formation could have taken place.

High-pressure experiments in the range of 2 - 24 GPa, temperatures of 1750 – 2600°C and low oxygen fugacities (ΔIW -1 to –5) have been performed using piston cylinder and multi-anvil devices. In two separate series of experiments, the metal-silicate partition coefficient for Ta was determined together with (a) Ga, In, Zn and (b) V, Cr, Mn, Ti, Nb. These elements were added as oxides in concentrations of 4-10 wt% to powdered starting mixtures of ~55 wt% synthetic peridotite and 35-40 wt% Fe-alloy (with 2 wt% Ni, 1 wt% Co, 9-17 wt% S).

Our data show that at pressures up to 6 GPa, Ta, Ga, In and Zn would have been strongly depleted from the mantle at the redox conditions required to extract V and Cr to the core. Moreover, the depletion of Ta would have been much greater than the depletion of Si required to explain the low Si/Mg ratio of the mantle compared to CI chondrite, if significant core/mantle equilibration occurred at low pressures. At higher pressures (≥18GPa) and very high temperatures, Si and V can be extracted into the core without depletion of Ta and without requiring strongly reducing conditions. This means that metal-silicate partitioning must have occurred in a relatively deep magma ocean during core formation and that the redox state of accreting material may, on average, have remained constant with time.

References  

Hf-Nd isotopic decoupling in enriched Icelandic lavas  

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The range in isotopic and chemical compositions of Icelandic lavas is commonly interpreted as resulting from mixing between isotopically depleted and enriched components, thought to originate by melting an entire section of recycled oceanic crust [1,2]. In these models the gabbroic section forms the depleted endmember and the crustal layer forms the enriched component. Lead isotopic data has shown the mixing relationships to be more complicated than simple binary mixing, indicating that at least 5 separate components are needed to account for the compositional range [3].

The lavas most enriched in incompatible elements in Iceland, representing the closest approach to an enriched endmember, are found in the Snaefellsnes peninsula (SNP) and in the central volcanoes of southern Iceland (SI). We present new Nd-Hf-Pb isotopic data from these areas. The SNP and SI show $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 0.283077–0.283192 and 0.283076–0.283149 respectively. Nd-Hf ratios correlate with incompatible element enrichment, as elsewhere in Iceland, and thus also with Sm/Nd and Lu/Hf ratios. These correlations give minimum ages for the isotopic variation in SNP and SI of 200-350Ma. However, more recent partial melting events probably have reduced these ages.

Sources originating from recycled slabs are expected to have flat HREE patterns. Samples from the SNP and SI exhibit elevated Dy/Yb$_N$ compared to other Icelandic regions. SNP shows lower Dy/Yb$_N$ than SI indicating smaller garnet facies contributions, consistent with higher Lu/Hf ratios, whilst the high Dy/Yb$_N$ and low Lu/Hf of SI are consistent with a larger contribution from the garnet field.

Samples from the SNP exhibit higher $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ for given $^{144}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Sm}/^{144}\text{Nd}$ than those from SI forming 2 sub-parallel trends on Hf-Nd isotope and the equivalent parent/daughter diagrams. This implies that the Hf-Nd isotope decoupling is a product of ancient source differences in Lu/Hf and Sm/Nd, which have not been eliminated by garnet-facies melting. Calculations using the differences between the 2 correlations give ages which are partially corrected for melting and so may provide insight into earlier differentiation processes. Lu/Hf ages calculated for Eastern SNP and SI gave ages of ~550Ma. These ages are consistent with the lower Palaeozoic age proposed for the recycled slab based on lead isotopes [3]. This could indicate that the Hf-Nd decoupling between SNP and SI reflects heterogeneity within the recycled component.

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Rutile solubility in albite-H$_2$O fluids at high P and T: Implications for HFSE mobility in subduction zones

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Ti and other HFSE are considered immobile in high-P fluids, but rutile is common in eclogite-facies veins. Rutile occurring with vein Na-Al-silicates motivates experiments on the role of NaAlSi$_2$O$_6$ (Ab) dissolved in H$_2$O on rutile solubility at 800-900°C and 0.5-1.5 GPa. At 800°C, 1 GPa, hydrothermal piston-cylinder (HPC) methods[1] indicate that rutile solubility rises linearly from 19±7 ppm (1σ) in pure H$_2$O to 275±10 ppm at 8.8 wt% Ab. Results give higher solubility than reported by [2] using hydrothermal diamond-anvil cells (HDAC). The discrepancy was examined by measuring rutile solubility in Ab-H$_2$O in HDAC by synchrotron XRF at ESRF, ID22. Ti solubility rose from 159±11 to 210±5 ppm with Ab increasing from ~2.5 to 8 wt % (P=0.7-1.1 GPa), in agreement with our HPC results but not [2]. The role of Ab is important. Rutile solubility in supercritical Ab-H$_2$O (HPC, 900°C, 1.5 GPa) increases from 85 ppm in pure H$_2$O to ~1500 ppm at the critical composition (X_{Ab}~0.09); solubility rose further to ~5000 ppm at albite saturation (X_{Ab}=0.52). Independent evidence points to polymerization of Na-Al-Si species in solution at these conditions[3], which implies that the solubility increase with X_{Ab} is controlled by access to more energetically favorable sites in the polymers. As a preliminary test, we carried out Ti K-edge XANES at APS (GSECARS) on quenched hydrous rutile-saturated Ab glasses (X_{Ab}=0.29-0.50). Ti pre-edge at 4970.5±0.1 eV and 0.23±0.01 normalized intensity indicates coordination by oxygen that is ~95% octahedral and 5% tetrahedral[4], in contrast to IV-coordinated Ti(OH)$_4$ in H$_2$O. Evidently, the higher Ti solubility arises from the change in coordination afforded by dissolved Ab components. Ti, and by extension HFSE, are surprisingly soluble in realistic subduction-zone fluids.

References

Changes in ion pairing across the H$_2$O liquid-liquid transition: Implications for planetary fluids

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Compression of H$_2$O at ambient temperature leads to a transition at 0.2–0.4 GPa from low-density water (LDW) to high-density water (HDW) [1,2] due to second coordination-shell collapse [3] or interstitial H$_2$O [4]. This transition may play an important role in fluid-rock interactions in cold, deep planetary settings, such as the interiors of the icy moons of Jupiter and Saturn. To explore potential effects, we studied pressure-dependent variation in contact ion-pairing in MgSO$_4$ solutions at 23°C by Raman spectroscopy using hydrothermal diamond-anvil cells. Solutions were 0.5, 1.75 and 2.0 m, as determined by freezing-point depression. Pressure (P) was determined from the frequency shifts of the 206 cm$^{-1}$ line of quartz [5].

Raman spectra in the region of the OH stretching mode of H$_2$O were collected for 2.0 m MgSO$_4$ and deconvoluted into 3 components. Frequencies of all peaks (1 atm positions: ~3280, ~3450, ~3580 cm$^{-1}$) decrease linearly with $P$. A well-resolved decrease in linear slope at 0.4 GPa is interpreted to record the liquid-liquid transition. A negative correlation between frequency and $P$ is consistent with strengthening of hydrogen bonding with compression; the lower slope at >0.4 GPa implies less strengthening with $P$ in HDW. Spectra in the v$_1$-SO$_4^{2-}$ region were deconvoluted into 2 components, v$_1^{CIP}$=993 cm$^{-1}$ (contact ion pairs, CIP), and v$_1^{*}$=980 cm$^{-1}$, which includes Raman-indistinguishable contributions from free SO$_4^{2-}$ ions and single and doubly solvent-separated ion pairs [6]. Values of v$_1^{*}$ increase linearly with $P$, and also display a well-resolved slope break at ~0.4 GPa. The fraction of CIPs decreased with $P$ to 0.4 GPa, but the trend reversed at >0.4 GPa, signifying increasing CIPs with $P$ in HDW. Salt reassociation with $P$ in deep, cool environments – e.g., beneath the ocean floors of icy satellites – will enhance the progress of dissolution reactions relative to expected values based on LDW, and result in higher mineral solubility in HDW.

References
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Evidence for dry mantle transition zone from the electrical conductivity of wadsleyite

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Micro-scale oxygen isotopic variation in 1.9 Ga Gunflint cherts: New constraints on their paleo-environmental significance

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Precambrian sedimentary cherts have the potential to preserve a record of O and Si isotopic composition (δ18O and δ30Si) of seawater and may give access to oceanic paleothermatures (Knauth and Lowe, 1973 ; Robert & Chaussidon, 2006). However, bulk δ18O of individual cherts at a given age show a typical 3-4‰ range (Knauth, 2005) which complicates paleo-temperatures reconstruction. In addition, some cherts may be of hydrothermal origin and δ18O-values may be altered by metamorphic fluids. We looked for μm-scale δ18O variations in the 1.9 Ga old Gunflint iron-formation (Canada), which contains among the least metamorphosed precambrian cherts, in order to (1) constrain their origin and (2) to assess their preservation.

Four cherts samples, containing different types of silica (microcrystalline quartz, druzy quartz, megaquartz, and quartz veins) and minor carbonates (siderite and ankerite), hematite and pyrite, were analysed (> 100 spots per sample) by multicollector Cameca ims 1270 ion microprobe, with an external reproducibility on quartz standards of 0.31‰ (1 σ, n=22).

The four Gunflint cherts show (i) large megaquartz with δ18O 10-12‰ lower than microcrystalline quartz, (ii) a typical 3-5 ‰ δ18O range for microcrystalline quartz and (iii) quartz veins with δ18O 5-7‰ lower than microcrystalline quartz. The variation in the proportion of the differences types of silica appears to explain bulk variations (i.e. sample 4 of 06/30/84 ; bulk = 22.75‰, δ18O calculated from modal proportions of silica = 23.18%). Considering microcrystalline quartz only, a δ18O range from 0‰ to 3‰ higher than previous bulk δ18O (Winter and Knauth, 1991) is found, which would correspond to a difference of temperature of 0-15°C. This approach may allow to better constrain oceanic paleo-temperatures in the Precambrian.

References


Iron isotope fractionation during hydrothermal ore deposition and alteration

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Iron isotopes fractionate during hydrothermal processes. Therefore, the Fe isotope composition of ore-forming minerals characterizes either iron sources or fluid histories. 51 samples of iron ores and iron mineral separates from the Schwarzwald region, southwest Germany, were analyzed for their iron isotope composition using multicollector ICP-MS. Further, the ore-forming and ore-altering processes were quantitatively modeled using reaction path calculations.

The Schwarzwald mining district hosts mineralizations that formed discontinuously over almost 300 Ma of hydrothermal activity. Primary hematite, siderite and sulfides formed from mixing of meteoric fluids with deeper crustal brines. Later, these minerals were partly dissolved and oxidized, and secondary hematite, goethite and iron arsenates were precipitated.

Two types of alteration products formed: (1) primary and high-temperature secondary Fe minerals formed between 120 and 300 °C, and (2) low-temperature secondary Fe minerals formed under supergene conditions (<100 °C). Measured iron isotope compositions are variable and cover a range in δ56Fe between -2.3‰ and +1.3‰. Primary hematite (δ56Fe: -0.5 to +0.5‰) precipitated by mixing oxidizing surface waters with a hydrothermal fluid that contained moderately light Fe (δ56Fe: -0.5‰) leached from the crystalline basement. Occasional input of CO2-rich waters resulted in precipitation of isotopically light siderite (δ56Fe: 1.4 to 0.7‰). The difference between hematite and siderite is compatible with published Fe isotope fractionation factors. The observed range in isotopic compositions can be accounted for by variable fractions of Fe precipitating from the fluid. Therefore, both fluid processes and mass balance can be inferred from Fe isotopes.

Supergene weathering of siderite by oxidizing surface waters led to replacement of isotopically light primary siderite by similarly light secondary hematite and goethite, respectively. Because this replacement entails quantitative transfer of iron from precursor mineral to product, no significant isotope fractionation is produced. Hence, Fe isotopes potentially serve to identify precursors in ore alteration products.

This iron isotope study illustrates the potential of the new technique in deciphering ore formation and alteration processes. Isotope ratios are dependent on and characteristic of fluid and precipitation histories. Therefore, they are less suitable to provide information on Fe sources. However, it will be possible to unravel the physico-chemical processes leading to the formation, dissolution and redeposition of ores in great detail.
Sodic pyroxene and sodic amphibole as potential micro-analytical reference material for Li isotopes

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Two large pegmatitic crystals of sodic pyroxene (aegirine) and sodic amphibole (arfvedsonite) from the agpaitic igneous Ilímaussaq Complex, South Greenland are suitable reference materials for in-situ Li isotope analyses.

Li concentrations [Li] and isotope compositions (δ7Li) determined by SIMS and micro-drilled material analyzed by MC-ICP-MS generally agree within analytical uncertainty. The arfvedsonite crystal is homogeneous with [Li] = 639 ± 51 µg/g (2σ, n = 69, MC-ICP-MS and SIMS results) and a mean δ7Li of +0.7 ± 1.2 ‰ (2σ, n = 10, via MC-ICP-MS) or −0.5 ± 1.1 ‰ (2σ, n = 23, via SIMS). Accordingly, we propose adopting of δ7Li = 0 ‰ for this crystal.

The aegirine crystal shows strongly developed sector zoning, which is a common feature of aegirines. Using qualitative element mapping techniques (EPMA), the homogeneous core of the crystal is easily distinguished from the outermost sectors of the crystals. The core has mean [Li] of 50.5 ± 3.6 µg/g (2σ, n = 33) as determined by SIMS, whereas the seven micro-drilled regions measured by solution MC-ICP-MS returned slightly lower concentrations, between 41 and 46 µg/g. The δ7Li of the core determined by SIMS (−3.4 ± 1.6‰, 2σ, n = 5) is in excellent agreement with the MC-ICP-MS data (−3.7 ± 1.2‰, 2σ, n = 7).

A limited quantity of these two crystals will be available upon request.

Kinetic Li isotopic fractionation in the alkaline plutonic Ilímaussaq complex, South Greenland

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Li concentrations [Li] and isotopic compositions (δ7Li) of mafic minerals (mainly amphibole and clinopyroxene) from the alkaline to agpaitic Ilímaussaq complex, South Greenland, track the behavior of Li and its isotopes during magmatic differentiation and final cooling of an alkaline plutonic system.

[Li] in amphiboles increase with magmatic differentiation from about 10 ppm in Ca-amphiboles of the least differentiated unit to >3000 ppm in Na-amphiboles of the highly evolved units. In contrast, clinopyroxenes are generally low in Li (15 – 84 ppm) and show no systematic variation with differentiation. The most important factors influencing the distribution of Li between these two phases appear to be changes in the major element composition of the minerals and changes in oxygen fugacity during differentiation. δ7Li of all minerals span an extremely wide range from +17 to −8 ‰, with the different intrusive units having distinct Li isotope systematics.

Amphiboles from the inner part of the complex have constant δ7Li of +1.8 ± 1.1 ‰ (n=15) indicating a homogeneous melt reservoir, consistent with their mantle derivation and in agreement with published O and Nd isotopic data. Clinopyroxenes of these samples are consistently lighter, with δ7Liamph-cpx as large as 8 ‰ and are thus not in Li isotopic equilibrium. These light values might reflect late-stage diffusion of Li into clinopyroxene during final cooling of the rocks, thus enriching the clinopyroxene in 6Li.

At the margin of the complex δ7Li increases systematically, from +2 to exceptionally heavy values of +17‰. This, coupled with the observed Li isotope systematics of the granitic country rocks, whose δ7Li dips to −9 ‰ 5 m from the contact and rebounds to +4 ‰ over 100 m away, supports post-magmatic open-system processes occurring during final cooling of the Ilímaussaq rocks. The country-rock profile reflects fluid infiltration from, and Li diffusion out of, the complex. In contrast, the fractionation within the pluton is too large and not of the right shape to represent diffusional loss of Li. Instead, the extremely heavy values reflect the ingress and circulation of an external fluid phase with a high δ7Li value (possibly seawater) along the chilled contact. This study demonstrates the power of Li isotopes in deciphering fluid- and diffusion-governed processes.
Sulfur speciation and metal transport in surface geothermal waters

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Geothermal waters are generally reduced with elevated hydrogen sulfide concentrations. When these waters assent to the surface sulfide mineralization occurs upon cooling, mixing and boiling (phase separation) as well as oxidation. The oxidation of hydrogen sulfide proceeds through a series of complex reactions with the formation of metastable sulfur species including sulfur (S\(^2\)), polysulfides (S\(_n\)), thiosulfate (S\(_2\)O\(_3\)), polythionates (S\(_i\)O\(_{i+}\)), and eventually to sulfate, often resulting in acid waters. The associated metal speciation and transport is largely influenced by the redox chemistry of sulfur.

We have developed methods for on-site determination and/or sample preservation and lab determination of the concentrations of redox sensitive sulfur and selected metal species in geothermal waters using both ion chromatographic and spectrophotometric techniques. In geothermal surface waters associated with basaltic and rhyolitic rocks in Iceland, H\(_2\)S, S\(_2\)O\(_3\) and SO\(_4\) are found to be the dominant forms of sulfur with concentrations up to 73, 22 and 5060 mg/L, respectively, and H\(_2\)S:S\(_2\)O\(_3\):SO\(_4\) molar ratios between 0.0:1 to 1.2:0.7:1. These waters are often enriched in trace elements like Al, Fe, Mn, Cr, V, Zn, Ni and As with concentrations in the range <1-390 mg/L, <1-756 mg/L, 0.04-4.64 mg/L, <0.01-754 µg/L, 7-890 µg/L, 1-698 µg/L, 0.06-1004 µg/L and 0.2-258 µg/L, respectively. The dissolved metals are predominantly transported in the reduced form as simple ions and hydroxide complexes as sulfur containing species.

Combined field and modeling study indicates that the main processes governing the chemistry of sulfur species are H\(_2\)S discharge (flux), H\(_2\)S oxidation via S\(_2\)O\(_3\), SO\(_4\) reduction, and native sulfur hydrolysis. These reactions are sometimes catalyzed by metals and metal surfaces as well as bacteria. Further, the sulfur redox chemistry and metal transport and precipitation are closely linked together.

Trace element composition of metasomatic reaction zones: Insights into the evolution of the slab-mantle interface

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The peridotite-gneiss reaction zone may be regarded as a natural window on the processes affecting crust-mantle interaction. A spectacular outcrop of the contact between garnet-peridotite and gneisses is located in the northern side of Mt. Hochwart (Ulten Zone, Italy). The ultramafic body consists of strongly serpentinitized metaperidotites associated to monomineralic zones that developed at the contact between the peridotite body and the garnet gneiss country rocks. The composition of monomineralic zones records an order of metasomatic zoning formed by phlogopite-rich to tremolite- anthophyllite-rich rocks from the host gneiss towards the peridotite. Phlogopite aggregates (phlogopitite) with accessory zircon, tourmaline and Cl-apatite also occur.

Whole-rock geochemistry and trace element (LA ICP-MS) composition of hydrous phases (phlogopite and amphibole) in different metasomatic zones indicate mobility of many elements, including elements such as Ta which are considered to have scarce mobility in fluids. Trace element composition of accessory minerals in the phlogopite-rich zone suggests that the trace element signature of subduction zone fluids may be fractionated in this zone. The progressive depletion in some trace elements (LREE) and enrichment in LILE and Li from the peridotite towards the gneiss suggests a strong influence of bulk composition on the trace element budget of hydrous minerals.

The reaction between mantle and gneissic rocks was enhanced by considerable influx of H\(_2\)O-B-Cl-rich fluids, causing crystallization of hydrous phases and release of a trondjhemitic residual melt. We interpret fluid flow responsible for metasomatism at the peridotite-gneiss contact to have occurred at \(≈700-800^\circ\)C, after the migmatization of crustal rocks and incorporation of the peridotite inside the slab. In this contribution we highlight that the chemical composition of fluids in collisional settings can be substantially modified by metasomatic reactions occurring in the mantle wedge.
Helium and argon solubility in silicate melts: Relationship between solubility and liquid structure

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The interpretation of elemental noble gas ratio in magmatic rocks requires the knowledge of the solubility of these elements in silicate liquids and crystals. Argon solubility in silicate melts appears to be controlled by tetrahedral units rather than oxides as previously reported (Marrocchi and Toplis, 2005). This model successfully accounts for reported argon solubility in Al-free systems, in simple Al-bearing systems and in natural liquids. It strongly suggests the link between melt structure and noble gas solubility.

In order to test this predictive model, we computed helium data available from the literature (Jambon et al., 1980; Shibata et al., 1998). As for argon, helium solubility is controlled by the molar silica content, whatever the nature of the network modifying cations. However, we did not observe the two linear segments with a break in slope at ≈ 67 mol% SiO₂ reported for argon (Marrocchi and Toplis, 2005). Such an observation suggests that helium solubility is less sensitive than argon to the polymerization state of the liquid but might be predicted using this parameter. We define partial molar helium solubility of Q₂ (-11.16), Q₃ (-13.87) and Q₂ (-15.11) MMR species as used in the argon model. Such species corresponds to fully polymerized units (Q₄), sheet like units (Q₅) and chain like units (Q₆).

In Al-bearing systems, the nature of the low-field strength cation plays an important role. Determination of helium solubility in such systems is underway in order to define the partial molar helium solubility of the NaAlO₂, Ca₁₋₃AlO₂ and Mg₆₋₄AlO₂ components. Comparison of the He and Ar solubility parameters will allow us to assess differences (if any) between the solubility mechanisms for both gases and thus, develop a predictive model for He/Ar fractionation during magmatic degassing.

References


Heavy lithium in subducted slabs

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Modelling of the Li budget of subducting oceanic crust during dehydration completed previously [1], suffered from a poor constriction on essential input data, such as the Li isotopic fractionation as a function of temperature, the partition coefficient between metamorphic rocks and fluids and the representative range of Li abundances and Li isotopic compositions of altered oceanic crust (AOC) and sediments. These values have been quantified since [2,3,4,5] and were used in this study to revisit the impact of dehydration on the Li isotopic composition of AOC. The results show that dehydration can account for a decrease in δ⁷Li of only ≤3‰, including the entire prograde metamorphic process up to the unhydrous eclogite stage. Dehydration can, therefore, not account for light Li in high-pressure metamorphic (HPM) rocks. Eclogites in subducting slabs are predicted to contain Li at MORB-like concentrations and to be moderately enriched in the heavy isotope. The fore-arc mantle will be strongly enriched in Li with a heavy Li isotopic composition.

We analysed Li abundances and Li isotopic compositions of 56 orogenic HPM rocks from 8 different localities. The investigated samples (together with eclogite samples from [1]) show a wide range in Li abundances from 1 to ~50 µg/g (one sample 77 µg/g). Li isotopic compositions of the rocks display both very heavy (δ⁷Li > 6‰) and very light (δ⁷Li < 0‰) compositions, as low as -21.9‰. However, the δ⁷Li histogram displays a strong peak between 0 and +4‰.

Li abundances in excess of 20 µg/g in orogenic HPM rocks of basaltic composition (eclogites) can only be explained by addition of Li after the onset of subduction, most probably during eclogitisation or exhumation. Light-δ⁷Li values are probably generated by kinetic fractionation of the Li isotopes during diffusive influx of Li from the country rocks into the exhuming eclogite bodies. The consequence of this hypothesis is that Li found in orogenic eclogites is not representative of rocks within subducting slabs. The investigation of subduction-related HPM rocks has always suffered from retrogression of the natural rock samples during exhumation. In the case of Li, this problem seems to be particularly vicious, due to the high diffusivity of Li, its fluid mobility and its liability to kinetic isotope fractionation. On the other hand, Li and its isotopes may be highly sensitive tools to detect HP and retrograde metasomatism in eclogites and peridotites.

References

Dust chemistry and accumulation rate in a long-term full-scale heater test at Yucca Mountain, Nevada, USA

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Yucca Mountain, an eastward-tilted fault block of Miocene-age volcanic rock in southwestern Nevada, is the proposed site for storage of high-level radioactive waste in the USA. The repository would be built within a ~300-meter (m)-thick welded tuff about 200 m above the water table. A full-scale heater test was conducted in a sealed 47.5-m-long, 5-m-diameter drift with concrete invert and partial concrete liner. Steel canister heaters within the drift and borehole heaters on the sides of the drift maintained an in-drift temperature of approximately 200°C for more than 2 years. After 4.2 years of cooling, samples of dust were collected from the upper surfaces of the canister heaters. The amount and composition of the dust, especially the water-soluble fraction, are important factors in understanding the chemistry of the near-field environment in the proposed repository.

Fine dust (~63 micrometers) accumulated on the canister heaters at rates from 0.8 to 4.3 milligrams/square centimeter/year. The major dust components were derived from the host rock (rhyolite), concrete, and oxidized steel. Calcite from limestone aggregate in the concrete constitutes as much as 18 percent. Iron oxides (6 to 9 percent) are derived from the host rock (average 1.0 to 1.8 weight percent of the accumulations beneath partially oxidized steel rock bolts. Water-soluble salts constitute 1.0 to 1.8 weight percent of the dust samples and are enriched in Na+, K+, Ca++, CI-, SO42-, F-, and Br-, and strongly depleted in Mg++, and NO3- relative to dust from ventilated tunnels at Yucca Mountain. The low NO3- in the soluble salts may indicate lack of dust supply to the heated drift via ventilation or may indicate consumption of NO3- through redox reactions that occurred on the canisters or within the wall rock or liner prior to dust fall.

Six of the dust leachates also were analyzed for strontium isotope composition. The samples from canister heaters beneath the concrete liner have 87Sr/86Sr ratios of 0.70930 and 0.70963, indicating derivation of Sr from the liner materials, rather than from the host rock (average 87Sr/86Sr = 0.71715). The four samples under areas with no liner have larger 87Sr/86Sr than the other two, but still lower than the host rock, indicating limited mixing of dust within the heated drift over the 8.3-year isolation period.

This study indicates that dust in the underground environment isolated from ventilation is derived locally from both the host rock and introduced materials. Chemical differences between dust samples and dust from ventilated areas may be due to isolation of the drift and (or) chemical reactions during the heater test.

REE and HFSE mobility from eclogite to amphibolite metamorphism (Vårdalsneset, Norwegian Caledonides)

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Hf and REE mobility during chemical diffusion and recrystallization controls the resetting of Sm-Nd and Lu-Hf geochronometers during metamorphism. It is therefore interesting to characterize HFSE and REE mobility at different scales - intergranular to outcrop scale - according to pressure, temperature and fluid circulation.

Hf and REE mobility is here exemplified by the retrogression of an eclogitic sample (16 kbars, 670 ± 40°C) into an amphibolitic sample (7.5 kbars, 640 ± 20°C) of identical protolith during Caledonian metamorphism, in the Vårdalsneset area (Western Gneiss Region, Norway). The initial eclogitic paragenesis (garnet, omphacite and rutile) is transformed in the amphibolite into a second paragenesis (amphibole, oligoclase, titanite and ilmenite), where garnets are partially resorbed and rutiles are present as relics.

Elemental data allow to discuss chemical mass balances in each sample and during amphibolitization. In eclogite, more than 40% of Hf but only 10 to 15% of LREE are is within paragenetic minerals. The remainder lies within accessory minerals (zircons). In the amphibolite, accessory minerals (zircons and epidotes) concentrate not only LREE but also Hf (85%). Thus, mass balance indicates mobility of Hf from cardinal minerals in the eclogite to accessory minerals in the amphibolite. Moreover, the increase in LREE contents (+ 20%) from eclogite to amphibolite indicates the contribution of fluids during retrogenesis, and reopening of the Sm-Nd system. By contrast, the HFSE content decreases only slightly (ca. 5%). However, isotopic data show significant difference for Hf between eclogitic isotopic ratio (176Hf/177Hf = 0.282804 ± 6) and amphibolitic ratio (176Hf/177Hf = 0.282620 ± 4). At the outcrop scale, whole rock isotopic ratios scatter from 0.2824 to 0.2828. This may be due either to limited reopening of the system during amphibolitization or to the isotopic heterogeneity of the protolith.

Four garnets fractions (three from the eclogite and one from the amphibolite) show a large variability in both 176Lu/177Hf and 176Hf/177Hf ratios and plot along a straight line. This line can be interpreted either as a mixing line between pure garnet and inclusions (e.g. zircons), or as a record of the reopening of Lu–Hf system. In this case, this alignment describes the reequilibration of Hf in garnet after eclogitic metamorphism, probably due to fluid circulation.
Magmatic timescales using diffusion profiles in olivine from Nea Kameni, Santorini, Greece

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Mafic enclaves, interpreted as fragments of replenishing magma batches, are abundant in all the dacitic lava flows of Nea Kameni, Santorini. Periodic replenishment of shallow crustal magma chambers with batches of mafic magma has been widely accepted as a potential eruption trigger. Thus, developing an understanding of the evolution of shallow magma chambers after replenishment, and the duration of any delay between the triggering mechanism and subsequent eruption, represents a significant advance in our ability to predict volcanic activity.

Glomerocrysts and xenocrysts of gabbroic cumulate material are present in a number of the mafic enclaves. Isotopic and chemical disequilibrium between the cumulate crystals and the andesitic host enclaves indicate that these fragments are derived from pre-existing gabbroic crystal mush piles that were pervaded by the replenishing andesitic melts as they migrated to shallow levels, creating disequilibrium between the cumulate mineral cores and the replenishing melts.

High-resolution back-scattered electron (BSE) images reveal that when in contact with enclave magma groundmass, the xenocrystic olivine crystals display narrow (10-30 µm) Fe-Mg diffusion profiles. This diffusion must have occurred after entrainment of the crystals in the replenishing magma, and thus can be used to estimate the interval between entrainment, replenishment and eruption.

Initial modelling of diffusion profiles from more than 60 crystals suggests short timescales, ranging from 6 to 46 days, for the combined migration-replenishment-eruption cycle at Nea Kameni. Such information may prove useful in terms of volcanic hazard prediction and mitigation.

Biogeochemistry of metalliferous peat cores: Distribution of Zn, S, Mn, Fe and dsrAB genes and sulfur and zinc speciation

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Biogeochemical processes have resulted in the accumulation of elevated concentrations of Zn and S in soils of the Manning peatland region in western New York. Peat cores were collected during dry and wet seasons across a transect of variable Zn concentrations. Element distributions, Zn and S speciation and detection of dsrAB genes were independent of season but related to peat depth. The pH increased with depth. The highest levels of S and Zn occurred at intermediate depths, whereas Mn concentrations were highest in topmost soils. Iron showed relatively uniform vertical distribution profiles. These data indicated vertical redox stratification in peat cores where topsoils were typically acidic and oxidizing and deeper soils were typically circumneutral and reducing. Surface peats contained >50% of the total S in reduced forms while deep peats contained <5% of the total S in oxidized forms. dsrAB gene detection followed redox stratification chemistry in peat cores closely.

Zn-EXAFS analyses of surface peats indicated Zn binds to O/N functional groups of soil organic matter. Zn-EXAFS analyses of deep peats identified ZnS minerals as the primary Zn specie while SEM, S isotopic analyses and synchrotron-based XRD showed that ZnS species occur as framboidal aggregates of biogenic nanocrystallites. We can therefore conclude that exposure to prolonged dry-wet cycles resulted in the formation of two redox stratified zones with distinct chemical and microbiological signatures.
Characterization of carbonate mineral formation by cyanobacteria and the implications in CO₂ sequestration

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Biomineral-fluid reactions, including dissolution, adsorption, nucleation, and precipitation minerals are key to solving pressing issues such as minimizing the risk of groundwater extraction, optimizing CO₂ sequestration, safe storage of radioactive waste products, and minimization of pollutant transport. Current understanding of the biomineral-fluid interface is only fragmentary. Although we have a good understanding of the reactivity of minerals in abiotic systems little is known about the kinetics and thermodynamics of biomineral fluid reactions. The major limitation of past biomineralization kinetic studies performed in batch reactors to quantify reaction rates is that it is not possible to control many rate influencing parameters, such as pH, solution saturation state, and bacterial activity and biomass. As such it is impossible 1) to determine the effect of each of these rate influencing parameters individually and thus 2) develop robust equations that can be applied to describe these rates in natural systems. These limitations were overcome in the present study by the modification and application of mixed-flow reactor systems to biomineralization.

Results from Synechococcus sp. photosynthetic cyanobacteria in supersaturated calcium carbonate systems presented are used to determine steady-state thermodynamic and kinetic parameters for the development of macroscopic models capable of predicting carbonate bio-mineralization rates as a function of bacterial cell activity/metabolism, biomass, temperature, pH, and pCO₂.

Different plutons, the same feeding zone

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Multidisciplinary studies integrating petrography, geochemistry, anisotropy of magnetic susceptibility (AMS) studies and gravimetry were carried out on Vila Pouca de Aguiar (VPA) and Águas Frias-Chaves (AF) porphyritic biotite granite plutons which distance ca 20 km one from the other. These plutons are spatially related to Penacova-Régua-Verín fault (PRVF), a late Variscan fault, which belongs to the NNE-trending brittle system that crosscuts the whole of Northern Portugal. VPA pluton is zoned and composed by two main facies: a peripheral biotite-rich medium-grained monzogranite (VPA granite) and a central medium- to fine-grained leucogranite. The AF granite pluton is composed by a marginal coarse-medium grained cordierite-bearing monzogranite (AF granite) and by a central two-mica medium-grained granite.

The modelling of the residual gravity indicates that the shapes from the two granite plutons are quite different: (i) VPA pluton is laccolithic in overall shape, less than 1 km in thickness on 60% of its thickness area; (ii) AF pluton has a greater thickness (~10 km) and is a thicker and deeply rooted body. However gravity data shows a connection of the two gravimetric anomalies. Assuming this connection, a possibility of a relationship between the two plutons was investigated. AMS studies yield magnetic susceptibility averages of 101.0 x 10⁻⁶ SI to VPA pluton and 80.7 x 10⁻⁶ SI to AF pluton. The magnetic anisotropy are quite low and similar, 1.4% to VPA pluton and 1.6 % to AF pluton, confirming their classification as late orogenic (post-tectonic) plutons wich agrees with field data.

The studied granites are slightly peraluminous monzogranites, 1.02<ASI<1.07, and have similar geochemical features (major, trace and REE). However biotite compositions are quite different, namely in content of octahedral Al and XMg wich are higher in AF granites. The tipology features of biotite from VPA granite indicates a sub-alkaline affinity while the biotites from AF granite suggest a aluminopotassic signature, wich are in agreement with the presence of cordierite. These features, the mantle-like isotopic data (Sr₀= 0.704-0.707 and εNd=-1.98 to -2.5) and the available δ¹⁸O (+10 to +11) led us to propose a model of mantle input followed by mantle crust interactions for the origin of these granites, although implying a major crustal contribution for AF granite.

We propose the PRVF as the same feeding zone for the two plutons This fault is also a preferential location for several CO₂ rich thermal water springs, that reach temperatures of 74°C near AF pluton, at Chaves, while in VPA pluton temperature is much lower, 15°C at Pedras Salgadas. A deeper circulation explain the hotter water from Chaves spring, wich is consistent with a deeper root and a thicker shape for AF pluton than for VPA pluton.
Geochemical evidence for extensive carbonate assimilation by CAMP tholeiites from Algarve (S Portugal)

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In the Algarve Basin (S Portugal), Lower Jurassic volcanic successions from CAMP include tholeitic flows, pyroclasts, rare dikes, peperites and volcanic derived sediments. Fine-grained porphyritic carbonate-contaminated lavas coexist in the same sequences with opthic uncontaminated flows. Carbonate contamination is expressed by low SiO$_2$(45.67 to 50.00 wt%), high CaO, Sr contents (12.5 to 20.4 wt% and 235 to 1337 ppm, respectively), and ($^{87}$Sr/$^{86}$Sr)$_{0}$ isotope ratios (0.70665 to 0.70746) relative to those parameters in the uncontaminated rocks (SiO$_2$ = 50 - 53 wt%; CaO = 9 - 12 wt%; Sr = 149 – 233 ppm; ($^{87}$Sr/$^{86}$Sr)$_{0}$ = 0.70539 – 0.70634).

High-CaO rocks also display distinct mineral assemblages, including An-rich plagioclase (An$_{nat}$), olivine (Fo$_{nat}$) and high-Al clinopyroxene (Al$_2$O$_3$ up to 9.1 wt%). Enrichment of Al$_2$O$_3$ in clinopyroxenes (reflecting extensive incorporation of Ca-Tschermak component) correlates with increasing CaO contents of the host rocks, consistent with the mineralogical/geochemical data which indicate a significant decrease of melt silica activity in the high-CaO domains relatively to the typical SiO$_2$ saturated character of the dominant tholeitic magmas.

Binary mixing models (SiO$_2$/CaO vs. 1/CaO; $^{87}$Sr/$^{86}$Sr vs. $^{18}$O/$^{16}$O; $^{87}$Sr/$^{86}$Sr vs. SiO$_2$/CaO; $^{87}$Sr/$^{86}$Sr vs. Sr ppm) indicate that contamination resulted from variable degrees of assimilation of 2-10% of an almost pure Ca-carbonate component. The contaminant component should have had high Sr contents (Sr ~ 6200 ppm) and relatively high $^{18}$O (3% to +25%) and ($^{87}$Sr/$^{86}$Sr) ($>$ 0.70771) isotope ratios, consistent with the chemical characteristics of Visean platform marine carbonates such as those present in the underlying Palaeozoic basement. Significant undercooling by CO$_2$ loss may have increased crystal nucleation rates, producing the fine-grained texture that characterizes the carbonate-contaminated rocks.

Clinopyroxene-liquid geobarometry indicates that the main fractionation occurred at an average depth of 26 ± 4 km, reflecting extensive magma underplating at the Lower Jurassic SW Iberia crust/mantle boundary (promoting assimilation of Visean carbonate basement) during the initial stages of the Atlantic opening.

Monazite preservation and formation during anatexis: An example from garnet-bearing migmatite, Brazil

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Backscattered images, Y and Th mapping and U-Th-Pb$_{(total)}$ electron microprobe dating reveal complex compositional and age zonings of monazite crystals from a garnet-bearing migmatite (Fig. 1).

Monazite chemistry reflects in part its textural position: late interstitial crystals are Y+HREE-poor and Th+LREE-rich, while crystals included in garnet and biotite are Y+HREE-rich. Cores of leucosome monazite have high Y and HREE, and are similar to mesosome monazite, suggesting that they are inherited, and were not dissolved during the melting reactions because of their textural position. Associated to compositional zones, at least two main age domains (~827 Ma and 645 Ma) could be recognized through in situ U-Th-Pb$_{(total)}$ electron microprobe dating (147 analyses). Monazite cores or Y-rich zones correspond to the oldest ages (827 Ma). Some monazite rims or Y-poor and Th-rich zones can be interpreted as products of anatectic melt precipitation at 600-610 Ma, the age of a well-recognized regional metamorphic event (750°C and 5 kbar). The meaning of some portions with intermediate dates (~670 Ma) and chemical contents is unclear (Fig. 1), and could record partly resolided monazite or reprecipitated domains that incorporated some Pb from the anatectic melt.
**Plume-lithosphere interaction at Santiago Island (Cape Verde)**

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Santiago Island belongs to the southern group of the Cape Verde archipelago which is implanted in old and thick oceanic lithosphere (140-120 Ma). This paper will address elemental and isotopic data for ≤6 Ma Santiago lavas, i.e. those that were formed after the erosive phase which exposed the basal (mainly) intrusive complex.

Santiago samples are ultrabasic alkaline lavas, with Nb and Ta enrichment and significant REE fractionation. Elemental characteristics of primitive lavas indicate complex and variable residual paragenesis including garnet, amphibole and phlogopite. The inferred hydrous residual parageneses are more obvious from geochemical characteristics of recent lavas (<3 Ma), reflecting lithospheric metasomatism by a carbonatic agent, consistent with their lower Ti/Eu, Sc/Ca, Sm/Sr and Pb/Ce ratios and aSIO2 values, as well as included carbonate bearing lherzolitic xenoliths. Santiago lavas exhibit a significant isotopic variation ([87Sr/86Sr = 0.703177 to 0.703907, εNd = -0.4 to 4.5 and εHf = 2.5 to 7.2), implying the involvement of HIMU and EM1 like mantle components, in accordance with the overall isotopic characteristics of southern Cape Verde islands.

Given that the evidence for both hydrous residual mantle parageneses and carbonatic metasomatism are best preserved in the more recent formations, metasomatism should have been developed during previous (>3 Ma) magmatic phases of Santiago building; thus, it is suggested that these features were related to interaction of plume derived magmas with the overlying lithosphere, induced by the intense carbonatite melt reaction/diffusibility through regional lithospheric mantle peridotites. Besides the carbonatic metasomatic component, the relatively low [143Nd/144Nd of Santiago lavas implies an enriched mantle component that must be distinct from typical EM1. This feature strongly suggest the influence of low [143Nd/144Nd, subcontinental lithospheric derived melts (lamproite – kimberlite) in Santiago magma sources. The data demonstrate the variable role of lithosphere to Santiago magma genesis; thus, endorsing the influence of plume-lithosphere interaction on oceanic island magmatism.

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**Impact of the late heavy bombardment on Earth**

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The Lunar cratering record is consistent with the occurrence of a late heavy bombardment (LHB), which marked the end of terrestrial planet accretion 3.8 billion years ago. At that moment, migration of the giant planets triggered a cascade of icy planetesimals from the outskirts of the solar system (i.e. ≥15 AU from the Sun) to the terrestrial planet formation region [1]. However, clear evidence of a LHB on Earth has not yet been identified. Here we show that the LHB did indeed occur on Earth and that we are breezing its aftermaths. The terrestrial atmosphere and hydrosphere is enriched in noble gases relative to the abundances of volatiles in the mantle. This noble gas composition is a signature of the LHB on Earth and requires a contribution of cold, noble gas-rich bodies formed in the outer solar system. The present day atmospheric composition is consistent with the estimated mass delivered to Earth during the LHB only if it consisted of ~0.5% Kuiper-belt objects mixed in with a population of largely chondritic (i.e. asteroidal) impactors. It seems likely that during the terrestrial LHB, considerable amounts of complex hydrocarbons were also delivered, conceivably providing essential building blocks for the near simultaneous rise of the biosphere

**Reference**

Genesis and the isotopic composition of nitrogen in the solar wind

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The isotopic composition of protosolar nitrogen is a long standing problem in planetary sciences. The goal of the Genesis mission (NASA Discovery class) was to determine the solar isotopic composition of some key elements in order to document the protosolar nebula and, by comparison, to investigate planetary formation processes that have led to the observed isotopic structures in planets and meteorites. Despite the hard landing of the sample return capsule, fragments of targets irradiated by the Sun during 27 months have been recovered and are currently analysed by several teams around the world. We have developed a new NB isotope analytical system in CRPG Nancy. The new line, partly automated, is made exclusively of stainless steel, Pyrex and quartz, and is pumped by fluid-free pumps. Targets were ablated with a UV laser having a wavelength of 193 nm over surfaces up to 1 cm². N₂ was concentrated on Pt at low temperature, then purified over CuO. Noble gases were purified classically in another section of the line. AuS spare targets implanted with ¹⁵N at energies mimicking those of SW N were ablated over surfaces of typically 1 mm² and we obtained a well reproducible recovery yield close to 100 %. The amount of implanted SW N (2 . 10¹² atoms N/cm²) is so low that contamination not only due to the crash but also resulting from target manufacturing is always dominant; Nevertheless, using the measured Ne amount and isotopic composition and the solar wind Ne/N ratio (from spacecraft measurement), we are able to put constraints on the N isotopic composition of the Sun. Results obtained so far suggest a terrestrial-like composition rather than a ¹⁵N-depleted one, which, if confirmed, will lead to a significant change in our view of the distribution of nitrogen isotopes in the solar system.

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Sulfur isotope geochemistry of sulfdic springwaters at Marche region, central Italy

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The genesis and development of caves are usually controlled by seepage of meteoric waters supplied from the surface. In contrast, some caves, known as hypogenic caves, are formed by fluids coming from the depth. Hydrogen sulfide is one of the most common gases in the springwaters related to cavern environments and has a great impact on the formation of hypogenic caves. The oxidation of H₂S to H₂SO₄ induces the corrosion of the host rock and the deposition of many secondary cave minerals, like gypsum. Gypsum is observed where the emission of H₂S occurs in limestone caves and at least some portion of the gypsum deposits survives long after its emission ceases (e.g., Galdenzi and Maruoka, 2003). The gypsum deposits are often observed as a crust covered on limestone walls above the watertable. Such vadose gypsum crusts have δ³⁴S values similar to those of H₂S in the springwater (e.g., Galdenzi and Maruoka, 2003), implying the oxidation of H₂S to H₂SO₄ and the reaction between calcite and sulfuric acid occurs above the watertable.

The δ³⁴S values of H₂S in the aquifer reflect the activity of sulfate-reducing bacteria. Therefore, those are not constant through the time. The δ³⁴S_S₂H₂S values in the past can be estimated from the δ³⁴S values of the gypsum in the cave where the emission of H₂S ceases. Therefore, the δ³⁴S_gypsum values of the hypogenic caves can be used as a paleoindicator for environmental factors that influence the activity of the sulfate-reducing bacteria. However, so far it is uncertain what is the primary factor that controls δ³⁴S values of H₂S in the aquifer. To clarify this problem, we determined δ³⁴S values of sulfide and sulfate collected from the springwaters related to hypogenic caves in Marche region, central Italy, and compared them with other parameters. In such parameters, sulfate concentration seems to be the most important factor that influences isotopic fractionation between sulfate and sulfide. Pure culture experiments demonstrated that the extent of isotope fractionation is not affected generally by sulfate concentration at concentrations above 1 mM; however sulfate concentrations in the springwaters studied here ranges from 1 to 18 mM. Therefore, the correlation between isotopic fractionation and sulfate concentration might reflect the difference of bacteria community compositions rather than the response of single bacteria community.

Reference

40Ar/39Ar ages of CAMP in North America (Hartford, Deerfield and Fundy basins)

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The Central Atlantic magmatic province (CAMP) is one of the largest igneous provinces on Earth (>1x106 km3) and spans four continents. Recent high-precision 40Ar/39Ar dating of mineral separates have provided important constraints on the age, duration, and geodynamic history of CAMP (e.g. [1]). Yet, the North American CAMP is strikingly under-represented in this dating effort.

Here we present 13 new statistically robust, mostly plagioclase separates, plateau and mini-plateau ages obtained on lava flows from the Hartford and Deerfield (n=3; USA) and Fundy (n=10; Nova Scotia, Canada) basins. Ages mostly range from 198.6 ± 1.1 to 201.5 ± 1.1 Ma (2σ), with 1 date substantially younger at 190.6 ± 1.0 Ma. Careful statistical regression show that ages from the upper (200.0 ± 2.0 Ma) and bottom (200.1 ± 0.9 Ma) units of the lava pile in the Fundy basin are statistically indistinguishable, confirming a short duration emplacement (<< 2 Ma). These results are in agreement with the minimum duration estimates (> 0.6 Ma) obtained by cyclostratigraphy for the Newark basin CAMP [2]. Three ages obtained on the Hartford (198.6 ± 2.0 Ma and 199.8 ± 1.1 Ma) and Deerfield (199.3 ± 1.2 Ma) basin were measured on sericite from the higher lava flow units. We interpret these dates as reflecting syn-emplacement hydrothermal activity within these units. Altogether, CAMP ages gathered so far (cf. compilation in [1] and this study) suggest a short duration of the main magmatic activity (2-3 Ma), but also address the possibility of a temporal migration of the active magmatic centers (e.g. Nova Scotia at 200.3 ± 0.7 Ma and Brazil at 198.0 ± 0.3 Ma). Such a migration challenges a plume model that postulates a radial outward migration of the magmatism and is more compatible with different models such as the supercontinent global warming hypothesis [3]

A possibly significant age at 191 Ma confirms a minor CAMP late tailing activity (190-194 Ma) already observed for dykes and sills in Africa [4] and Brazil [5]. We speculate that this late activity may be due to a major extensional event, possibly heralding the oceanisation process at ~190 Ma [6].

[1] Nomade et al, PPP 234, 326-344;
[3] Coltice et al., Geology in press

The model of the four-sub-grate ferrimagnetic

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There were investigated the magnetic properties of Ferrous sulphides in a metastable phase condition and the change of magnetization of non-stehiometric pyrrotites depending on the concentration of vacancies in their structure. Ferrous sulphides with composition Fe1+xS decrease of magnetization practically to a zero when hardening with the temperature of synthesis. It is shown that the observed effect is explained not only by the redistribution of the vacancies of iron in a base plane of the crystalline structure of the type NiAs, but by the process of the spin flip on the node. For the first time in the frame of the model of the four-sub-grate ferrimagnetic it is given a theoretical description of magnetic transformations in non-stoechiometric ferrimagnetics. For explaining the effect of the ordering of vacancies it is used the method of the secondary quantization. It should be noted that the operators correspond to the quantum statistics of Pauli. The calculations are made considering the interactions between the cation vacancies. It is noted that the appearance of the vacancy interaction is explained by breaking the connections of d-electronic tracks and forming of non-compensated electrical charge on the vacant unit consequently.

Based on the proposed model of the vacancies theoretically possible magnetization depending on the temperature are presented.

**Figure 1:** Theoretical dependence relative magnetization of non-stehiometric ferrimagnetic from temperature.
**Organic Carbon Oxidation State (C_{ox}): A new proxy for the Earth's C and O cycles**

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Carbon oxidation state (C_{ox}) is a basic property of the Earth's carbon pools, and has the potential to be used as a tracer in a broad range of ecological and Earth system questions. It is relevant to questions such as the controls on tracer in a broad range of ecological and Earth system questions. It is relevant to questions such as the controls on tracer in a broad range of ecological and Earth system questions. It is relevant to questions such as the controls on tracer in a broad range of ecological and Earth system questions. It is relevant to questions such as the controls on tracer in a broad range of ecological and Earth system questions. It is relevant to questions such as the controls on tracer in a broad range of ecological and Earth system questions.

**Fig. 1:** Natural variation in C_{ox} values (lower axis) and oxidation state values (OR, upper axis, assuming N from NH_{3}).

C_{ox} varies with 1) initial form of organic matter (e.g. marine vs terrestrial organisms) and 2) degree of diagenesis. On short timescales (decades) precursor organism controls organic pool C_{ox} values. Organism C_{ox} values are themselves likely controlled at a fine scale by ecosystem N status and CO_{2} concentration at the time of C fixation, as well as the history of ecosystem disturbance (Randerson et al., 2006). On longer timescales, degree of diagenesis is at least as important as precursor organism in controlling C_{ox} values.

The utility of C_{ox} is enhanced by its linear relationship with another C cycle parameter, oxidative ratio (OR), defined as ratio of mols O_{2} released/mols CO_{2} fixed by photosynthesis. Currently, the global terrestrial OR value is both unconstrained and required in calculations of the fate of fossil fuel CO_{2} in the environment (Manning and Keeling, 2006). On both long and short timescales, organic matter OR values record the efficiency of the biosphere's production of O_{2}.

**References**


**Sulfur isotopes in barite deposits from the lower Onverwacht Group, Barberton Greenstone Belt: Evidence for microbial sulfate reduction at >3.5 Ga?**

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Convincing stable isotopic evidence for microbial sulfate reduction is limited to only one locality in the early Archaean rock record at the 3.48 Ga North Pole dome in the Pilbara Block (Shen et al. 2001), even though molecular phylogeny suggests it to be one of the most ancient metabolic processes on Earth. Here we studied some of the oldest barite-rich deposits of both hydrothermal and sedimentary origin in the Barberton Greenstone Belt, South Africa, where excess sulfate could have led to significant δ^{34}S fractionation. We focus on samples from the Theespruit formation of the lower Onverwacht group (3.54-3.50 Ga, Kroner et al. 1996). The rocks, from localities at Londozi and Stentor, contain massive barite, chert- and re-worked barite-rich layers of sedimentary origin with abundant pyrite that in places shows petrographic evidence for detrital deposition. Trace elements within the sedimentary pyrites support a low temperature origin with Co/Ni of 0.1 to 1 and low Se/S of <5 x 10^{-5}.

δ^{34}S in bedded and fine grained barite varies between +4 and +6‰, that could represent the isotopic composition to sulfide derived from seawater or an enclosed basin. Pyrite included within and closely associated with the barite, measured by both bulk and in situ techniques, shows δ^{34}S that varies between -4 and -13‰. Individual pyrite grains reveal mass independent fractionation (δ^{33}S) of up to -2‰ consistent with an atmospheric-derived sulfate component. If both barite and pyrite were in isotopic equilibrium then the shift recorded here would match enrichment factors for microbial sulfate reduction in modern sediments (Canfield, 2001). The variations we show here represent the largest amount of fractionation yet found in early Archaean sedimentary sulfides outside the North Pole locality.

**References**


Copper addition by organic matter degradation in the freshwater reaches of a turbid estuary (Gironde Estuary, France)

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The Gironde Estuary is a macrotidal estuary with a permanent maximum turbidity zone (MTZ) that moves upstream and downstream depending on hydrologic conditions. In 2004, monthly samples have been conducted in the freshwater reaches of the estuary (from the limit of the tidal zone to the beginning of the salinity gradient). In May and September 2005, longitudinal profiles of surface water have been sampled in the freshwater reaches. Additionally, sampling was carried out in the salinity gradient of the estuary in May 2005. Dissolved Cu (<0.2 µm and <0.02 µm) concentrations and C18-Sep-Pak extracted metal-organic complex fractions were analysed. The organic matter (OM) was quantified by measuring dissolved and particulate organic carbon, the dissolved OM was then characterized using 3D-fluorescence and transmission electronic microscopy.

The presence of the MTZ in the freshwater reaches of the estuary induces significant Cu addition, mainly in the “truly” dissolved phase (<0.02 µm). In addition, major transformations of OM (e.g. humification index) were observed in the MTZ which suggests that degradation of fluvial OM plays a strong role in Cu addition. In 2004, dissolved Cu addition (~5 t a⁻¹) represented ~25% of the annual dissolved Cu fluxes entering into the estuary (~21 t a⁻¹). Copper addition occurred mainly in the “truly” dissolved (<0.02 µm) phase, increasing fluxes of hydrophobic (C18-extracted) metal-organic Cu complexes.

Experimental simulations of freshwater inputs into the MTZ were performed by mixing river water with different concentrations of MTZ particles. Important and rapid (inferior to tidal period) Cu desorption followed pseudo-second order kinetics and depended on particle concentration. The amount of Cu desorbed (qₐ) represented ~40% and ~2% for particle concentrations of 20 mg l⁻¹ and 2000 mg l⁻¹, respectively. The relationship between Cu desorption and particle concentration can be described as follows: log (Cu) = a*log(MES) + b. The coefficients a and b obtained for both, the experimentation and in-situ observations were found to be similar. This supports the hypothesis that Cu addition is closely related to particulate OM degradation in highly turbid estuaries.

Origin, migration, fate and impact of hydrocarbon gases from mud structures in the Nile deep sea fan (eastern Mediterranean)

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At all investigated mud volcanoes in the Nile deep sea fan, not only methane but also heavier hydrocarbons have been measured in the sediment column. At Isis and Amon MV’s the origin of CH₄ is mainly thermogenic with variable microbial contribution. However, in regards to the stable carbon isotopic composition of the heavier hydrocarbons, two distinct thermal source are found for Isis and Amon MV’s.

Gas advection occurs mainly at the centre of the mud structures, while at off centre sites. Moreover, another important process occurring at those mud volcanoes is a downward flow of seawater following each gas expulsion, as indicated by the compositional and isotopic signature of the pore water indicating a pure seawater signature within the upper sediment column.

In the upper sediment section, anaerobic oxidation of methane occurs within the Sulfate-Methane Transition Zone (SMTZ). In addition, major shifts in the δ¹³C and δD of propane and n-butane have been observed in the upper 20 cm of the sediment column. This indicates that these hydrocarbons are also efficient terminal electron donors for sulfate reducing bacteria.

Finally, and despite that microbial filter, enhanced fluxes of hydrocarbons are encountered in the water column, with up to several tens of µmol/L. These gas plumes can extend to several hundreds of meter up in the water column and, for the shallowest mud structures, can even reach the sea surface.
Earth’s mantle Th/U and U/Pb evolution in the Archean

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The present Th/U ratio of depleted mantle at $\kappa \approx 2.5$ is clearly lower than the time-integrated value as calculated from Pb isotope ratios ($\kappa_{Pb} \approx 3.75$) or the estimates for the $\kappa$ value of the primitive mantle. This Th/U decrease has been ascribed to post-Archean deep-mantle U recycling. However, such models are not compatible with: 1) increasing geochemical evidence severely limiting the amount of recycled U; 2) the Collerson and Kamber (1999) compilation showing that Th/U decrease in the upper mantle started in the Archean, an eon whose anoxic atmospheric conditions were not suitable for U mobilization and subsequent recycling. Archean continental crust formed dominantly from TTG liquids generated by slab melting under higher geothermal gradients. For slab melting, $D_U > D_{Pb}$, such that Archean arc crust has high Th/U and a complementary residual slab was recycled, decreasing mantle Th/U and $\kappa_{Pb}$ down to circa 3.82 and 4.09, respectively. The feasibility of this hypothesis was numerically tested by box-modelling. The obtained results (lines) compare favourably with the observed (black dots) Th/U variation in the upper mantle.

Archean crustal extraction being dominated by slab melting also caused a significant U-Pb fractionation ($D_U < D_{Pb}$) which was responsible by the U enrichment of Archean crust as testified by the relatively high $^{207}Pb/^{204}Pb$ signatures of sediments. The recycling of the complementary low U/Pb residue can explain the Archean $\mu$ decrease from $\approx 9.2$ to $< 8$ inferred from the two-stages model for recent oceanic basalts. In conclusion, the Archean mantle evolution was characterized by Th/U and U/Pb decrease caused by the extraction of continental crust through slab melting.

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Reference

Mineralogy and genesis of Lashak plain clay deposit in the North of Alborz Mountain, Iran

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The studied area is situated in North of Alborz Mountains. Expound of drainage basin is 75 Km2 and its cirque is 15 km2. The purpose of this study is investigation of mineralogy and genesis of Lashak plain clay deposit. Fifty profiles pedology are provided and three boreholes (360m) are excavated. Pedology profiles are shown three groups of inceptisol, mollisol and alfisol. XRF and ICP analysis show that TiO$_2$ and K$_2$O oxide and Ag, V, Ni, Mo, Cr, Co elements are dominant. Illite, Mica and kaolin are main mineral percentage in the upper top soil. Minerals size is less than 2 micron that originate from bed rock and alluvium deposit. Boreholes sedimentology studies indicate that pasadenian orogeny phase effect on this area and filling cirque since 500,000 years. Usually, boreholes lithofacies is high thickness mud, gravelly mud and muddy gravel. Illite, mica and kaolin are major minerals in the boreholes samples and X-Ray analysis show that their crystalline shape. Chlorite, Smectite, Palygorskite and Nontronite are existed in the samples, occasionally. Abundance of these minerals and lack of sedimentary are shown that basal bed rock changing to clay minerals in a burial stages. Palygorskite subhedral crystalline and Illite as a result upper soil PH and lower aluminum oxide in this area.
Potential utility of Cu isotopes to recognize secondary Cu mineralization and the degree of enrichment


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In this contribution we examined the copper isotope ratio of both Cu-oxides and Cu-sulfides from hypogene and supergene mineralization in porphyry copper deposits (PCD). Copper isotope ratios are reported as $\delta^{65}\text{Cu}_{\%} = \left(\frac{^{65}\text{Cu}_{\text{sample}}}{^{65}\text{Cu}_{\text{NIST 976 standard}}} - 1\right) \times 10^3$. Errors for the all analyses are $\pm 0.14\%$ (determined by multiple analyses of the samples) and mass bias was corrected through standard-sample-standard bracketing. Primary high temperature chalcopyrite and bornite (hypogene mineralization) from 15 PCD varied between -0.72 to 0.92‰. In comparison, Cu-chalcocite from 8 enrichment blankets (supergene mineralization) varied between 0.45 to 5.4‰. Although the collected dataset is relatively small (n=54 total minerals analyzed), a distinct pattern shift to heavier copper in supergene samples exists. The heavier copper isotope signature present in the supergene samples is consistent with experimental batch leach experiments. The causes of fractionation could relate to kinetic, biologic, crystallographic and/or equilibrium isotope effects. Regardless of the cause, the magnitude of isotopic fractionation can be modeled using Rayleigh fractionation trends to indicate the degree of leaching that occurred.

The diurnal variation of carbon isotopic ratios of carbon dioxide in human breath

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The carbon dioxide of our human breath reflects the digestion and assimilation of our human body and could be a good indicator of our health condition. Dodds (1920) first measured the partial pressure of CO$_2$ in the breath to examine the digestive function. Nowadays, $^{13}$CO$_2$ breath tests are widely carried out using $^{13}$C-labelled compounds. Among them, the most famous one is the $^{13}$C-urea breath test (UBT). This test is very sensitive and safe to check Helicobacter pylori infection. In these tests, infrared spectroscopy is generally used to measure the carbon isotopic ratios.

It is also known that the carbon isotopic ratios reflect those of the diet in our daily life. For example, the carbon isotopic ratios of the hair correlated with the calculated values of the dietary protein on the country where the individual lives (Nakamura et al., 1982). The changes in the carbon isotopic composition of beard samples were 2-3 per mil when German residents traveled to Japan and United States.

In this study, we have examined the diurnal variation of the concentration and the carbon isotopic ratios of carbon dioxide in our human breath using the mass spectrometer ANCA-SL installed in Osaka University. We found that there is about 2.5 per mil variation of carbon isotopic ratios during a day. This variation is rather large, comparing to the beard variation of 2-3 per mil reported by Nakamura et al. (1982). We also carried out the measurement of blood pressure, body temperature, and blood sugar level at the same time. There was no correlation between carbon isotopic ratios and these fundamental data values. Thus it was supposed that the variation of carbon isotopic ratios of the human breath depend on the diet itself rather than the digestion and assimilation inside the human body. To confirm this, we carried out the experiment in case that examinee did not take diet. The variation of carbon isotopic ratios of the breath was only 1 per mil in this experiment. Thus we can conclude that the diurnal variation of 2.5 per mil is mainly attributed to the variation of carbon isotopic ratios of the diet that the examinee took in his human bodies.

References
Water content variation in low temperature eclogite inferred from the Sesia Zone, Western Alps

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H₂O derived from dehydration in a subducting slab has important roles in causing various geological/geophysical processes in the subduction zone, such as the island arc magmatism, the enhancement of serpentinization of mantle wedge and the induction of intraslab earthquake. However, the systematics of fluid activity in the subduction zone has not been unraveled yet, such as how much fluid subducts into the mantle, how much fluid is released from the subducting slab, and what kinds of reactions control the dehydration. Due to uncertainties in these fluid activities, there are various perspectives on the nature of subduction system.

We examined the water content variation and the systematics of dehydration reaction in the glaucophanite and eclogite from the Orco Valley area in the Eclogite Micaschist Complex of the Sesia Zone, using the modal analysis and the pseudosection modeling. The application to the conventional geothermobarometry for eclogite yields ca 500°C and 15kb in the southern Orco Valley and 560°C and 17kb in the northern Orco Valley, suggesting that a regional metamorphic gradient (ca 9°C/km) exists in the Orco Valley area.

The result of the modal analysis shows that the eclogites in the southern and northern Orco Valley contain ca 0.9 and 0.8 wt%H₂O, respectively, and the Lws-free glaucophanites in the Orco Valley contain an identical water contents of ca 1.8 wt%. The water content of Lws-bearing glaucophanite is estimated as ca 3.0 wt%. These data suggest that prograde Lws decomposition can supply a significant amount of H₂O (ca 1wt%) from subducting slab by overstepping the Lws decomposition reaction [Lws+Jd/Ab=Czo+Pg+H₂O] at 450°C and 12-13kb. The pseudosection modeling predicts that the water content in the eclogite gradually decreases by a ratio of ca 0.4 wt%/100°C with increasing metamorphic temperature from ca 500 (1.5 wt%H₂O) to 700°C (0.7 wt%H₂O). Therefore, we conclude that a prograde Lws dehydration is a substantial fluid supplier at ca 35-45km depth (12-13kb) in subducting slab.

The metamorphic field gradient of the Orco Valley area is well concordant with the inferred thermal structure along the subducting Philippine Sea slab beneath SW Japan. Recently, the deep low-frequency (DLF) earthquakes and tremors observed at ca 25-45 km depth around the plate boundary below the non-volcanic area of SW Japan. The DLF earthquakes and tremors are considered to be a result in the fluid activity caused by the dehydration in subducting slab. As most of DLF earthquakes and tremors take place at ca 25-45 km depth in SW Japan, where are coincidence with the expected depth of Lws decomposition in SW Japan, we emphasize that the lawsonite decomposition is one of the candidates for causing DLF earthquakes and tremors.

Gravitational trapping of carbon dioxide in deep sea sediments: A geomechanical analysis

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Carbon dioxide is denser than the surrounding pore water at great depth and relatively cold temperature found in geological formations below the deep ocean floor and thus would be trapped by gravitational forces (House et al. 2006). Gravitational forces will drive the CO₂ from above and below toward the level of neutral buoyancy (Lnb), below which warm CO₂ is less dense than the surrounding pore water and thus will rise and above which the CO₂ is denser than water and thus will sink. CO₂ storage near the neutral buoyancy level is therefore stable. Storage capacity varies with seafloor depth, geothermal gradient, pore water salinity, permeability, and porosity of deep-ocean sediments. Using field data from pelagic sediments from the Atlantic, Pacific, and Indian Oceans, we show how in-situ conditions would affect storage capacity by shifting the level of neutral buoyancy and therefore the sediment depth available for CO₂ accumulation. We also measured permeability and porosity in core samples from relevant sites.

The majority of tectonically stable ocean sediments at the minimum required water depth of 2700m is composed of calcareous sediments or clays. Pelagic clays have very low permeabilities unsuitable for injection. Our data illustrate that pelagic carbonates have low to moderate permeabilities (μD to mD), suggesting that reservoir stimulation techniques such as hydraulic fracturing would be necessary to increase the injectivity. We evaluate the potential for CO₂ injection in calcareous sediments based upon a geomechanical analysis. Young basalts located under pelagic sediments and turbidites may offer attractive alternatives with higher permeabilities for injection.

Reference
Ore deposits: An interface between the metallic and light stable isotopes

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The light stable isotopes (H, C, O, S) have proved powerful geochemical tracers of ore deposition processes in a wide variety of areas such as: geothermometry; identifying magmatic-hydrothermal and meteoric hydrothermal fluid systems; sulphide-sulphate fluid equilibria and speciation; the role of bacterial processes. In contrast, the metallic isotopes are most strongly fractionated in chemical sedimentation processes, where the transition metal elements (Fe, Cu, Mo) serve as potential tracers of both biogenic and abiogenic reduction processes and corresponding oxidation reactions. Can these two types of stable isotope system be integrated to promote the understanding of ore deposition processes? Two promising areas appear to be the combination of metallic stable isotopes with sulphur isotopes in sulphide ore mineral deposits and metallic isotopes with oxygen isotopes in oxidized ores. Studies of metal-sulphur isotope covariations are particularly suited to sedimentary ore deposition processes such as banded iron formations, stratiform sedimentary copper deposits, supergene alteration, where they can identify the involvement of bacterial processes and be used to trace redox cycles. However, use of such covariations is not limited to sedimentary processes. Low temperature continental hydrothermal processes, sea-floor hydrothermal systems and even magmatic-hydrothermal systems, may provide unique isotopic signatures. During processes such as supergene oxidation, the combination of metallic isotopes with oxygen isotopes can tell us about the evolution of the fluid-metal system.

One of the potentially important fields for the application of metallic isotopes is the use of speciation-isotope diagrams of the type developed by [1] for sulphur and carbon isotopes. Just as the SO₂–H₂S equilibria potentially control the isotopic composition of sulphide and sulphate minerals in hydrothermal systems, so speciation between oxidized and reduced solution complexes (e.g., Cu²⁺ and CuCl₂⁻) or between oxy- and thio-anion complexes (e.g., MoO₄²⁻ and MoS₂⁻), can help understand the controls of metal isotope compositions in ore deposits.

Examples illustrating the above ideas, taken both from published and our own work, will be presented. Ultimately, the power of metal stable isotopes in ore deposit studies lies in their ability to explore metallic element cycling. Careful combination with the appropriate light stable isotopes can both enhance and refine the insights provided by metal stable isotopes.

Reference


OH in mantle olivine: Experiment vs. nature

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Olivine is the principal rock-forming mineral in the mantle lithologies. Its effect structure depends on conditions of crystallization or re-equilibration and thus can be used as an indicator of magmatic and metasomatic processes. Protonated defect structure of olivine, i.e. defect structure in which cation vacancies are charge-balanced by H⁺ bonded to oxygen, is conventionally studied using FTIR (Fourier Transform Infra Red) spectroscopy. It has been shown experimentally that the frequency of OH IR absorption bands depends on a number of parameters, the most important of which have been proposed to be: aSiO₂, aTiO₂, and O₂. Variation of these parameters may have similar effects on OH IR absorption, hampering interpretation of the spectroscopic results.

In order to isolate the major parameters controlling OH IR absorption at the conditions of the lithospheric mantle we studied olivines from mantle peridotitic xenoliths and kimberlitic phenocrysts using FTIR and EPMA. We did not observe correlation between OH IR absorption and TiO₂ content in olivine. Atomic proportion of H typically exceeds atomic proportion of Ti. We assume that Ti does not control the position and concentrations of H in olivine from the lithospheric mantle.

At increasing fO₂, concentration of ferrous iron increases and one anticipates stabilization of hydrous defects associated with Fe³⁺ (lower frequency OH IR absorption). However, spectra indicative of OH associated with Me²⁺ were measured in olivines from contrasting fO₂ environments: spinel peridotites, relatively reduced diamondiferous garnet peridotites, as well as kimberlitic pheno- and xenocrysts. Thus at relatively oxidized conditions of the lithospheric mantle fO₂ does not significantly affect OH occurrence in mantle olivine. At the same time reduced conditions of the adiabatic upper mantle may cause preferential stabilization of the hydrogarnet-type defects (higher frequency OH IR absorption) rather than defects associated with Me²⁺. Hydrogarnet-type defects are significantly more capable of storing OH. In that case oxidation of mantle material at the asthenosphere can cause partial dehydrogenation of olivine and thus assist melting.

We propose that the primary factor controlling OH solubility in olivine at conditions of the lithospheric mantle is aSiO₂. Peridotitic olivine in equilibrium with orthopyroxene (high aSiO₂) should show lower frequency OH IR absorption bands. However many olivine samples from mantle xenoliths show higher frequency OH IR absorption bands suggesting that these samples are not in equilibrium with orthopyroxene. This implies that a significant proportion of available mantle material may have been modified by transporting melts and/or metasomatic fluids, which were characterized by lower silica activities.
Zircon growth and recycling during the assembly of the Tuolumne Batholith, Sierra Nevada, California

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The Cretaceous Tuolumne Batholith represents a classic example of a large (~1200 km²), compositionally zoned pluton and provides a natural laboratory for the study of magmatic processes. Eruptions of large volumes of felsic magma demonstrate that large magma bodies exist in Earth's crust, but the geochemical and geophysical path that links these large magma volumes to the frozen remnants of magma input (plutons) is still obscure. Deciphering the intrusive record of magma systems is essential to understanding the relationship between surface volcanism and the long-term storage and evolution of magma reservoirs. U-Pb zircon TIMS analyses from several locations in the batholith exhibit appreciable dispersion of single crystal or crystal fragment ages (several 10⁷ yrs to 1x10⁸ yrs) and, in addition, display distinctly older ages that likely represent zircon crystals entrained from older parts of the Tuolumne magmatic system. Since techniques aimed at eliminating Pb loss (and thus age scatter) have been employed prior to analysis, we interpret the age dispersion to reflect real variation in the timing of zircon crystallization. Two samples that show a high degree of age dispersion (> 1 Myr) were selected for trace element analysis and Ti-in zircon geothermometry by SHRIMP-RG. Crystallization temperatures ranged from 780-640°C and averaged 695°C (Δν102 ~ 0.75 based on presence of titanite). No clear correlation exists between crystal age and temperature. In most cases, the temperatures from crystal centers were within uncertainty of the temperatures at the rims or show a slight core to rim decrease in temperature. Trace element ratios vary systematically with temperature (e.g. decreasing Th/U ratio with decreasing T) and are attributed to fractionation, although neither sample represents strongly fractionated melt. Low total Zr indicates that the magmas were initially undersaturated in zircon when emplaced, which is also consistent with late zircon crystallization. Entrainment of zircon from older parts of the magmatic system occurred late in the history of the batholith, and recycling of zircon crystals during successive magmatic injections is compatible with progressive growth of a large, long-lived, crystal mush body. Similar studies, applied to magmatic systems where both the plutonic sources as well as the volcanic products can be studied, are expected to shed further light on linking the former with the latter.

On the primitivity of the Wild 2 cometary dust

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We were impressed by the analytical results obtained by 183 scientists on a 0.2 μg of dust from the Wild 2 comet (W2-dust) returned by Stardust [1]. What is less impressive is the way the data are interpreted and sold as a "big surprise".

We already argued that the unmelted chondritic dust recovered from the stratosphere and polar ices and snows (micrometeorites or MMs) that we and many other analyzed are cometary dust particles. In 1998, we thus pointed out that cometary dust particles would be similar to MMs, being made of a material related to the CM-type hydrous-carbonaceous chondrites containing refractory phases, kerogen, and being depleted in chondrules [2]. This "ordinary" dust was formed in the inner solar system and then forwarded to the outer solar system by huge surges of nebular gas [3].

The W2-dust analyses confirm these earlier deductions because they establish strong similarities with MMs for: (i) the abundance of Ca-Al-rich inclusions and pre-solar grains; (ii) the H, C, N, and O isotopic compositions; (iii) the chemical composition of the refractory magnesian silicates and of Fe sulfides. These similarities imply that hydrous silicates must also be present in the W2-dust, and that they should be dominated by saponites, which are the major hydrous silicates of unmelted MMs. However, the Stardust team repeatedly emphasized that "hydrous silicates are missing" in the W2-dust. The fate of these missing silicates, which is not discussed, is just pictured in the bulb-shaped aerogel track reported on the cover page of Science [1]. It documents the microscopic explosion of a dust particle containing saponite during its μs deceleration in the aerogel. Only the most massive and refractory particles can be found at the termini of the tracks.

Indeed, saponite contains both OH groups and very labile H₂O, which starts to be released at about 100°C. Consequently, it should be "instantaneously" released during the pulse heating of the particles and form an explosion bulb in the aerogel – with the result that saponite is now missing. In contrast, "dry" crystalline particles produced "carrot"-shaped tracks.

References
Insights on the enriched isotopic nature of Proterozoic dyke swarms in the Northeastern Superior Province

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The origin of the enriched signature commonly seen in continental flood basalts has fueled a long standing debate about the relative roles of sialic crust and lithospheric mantle in the contamination of asthenosphere-derived magmas. Many Proterozoic mafic dykes have the chemical characteristics of continental flood basalts (CFB), displaying light rare earth element and large ion lithophile element enrichments relative to primitive mantle, associated with depletions in Nb and Ta relative to Th and La.

Many Proterozoic mafic dykes have the chemical characteristics of continental flood basalts (CFB), displaying light rare earth element and large ion lithophile element enrichments relative to primitive mantle, associated with depletions in Nb and Ta relative to Th and La.

In the Northeastern Superior Province of Canada (NESP) numerous mafic dyke swarms range in age between 2.51 and 2.00 Ga, with many being ca. 2.21 Ga. The mafic dykes that cut the isotopically-juvenile Archean crust ($T_{DM} = 2.8-3.1$ Ga) of the Riviere Arnaud Terrane in the North have lower La/Nb and Th/Nb ratios, and positive $\varepsilon$Nd values (+4.2 to +0.4). In contrast, the mafic dykes in the older crust ($T_{DM} = 2.9-3.8$ Ga) of the Hudson Bay Terrane, to the South and West, have higher La/Nb and Nb ratios and Th/Nb ratios, and low to negative $\varepsilon$Nd values (+0.5 to -10.5). These differences are independent of age, but rather coincide with the nature of the crust and lithosphere in which the mafic dykes were emplaced. Although enriched alkaline basalts occur along the periphery of the NESP craton (Kenty Lake; 1.96 Ga) and alkaline lamprophyres intrude the craton (Lac Aigneau dykes; 1.94 Ga), these rocks cannot represent the enriched component seen in the mafic dyke swarms, because they are characterized by low La/Nb and Th/Nb ratios coupled with positive $\varepsilon$Nd values (+3.7 to +0.5). These differences are incompatible with the involvement of a lithospheric component in the petrogenesis of the mafic dyke swarms of the NESP and suggest a significant role for old enriched Archean crust ($\varepsilon$Nd$_{3.0 Ga}$ -1 to -20).

Geochemical, lithologic and biotic variations of the K/P boundary record, implications for seiche-like movements as causal factors in the observed mix-up

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A comparison of temporal and spatial distribution of iridium and various stable isotope records [e.g.1, 2]; in marine deposits affected by the K-P bolide impact, c. 65.0 Ma [3, 4] shows wide discrepancies indicative of unusual conditions of sedimentation. Similarly, the boundary zone displays heterogeneities in texture and microfossil contents, even within short distances of a given basin, as faunal mixing has been, indeed, the hallmark of the boundary layer worldwide. Furthermore, the boundary zone displays considerable variation in thickness within a same area, and most importantly it also includes consistent delicate primary sedimentary structures such as cross-lamination, and rip-up clasts.

These features may occur irrespective of the paleodepths of the basins. Repetitive occurrences of these primary sedimentary structures indicate vigorous multiphase subaqueous flow processes of cohesionless particles. The complexity of the structures together with reversal of directional pattern is consistent with structures related to oscillatory movements [5].

Thus, shock waves generated by the impact and subsequent major crustal readjustments not only triggered tsunamis [6,7], but they apparently generated oscillatory waves such as those observed in seiches, a phenomenon not yet studied in present deep ocean basins. This mechanism may explain the effects of exceptional subaqueous flow processes that led to the sedimentological, faunal and geochemical discrepancies observed at the K-P boundary.

References
**In situ fluid inclusion analysis: Why bother?**

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In situ studies of solutions in fluid inclusions, both natural and synthetic, are becoming increasingly popular, mostly due to technical advances in recent years. We are now, for the first time, able to directly measure inclusions of hydrous fluids, as well as silicate, sulfide, carbonatite and salt melts. Synchrotron XRF and PIXE allow elemental compositions of individual inclusion, but are strongly dependant upon independent estimates of inclusion geometries and depths. LA-ICPMS provides high precision elemental ratios of inclusion compositions, but requires a priori knowledge of one element within each inclusion as an internal standard. Thus synchrotron XRF, PIXE and LA-ICPMS all have specific difficulties that are rarely admitted publicly.

Synchrotron absorption studies provide the only means to measure oxidation states and bonding within inclusions at high P and T. This technique, although not straightforward, is likely to be the only way to directly measure molecules in melts and hydrous solutions. The small sample size of individual fluid inclusions, however, may limit how much information we can extract from them. Hydrothermal cells and diamond anvils may provide better data due to longer path lengths through solutions, but absorption by window materials may be a limiting factor here.

We are only now getting to the point where we can routinely measure inclusion compositions. But what will we really learn with this new capability? If one cannot connect a specific inclusion to a geological event, what is the point? So far, most studies have concentrated on highly saline brines, which contain very high metal contents. However, most ore-forming fluids contain very low levels of dissolved metals, and until we can detect these, we may not be unravelling ore-forming processes, which is our obvious goal.

**Characterisation of Methanotrophic bacteria in volcanic soils through time-series \(^{13}\)CH\(_4\) PLFA labelling**

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Methanotrophs are a unique group of microorganisms in the Earth system acting as both a sink for atmospheric CH\(_4\) (high affinity methanotrophs) and a robust barrier against CH\(_4\) flux to the troposphere from anoxic environments (low affinity methanotrophs). As they have yet to be successfully cultured few details are known about high affinity methanotrophs with the main evidence supporting their activity from indirect CH\(_4\) oxidation rate studies. Moreover, the fate of methanotrophically fixed carbon in the extensive range of natural and anthropogenic environments that they inhabit is unknown.

Through the use of compound-specific \(^{13}\)C stable isotope analysis of microbial biomarker PLFAs we have simultaneously assessed high affinity methanotropic biomass and taxonomic identity from a range of different mineral soils under atmospherically relevant CH\(_4\) concentrations (Maxfield et al., 2006). This paper presents the first detailed investigation of high affinity methanotrophs in volcanic soils (andisols) from Tenerife. The results show substantial levels of \(^{13}\)C incorporation following incubation under 2 ppmv \(^{13}\)CH\(_4\), indicating an extremely high abundance of methanotrophic bacteria in these environments. This suggests that Andisols, a previously unstudied soil class with respect to methanotrophic bacteria, may oxidise significant amounts of atmospheric methane despite their low areal coverage globally. The preliminary fate of methane-derived carbon in soils will also be considered, as will the relationship between these findings and previously studied temperate soils (Evershed et al., 2006).

**References**


The structure of REE aqua and chloroaqua complexes in hydrothermal fluids

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Our understanding of the association of rare earth ions with ligands common in the Earth’s crust (e.g. chloride, fluoride, phosphate, and carbonate ions) at elevated pressures (P) and high temperatures (T) is incomplete. Data on the stability and structure of REE ion complexes at elevated P-T conditions are necessary in order to understand fully the geochemistry of hydrothermal rare earth mineralization. We discuss structural data for several rare earth ions measured using synchrotron x-ray absorption spectroscopy (XAS) in aqueous solutions under elevated P-T conditions on the PNC-ID 20 beam line at the Advanced Photon Source, Argonne National Laboratory. Analysis of XAS spectra measured from Eu3+, Gd3+, and Yb3+ ions, at concentrations ranging from 0.006 to 0.07 m in 0.16 m HNO3 aqueous solutions, shows that the number of H2O ligands of the Gd3+ aqua ion decreases at a rate (0.41/100 °C) which is roughly half of the rate of H2O-ligand reduction for the Yb3+ aqua ion (0.84/100 °C) and for the Eu3+ aqua ion (0.77/100 °C) over the 25 to 500 °C temperature range. These results suggest that the Gd3+ aqua ion is more thermodynamically stable than the Yb3+ and Eu3+ aqua ions. We conjecture that this may be due to the tetrarad effect, as evidenced in a strengthening of the bonding of aqueous ion complexes derived from enhanced quantum mechanical interelectronic repulsion energy of the half-filled 4f electronic shell configuration of the Gd3+ ion. XAS measurements of Nd3+, Gd3+, and Yb3+ ions, at concentrations ranging from 0.006 to 0.1 m in low pH chloride (0.02 – 0.3 m) aqueous solutions reveal that significant association between these REE ions and the chloride ligand occurs in the 300 to 500 °C temperature range forming stepwise inner sphere chloroaqua complexes of the type REE(H2O)δ− nCl+n−δ+, where δ = 7 – 8 and the number of Cl− ligands (n) increases steadily with temperature from an average of roughly 0.5 to a value close to 2. This demonstrates that chloride species may be important for transport of REE in low pH chloride-bearing hydrothermal fluids at elevated temperatures (300 to 500 °C). Our results are found to have negligible pressure dependence for the pressure range of this study. The structural results for the REE chloroaqua complexes under elevated P-T conditions are discussed in terms of variability (or lack thereof) across portions of the REE series.

Identifying sources of riverine sulfate by combining hydrological, chemical and isotopic approaches

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A series of case studies will be presented in which sulfate in surface water systems was sampled frequently, 34S and δ18O values were obtained, and interpreted in conjunction with hydrological and chemical data. Using this approach in selected forested headwater catchments in New Hampshire, New York, and Vermont (USA), it was demonstrated that a significant portion of stream water sulfate during base flow was derived from weathering of bedrock, particularly in catchments with sulfur-rich lithology. During storm events after a dry summer season, sulfate concentrations in stream water increased significantly and δ34Ssulfate decreased to minimum values in some catchments. This suggests that sulfate derived from oxidation of sulfide minerals, e.g. in wetland areas or the hyporheic zone, contributed to the increased sulfate load in these streams following storm events. Monitoring of stream water during spring snowmelt events at the Sleepers River Research Watershed (Vermont, USA) revealed elevated contributions of sulfate from pedospheric sources, but little direct contribution of sulfate from the melting snowpack.

Investigations in two large watersheds in the Rocky Mountains of Alberta (Canada) indicated that riverine sulfate in headwaters was mainly derived from evaporite dissolution. In the agriculturally dominated downstream portions of the watersheds, oxidation of pyrite in tills was identified as an additional source of riverine sulfate evidenced by increasing sulfate concentrations and decreasing δ34S values. Using a combination of hydrological, chemical and isotopic approaches, it was also demonstrated that urban centers, such as Calgary in southern Alberta, had a significant impact on riverine sulfate loads that was evident from the distinct isotopic composition of sulfate released from the waste water treatment plant.

In watersheds with forested, agricultural and/or urban land use, there is a variety of natural and anthropogenic sources of riverine sulfate. The relative contributions of these sources to sulfate in rivers and streams can vary significantly depending on hydrological conditions that have distinct seasonal patterns. To identify these different sources and to assess their relative contributions, it is essential to determine the isotopic composition of sulfate from spatially distributed sites along headwater creeks, rivers or streams under different hydrological regimes. These isotopic data, when combined with hydrological and chemical results, provide information that can be used to markedly improve the quantification of riverine sulfate sources.
The geochemistry, mineralogy and consideration of AMD of Karmozd coal mine and Zirab coal cleaning factory, Mazandaran, Iran

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The Karmozd mine and Zirab coal cleaning factory in Mazandaran Province are one of the largest and oldest coal extraction and coal concentration in Central Alborz Coal Basin. These coals are classified as low sulphur, low ash coals. Mineralogy and geochemistry studies show that excluding P2O5, all other main oxides are related to the minerale within the coal layers. The concentration of some major, trace and rare elements such as Ti, Mn, Sr, Ba, Nb, Ce, Zr, Rb, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, W, Th, and U in Karmozd are much more higher compared to the most coals in the world.

Two types of drainage exists in Karmozd: Acid drainage of Mg-SO4 type (pH≈4.59) and alkali drainage of Na-HCO3-SO4 type. Hydrogeochemistry modeling indicates that minerals such as jarosite, alunite, iron and aluminum oxides and hydroxides are basically oversaturated, whereas carbonate minerals like calcite, dolomite and aragonite are undersaturated. Bledite and secondary minerals are formed in arid seasons due to evaporation of hydrosulphate solutions. The river water tends to change from Ca-HCO3 type to (Na-Ca-Mg)-HCO3-SO4 type in arid seasons. Potential consideration of water shows that in acid mine drainage: EC, TDS, SO4, PO4, NO3, Mg,y) Fe, Sr, As, and Mn and in neutral to alkali mine drainage (as well as seepage water from tails and coal cleaning factory) SO4, PO4, Ca, As, Sr, Sb and Bi are more than standard value, which may leads to surface and underground water pollution in this region.

According to acid mine drainage management standard methods, limestone pond is suggested in order to control AMD in Karmozd. However, because the Zirab coal cleaning factory tail dumps are discharged in the riversides, using precipitation ponds and constricted wetlands seems to be suitable controls.

Carbon dioxide degassing and estimation of thermal energy release from volcanic lakes

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Introduction

Periodical surveys are carried out in geochemistry since 1993 to understand the hydrothermal system of Kelud volcano (Indonesia). The last eruption of Kelud volcano was occurred in 1990 and it contains a crater lake with near neutral waters (pH≈6): a part of CO2 is dissolved as bicarbonates, and another part of CO2 escape through the lake as bubbles and by diffusion to the surface.

CO2 flux degassing

From 2001 to 2006, measurements of CO2 flux emitted by the surface of the lake were performed by using the accumulation chamber method (Chiodini, 1998) modified in order to work at the surface of a crater lake. Two statistical methods were used to process data: the graphical statistical approach (Sinclair, 1974) and stochastic simulation methods (Deutsch and Journel, 1998). The results of graphical statistical approach permit to quantify the different degassing processes that are acting at the lake surface: one corresponding to CO2 fluxes resulting from rising bubbles close to the lake shore (from 2633 to 9072 g/m2/d); the second corresponding to CO2 fluxes from rising bubbles in the middle of the lake (from 478 to 945 g/m2/d); and the last corresponding to equilibrium diffusion of dissolved CO2 at the water-air surface (from 151 to 209 g/m2/d). Total CO2 emission rate estimated by stochastic simulation ranges from 105 t/d for 2001 to 35 t/d for 2006.

Thermal energy

Thermal energy released by the lake was estimated by using physical characteristics of the lake and meteorological data (wind speed, rainfall rate). The results of gases analysis and CO2 fluxes have provided a new constraint in the quantification of the input of steam and brine from the hydrothermal system. The thermal flux decreased from 200 MW (2001) to 60 MW (2006) and estimated inflow steam from 12 to 4 kg/s and inflow brine from 429 to 235 kg/s.

References

Provenance studies, which provide crucial insight into crustal evolution and palaeogeography, are particularly important in deformed and metamorphosed cover sequences that may be displaced during orogeny thereby obscuring the link with their original basement. Of the various sedimentary provenance techniques available (e.g. whole-rock major and trace element analyses and single grain U-Pb zircon dating), none can be described as the definitive tool and as such integrated, multi-method approaches are necessary.

This contribution presents the first in situ ion microprobe U-Pb study of detrital titanite, applied in conjunction with petrography, whole-rock Sm-Nd and U-Pb detrital zircon data. These techniques were used to investigate the provenance of two enigmatic, probable Neoproterozoic, metasedimentary cover sequences in the Inner Hebrides, SW Scotland – the Colonsay Group, which unconformably overlies the Palaeoproterozoic Rhinns Complex on Islay and the Iona Group, unconformably overlying Archaean Lewisian gneisses on Iona. U-Pb detrital zircon data point to the Rhinns Complex (c. 1780 Ma) as the major source of both successions and are consistent with whole-rock Sm-Nd data. Detrital titanite data, for the most part, support predominant derivation from the Rhinns Complex, but yield younger maximum ages, for the most part, support predominant derivation and are consistent with whole-rock Sm-Nd and U-Pb detrital zircon data. These techniques were used to investigate the provenance of two enigmatic, probable Neoproterozoic, metasedimentary cover sequences in the Inner Hebrides, SW Scotland – the Colonsay Group, which unconformably overlies the Palaeoproterozoic Rhinns Complex on Islay and the Iona Group, unconformably overlying Archaean Lewisian gneisses on Iona. U-Pb detrital zircon data point to the Rhinns Complex (c. 1780 Ma) as the major source of both successions and are consistent with whole-rock Sm-Nd data. Detrital titanite data, for the most part, support predominant derivation from the Rhinns Complex, but yield younger maximum depositional ages of c. 942 Ma and c. 1482 Ma for the Colonsay and Iona groups, respectively. One sample (from the Dun Gallain Grit Formation of the Colonsay Group) exhibits a markedly different titanite age distribution to that of the zircon, with a pronounced peak at c. 1.0 Ga. This difference could reflect additional source contributions, lacking in zircon but containing titanite. Alternatively the titanite may be recording metamorphic events in the source(s). As detrital titanites from this sample are found overgrowing ilmenite (implying a metamorphic origin) the latter explanation seems more plausible. The pronounced peak at c. 1.0 Ga suggests that these titanites are recording Grenville events in the source(s).
Kaersutite in the Chassigny martian meteorite: How much water?

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Kaersutite (Ti-rich amphibole) occurs within olivine-hosted polyphase melt inclusions within the Chassigny martian meteorite. Extensive work has been conducted to assess the compositional characteristics of this mineral because of the potential implications for water on Mars (i.e. Johnson et al., 1991; Monkawa et al., 2006; Watson et al., 1994). Microprobe analyses of F and Cl contents of this kaersutite (Johnson et al. 1991) yielded 0.50 and 0.10 wt.% respectively. These low values led to the presumption that much of the amphibole O(3) site was filled with OH-. However, Watson et al. (1994) found very little water in the kaersutite (~0.15 wt.% H₂O), implying that the kaersutite O(3) site is largely occupied by O²-. However, Fe micro-XANES data collected by Monkawa et al. (2006) showed that Fe³⁺ comprised only ~5% of the Chassigny kaersutite, which is uncommon for typical terrestrial oxy-rich kaersutites.

When all of the above published data are considered, a structural formula for the Chassigny kaersutite can be calculated based on normalization to 24 anions [best normalizatin scheme for well characterized O(3) occupancy]. The resulting structural formula yields an over-occupied A-site (by ~ 11-15%), which is consistent with having too much O²⁻ in the O(3) site. This inconsistency suggests either that at least one of the above published data is inaccurate or that the Chassigny kaersutite is not currently representative of its chemical state at the time of crystallization. The first case requires (i) a higher concentration of monovalent anions is present within the O(3) site to decrease the apparent amount of O²⁻ in O(3), (ii) a higher concentration of Fe³⁺ in the M(1-4) sites to diminish the effects of the extra negative charge imposed by O²⁻, or (iii) a combination of both. The second case would imply that the above data are accurate and the Chassigny kaersutite has changed to an unstable or charge-imbalanced phase subsequent to crystallizing within the melt inclusions. Such a change may have been induced by the shock event that removed the Chassigny dunite from the martian surface (dehydroxylation?). Analyses are ongoing to further assess these possibilities.

References

Coral reefs and global change: the roles of increasing ocean acidity, ocean temperatures, sea-levels and direct human impacts

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Although coral reefs make up less than 1.2% of the world’s continental shelf area, they represent a disproportionately large and essential resource to people as well as being of immense ecological value. Coral reefs are however sensitive to the threats from global climate change as well as direct human impacts from degradation of their local marine environment, both of which are now occurring at unprecedented rates. Higher levels of atmospheric CO₂ from fossil fuel burning are causing global warming, but also importantly increasing the acidity of the world’s oceans. Increasing ocean acidity and the resultant decrease in the carbonate saturation state of seawater, has the potential to cause substantial reductions in coral calcification. Warming of the world’s oceans has also increased the frequency of unusually warm events resulting in widespread mass coral bleaching, such as occurred in 1998 and 2002. These effects, and the apparent lack of adaptability of corals, is more than counter-balancing any possible beneficial effects from climate change such increased calcification and reduced uptake of CO₂ with higher sea surface temperatures as well as increased accommodation space for coral growth from rising sea levels.

However, arguably the most severe impacts on coral reefs are still those that arise from direct human activities. Locally, landuse changes in river catchments, wetlands and estuaries is leading to increased supplies of sediment and nutrients to many inshore coral reefs. In some cases these, together with pressures from other activities such as trawling and overfishing are now resulting in an evolutionary trajectory that may ultimately result in an abrupt phase shift from a coral to macro-algae dominated ecosystem. It is thus clear that the long-term sustainability of coral reefs is not only dependent on the still poorly understood effects of global climate change and coral adaptability, but also on increasing the resilience of reef systems by mitigating direct human impacts.
Microbes, sedex deposits and siderophile seawater at ~1.65 Ga in northern Australia

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Late Palaeoproterozoic to earliest Mesoproterozoic sequences in northern Australia host nearly a quarter of the world’s zinc reserves [1]. Individual sedex (‘sedimentary-exhalative’) deposits may contain tens of millions of tonnes of base metals. Furthermore, the deposits and their primary dispersion halos contain several orders of magnitude greater amounts of iron (as pyrite and/or iron carbonate) than base metals [2]. This talk will discuss the origin of northern Australian sedex zinc deposits in the light of new ideas about the oxidation state and sulfur content of Proterozoic oceans [3,4].

These deposits are thought to form from oxidised fluids that already contained dissolved S (as sulfate) or obtain sulfate when the exhaling fluid mixed with seawater, or both [1]. Sulfide was produced through biogenic reduction at the site of ore deposition and local water column euxinia must have been important to fix (and preserve) base metal- and Fe-sulfides in the sediments. However, Fe enrichments expressed as carbonates, rather than sulfides, imply S-poor (and perhaps CO\textsubscript{2}-rich) bottom waters. Such waters may have been anoxic, but were not euxinic.

We will present textural evidence from distinctive bottom precipitated carbonates, as well as S isotope data (sulfide and CAS) from the mineralised and unmineralised sequences, that support arguments for a low-S reduced ocean at this time. The extent of the influence of giant ore-forming exhalative systems on coeval ocean chemistry will be discussed.

References

Microscale controls on contaminants at the Hanford Site

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Hanford was the site of intensive plutonium production from 1943 to 1989, the operation of reactors, chemical processing facilities, and waste storage and disposal facilities resulted in environmental contamination on a large scale. The vadose-zone mobility of these contaminants was controlled by microscale reactions with unconsolidated surface sediments. Waste-sediment interactions modified migrating solution compositions along the flow path, resulting in immobilization by precipitation or sorption. We used autoradiography, x-ray microprobe, electron microprobe, and scanning electron microscopy to determine the microscale controls on mobility for U, \textsuperscript{90}Sr, \textsuperscript{137}Cs, and Cr.

Uranium diffused into microscale fractures in granitic sediment clasts, and precipitated as sodium boltwoodite. The reaction was sustained by dissolution of silica from feldpars and by continued diffusion of uranyl from the pore-filling waste solution. Sequestration of uranyl in microfractures implied a limited possibility of subsequent dissolution and remobilization. \textsuperscript{90}Sr was entrained in Na\textsuperscript{+} rich solutions that displaced Ca\textsuperscript{2+} from ion exchange sites on sediment smectites, causing saturation and Sr coprecipitation with secondary calcite, suggesting that remobilization by subsequent dissolution would be moderated by exchange with Na\textsuperscript{+}. \textsuperscript{137}Cs was found to be bound to interlayer sites on biotite and muscovite. The extent of weathering within the micas was critical to the penetration of \textsuperscript{137}Cs; more weathered biotites included internal concentrations, while muscovite held \textsuperscript{137}Cs predominantly along the muscovite clast boundaries. Chromate was observed associated with aluminosilicate coatings on sediment clasts, and as concentrated, reduced precipitates in interclast space. The mobility of these contaminants was limited by reaction within distinct reactive components not evident during macroscopic investigations.
Evaluating environmental response trends using an integrated paleolimnological approach

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We examine the hypothesis that ecosystems highly perturbed by human activities cannot return to their original unperturbed state and with the influence of climate change, new ecosystem balances are obtained. A problem is that ecosystems are perturbed by various stressors that operate at different timescales and intensities. Our approach is to integrate observations of various ecological/environmental indicators over time. An investigation of lacustrine sediments was used to examine this hypothesis and determine rates of response and recovery from environmental stressors.

The study area is Muskegon Lake (Great Lakes region, USA) which is in a watershed highly perturbed by human activity since the early 1800s. Logging, dams, agricultural runoff, urbanization and industry have resulted in altered hydrology, disrupted biological communities and chemical contamination. Sediment were analyzed for vertical profiles of pollen stratigraphy, diatom community structure, 210Pb activity (sedimentation rates, age, focusing), and corresponding geochemistry that includes a suite of elements including trace metals and nutrients.

Three distinct paleoecological phases are represented in the sediment geochemistry chronology and diatom community structure of the core. Select relationships observed include: 1) Top section (<16cm depth) shows diatom species indicative of high nutrient conditions, specifically, Achnanthes minutissimum and Amphora pediculus, which correspond to increasing phosphorus concentrations near the surface; 2) The 60 – 90cm depth reflects an increase in Cocconeis placentula and C. placentula v. euglypta, that predates the peak in anthropogenic loading of lead and mercury, after which, both species decline; 3) Bottom of core (>100cm depth) is abundant in Cavinula scutelloides, benthic diatom species associated with cooler climate (Little Ice Age), Ophephora martyi, and geochemistry that reflects apparent background conditions.

Preliminary results are consistent with the hypothesis and are interpreted to indicate that ecosystems will work to attain new balances in the Great Lakes region as climate changes, but the magnitude of human disturbances further influences these new balances. It is hoped that this integrated approach will facilitate not only a better understanding of ecosystem response to stressors, but also a more realistic assessment of new states of balance after the stressors are removed.

LIBS analysis of gem beryls: Single-pulse, double-pulse, and provenance determination

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Laser-induced Breakdown Spectroscopy (LIBS) is an attractive emerging tool for chemical analysis, including potential for real-time, in-field, minimally destructive analysis. LIBS is simultaneously sensitive to all elements, especially for those with low atomic weights. Based on the premise that every material produces a unique broadband LIBS emission spectrum, averaged LIBS spectra (200-980 nm) were collected for a wide variety of samples of the cyclosilicate gem beryl (Be3Al2Si6O18). Spectra were collected for single-pulse LIBS in air and Ar atmospheres, and for double-pulse LIBS in air. A methodology for comparing spectra was developed to determine provenance of gem beryls based on the premise that specimens from the same mine, mine field, or tectonic region should share a common geochemical signature. Analysis of over one hundred beryls from 27 localities worldwide demonstrates that this should be possible, given the appropriate database. However, ionic substitutions in beryl are sufficiently complex that within-pegmatite variations controlled by magmatic differentiation and subsequent recrystallization add a significant amount of chemical variability to the beryls. Despite this complexity, the analytical and data processing protocols demonstrate that the provenance of beryls can be successfully identified at the scale of a pegmatite mine, if the database contains a sufficient number of samples to capture the chemical variability in the field. The precision of provenance studies also depends on the quality of geographic metadata associated with each sample.
Crustal contamination in the British and Irish Palaeogene Igneous Province: Mechanisms, timing and implications for the formation of granitic magmas

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Old and lithologically variable terranes, such as those in the northern British Isles, preserve distinct and diverse crustal isotopic end-members. Similarly, individual crustal lithologies comprise various isotopic sinks, representative of various sources. Hence, while a partial melt/restite of these crustal lithologies may not be fully representative of the original protolith, it can be identified individually, further constraining crustal contamination. Therefore a magma’s course may be traced isotopically, providing a picture of a granite’s ascent and storage at both a local and crustal scale. Samples from the Drumadoon Igneous Complex, Isle of Arran, Scotland, and the Carlingford Igneous Centre, NE Ireland, were analysed for major and trace elements and Sr and Nd isotopes, aiming to reveal both magma chamber-scale processes and larger-scale crustal pathways. The Arran data point towards major involvement of the Grampian terrane, despite the Drumadoon Igneous Complex being within the Midland Valley. Therefore, while the magmas originated at depth on the northern side of the Highland Boundary Fault (HBF), they have crossed this boundary during their evolution and ascent, most likely during shallow-level emplacement. The HBF has a sub-vertical orientation, therefore the magma is unlikely to have taken a direct vertical traverse through the crust, but rather experienced significant lateral transport. At Carlingford, all samples trend markedly towards local Silurian crust, reflecting the involvement of a single crustal end-member. Nevertheless, our data imply contamination was not straightforward. We see a time sequence of variably overprinted processes, from initial contamination by crustal partial melts, to bulk contamination, and final assimilation of the remaining restite during transport and emplacement. At both centres, granitic magmas appear to result from high levels of contamination during differentiation, producing a characteristic bimodal “Bunsen-Daly Gap”. Significantly, the intermediate compositions that bridge this gap at Drumadoon and Carlingford are not the products of fractional crystallisation, but rather appear to be the result of both mixing of end-member compositions and variable amounts of crustal contamination during storage, transport and emplacement.

Silicon isotopic fractionation: Assessments from first-principles methods

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Equilibrium isotopic fractionation between solids is a thermodynamic property, which is determined by the vibrational properties of the system. In this work, we employ an ab initio method (Density Functional Perturbation Theory) to obtain the complete phonon dispersion, which in turn, is used to calculate the free energy of a material of a given isotopic composition. Finally, the equilibrium isotopic fractionation is determined from the difference in free energy of materials of different isotopic compositions. We use PBE functionals, combined with the use of pseudo-potentials and planewave basis sets. This methodology has proved to be successful in reproducing the physical and chemical properties of complex systems. Within this framework, we have recently developed a methodology to predict equilibrium fractionation factors as a function of temperature [1].

Silicon is a major component of Earth crust. Measurements of various isotopic compositions in Nature show that, in general, the silicon composition follows the oxygen composition, and shows a positive correlation with silicon content [2]. Further observations, as well as theoretical arguments, predicted that silicon isotopic fractionation properties could be related to the degree of polymerization of silica units in silicates[3].

In this study, we have focused on the study of the systematic trends in Si fractionation, and on its relationship with oxygen fractionation or silicate polymerization. Our work consists in a comparative study of materials presenting several degrees of silicate polymerization: nesosilicates (forsterite), inosilicates (clinoenstatite), phyllosilicates (kaolinite and lizardite), and tectosilicates (quartz). Oxygen isotopic fractionation has been computed and compared to existing experimental data with which they agree well given the calculation uncertainty. Silicon isotopic fractionation has also been computed and compared to their oxygen counterparts. Silicon fractionation between quartz and other materials is systematically positive and range from 0.2 to 0.8 permil at 1000°C. Beyond that, they roughly follow the trends of oxygen fractionation. Nevertheless, a clear correlation between silicate polymerization and silicon fractionation has not been observed.

References

Iron sulfide formation under low pH conditions in sulfate reducing enrichment cultures obtained from acidic pit lake sediments

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Dissimilatory sulfate reduction often plays a key role in bioremediation systems treating acid mine drainage as it leads to alkalinity generation and precipitation of metal ions. However, both, microbial sulfate reduction and metal sulfide formation, are pH dependent and are inhibited under low pH conditions. The aim of this study was to investigate iron sulfide formation under sulfate reducing conditions in systems mimicking low pH environments. Experiments were performed at 18°C with indigenous sulfate reducing populations originally enriched from sediments of an acidic pit lake. The artificial pore water media contained elevated concentrations of sulfate (20 mM), Ca (6 mM), Fe(II) (5 mM), Al (4 mM), and Mg (1 mM) and a H2/CO2 gas mixture was used as electron donor/carbon source. The pH was initially set to pH 3.3, 3.8, 4.8, and 5.9. Over an incubation time of 12 weeks, pH, concentrations of soluble Fe(II), sulfate, and sulfide, and partial pressures of H2 and CO2 were monitored. In the less acidic systems (pH 4.8 and pH 5.9), sulfate reduction started shortly after inoculation. In the systems with an initial pH of 5.9, immediate precipitation of iron kept the concentration of free sulfide very low (< 30 µM), whereas in the systems initially set at pH 4.8, free sulfide concentrations built up to 300 µM during iron precipitation. In the more acidic systems, sulfate reduction occurred after a lag phase of 20 – 40 days but it proceeded at a much higher rate than in the less acidic systems. A decrease of soluble Fe(II) was only observed at pH > 4.3 when the amount of sulfate reduced exceeded 5 mmol per ml of culture medium. The results show that free sulfides form at low pH when high concentrations of free sulfide are present. Sulfate reducing prokaryotes thriving under these conditions need not only to be acidotolerant but must also tolerate high concentrations of free sulfide. Different cell morphologies revealed by microscopic observations as well as microbial community analysis based on 16S rRNA gene amplicons suggest that different sulfate reducing species were enriched. Mineral precipitates formed in the different system will be characterized by electron microscopy (SEM/TEM). Geochemical equilibrium modeling will be used to calculate saturation indices and predict iron-rich mineral formation in the various systems.

Determination of siderophile and chalcophile elements in peridotites by sector field ICP-MS

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Obtaining complete and accurate data sets on all highly siderophile elements in peridotites and related rocks is challenging because of digestion issues, low abundances and the monoisotopic nature of Au and Rh. Similarly, moderately siderophile and chalcophile elements such as Mo, Ag and Cd are poorly constrained in such rocks, again because of digestion issues, low abundances and a wealth of interferences in ICP-MS. Here, we report initial results on highly siderophile elements including Rh and Au and a new approach for the precise analyses of some moderately siderophile and chalcophile elements. Analyses are carried out at the Freie Universität Berlin using a Thermo Element XR sector field ICP-MS equipped with an Aridus desolvating system, glass spray chambers and microconcentric nebulizers.

The analysis of PGEs, Re and Au follows a modification of previously published protocols (Meisel et al., 2003, JAAS 18, 720-726). Up to two g of powdered samples are digested in inverted aqua regia using carious tubes or a high pressure asher. Osmium is separated by solvent extraction and analyzed by TIMS, the other PGEs and Re are separated from the rock matrix in 0.2 M HCl using cation exchange resin. Rhenium and all PGEs except Rh are quantified by isotope dilution (ID). Rhodium is quantified relative to Ir by using the Ir abundance from the ID analyses and a response factor derived from a Rh-Ir calibration solution.

Gold abundances have been determined by the standard addition method for two samples, a serpentinitized herzolite reference material (UB-N) and a Al-rich peridotite (TUR-7) from France. Four rock powder aliquots were spiked with 0, 2, 4 and 6 ng Au before carius tube digestion. Prior measurement, the samples were centrifuged and diluted with 0.5M HCl to a solution weight 50 times the initial sample weight. During the analysis, drift was compensated for by internal normalisation to sample Ir. Very good correlations were obtained despite the independent digestions for each aliquot, which suggests that Au and Ir are homogeneous at the 2g sample scale and that the digestion method is reproducible. The Au abundance in UB-N and TUR-7 was found to be 1.49 (+0.04; -0.05) and 1.34 (+0.11; -0.20) ng/g at the 95% confidence level.

The abundances of many moderately siderophile and chalcophile elements are poorly constrained in the Earth’s mantle. To obtain high precision data, we started to prepare enriched isotope spikes and developed a chemical separation protocol for Cu, Zn, Ga, Mo, Ag, Cd, In, Sn, Te, W and Tl.
Hardpan formation in mine tailings: Reactive transport modelling of column experiments

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Hardpan formation in low-sulphide low pH mine tailings was studied using laboratory column experiments. The main reactive components of these tailings are metal-sulphides and sheet-silicate minerals like biotite (Graupner et al., 2007). Artificial rain water was allowed to enter at the bottom of a 5 cm Ø column, which was filled with 35 cm of loamy tailings beneath a 15 cm layer of fine-grained quartz sand. Upward capillary transport of water followed by evaporation at the top of the column resulted in partially saturated conditions within the upper part of the column, an upward directed transport of solutes and colloids into the quartz sand, as well as the formation of a hardpan at the capillary fringe.

Figure 1: Bulk chemical profiles after 146 days (circles: measured data, lines: reactive transport model (single porosity model, transport of solutes only))

The reactive transport code FLOTRAN (Lichtner, 2005) was used to model the relevant reactive transport processes leading to the formation of the observed hardpan. The observed concentration profiles (Fig. 1) cannot be explained by reactive solute transport on the basis of single porosity models. A dual porosity approach, which considers mobile and immobile pores, is required to explain the observed retention of e.g. aluminium, zinc, and copper within the quartz sand layer. Furthermore, the observed extremely high transport rates for e.g. aluminium can only be explained assuming colloid and/or mechanical transport. These additional processes would positively affect hardpan formation rates.

References

Identifying the sources of PGE, Re and Sb in road dust and soils along highways

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Automobile catalytic converters are a known source of Rh, Pd and Pt deposited in road dust and soils along highways. Since Ir is now also used in catalytic converts an increase in concentrations in the environment could be detectable. In addition Os, which can occur in toxic species, with a close to Earth mantle isotopic composition was detected in car exhaust. Thus a almost the whole range of PGE in the environment are related to anthropogenic emissions. In this work we studied soils from an Austrian highway section sampled in 2002, 2005 and 2007. Soils, grass and road dusts where analyzed for platinum group elements (Ru, Rh, Pd, Os, Ir and Pt), Re, Sb and the 187Os/188Os isotopic composition. Samples where taken in 0, 2 and 10 m distance and in 0-5 and 5-10 cm respectively. In addition to trace element concentration data, magnetic susceptibility of the soils were measured.

The combination of all data and information allow the following observations. Very strong correlations between Re, Sb, Cu and magnetic susceptibility point to brake liners as the source of the enrichments observed in the top layers of the soils close to the highway. The strong increase of Ru, Pd and Pt enrichments within the last 5 years is clearly a attributed to catalytic converters. The high Ru, Os and Ir concentrations of soils close to the highway are explained by the use of serpentinite gravel from a quarry close to the sampling site used for the construction of the highway dam. Since a very strong correlation between Os isotopic composition and the inverse concentration of Os exists a mixing of two endmembers is evident. The two endmembers coincide with estimations of upper mantle and a continental crustal composition. A mixture with a third component representing the composition of catalytic converter can be excluded based on the current data. Either the concentrations of Os are too low to be detected or Os occurs in a volatile species that is easily dispersed compared to the Rh, Pd and Pt which are associated with Al-Ce bearing particles. Since Ir/Os and Ru/Os ratios are similar to mantle estimates and their concentrations relatively high, an anthropogenic source of Ir cannot be detected at this site.

In conclusion we can attribute the observed distributions of measured trace element concentrations to the following sources: automotive converters (Rh, Pd and Pt), brake liners (Sb, Cu and Re?) and serpentinite gravel (Ru, Os and Ir).
Equilibrium experiments and theoretical studies in the MgO-SiO$_2$-H$_2$O system at high pressures: Clarification of stabilities and thermodynamic properties of phase A, clinohumite and chondrodite

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The stabilities of clinohumite, chondrodite and phase A were investigated in phase equilibrium experiments using a rocking multi-anvil apparatus at pressures of 7.5-12.5 GPa and 800-1350 °C. The rocking technique, i.e. regular inversion of the experimental apparatus including the capsule, results in nearly homogeneous run products. This overcomes the problem of experimentally producing more phases than can be in equilibrium and thus allows unequivocal determination of stability fields.

Seven reactions were bracketed by equilibrium experiments (every starting material consisted of crystalline phases both, products and reactants).

Our results show that phase A, clinohumite and chondrodite have wider P-T stability fields when compared to the previous studies. More over, above 10 GPa, clinohumite has a lower temperature stability compared to chondrodite. These results contradict works by Wunder, (1994) and Kawamoto, (2004).

Thermal expansivities for clinohumite and chondrodite and the C$_P$ function of chondrodite were predicted from the Debye model. Thermal expansivities correspond to 2.64 ·10$^{-5}$ and 2.71 ·10$^{-5}$ K$^{-1}$, respectively. Standard state entropy and enthalpies for phase A, clinohumite and chondrodite were deduced from the fluid absent reactions by mathematical modelling.

References

Effect of montmorillonite dissolution on U(VI) sorption in bentonite

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Along with the fulfilling of other safety functions relevant for the final disposal of radioactive waste, bentonites should also retard the release of radionuclides in case of groundwater inflow. This study shows that U(VI) interaction with bentonite depends on its aqueous complexation and is strongly influenced by the dissolution of montmorillonite.

Results and Discussion
A comparison of the time-dependent changes in Mg and U(VI) supernatant concentrations as a result of clay-solution contact at circumneutral conditions reveals their strong correlation. SEM-EDS and FEM analyses of the bentonite samples indicate further that U(VI) is adsorbed at montmorillonite edges, which supports the findings of previous studies (Catalano and Brown, 2005). Time-dependent changes in the solubility of colloidal silica evidence silica release from montmorillonite and its relation to Mg release occurring at montmorillonite edges as well.

Application of the periodic bond chains (PBC) theory (Hartman and Perdock, 1955) to the observed data and taking into account the mechanism of alkali feldspar dissolution (Oelkers et al., 1994) allows to suggest the following mechanism of the non-stoichiometric montmorillonite dissolution as related to U(VI) adsorption on its edges: (1) surface complexation of U(VI) with Mg edge sites; (2) detachment of Mg; (3) surface complexation of U(VI) with Al, Fe edge sites; (4) diffusion and release of Mg from the outermost but one PBC; (5) hydrolysis of Al-O-Si bonds and release of Al; (6) Si release after dissolution of at most three PBCs. Taking into account the proposed mechanism of orthosilicate dissolution (Casey and Westrich, 1992), we hypothesize that the preferential complexation of dissolved U(VI) with Mg edge sites may be explained by very similar rates of water exchange on UO$_2$(H$_2$O)$_5^{2+}$ and Mg(H$_2$O)$_6^{2+}$.

Conclusions
The study proposes a mechanism of montmorillonite dissolution as related to U(VI) adsorption, which provides molecular scale information about the involved processes.

References
Oldest terrestrial diamonds in zircon from Jack Hills, Western Australia

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Recent geochemical and mineralogical studies of >3,900 Myrs old, detrital zircons from the Jack Hills metasedimentary belt, Yilgarn Craton, Western Australia, implied that granitic, continental crust and oceans on the Earth already existed as early as 4,400 Ma. However, this hypothesis is still a matter of debate as it contrasts with the conventional view that early Earth’s evolution was dominated by mafic and ultramafic magmatism. Importantly, we have now discovered diamond inclusions in Jack Hills zircons using micro-Raman spectroscopy. The ages of the diamond-bearing zircons range from 3 to >4 Ga, thus providing a completely new dimension in the formulation of ideas regarding the evolution of the early Earth. This spread of ages indicates that either the conditions required for diamond formation were repeated several times during early Earth history or that there was significant recycling of ancient diamond. Most diamonds are surrounded by graphite, suggesting a retrograde diamond-to-graphite transformation. Graphite is known to be associated with metamorphic diamonds formed during ultra-high pressure (UHP) metamorphism. This, together with other mineralogical features, demonstrates that the Jack Hills diamonds most closely resemble diamonds formed during UHP metamorphism. Unless conditions on the early Earth were unique, this implies the presence of a relatively thick continental lithosphere and that crust-mantle interaction occurred on Earth as early as ~4.2 Ga.

References

Organic speciation of hydrocarbon-derived carbonate chimneys (Gulf of Cadiz, SW Iberia)

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Dolomite-rich chimneys associated with hydrocarbon-rich fluid venting were discovered in September 2000 in the Gulf of Cadiz. Chimneys show a wide variety of shapes and range in size from several centimetres to a few decimetres. Basically, they are made of a fine groundmass of major Fe-rich dolomite, ankerite and calcite, small grains of quartz and phyllosilicates, and foraminifer tests and ostracod shells. The possibility of anaerobic oxidation of methane mediated by a community of anaerobic methanotrophic archaea and sulphate reducing bacteria, along with the proposal that the iron oxides and sulphides, present in the carbonate matrix of the chimneys, are probably formed by biomineralization processes justify the organic speciation of samples and study of biomarkers. We found linear hydrocarbons with C<20, isoprenoids but not hopanoids and PAHs as indicators of petroleum or anthropogenic contaminations. It is interesting the presence of a complete series of terminal monochloroalkanes in the same C range of the n-alkanes found in the sample (Fig. 1.) We suggest that chloroalkanes were formed during the hydrothermal process in the seafloor.

Figure 1: SPME-GC/MS chromatogram showing the 1-chloro-n-alkanes profile in hydrothermal chimney samples.
Generating the aromatic world: Synthesis of aromatic compounds in icy environments

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The aromatic hydrocarbons are recognized as astrophysically important molecules and their presence in interstellar ices may contribute to the materials incorporated into planets, satellites, asteroids and comets. Ultimately, PAHs are recognized as key molecules in the study of the origin of life, due to their photochemical properties that could allow to PAHs to play the role of primitive pigment systems that drive synthesis of amphiphilic compounds; assemblies based on aromatic hydrocarbons were proposed as components of informational polymers, containers and mediators in metabolic pathways (1). The availability and stability of such aromatic compounds plus their capacity for self-assembly driven by pi-pi stacking interaction and weak forces made the aromatic hydrocarbons good building blocks for protocellular structures. Indeed, it has been demonstrated that amphiphilic polycyclic aromatic compounds are capable to self-assemble and form bilayer structures (2). We demonstrate that complex mixtures of aromatic compounds could be synthesized in cold systems with water ice and methane as carbon source. Using spark discharges as energy source and generating a “ice reactor” by means of a cycle of freezing-melting we found benzene derivatives as acetophenone, benzaldehyde and benzonitrile and PAHs.

References

Figure 1: SPME-GC/MS chromatogram showing main aromatic compounds obtained in an icy environment.

Dating carbonate rocks with in situ produced cosmogenic $^{10}\text{Be}$: Why it often fails

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In situ produced cosmogenic $^{10}\text{Be}$ has proved to be valuable tools for environmental and Earth sciences. Progress in the field of accelerator mass spectrometry (AMS) allows the determination of radionuclide concentrations as low as of $10^3$-$10^5$ atoms/(g rock) that makes quantifying Earth’s surface processes possible. However, surface dating of carbonate rocks using the cosmogenic radionuclide $^{10}\text{Be}$ is still problematic. In order to investigate the reasons for this, we have performed extensive step-wise leaching of calcite-rich samples. Results on different grain size fractions clearly indicate the sources of atmospheric $^{10}\text{Be}$ being small clay minerals. We demonstrate that partial-leaching procedures that result in moderate pH levels will not release $^{10}\text{Be}$ (in-situ produced or atmospheric) due to the instant re-absorption on grain surfaces. Under strongly acidic conditions all absorbed atmospheric $^{10}\text{Be}$ is leached from aluminosilicates giving abnormally high $^{10}\text{Be}$ concentrations and consequently exposure ages that are too old (Merchel et al., submitted).

Now, that we understand the main obstacles in analysing $^{10}\text{Be}$ from carbonate rocks, the next steps are clear: We need to concentrate on samples that do not contain clay minerals. This might require working on coarser grain size fractions or recrystallized material. Or we need to find a way to physically and/or chemically separate clay minerals from carbonates before dissolving them. This task is most challenging because clay is generally much more resistant to chemicals than carbonate minerals. After testing several analytical methods, i.e. XRD, IR, TEM-SAED, ICP-OES, SEM-EDX, we are still searching for a “simple and fast” method which could quantify clay concentrations in our samples and could help monitoring the efficiency of future separation procedures.

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References
New spectroscopy developments to study water in basaltic melts

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Micro-Raman spectroscopy is a powerful technique to assess the water content and diffusion profiles in silicate glasses, at micrometer scale. The potential of Raman spectroscopy to quantify water has been recently demonstrated for hydrous, silicic glasses [e.g., 1-2]. However, Raman analysis of hydrous, basaltic glasses is more delicate. We examine here the effects of laser beam (heating and oxidation) on these glasses and the dependence of Raman calibrations on iron redox state and compositions of glasses. We studied 28 dry natural glasses having a large range of polymerization degree (NBO/T: 0 to 1.17), 2 sets of basaltic glasses with variable Fe3+/ΣFe ratios and 4 sets of synthetic hydrous mafic glasses (H2O: 0.4 to 5.3 wt%). In order to prevent analytical condition bias, Raman calibration for water (internal calibration) has been based on the ratio of the H2O total stretching band (3500 cm−1) relative to spectral features (LF: 490 cm−1 and HF: 960 cm−1) of the glass network. Internal calibration is glass composition dependent. Our results on dry glasses demonstrate that the ratios between LF and HF spectral bands correlate with the sum of structural modifiers (SM). It thus allows us to predict the composition dependency of Raman internal calibrations. Moreover, the iron oxidation state of basaltic glasses does not influence the Raman calibrations. We demonstrate that internal calibration of water is reliable, using the HF and LF bands, respectively, for depolymerised and polymerised glasses.

References

Growth of calcium carbonates in gels in the presence of organic and inorganic additives

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Biomineralisation provides a great variety of crystal morphologies. For example the brachiopod Mergelia Truncata [1] forms extremely tortuous strands of calcite crystals. In order to understand the biologically induced crystal morphologies, the growth of crystals in gels is an excellent method to study the influences of additives on the morphology of the growing crystals. Different striking effects on the morphology of calcite crystals have been shown for inorganic [2] as well as organic additives [3] using this method. Additionally, biomineralisation often results in crystals with incorporated cations (e.g. Mg2+ in calcite [1]). The focus of this work, therefore, is the investigation of the combined influences of organic and inorganic additives on the crystal morphologies and polymorph formation of calcium carbonate. We used acrylamide as well as sodium silicate hydro-gels with MgCl2, SrCl2, aspartic acid, and succinic acid as additives. The crystals were investigated using XRD, micro-raman spectroscopy, and SEM. We obtained vaterite, aragonite, and calcite polymorphs. The crystal morphologies range from spheres (Fig. 1) and morphologies known from inorganically grown crystals (rhombohedra, aragonite twins) to crystals with strongly distorted morphologies such as dumbbell-shaped crystals. The experiments show that the combined influences of inorganic and organic additives are able to change the growth behavior of calcium carbonate, generating a variety of crystal morphologies.

Figure 1: Calcite sphere grown in an acrylamide cryogel (gelation at -20°C).

References
**40 Ar/39 Ar ages and geochemistry of Maranhão CAMP tholeiites (Brazil): Implications for low and high-Ti basalts sources**

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The Central Atlantic magmatic province (CAMP) emplaced at the Triassic-Jurassic boundary, is composed of prevailing low-Ti (TiO2 < 2.0 wt%) and of rare high-Ti basalts (TiO2 > 2.0 wt%). The latter are generally confined to the circum-Atlantic regions of northernmost South America (French Guiana, Surinam and Cassiporé area of Brazil) and of western Africa (Liberia, Sierra Leone). Here we report first separates for intermediate-Ti (198.5 ± 0.8 Ma) and to the mean 40Ar/39Ar age of the brazilian CAMP (mean 199 ± 2.4 Ma).

The Maranhão tholeiites are generally evolved basalts to basaltic andesites (MgO = 2.6-7.9 wt%). Three chemical groups are defined: low-Ti (TiO2 ≈ 2.0 wt%), high-Ti (TiO2 > 2.0 wt%), and intermediate-Ti tholeiites (TiO2 ≈ 2.1 wt%; K2O ≈ 0.3 wt%). The three chemical groups display almost flat to slightly enriched REE patterns precluding a garnet-bearing source. In particular, the intermediate-Ti tholeiites display almost flat REE patterns (LaCN/YbCN ≈ 2.1) relative to low-Ti (LaCN/YbCN = 3.5-4.0). The high-Ti tholeiites are more enriched in LILE and LREE (LaCN/YbCN = 4.4-5.0). All the low-Ti tholeiites display strong negative Nb and positive Pb anomalies, which are indicative of crustal assimilation. By contrast, such effects of crustal contamination.

**Chromitite alteration in serpentinite mélanges of Nurali and Kalan massifs (Russia)**

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Studies on the genesis and evolution of Cr-mineralization in ophiolites usually do not consider the metamorphic processes that influenced the mineralization in later stages. Kalkan and Nurali chromitites from Urals mélanges exhibit different alteration. During post-serpentinization reactions Al diffuses out of magmatic spinel leaving behind a ferritchromite and promoting the formation of chloride aureoles (Mellini, 2005). Kimball (1990) describes the alteration of spinel to ferritchromite and the formation of chloride by the reaction:

\[
\text{MgAl}_2\text{O}_4 + 4\text{MgO} + 3\text{SiO}_2 + \text{H}_2\text{O} = (\text{Mg}_3\text{Al})(\text{AlSi}_2\text{O}_8)(\text{OH})_8
\]

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\]

with MgO, SiO2 and H2O coming from the fluid.

At Kalkan post-serpentinization processes led to the formation of chloride and ferritchromite by reaction of fluid with spinel and serpentine, with MgO and SiO2 coming from serpentine. Only rare serpentine relics testify the serpentinization stage. At Nurali no evidences of chloride and ferritchromite formation have been observed and post-serpentinization processes led to partial reabsorption of chromite. Serpentinization did not affect chromite and led to the formation of magnetite as coronae around chromite crystals or as small scattered magnetite grains in the matrix. According to the mineral chemistry of involved phases we propose the following reaction for ferritchromite formation:

\[
2(\text{Mg}_{0.60}\text{Fe}_{0.40})(\text{Cr}_{1.10}\text{Al}_{0.70})\text{O}_4 + 3/2(\text{Mg}_{0.57}\text{Al}_{0.43}\text{Fe}_{0.10})\text{Si}_2\text{O}_5\text{(OH)}_4 + \text{H}_2\text{O} + 1/12\text{O}_2\rightarrow 7/6(\text{Fe}_{0.60}\text{Mg}_{0.40})(\text{Cr}_{1.85}\text{Fe}_{0.15}\text{Al}_{0.00})\text{O}_4 + 1/2(\text{Mg}_{0.18}\text{Fe}_{0.82}\text{Al}_{0.00}\text{Si}_{0.00}\text{O}_{16})(\text{Al}\text{Si}_2\text{O}_8)\text{(OH)}_8
\]

Magnetite formation during serpentinization without involving chromite can be described by the reaction:

\[
4(\text{Mg}_{1.8}\text{Fe}_{0.2})\text{SiO}_4 + 2(\text{Mg}_{0.6}\text{Fe}_{0.4})\text{Si}_3\text{O}_5 + 6\text{H}_2\text{O} + 1/6\text{O}_2\rightarrow 3\text{Mg}_2\text{Si}_3\text{O}_8\text{(OH)}_4 + 1/3\text{Fe}_2\text{O}_4
\]

**References**


Interactions of U(VI) and Eu(III) with natural bacterial isolates

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The presence of the actinides uranium, plutonium, neptunium, americium and curium as well as of lanthanides in radioactive wastes is of major concern because of their potential for migration from the waste repositories and long-term contamination of the environment. It was demonstrated that abiotic processes strongly affect the migration of these elements in the environment. However, it is becoming increasingly evident that microbial processes are of importance as well. Microbial processes will act immobilizing or mobilizing radionuclides, depending on the type of process and the state of the microbes. The present work investigated the interaction of bacterial strains isolated from different uranium contaminated sites as well as from groundwater at a deep-well monitoring site of the radioactive waste repository Tomsk-7, Siberia, Russia with U(VI) and Eu(III) (as non radioactive analogue of the trivalent actinides). A highly multidisciplinary approach consisting in a combination of wet chemistry (batch sorption), microbiological, spectroscopic (EXAFS, XANES, TRLFS) and microscopic techniques (TEM/EDX) is used. The results of this work will help in understanding the role of microbiological process in the chemical behavior of actinides in geological and environmental context for future nuclear waste disposals as well as in the optimization of bioremediation processes using these natural bacteria.

Seasonal element and Sr isotope ratio variations in Late Miocene corals from Crete, Eastern Mediterranean

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Trace and minor element profiles of coral skeletons may be used to infer temporal changes in environmental conditions. In paleoclimate and paleoenvironmental studies diagenetically unaltered materials are required which are generally only available from Pliocene or younger localities. However, exceptionally well-preserved Porites corals of Late Miocene age (~9 Ma) can be found on Crete (Eastern Mediterranean) which have retained their original aragonite mineralogy. Previous stable isotope (δ¹⁸O, δ¹³C) profiles yielded geologically significant seasonal signals, similar to those found in present-day corals.

Here, we report element profiles of these corals by laser ablation along the axis of maximum growth at a spatial resolution of 500 µm, corresponding to eight to eleven samples per year. Analyses were done using a 213 nm Nd:YAG laser coupled to an Element2 ICP-MS (ThermoFisher). In addition, two Sr isotope profiles of several years each were measured by TIMS by microdrilling (0.8 mm bit) at a resolution of ~4 samples per year.

The ⁸⁷Sr/⁸⁶Sr ratios mostly cluster closely around 0.7089 which confirms the ~9 Ma-old age of the corals, and suggest a working connection of the Eastern Basin to the open ocean at that time. Nevertheless, several isotopic excursions to lower values are seen in the profiles, which could be interpreted in terms of a semi-closed basin with Nile-like (unradiogenic) influence.

Variations in many lattice-bound elemental ratios (e.g. Sr/Ca, U/Ca) co-vary with those of δ¹⁸O, and thus closely reflect sea surface temperature (SST) seasonality. Other element ratios in the profiles (e.g. Al/Ca, Ba/Ca, Mn/Ca, Zn/Ca) do not correlate with δ¹⁸O (and thus SST), but do however exhibit strong peaks in the winter months. Therefore, this signal cannot plausibly originate from diagenetic alteration or post-growth contamination. Rather, the Al, Ba, Mn and Zn most likely represent seasonal terrigenous input into the coral reef environment syn-genetically incorporated into skeletal porosity during coral growth, though the exact mechanism of sediment inclusion remains unclear in detail. However, because of its winter dominance, we interpret it in terms of variations in riverine suspended load from Crete into the near-shore environment of the corals caused by winter rainfall. If so, our profiles are a proxy for the frequency and/or severity of winter storm events in the Eastern Mediterranean during the Late Miocene.
Petrogenesis and tectonic evolution of the meso-Proterozoic felsic volcanic suite of the Sakoli Group in the Bhandara Craton, Central India

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The Sakoli supracrustal rocks encompassing an area of about 3600 sq km known as ‘Bhandara Triangle’ of Central India are surrounded by the Amgaon granitic gneisses forming the basement for Sakoli Group with highly tectonised contact. Chemically the felsic volcanics of Sakoli Group lie in rhyolite-rhyodacite field and the relationship of Zr/TiO2 vs Nb/Y shows that felsic pyroclastics are relatively less evolved members of the felsic suite that fall in the rhyodacite-dacite-trachyte field. Other members of the felsic suite shows a spread in comendite-pantellerite-trachyte field. The pyroclastics are the least alkaline, hence least evolved members of the felsic suite, while the lavas emplaced at conduit are most evolved.

The geodynamic setting of the felsic lavas is interpreted by using various discrimination diagrams and ratios of incompatible elements. The La/Yb vs Sc/Ni discriminant function shows that the felsic suite was evolved in ‘continental margin arc’ to ‘evolved oceanic arc’ like mixed setting. The La/Yb vs Yb discrimination indicates extensional set up for the pyroclastics and the La/Yb vs Th/Yb functions suggest that the lavas were evolved in immature transitional to marginal arc setting with evolutionary trends towards Andean (continental) arc. Overall the ratios of incompatible trace elements for the felsic volcanics indicate a continental marginal arc to marginal extensional basin set up, suggestive of a back arc rifting at the continental margin. Pyroclastics in general have highest LREE enrichment as well as high HREE content of the felsic suite. Hydrothermally altered Pyroclastics have HREE levels compatible to felsic suite, but the depleted middle and LREE are similar to the REE pattern of granite dykes from the area. The hydrothermal fluids that caused this alteration may hence be related to granite emplacement. The hydrothermal fluids have been enriched in HREE possibly because these fluids were generated by partial melting of the residuum of the first partial melt that generated felsic magma.

Overall REE pattern and incompatible trace element ratios suggests that the magma for the Sakoli felsic volcanic suite was generated by a mixed process. An initial enriched mantle partial melting event unrelated to the subduction process generated primary melt. Its emplacement at deep continental levels, possibly related with subduction regime that generated a subsequent deep continental crustal partial melt. Mixing up of both the melts resulted in the mixed transitional character of the felsic suite. The resultant mixed melt possibly had short, shallow crustal residence after initial emplacement and fractionation.

Submicrometer organic grains: Widespread constituents of the early Solar System

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Primitive meteorites and interplanetary dust particles (IDPs) contain remnants of interstellar organic matter, marked by anomalous H and N isotopic ratios [1]. These isotopic anomalies are attributed to mass fractionation during chemical reactions at cryogenic temperatures (10 – 100K) in a cold molecular cloud. Significant variations in the chemistry and isotopic compositions of organic compounds within and between these samples suggest varying histories of alteration and dilution of the presolar components.

Recent studies have reported large H and N isotopic anomalies preserved in sub-µm organic inclusions in both meteorites and IDPs [2]. In the Tagish Lake meteorite, the largest H and N isotopic anomalies are associated with sub-µm, hollow organic globules [3]. The common physical, chemical, and isotopic characteristics of these globules suggest that they formed before being incorporated into their parent meteorite. These organic globules probably originated as organic ice coatings that formed on preexisting ice or mineral grains in a cold molecular cloud. Radiation driven photochemistry may have processed them into refractory organic grains. This model implies that submicrometer organic grains were widely distributed throughout the solar nebula during the epoch of planet formation.

Submicrometer organic particles were detected by the Giotto and Vega encounters with comet Halley, termed CHON particles based on their major element chemistry. The first direct samples of cometary dust (comet Wild-2) were returned by the Stardust spacecraft in January 2006. These samples exhibit widely varying, fine grained mineralogy similar to anhydrous IDPs, including submicrometer carbonaceous grains. The submicrometer organic grains from comet Wild-2 exhibit H and N isotopic anomalies of similar magnitude to those commonly observed in primitive meteorites and IDPs [4,5].

Isotopically anomalous, submicrometer organic grains have now been observed in meteorites, IDPs, the Oort-cloud comet Halley, and the Kuiper-belt comet Wild-2, suggesting that such grains were prevalent throughout the protoplanetary disk.

References

Trace element and volatile signature of Etna magma source(s): A melt inclusion approach

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OIB-type alkaline magmatism at Mt Etna is related to mantle upwelling and tensional tectonics at the collision boundary of the African and European plates, promoted by differential roll-back of subducting Ionian oceanic lithosphere. During the last 4 ka Mt Etna produced rare H2O, Ca-rich picrite magma [1] and recurrently, water-rich basalts-trachybasalts variably enriched in alkalis [2]. Trace elements, Cl H2O and CO2 have been analyzed in the olivine-hosted melt inclusions in order to better constrain magma genesis, the mantle source processes and the evolution of the volcano plumbing system. Both picritic and basaltic melt inclusions display closely similar Th/U, La/Th, Ce/Th, Ta/Nb ratios indicating their derivation from a bulk HIMU-type OIB mantle source. However, the Ca-rich picritic magma is distinguished by a stronger negative anomaly in Nb, high U/Nb, Cl/Ce, H2O/Ce ratios, and moderately high Ce/Pb, Ba/Th and Sr/Nd ratios which evidence the imprint of a subduction-derived fluid component. This imprint is diluted in historic and present-day basalts that show moderate water enrichment and nearly constant H2O/Ce and Nb/U ratios. A main feature is the decoupled behaviour of alkalis and volatiles (H2O-Cl). Compared to historic basalts, the present-day magmas are significantly enriched in alkalis, but preserve alkalis/La ratios similar to those of the picrite. This suggests the separate involvement of an alkali-rich component during either mantle processes (melting, magma production rate) or interactions with the lower crust, as will be discussed.

References

Probing the Organic-Mineral Interface (OMI) at the molecular level in Model Biominalers

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The process of biomineralization involves exquisite control of organic and mineral components by biological systems [1-3], which harness chemistry and physics, drawing the attention of material scientists, geochemists, physicists, and biologists [4-5]. The key to understanding biomineralization is in the interaction, at the molecular level, between the organic and mineral components [4]. In this study we employ x-ray absorption near edge (XANES) spectromicroscopy to investigate bond changes and electronic structure of both calcium carbonate mineral crystals and peptides at the OMI. We acquired XANES spectra from calcium carbonate crystals grown in the presence of three nacre-inspired peptides (AP7N, AP24N, n16N) and a sea urchin spicule matrix protein, LSM34.

All model biomineral systems examined show disruption of surface C–C bonds in calcite and the enhancement of the peak associated with C–H bond, indicating ordering of the amino acid side chains. We show that these changes do not occur when Asp and Glu are replaced in the n16N sequence with Asn and Gln, respectively, demonstrating that the Asp and Glu amino acids participate in peptide-mineral molecular associations.

References
Mother-of-Pearl: Architecture and possible formation mechanism

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Biominerals in general [1-4] and nacre, or mother-of-pearl, in particular [5-8] attract the attention of scientists in biology, material science, and geochemistry because of their remarkable mechanical properties and the fascinating mysteries that still surround the formation mechanisms of these materials.

The structure and formation of aragonitic mollusk shell nacre are widely studied but still poorly understood. In this work we analyze Haliotis rufescens (red abalone) nacre with synchrotron spectromicroscopy, using linearly polarized soft-x-rays as illumination, and x-ray absorption near-edge structure (XANES) spectroscopy. We demonstrate high imaging contrast between adjacent individual nacre tablets, dependent on their crystal orientation with respect to the polarization vector. We compare data from previous reports and our new data with models for columnar nacre growth and polarization vector. We compare data from previous reports and our new data with models for columnar nacre growth and polarization vector.

Experimental study on the B-isotope fractionation between tourmaline and fluid: A re-investigation

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The boron isotopic composition of magmatic and metamorphic tourmaline shows a wide spread in δ11B-values which may range up to 40‰. Fractionations of boron isotopes between tourmaline, fluids, and melts have been used to infer quantitative information on fluid-rock and melt-rock processes in which tourmaline is involved. However, experimental data on ∆11B_{tourmaline-fluid} are scarce and restricted to hydrothermal experiments by Palmer et al. (1992) performed at 350 to 750°C and 50 to 200 MPa.

We reinvestigated the boron isotopic fractionation between tourmaline and fluid by hydrothermally synthesizing dravite with excess fluid between 400 and 700°C at 200 MPa, and at 500°C, 500 MPa using different synthesis techniques. One series used oxides, water and boric acid (90% excess) in a single capsule; the other boric acid (10% excess) and a two-chamber capsule (von Goerne et al. 1999). Run products were characterized by XRD with Rietveld refinement, SEM, EMP and P-TIMS.

Dravitic tourmaline was always the main solid phase sometimes accompanied by traces of other phases, which essentially are boron-free. Dravites from the first series are uniform in size (about 20 µm long), the second series produced a bimodal distribution consisting of small dravite aggregates plus large needles up to 350 µm long. Fractionation of boron isotopes between tourmaline and fluid from the first series give consistent results of -0.4‰ at 700°C and -2.6‰ at 400°C. The temperature dependence is approximated by ∆11B_{tourmaline-fluid} = -3.82 (1000/T[K]) + 2.88, R2 = 0.61.

References

References
Quantification and geochemical characterization of total mass fluxes in river catchments of the Rhenish Massif and the Black Forest, Germany

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We aim to constrain long-term erosion rates from the concentration of cosmogenic \(^{10}\text{Be}\) in stream sediments in order to quantify the Late Quaternary denudation history of mountain ranges in central Europe. Four different catchments in Germany, ranging in size from 8 to 379 km² are being investigated. Two of them, the Aabach and Möhne catchments in the Rhenish Massif, drain predominantly low-grade Paleozoic metasediments. The other two, the Gutach and Acher catchments in the Black Forest are situated in late Paleozoic granites. Initial samples from river catchments in the Rhenish Massif yield preliminary erosion rates between 30 and 50 mm/ka. These spatially-averaged erosion rates integrate over the past 10 to 20 ka. Central to our investigation are questions concerning the relative importance of lithology and catchment relief on long-term erosion rates.

Short-term erosion rates for all catchments will be quantified by combining the amounts of suspended and dissolved loads in water samples with water discharge data and basin area. By analyzing the stable isotopic signatures \(\delta^{34}\text{S}\) and \(\delta^{18}\text{O}\) of sulfate and \(\delta^{13}\text{C}\) of dissolved inorganic carbon we aim to correct the suspended and dissolved load for organic, atmospheric and anthropogenic inputs. These results will be complemented by erosion rates derived from the volume of sediment stored behind reservoirs of known age. Preliminary erosion rates, based on accumulated suspended matter from both reservoirs in the Rhenish Massif vary between 4 and 24 mm/ka over a period of 13 to 28 a.

Carbon, nitrogen, and sulfur cycling in a euxinic end-Permian ocean

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Abundant isotopic, geochemical, and biomarker evidence suggests the end-Permian mass extinction coincided with widespread anoxia and possible euxinia (anoxic and sulphidic waters). Anoxia might have resulted from a coincidence of warm surface ocean temperatures, low atmospheric oxygen content, and high \(\text{O}_2\) demand in the deep ocean. Subsequent organic matter remineralization by bacterial sulphate reduction would produce euxinic conditions. Phosphate release from shallow sediments under a sulphidic water column would further enhance oceanic euxinia through positive feedbacks to primary productivity. Here we use earth system modelling to investigate the physical and biogeochemical conditions necessary for the development of intense euxinia during the end-Permian. We hypothesize that reasonable variations in oceanic nutrient content will induce deep ocean euxinia.

We use the end-Permian configuration of GENIE (www.genie.ac.uk), an energy-moisture-balance atmospheric model coupled to a 3-D, non-eddy-resolving, frictional geostrophic model to evaluate this hypothesis. The model includes marine carbon, nitrogen, and sulfur cycles and accounts for metabolisms critical for the transition to ocean euxinia. We performed model simulations over a range of oceanic phosphate concentrations to relate nutrient content to the buildup of widespread euxinia and subsequent chemocline (oxygen-sulphide interface) destabilization. Deep-water \(\text{H}_2\text{S}\) appears with a doubling of oceanic phosphate, and we observe the greatest deep-water sulphide concentrations in the Paleo-Tethys Ocean. The metabolic activities of sulfide-oxidizing phototrophs and denitrifying organisms delay, but do not prevent \(\text{H}_2\text{S}\) buildup. Additionally, \(\text{H}_2\text{S}\) in equatorial and high latitude upwelling zones is released to the atmosphere when the upwelling flux of sulphide exceeds the downward oxygen flux from the atmosphere. Under modern atmospheric oxygen levels, significant air-sea \(\text{H}_2\text{S}\) fluxes result from 6- to 10-fold increases in oceanic phosphate. This destabilization of the chemocline causes sulphide poisoning in both marine and terrestrial environments, imposing environmental stress that may promote extinction. These simulations support the hypothesis that extreme euxinia and episodic \(\text{H}_2\text{S}\) eruptions can result from modest changes in the ocean’s nutrient content. Comparing these spatially resolved predictions to the rock record will help constrain the geochemical environment in which the end-Permian mass extinction appears.
Crustal – mantle melt interactions during continental breakup at the Early Paleocene Vøring Plateau, North Atlantic igneous province

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Drilling during ODP Leg 104 Hole 642E showed that the Volcanic Rifted Margin (VRM) at the Vøring Plateau is built up of mafic Seaward Dipping Reflector Sequences (SDRS) of Transitional T-MORB character, underlain by silicic volcanic formations (“Lower Series”), LS. The latter are dominantly peraluminous dacites formed by anatexis of crustal material. The core samples not only provide a unique sequence to study the geodynamic processes leading to continental breakup, but they provide the opportunity to investigate in space and time geochemical variations before and during excess magmatism. The samples from the LS allow to identify the crustal components that were potential contaminants of tholeiitic dykes within the LS and the tholeiitic T-MORB Upper Series sequence. These are essential data to determine the intrinsic geochemical characteristics of the mantle sources of the mafic melts. Trace element data, and Sr, Nd and Pb isotopes indicate that a lower crustal component and a upper crustal component contributed to the isotopic signatures, either through melt mixing or through mechanical mixing of pyroclastics. In order to better understand mixing processes we have analyzed a number of selected samples for the element caesium with a low-blank ICP-MS procedure. The Cs signature of the LS rocks (6.13–0.12 ppm) confirms the crust anatectic contribution of these rocks, and the data of the Upper Series tholeiites (0.14–0.01 ppm) indicate that a minor amount of crustal material might have been involved during the SDRS formation. A systematic investigation of Cs in the Hole 642E core defined a decreasing influence of continental crust during the magma formation. The tholeiitic “Upper Series” of both the Vøring and the SE Greenland VRM are isotopically rather similar. In contrast, the “Lower Series” from the two areas are isotopically fundamentally different, due to a different composition of the crust at the two locations. The LS of the Vøring Plateau interacted with high ⁸⁷Sr/⁸⁶Sr lower to upper crust. At the SE Greenland margin the isotopic composition of Sr, Nd and Pb point to a crustal contaminant of granulitic to high grade amphibolite nature (relatively low ⁸⁷Sr/⁸⁶Sr and rather negative εNd). This marked asymmetry of the geochemical signature of the crust at both sides of the nascent North Atlantic should be taken into account into models of the geochemical evolution of the ‘Iceland Plume’ system or alternative models for the formation of the NAIP LIP.

Microbial diversity and SIP investigations of streamer biofilm communities in Yellowstone National Park

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Streamer-forming biofilm microbial communities (SBCs) are common in some alkaline-chloride geothermal systems. Examples of SBCs have been reported in a variety of terrestrial thermal habitats [1], including Yellowstone National Park (YPN). 16S rRNA surveys of SBCs in one YNP location (Octopus Spr.) revealed that those communities were largely composed of presumably autotrophic Aquificales-like Bacteria [3]. However, further investigation of in situ metabolic characteristics of those SBCs by SIP (Stable Isotope Probing) techniques have indicated potential heterotrophic activity [4].

The physicochemical parameters of growth of SBCs down a thermal gradient at “Bison Pool” were investigated, in the context of the geochemical environment. While “Bison Pool” is geochemically similar to Octopus Spring, 16S rRNA and total lipid extract analyses have revealed a significant crenarchaeal component to the “Bison Pool” SBCs. At “Bison Pool”, the SBC bacterial component increases in complexity (going from 3 to 11 genera) while the archaeal component varies little (from 3 to 2 genera) in a 14°C gradient down the outflow channel, crossing the chemotrophic-phototrophic fringe.

Octopus Spring and “Bison Pool” SBCs were used as inoculae for SIP investigations of metabolic function. Microcosm experiments using ¹³C labeled salts of acetate, formate and bicarbonate were conducted over an incubation period of 3-4 days at in situ conditions. Following incubation, cells were extracted by a modified Bligh and Dyer technique in order to isolate various metabolic pools for evaluation of overall carbon uptake and its pathway into cellular metabolism.

SBC lipids showed uptake of ¹³C-labeled acetate and uptake was preferentially seen in archaean lipids after a short incubation (several hours), especially in caldarchaeol and its cyclic counterparts. Non-isoprenoid lipids also showed selective uptake, with the lipids diagnostic of Aquificales showing little or no isotope uptake. Further detailed analyses of these samples should shed light on the uptake of inorganic carbon and its incorporation into cellular metabolism.

References

Chemical erosion in the Himalayas-Tibet for the past 4 million years studied by Pb and Nd isotopic stratigraphy

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A record of the $^{143}$Nd/$^{144}$Nd ratio of Northern Indian Ocean seawater has been obtained for the past 4 Ma using a new method of differential dissolution on marine sediments. We studied ODP Sites 758 and 757 both located on the Ninetyeast Ridge. At Site 758, the $\varepsilon$Nd and $\delta^{18}$O curves fluctuate in conjunction during the glacial-interglacial periods. The largest variation occurred during the last 20 kyrs where $\varepsilon$Nd varies from -7.5 at Last Glacial Maximum to -10.5 during the Holocene, whereas the amplitude of the variation of the seawater signal is less than 1 $\varepsilon$Nd unit 2.5 Ma ago. The correlation between maxima and minima of $\varepsilon$Nd and $\delta^{18}$O is excellent (r=0.95). However, a detailed comparison of the two signals show that $\varepsilon$Nd and $\delta^{18}$O vary simultaneously during warming while $\varepsilon$Nd is delayed with respect to $\delta^{18}$O during cooling.

The southern ODP Site 757 shows little variations in Nd isotopic ratio. We thus interpret the $\varepsilon$Nd fluctuations at Site 758 as being linked to the erosion regime in the Himalayas-Tibet rather than to variations in the intensity of the deep ocean conveyor belt which flows from the South to this area. A simple quantitative model assuming that seawater Nd is a mixture of Nd that was chemically eroded in the Himalaya-Tibet with Nd coming from Indonesian island arcs indicates that chemical erosion in the Himalaya-Tibet was 2 to 4 times more intense during interglacial than during glacial periods.

We have shown by chemical tests that the same technique of partial dissolution can be also applied for lead isotopes. At Site 758, the lead isotopes ratios fluctuate following glacial interglacial alternation, but within a very small range. Indeed, $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb, $^{208}$Pb/$^{204}$Pb varies from 18.9 to 19.0, 17.73 to 17.77, 39.23 to 39.42 respectively. These variations are extremely well correlated suggesting a binary mixture. We suggest that the two component are the Trans-Himalaya-Belt and the High-Himalaya-Chain.

These results gives strong constrains on the enhancement of monsoon rainfall during Interglacials but also on the glacier occurrence in the Himalaya-Tibet highlands during glacial periods.

References


Assimilation beneath Mid-Ocean Ridges: Cl and H$_2$O constraints

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Many submarine basalts have assimilated hydrothermally influenced material before they erupt. High Cl and Cl/K in mid-ocean ridge basalts (MORB), submarine ocean island basalts (OIB) and submarine back-arc basin basalts (BABB) are often correlated with Mg#, and suggest that altered rock or brine is involved. It is possible to constrain the H$_2$O/Cl of the assimilated material if it is assumed that mantle derived H$_2$O/Ce ratios are fairly constant at 180 – 250 for Pacific MORB and many Pacific OIB sources, and that mantle-derived Cl/K is fairly low; ≤0.06 in MORB and OIB. (Robust values for low-Cl MORB and OIB). The maximum H$_2$O/Cl ratio in assimilated material can be determined by subtracting Cl from basalt analyses to obtain mantle Cl/K values, and subtracting H$_2$O up to the amount where H$_2$O/Cl constraints are violated. This exercise works best using samples that have very high Cl/K >0.30, such that the mantle contribution is relatively small and the uncertainty on the mantle contribution to Cl is negligible. For samples from the Galapagos Spreading Center (GSC) 86°-92°W, many glasses have <0.4Cl/K<0.6. The maximum H$_2$O/Cl content that does not violate H$_2$O/Ce constraints is H$_2$O/Cl = 1.0. If low-Cl/K samples from the nearby Galapagos Platform can be used to more tightly constrain the mantle H$_2$O/Ce, then the best fit is obtained with H$_2$O/Cl=0: e.g., halite addition. The requirement of a very dense brine or halite means that assimilation involves rocks at very high temperatures, consistent with assimilation of a narrow magma-hydrothermal transition zone.
Martian clay minerals: Context and implications for weathering of a basaltic crust

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The Mars Express OMEGA team discovered clay minerals on the Martian surface from near infrared remote sensing spectra [1-4]. In this paper, I examine some of these clay deposits using near infrared (\(\lambda \approx 0.4-3 \mu m\)) OMEGA data as well as thermal infrared (\(\lambda \approx 6-40 \mu m\)) spectra from the Mars Global Surveyor TES instrument. I also use high resolution images and thermophysical data to constrain the geologic context of these deposits.

At least two clay mineral types are detected (Al- and Mg/Fe-bearing) [1-3] and, in general, the Martian clay deposits correspond to extremely ancient rocks. The occurrence of clay minerals is usually tied to specific photogeologic units; the clay mineral distributions do not cut across multiple terrain units. Based on thermal infrared spectral observations, the clays are usually associated with other silicate minerals (plagioclase, ± mafic glass, ± pyroxene, ± olivine). To date, none of the clay mineral occurrences are associated with detectable quartz, opal-CT, zeolites, or carbonates. Thermal infrared spectra do not show the same strong evidence for clay minerals as the near infrared observations show.

The geologic scenarios that are most consistent with these observations are: 1) erosion and redistribution of a basaltic protolith where the clay minerals occur as clasts or cement in clastic rocks, or 2) diagenetic alteration of mafic ash or sediments. The geologic context of localized Martian clay mineral deposits detected to date is not consistent with origin by volcano-ice interaction, regional metamorphism, or low-temperature weathering of rock surfaces or varnish-like rock coatings. These deposits on Mars provide insight into early Solar System aqueous surface processes at a time when the surfaces of Mars and Earth may have been much more similar.

References

Native PAHs in hard coal particles as a possible source of increased PAH concentrations in river sediments

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Due to coal mining, transport and incomplete coal combustion, coal particles can be dispersed into soils and sediments where they can present a source of polycyclic aromatic hydrocarbons (PAHs) [1]. Once released into the environment, they play a pivotal role (amongst char coal, coke and soot) by carrying the predominant part of e.g. PAHs present in the sediment-water system. These particles together with their carcinogenic load can be taken up by organisms and the emanating risks have rarely been investigated [2]. While pyrogenic PAHs are known to be ubiquitous in environment, it is hardly recognized that native PAHs are the reason for elevated PAH concentrations in hard coals [3] being released into the environment during coal mining and transport. Although native PAHs have been in focus of previous research, [4, 5], a general overview of PAHs in hard coals from various large hard coal mining areas has not yet been reported.

The aim of this study is to elucidate (1) whether increased native PAH concentrations are present in hard coal samples from large mining areas and (2) whether PAH amounts and patterns correspond to hard coal rank.

In this study, for the analysis of PAHs in hard coal samples from some large mining areas (i.e. China, US, Australia, Indonesia, Poland, Germany, Ukraine, Kazakhstan), we applied accelerated solvent extraction using dichloromethane and fractionation according to polarity by column chromatography. Subsequently, fractions containing PAHs (~50 PAHs) were analyzed by GC-MS. First results of the study will be presented.

References
The source and the character of enrichment of Tholeiitic magmas developed on the spreading ridges near the Bouvet triple junction

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The Bouvet Triple junction Zone (Bouvet TJ) is characterized by mutual influence of three slow-spreading zones of the South Ocean – MAR, AAR and SWIR, position of which relatively each other has been changing in space and time. Within these zones there are different types of tholeiite magmas but their geochemical features are close by many parameters. By enrichment type the tholeiites belong to E-MORB developed in some segments of the MAR which are under the influence of Discovery hot-spot and at less degree of Shona plume (leRoux et al., 2002). Normalized spectrums of incoherent elements of Bouvet TJ basalts are characterized by relative maxima for Nb, Ta, La and minima for Pb and less pronounced for Th and U, and by these parameters are close to the enriched tholeiites of the southern part of the MAR. At the same time, these basalts differ from the plume magmas of Etendeka-Parana – the preceding to the opening of South Atlantic in the region 36-38° S. Normalized spectrums of Etendeka evolved basalts are characterized by U, Pb and Zr maxima and Nb and Ta minima, which evidence to crust contamination.

Similarities in geochemical and isotope data, in particular, for Sr, Nd, Pb in magmas of the Bouvet triple-junction region and Quaternary alkaline basalts of Antarctica (Hart et al., 1997) evidence to the participation in the melting process of material from enriched source, which is developed in the region of west Antarctica and stretches to the west extremity of the SWIR. The enriched component is characterized by high-radiogenic isotope ratios of Pb and Sr and low-radiogenic of neodymium ratio. All these events took place together with destruction of the old and formation of the new Bouvet TJ. As there have been some changes in relative movement of plates in the course of mantle flows migration during the oceanic rift propagations (the western part of the SWIR) and spreading ridges jumping, the melting of the low parts of the earlier formed oceanic lithosphere metamorphosed by the melts of earlier rifiting stages was occurred. During rift propagation and jumping of spreading ridge axis within all ridges of the South Atlantic areas have been forming with wide distribution of enriched tholeiites with similar geochemical characteristics. About 2-2.5 Ma ago development of the triple-junction was complicated by Bouvet hot-spot formation in pull-apart style. Such mechanism is suggested for the formation of many islands of the Antarctic peninsula (Hole et al., 1993).

The impact craters and linear magnetic anomalies.

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The method description

The big literature where modern representations about methods of the geochronological studying an anomaly magnetic field of the ocean and a structure of inversion magnetic-active layer ([1] etc.) are stated has already collected. A new maps of ocean bottom age are constructed. As an example it is possible to result the Tectonic globe of RSRI “ForeignGeology”, served by a cartographical basis for electronic variant [2]. The geometrization of LMA constructions and break structures allows to draw a conclusion on influence on them of various nonlinear geodynamic effects which may be caused as deep processes in geospheres, and various external influences on the ground.

New Results

The analysis of the LMA map [2] allows to locate the clearly circular anomalies in arrangement areas of the known impact craters (see the catalogue [3]). Three of them: a: Pribalhash-Iliyskaya (D=720 km), b: S. Atlantic G.A. (D=300 km) and Popigai (D=100 km) are shown in figure 1.

Figure 1: LMA of known impact craters

Conclusions

Proceeding from these supervision, it is possible to assume, that ring structures may become predicting attribute for a task of new astroblems detection. In Figure 2 the examples of similar structures are shown.

Figure 2: LMA of Barbados and Jan Mayen Islands

References

Relating siderophore-promoted dissolution to properties of ferrihydrite-exopolysaccharide coprecipitates

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Little is known about the properties and reactivity of Fe oxyhydroxides formed in the presence of exopolymers of microbes and plants. We synthesized ferrihydrite (Fh) in the presence and absence of acid polysaccharides (polygalacturonic acid, PGA; alginate, xanthan) and characterized the solids with micro-spectroscopic techniques, gas adsorption, and electrophoretic light scattering. The desferrioxamine B (DFOB)-promoted dissolution of the solids was studied in batch experiments at pH 7 in the presence and absence of citrate or malate. The total ligand concentration was ≤100 µM. In all cases 2-line ferrihydrite (Fh) was the main product of the synthesis. Mössbauer spectroscopy indicated a smaller particle size and a magnetic dilution of Fh in the coprecipitates. The embedding of Fh clusters in the polysaccharide matrices was confirmed by C-1s NEXAFS images. Compared to pure Fh, the coprecipitates comprised an up to 84% lower microporosity. Pure Fh sorbed about four times less DFOB than a PGA-Fh coprecipitate, and its ligand-promoted dissolution in the presence of 50 µM DFOB was two orders of magnitude slower. Our dissolution experiments indicated that, due to Fh coagulation (pH supplementation = 7.1), only a small fraction of the Fh surface was accessible to ligands. In contrast, Fh in the coprecipitates was sterically and/or electrostatically stabilized by the polymers. We show that ‘ligand-accessible surface area’ was the key control of the dissolution reaction and that ligand/adsorbent charge or crystallinity/particle size effects were of minor importance. The solubility of biogenic Fe oxyhydroxides may thus exceed that of pure phases by several orders of magnitude at circum-neutral pH.

History of trace metal contamination in Tagus prodelta cores, Portugal

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Favourable oceanographic and environmental conditions allow the formation of a fine-grained deposit (Tagus prodelta) located at the mouth of the Tagus river. This fine-grained deposit results from the sink and accumulation of terrestrial and marine derived materials. Three short sediment cores dated with 210Pb were analysed to determine historical trends in trace metal concentrations in the Tagus prodelta. The geochemical composition of this fine-grained deposit reflects the accumulation of marine biogenic materials, terrestrial and anthropogenic materials transported by the Tagus river. Historical trends indicate significant anthropogenic enrichments for Hg, Pb, Zn, Cu, Sb and Sn since the fifties. Hg presents the highest level of anthropogenic enrichment (ca. EF_mhg=20) in cores PO287-26-1B and PO287-27-1B. Core PO287-28-1B is characterised by high Ca contents that acts as a diluting factor of trace metal concentration derived from anthropogenic activities. Despite the improvement in the treatment of domestic and industrial effluents since the eighties, only slightly decreases in up-core metal trends were observed, revealing the importance of sediment re-working.
Natural Rhenium Isotope Variations

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Analyses of industrial and natural Re, expressed as $\varepsilon_{187}\text{Re} = [(187\text{Re}/185\text{Re}_{\text{smpl}}/187\text{Re}/185\text{Re}_{\text{std}}) - 1] \times 10,000$ with $\varepsilon_{187}\text{Re} = 0$ provisionally defined as $187\text{Re}/185\text{Re} = 1.7025$ [1], show ‰-scale isotope variation. External reproducibility of standards is currently ~2 $\varepsilon$ units.

Re is extracted and purified from sample powders with an aggressive leach and anion chromatography. Column-induced fractionation occurs, but is unimportant due to quantitative recovery. Solutions with 20 ng Re g$^{-1}$ are analysed by MC-ICP-MS (ThermoFinnigan Neptune) after doping with natural W to exponentially correct for instrumental fractionation ($^{186}\text{W}/^{183}\text{W} = 1.98594$; [2]). $^{189}\text{Os}$ is monitored to correct $^{187}\text{Re}$ when necessary. Re-rich samples with unknown but very large $^{187}\text{Os}/^{189}\text{Os}$ are stripped of Os by sparging. Other interferences, tailing, and sample matrix effects are insignificant.

Standards prepared in house from high-purity commercial Re and HReO$_4$ are identical ($\varepsilon_{187}\text{Re} = -26$) while an Alfa Aesar Re standard has an $\varepsilon_{187}\text{Re}$ of -28.

Natural samples consist of sulphides, shales, and water samples from an acidic pit lake. Sulphides show ~1‰ variation from $\varepsilon_{187}\text{Re} = -20$ (Archaean MoS$_2$) to a modern rhenite ($\varepsilon_{187}\text{Re} = -29$). Varibly-weathered Devonian black shales span $\varepsilon_{187}\text{Re}$ from -28 to ~32. Acid pit waters from both surface and depth (-76 m) are isotopically indistinguishable ($\varepsilon_{187}\text{Re}$ of -27 and -28).

Detection of natural Re isotope variations mandates a careful study of their utility as a geochemical tool. As Re has no known biogeochemistry, comparison with Mo and Se could prove useful as Re may quantify the strictly abiotic proportion of isotope fractionation.

References


Fine-scale isotopic structure in OIB trends: New insights from São Jorge Island, Azores

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Sr, Nd and Pb isotopic compositions (and, at a lesser extent, Os, Hf, He) of Oceanic Island Basalts (OIB) are commonly used to constrain the nature of mantle sources. However, isotope variations measured in OIB can be related either to variable proportions of the various components present in the deep source of basalts, or to interactions between pristine melts and the environments encountered during their ascent to the surface. Therefore, extracting the part of shallow-level processes from the global geochemical signature of OIB is a key to retrieve the source information and to investigate mantle topology in greater details. Consequently, fine-scale studies of OIB, at a single island or archipelago scale, are mandatory.

Here, we present a detailed study of São Jorge Island, Azores archipelago. We report new major-, trace-element concentrations and Sr-Nd-Pb isotope ratios measured for 22 basaltic samples covering most geological formations of the island. We observe variations in agreement with previous studies of the whole archipelago; notably our samples plot on the Pico-Terceira trend that was already documented in the different isotope variation diagrams. We also reveal the existence of a fine-scale structure of isotopic data best evidenced in the $^{206}\text{Pb}^{204}\text{Pb}$ vs. $^{206}\text{Pb}^{204}\text{Pb}$ plot. Our samples indeed draw two sub-parallel trends corresponding to distinct Sr and Nd average values, defined as the unradiogenic (low $^{87}\text{Sr}^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{206}\text{Pb}^{204}\text{Pb}$) and radiogenic (high $^{87}\text{Sr}^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{206}\text{Pb}^{204}\text{Pb}$) trends. This isotopic grouping shows a complex relationship with the geographical location of basalts. The radiogenic trend is composed by samples all collected on the eastern part of São Jorge. Conversely, the unradiogenic trend brings together basalts coming from various locations on the island. We will discuss these observations in terms of shallow-level vs. source information in a context of plume-ridge interaction.
Palaeoproterozoic metamorphism in the Limpopo Belt: New petrological and geochronological constraints

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Metasediments closely associated with the 3.28 Ga Sand River gneiss of the Central Zone of the Limpopo Belt, South Africa, were deposited after 2.615 Ga and underwent a structural- metamorphic overprint at 2.035-2.025 Ga. This is supported by CL-images in combination with \textit{in situ} LA-ICP(MC)-MS U-Pb, and new petrological results. Zircon core analyses reveal that the investigated metasediment succession consists of detritus of weathered Archean granitoids, predominately formed at ~2.61 Ga and minor at ~3.3 Ga. Zircon overgrowths yield an age of 2027 ± 6 Ma, which is interpreted to reflect the timing of the high-grade metamorphic overprint. This age is identical within error with an U-Pb monazite ages of 2036 ± 8 Ma, but distinctly younger than U-Pb monazite ages of ~2.61-2.64 Ga analysed from the same respective sample. The Neoarchean monazite grains are interpreted to be of detrital origin. This is supported by the finding of both monazite generations enclosed in syndeformative garnet. These structure-age relationships unambiguously show that the observed mineral assemblage sequence: Grt+Bt, Grt+St+Bt, Grt+St+Ky+Bt, Grt+Pt+Ksp/Liq., and Grt+Pt+Ksp/Liq.+Crd was formed during a single orogeny at ~2.03 Ga, characterized by a prograde $P$-$T$ path from 600°C/5kbar to 800°C/10 kbar, and followed by decompression and cooling to 750°C/5kbar.

Lithium isotopes in geothermal systems

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We measured the lithium isotopic composition of water samples (geothermal wells, thermal springs, thermal submarine springs and surface waters) and rock samples from different geothermal reservoirs. The overall objective of the present work was to establish the nature, extent and mechanism of Li isotope fractionation between 100 and 250°C during water/rock interaction.

For that purpose, a new analytical procedure was developed, based on the Neptune multi-collector ICP-MS in operation at BRGM, that enabled the analysis of Li isotopic ratios in liquid (water) and solid (rock) matrices with a level of precision of ±0.5‰ (2 standard deviation) for $\delta^7$Li values on quantities of 10-50 ng of Li.

Geothermal reservoirs located in the French West Indies (Guadeloupe and Martinique islands) were studied and particular emphasis was placed on the characterization of the behavior of Li isotopes during water/rock interaction in a volcanic context at high temperature. In addition, we also determined Li, B and Sr isotope compositions on waters collected from different geothermal sites in metropolitan France in order to characterize geothermal reservoirs by coupling a multi-isotopic approach with in-depth temperature of the reservoir calculated using chemical geothermometers.

The deep waters collected from geothermal wells and thermal springs in the Guadeloupe and Martinique islands indicate that Li isotopic signatures are very homogeneous for a given site but remain however very different from one site to another, probably due to not only lithological differences (reservoir rocks) but also highly variable water/rock interaction temperatures (90-120°C, 180-200°C and 250-260°C) for the Lamentin plain, the Diamant-Mount Pelée areas and the Bouillante geothermal fields, respectively.

Experiments of seawater/basalt interaction were also carried out at different temperatures (from 25°C to 250°C) and the results of isotope exchange experiments confirm the temperature dependence of Li isotope fractionation, ranging from +19.5 to +6.8‰ ($\Delta_{\text{solution-basalt}}$) between 25°C and 250°C, in agreement with field and experimental data reported in the literature.

The variations in B and Sr isotope tracers in geothermal waters appear to be largely controlled by the dominant host lithologies. In contrast, temperature plays an important role in controlling the lithium isotope composition of the geothermal fluids. This result seems to prove that lithium isotopic systematics represents a useful tool suitable for the study of geothermal waters and suggests that the $\delta^7$Li composition of geothermal waters may be utilised not only to characterize the geothermal reservoir (lithology, depth) but also to constrain the temperature of water/rock interaction.
Contribution of bacterial biomass components to the formation of refractory soil organic matter

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In general, plant material is regarded as the main precursor of soil organic matter (SOM). Recently however, evidence has been shown that also microbial compounds contribute to the formation of refractory SOM. Although microbial biomass in soils is regarded as rapidly decomposable, about 50% of the C derived from 13C-labelled Gram-negative bacterial biomass (Escherichia coli) persisted in soil after 224 days of incubation. About a fifth of this C was channelled into the microbial food web, the remainder was stabilized in non-living SOM. Further studies of this process are needed to elucidate the consequences for the chemical composition and the stability of SOM. We therefore studied the fate of E. coli-derived fatty acids and amino acids in soil. For both compound groups we distinguished the microbial fraction from the bulk soil fraction. Total amino acids did not decline during degradation, but we found a shift from the microbial to the non-living fraction at the beginning of the incubation. During this process, neither the amino acid pattern nor the isotopic composition of the amino acids changed. This suggests that whole peptides were transformed by the microorganisms, that E. coli-derived peptides were not utilized preferentially and that peptides are potentially refractory. The 13C declined in both the total fatty acids and the microbial (PLFA) fraction by about 80%. Also here a shift from the microbial to the non-living fraction was observed, which continued until the end of the experiment. The isotopic composition of the PLFA shows the redistribution of the labelled C from E. coli to the members of the soil microbial community. The half lives of the 13C-labelled compounds, in particular those of the non-living fractions show that both amino acids and fatty acids derived from E. coli contribute to the formation of refractory SOM thus imprinting a microbial-derived chemical structure on it. The distribution between the microbial and the non-living fraction was compound-specific with the proteins tending more strongly to accumulate in the non-living fraction. Together with the stabilization of compounds which are readily degradable as monomers, this shows that both the chemical structure and the molecular environment of a compound determine its fate in the soil.

Oxidative dissolution of Cr(OH)$_3$(s) by manganese oxides under circumneutral conditions

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Chromium generally exists in the +VI and +III oxidation states under surface and subsurface conditions. Cr(VI) is highly mobile and has deleterious health effects. Cr(III), by contrast, is generally immobile in the subsurface under neutral to alkaline conditions because it precipitates as sparingly soluble Cr(III)- or mixed Cr(III)-Fe(III) hydroxides. However, when these solids may be a potential source of toxic Cr(VI) under natural conditions when they are exposed to oxidants. Among the oxidants in nature, manganese oxides are ubiquitous and known to readily oxidize dissolved Cr(III).

This study investigates a possible pathway for the release of Cr(VI) to groundwater through the oxidative dissolution of Cr(OH)$_3$(s) by manganese oxides under circumneutral conditions. In this study, dissolution of synthetic Cr(OH)$_3$(s) was conducted in the absence or presence of MnO$_2$(s) at pH~8 in 0.01 M NaNO$_3$. The concentrations of dissolved Cr(VI) was determined by diphenylcarbazide method using UV-vis spectrophotometer and those of total Cr and Mn by atomic absorption spectrometry (AAS). During the dissolution of Cr(OH)$_3$(s) for 165 h, the concentrations of dissolved Cr(VI) were all below detection limit (50 µg/L) in the absence of MnO$_2$, whereas it increased with time and reached up to ca. 500 µg/L in the presence of MnO$_2$. The results of this study indicate that a small amount of dissolved Cr(III) ([Cr(OH)$_3^{+}$] = K$_{sp}^{conc} < 10^{-6.84}$) in equilibrium with Cr(OH)$_3$(s) is readily oxidized to Cr(VI) by MnO$_2$ and that this process can accumulate dissolved Cr(VI) in usual groundwater systems.
Radiocarbon and $^{13}$C variations during the last 300 years in lacustrine sediments of Lake Biwa, central Japan

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Lacustrine sediment cores collected from the northern and southern basins in Lake Biwa were measured for carbon content, $^{13}$C and $^{14}$C. Acid-alkali-insoluble fraction (residue) and acid-soluble fraction obtained by acid-alkali-acid treatment of the sediments were analyzed. The sedimentation rates of the northern basin sediment (KAN) and the southern basin sediment (KAS) were estimated to be ca. 0.13 cm/y and ca. 0.50 cm/y, respectively, by the $^{210}$Pb or $^{137}$Cs method. Carbon content of KAN is very high at the upper layer than 5cm depth and that of KAS has a highest peak at 19cm depth. $^{13}$C of KAN is the highest at 3cm depth layer and that of KAS is the highest at 20cm depth. The highest peaks, both corresponded to ca. 1960 A.D., might be due to nourishing in Lake Biwa.

$^{14}$C suddenly increases from 1950 A.D. to 1985 A.D. in the vertical distribution of KAN residue (Fig. 1). This high $^{14}$C is due to contribution of artificial $^{14}$C produced in atmosphere by nuclear tests after 1950 A.D. with maximum peak of 1964 A.D. $^{13}$C of KAN residue has a wide peak between about 1920 A.D. and 1980 A.D. This suggests the sediment in the southern basin could be a little disturbed. The $^{14}$C of KAN at the lower layer than 20cm, which might have no artificial $^{14}$C produced by atmospheric nuclear tests, shows ca. 4000 BP, older than the age obtained from $^{210}$Pb or $^{137}$Cs, and the true sedimentation age is difficult to be decided from $^{14}$C data of the bottom-surface sediments in this study.

Acknowledgements

We thank Dr. Oda (Center for Chronological Research, Nagoya University) and Dr. Yokota (Lake Biwa Research Institute) for arranging collection of soil samples in Lake Biwa.

Figure 1: $^{14}$C vertical distributions of Lake Biwa sediments.

Equilibrium iron isotope fractionation factors for magnetite from Mössbauer spectroscopy and inelastic nuclear resonant X-ray scattering data

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Mössbauer spectroscopy and inelastic nuclear resonant X-ray scattering (INRXS) in synchrotron radiation experiments are two independent experimental techniques for determination of equilibrium iron isotope fractionation factors ($\beta$-factors). The iron $\beta$-factor for magnetite evaluated from our Mössbauer studies of two natural samples is presented on Fig. 1 along with the $\beta$-factor computed using the INRXS-derived partial density of states (Seto et al., 2003). The Mössbauer temperature is 494 ± 15 K for the A ($Fe^3+$) site and 429± 20 K for the B ($Fe^{2+} + Fe^{3+}$) site.

Mössbauer spectroscopy and inelastic nuclear resonant X-ray scattering (INRXS) in synchrotron radiation experiments are two independent experimental techniques for determination of equilibrium iron isotope fractionation factors ($\beta$-factors). The iron $\beta$-factor for magnetite evaluated from our Mössbauer studies of two natural samples is presented on Fig. 1 along with the $\beta$-factor computed using the INRXS-derived partial density of states (Seto et al., 2003). The Mössbauer temperature is 494 ± 15 K for the A ($Fe^3+$) site and 429± 20 K for the B ($Fe^{2+} + Fe^{3+}$) site.

Figure 1. Temperature dependence of the Fe $\beta$-factors for magnetite (different evaluations).

Seto et al. (2003) used oxidized magnetite (A and B sites ratio is 1.3:1.0) instead of stoichiometric (A/B=1:1) magnetite used in our Mössbauer study. This may explain the slight difference between INRXS- and present Mössbauer-derived $\beta$-factors (Fig. 1). New Fe $\beta$-factors for magnetite are in agreement with isotope fractionations observed in natural and laboratory conditions and obey the general correlation between the $\beta$-factor and the potential energy of the Fe-occupied site, unlike $\beta$-factors previously computed by Polyakov and Mineev (2000) using Mössbauer data by Persoons et al. (1993).
Aqueous alteration of basalts: Earth, Moon, and Mars

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The geologic processes responsible for aqueous alteration of basaltic materials on Mars are modeled beginning with our knowledge of analog processes on Earth, i.e., characterization of elemental and mineralogical compositions of terrestrial environments where the alteration and weathering pathways related to aqueous activity are better understood. A key ingredient to successful modeling of aqueous processes on Mars is identification of phases that have formed by those processes. The purpose of this paper is to describe what is known about the elemental and mineralogical composition of terrestrial systems. Although aqueous alteration has not occurred on the Moon, it is crucial to understand the behaviors of basaltic materials exposed to aqueous environments in support of human exploration to the Moon over the next two decades.

Several methods or indices have been used to evaluate the extent of basalt alteration/weathering based upon measurements made at Mars by the Mars Exploration Rover (MER) Mössbauer and Alpha Particle X-Ray Spectrometers. The Mineralogical Alteration Index (MAI) is based upon the percentage of total Fe (Fe₂) present as Fe³⁺ in alteration products (Morris et al., 2006). A second method is the evaluation of compositional trends to determine the extent to which elements have been removed from the host rock and the likely formation of secondary phases (Nesbitt and Young, 1992; Ming et al., 2007). Most of the basalts that have been altered by aqueous processes at the two MER landing sites in Gusev crater and on Meridiani Planum have not undergone extensive leaching in an open hydrolytic system with the exception of an outcrop in the Columbia Hills. The extent of aqueous alteration however ranges from relatively unaltered to pervasively altered materials.

Several experimental studies have focused upon the aqueous alteration of lunar materials and simulants (e.g., Keller and Huang, 1971; Eick et al., 1996). Lunar basalts are void of water and highly reduced, hence, these materials are initially very reactive when exposed to water under oxidizing conditions.

References

Crystal Water on Mars: Insights from the Mars Exploration Rovers

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The purpose of this paper is to constrain the total water contents from crystal H₂O and OH in several materials analyzed by the Mars Exploration Rovers (MER). Crystal H₂O is part of the unit cell and cannot be removed without changing the structure. Minerals that contain only OH in their structures are anhydrous minerals containing hydroxyls, although they are formed as a product of aqueous activity and will decompose with evolution of H₂O when heated.

The crystal water and OH contents of a bulk material at the MER landing sites can be estimated from mineralogical composition, which is determined by a combination of Fe-mineralogy obtained by the Mössbauer Spectrometer and mineral abundances based upon the chemical composition determined by the Alpha Particle X-ray Spectrometer.

Jarosite, along with Ca- and Mg-sulfates, have been suggested as the sulfur-bearing phases in Meridiani Planum outcrop. Models of various hydration states of Fe-, Ca-, and Mg-sulfates and other possible secondary phases suggest that 6 to 22 wt.% of the outcrop may occur as crystal H₂O and/or OH (Clark et al., 2005). This estimate of water is consistent with measurements from the Odyssey orbiter, where 7 % H₂O-equivalent H was measured down to a depth of approximately 1 m for the region (Feldman et al., 2004).

The Peace outcrop material, which is composed of basaltic sands cemented by Mg- and Ca-sulfates, exhibited the highest water content (1.2 to 6.9 wt.% H₂O) of rocks and outcrops encountered on the northwestern flank of Husband Hill in Gusev crater (Ming et al., 2006, 2007). Paso Robles soil on Husband Hill contains Fe³⁺-, Mg-, Ca-bearing and other sulfates, Ca-phosphates, and other secondary phases (Ming et al., 2006). The water content derived from these materials ranges from 2.4 to 16.9 wt.% (Ming et al., 2007).

Unfortunately, the MER Athena instrument payload has not identified the secondary aluminosilicates in outcrops, rocks, and soils at the two landing sites. Therefore, it is likely that the total water constraints listed above are higher than suggested if hydrated secondary aluminosilicates are present.

References
Study at the nanoscale of the alteration of submarine basaltic glass from the Ontong Java Plateau

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Frequent observations of tubular to vermicular microchannels in altered basalt glass have led to increasing appreciation of a possible significant role of microbes in the low-temperature alteration of seafloor basalt. We have examined such microchannel alteration features at the nanoscale in basalt glass shards from the Ontong Java Plateau using a combination of focused ion beam milling, transmission electron microscopy and scanning transmission x-ray microscopy. Three types of material were found in ultrathin cross-sections cut through the microchannels by FIB milling: fresh basalt glass, amorphous Si-rich rims surrounding the microchannels, and clays within the microchannels. X-ray absorption spectroscopy at the C K-edge and Fe L2,3-edges showed the presence of organic carbon in association with carbonates within the microchannels and partial oxidation of iron in palagonite compared with basalt glass. Although these observations alone cannot discriminate between a biotic or abiotic origin for the microchannels, they provide new information on their mineralogical and chemical composition and thus better constrain the physical and chemical conditions prevailing during the alteration process. Finally, we will compare these results on modern samples with preliminary observations we made using the same analytical approach on altered archean (3.5 Ga old) basalts from Barberton (South Africa).

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Age constraints on the Late Cretaceous alkaline magmatism on the West Iberian Margin

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The post-Paleozoic magmatic activity of the West Iberian Margin (WIM) has been subdivided in three major magmatic cycles occurring at 190-160 Ma, 130-135 Ma, and 100-70 Ma (Ferreira and Macedo, 1979). Magmatic occurrences produced during the last cycle have been grouped along with other intrusions in the Pyrenees in the Late Cretaceous Alkaline Igneous Province of Iberia (Rock, 1982) and in the Circum-Mediterranean Anorogenic igneous province (Lustrino & Wilson, 2007). The onshore magmatic activity postdates by at least 40 Ma the end of the rifting that preceded the opening of the North Atlantic (Rasmussen et al., 1998).

In order to better constrain the sequence of events that characterized the Late Cretaceous magmatic cycle, we present several LA-ICP-MS U-Pb, Ar-Ar, K-Ar and Rb-Sr datings on several intrusions distributed along the WIM.

The new age determinations, combined with the previously published data, allow us to define two distinct pulses of magmatic activity. The first one (94-80 Ma) occurred synchronously with the rotation of Iberia and consequent opening of the bay of Biscay (123-80 Ma; , Sibuet et al., 2004) and clusters around the Lisbon area (above N38º20').

The second pulse (75-72 Ma) has a wider geographical distribution between Algarve in the southermost Portugal (N37º20') and the Lisbon area.

Trace element geochemistry and isotopic data indicate that different mantle sources supplied the two Late Cretaceous pulses, with the more recent one being characterized by more important enrichment in incompatible elements, but less radiogenic Sr and more radiogenic Nd isotopic signatures.

References
Experimental re-examination of the phase transition quartz-coesite – The reaction in presence of H₂O and at anhydrous conditions

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The quartz-coesite phase transition has been studied extensively because of its outstanding significance in petrology (cf. Hemmingway et al., 1998). Despite a nominally anhydrous composition, the two SiO₂ polymorphs may contain small amounts of H₂O (e.g. Lathe et al. 2005). Most experimental studies were conducted in presence of H₂O (e.g. Mirwald & Massonne, 1980; Bohlen and Boettcher, 1982). Contrasting results obtained by anhydrous experiments (Walter et al., 2002) gave rise to a re-examination.

The study was performed with a piston cylinder apparatus (400-1100°C, up to 3.5GPa) using pure synthetic SiO₂ as starting material. The phase transition was monitored by differential pressure analysis (DPA) and was controlled by additional quench experiments.

The „wet“ data (400-900°C) confirm previous studies in general reveal, however, a pronounced inflection at 2.7GPa/600°C. (boundary <600°C: P = 2.11 + 0.00096*T). Preliminary data of the anhydrous experiments (700-1100°C) suggest a significantly different P-T course of the transition boundary. (P/GPa = 2.7 + 0.00025*T[C]). The different P-T location of the „wet“ and „dry“ boundary indicates that H₂O incorporation in these phases has a considerable effect on their P-T stability. The observed inflection at 2.7GPa/600°C is attributed to a PVT anomaly of H₂O as similarly found for the nominally anhydrous reaction albite = jadeite + quartz (Mirwald 2005a) and for the brucite dehydration boundary (Mirwald, 2005b).

While in „wet“ experiments the sample material was wetted by breathing into the filled capsule, in dry experiments the capsules were heated to 1000°C for 5-12 hours before welding.

References

Interrogating a paleo-cratonic margin – The Peruvian Cordillera Oriental batholiths

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Batholiths of the Eastern Cordillera of Peru exhibit profound variations in chemistry and timing of emplacement from north to south. As products of long-lived, craton-peripheral, intrusive flare-ups, these plutons mark tectonic boundaries between the Western Gondwana and variable Proterozoic to Paleozoic crustal domains accreted during the final assembly and the ultimate break-up of Pangaea.

A striking geochemical relationship exists between three principal plutonic belts: 1) Mississippian to Pennsylvanian, metaluminous, hornblende and magnetite bearing, I-type granitoids are restricted to the segment north of 10°S, and display calc-alkaline evolutionary trends with elevated LILE/HFSE ratios and Nb-Ta anomalies characteristic of subduction zones; 2) Permian to Early Triassic, peraluminous, S-type, mica and ilmenite rich granitoids of the east-central Peru (10-14°S), are characterized by restricted bimodal compositional range, moderate Fe enrichments, low LILE/HFSE values which are associated with transitional, post-orogenic (within-plate) suites; 3) Late Triassic, initially Caledonian I-type monzogranitoids of the southern Cordillera de Carabaya terminate as peralkaline, SiO₂-undersaturated nepheline syenites (Allincapac Gr.) emplaced contemporaneously with eruption Mitu Gr. basanites. The Allincapac Gr. Intrusives and lavas display extreme Fe enrichments, steep REE profiles, and overall low LILE/HFSE ratios. Combined Sr-Nd-Pb-Hf isotope systematics from all three intrusive provinces however lack variation, and suggest uniformly large degrees of assimilation of the Proterozoic Amazonian basement. In addition to the systematic change in the plutonic chemistry, the U-Pb and ³⁹Ar/⁴⁰Ar chronometries reveal a general younging-southward trend from 345 to 188 Ma with the exception of the 310-275 Ma magmatic lull.

Our preliminary geodynamic model envisions, initially orthogonal, eastward subduction of the paleo-Pacific crust below the Western Amazonia during Carboniferous, which was terminated by accretion of a buoyant segment of oceanic crust. This scenario explains the sudden termination of arc-related magmatism in Pennsylvanian as well as uplift and eventual relaxation of the cratonic margin which in turn might have facilitated emplacement of the central Permo-Triassic granites. Simultaneously, a change in conversion angle to southeast during Permian induced development of transtensional, ensialic basins and subsequent back-arc extension along the inherited suture between the Gondwanan craton and the Neoproterozoic Arequipa-Antofalla terrane. The southernmost Carabaya plutons seem to reflect a phase of incipient rifting and re-accretion of the Arequipa terrane.
Sulfate Reduction and Sulfur Isotope Fractionation in Modern Evaporite Ponds

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The oldest evidence for sulfate reduction is found in ~3.5 billion year old barites from North Pole, Australia (Shen et al., 2001). These rocks are thought to have first precipitated as gypsum in a marine evaporitic setting. Sulfides are fractionated compared to sulfate by 8 ‰ to 22 ‰, with a mean of 11.6 ‰. This is well within the range of fractionations observed for pure cultures of sulfate reducers, ~10-25 ‰ (Kaplan and Rittenburg, 1964).

A modern analogue to this ancient environment is found in the concentrating ponds of the Eilat Salt Company, Israel. Here, stratified populations of microbes exist in gypsum crust which house active sulfate reducers (Sørensen et al., 2004). These communities are well adapted to the high salinities found in the evaporation ponds (Sørensen et al., 2004).

Fractionation and sulfate reduction rate studies were carried out using a plug flow-through reactor (Roychoudhury et al., 1998). The crusts were separated into two layers, the top 2 cm containing the colorful, phototrophic organisms and the bottom 2 cm, with the non-phototrophic communities.

Fractionations of 25 ‰ were found in both the top (oxic) and (anoxic) bottom layers. Sulfate reduction rates in the bottom 2 cm ranged from 0.02 to 2.65 nmol cm⁻¹ hr⁻¹. The sulfate reduction rates found in the upper 2 cm are higher, ranging from ~13 to ~20 nmol cm⁻¹ hr⁻¹.

The sulfur isotope fractionation found in modern gypsum crust microbial communities is of the same magnitude as found in Archean barites, lending support to the hypothesis that the sulfides here were produced by microbial activity.

References

Mobility of REE, Sr, Zr and other rare elements during late stage processes in peralkaline rocks: A mineralogical perspective

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Both over and undersaturated peralkaline syenites are notable for their enrichment in rare elements and complex mineralogy. In contrast to common plutonic aluminous granites and syenites, peralkaline syenites are typified by extended crystallization intervals (~1000-450°C) with a continuum from late-stage magmatic crystallization to alkaline hydrothermal residua. Interaction of the latter with previously-formed minerals can result in distinctive auto-metasomatic processes that result in the mobilization of many elements which are commonly considered as incompatible and/or immobile. Peralkaline complexes are characterized by distinctive styles of low temperature alteration and replacement depending upon whether the hydrothermal residua have either formed discrete pegmatites (e.g. Lovozero) or reacted in-situ (e.g Pilansberg), with previously-formed mineral assemblages. In some instances, (e.g. Strange Lake) externally-derived fluids have had a significant influence on the style of alteration. Elements which can be redistributed during metasomatic transformations involving alkaline-Cl-F-bearing low temperature fluids include the rare earths, Zr, Hf, Nb, Ta, and Sr. This mobility has consequences for ore deposits associated with alkaline rocks, whole rock geochemical studies and for geochronology based on the Lu-Hf, Sm-Nd and Rb-Sr systems. Examples illustrating the mineralogy of metasomatic micasitic, agpaitic and hyperagpaitic replacements are presented for eudialyte and other minerals from Ilimaussaq, Pilansberg, Pocos de Caldas, Gordon Butte, and Pajarito Mountain together with experimental data on the solubility of Nb and Ta in Ca-O-H-F fluids.
Analyses of drilled and surface samples of Ries, Sierra Madera and Takamatsu craters

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Example Co, Ni and Ir contents of drilled samples

Iron-group elements (Fe, Ni, Co) and platinum-group element (Ir) are measured on drilled samples of Ries (1,000m in depth) and Takamatsu (930m and 960m in depth), compared with surface breccias of Sierra Madera (Texas, USA) as shown in Fig.1.

Discussion

Meteoritic craters show considerable amounts of iron-and platinum-group elements from meteoroids.

Fig.1. Co, Ni and Ir contents of Ries, Takamatsu and Sierra Madera craters.

Significance of chloritite bodies found from the dike-gabbro transision of the Oman ophiolite

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Chloritite body with abnormal bulk compositions was first found from the south branch of Wadi Hilti area in the northern Oman ophiolite (Neo et al., 2004 JPGU meeting). Furthermore, another chloritite bodies were found from two localities, north-branch of Wadi Suhayli and north-branch of Wadi Bani-Umar. These three bodies have a similar size and extend about 100x70 m. Original textures are completely obliterated except for a remnant of the primary grain-size. The chloritites are composed of iron-rich chlorite with accessory epidote, titanite, hydrated rutile (anatase) and apatite.

It should be emphasized that these three bodies occur at the same stratigraphic position, i.e., uppermost horizon of the upper gabbro unit, corresponding to a root zone of sheeted dike complex. Sharp but gradual contacts between the black bodies and host rocks (mainly varitextured gabbro and dolerite dikes in places) confirm that the black bodies were altered products. The fact that they occur at the same stratigraphic horizon suggests strongly that the genesis of the chloritites is controlled by a stratigraphic control.

Chlorites of the chloritites are more Fe- and Al-rich than those of host rocks. Surprisingly, calcic plagioclases that are invaded by chlorites along the margin of the chloritites keep the primary composition. These lines of evidence suggest that temperature conditions during the hydrothermal alteration were higher than greenschist facies conditions. Abundant epidotes occur near the margin of the chloritites, but decrease rapidly away from the contact (inward the chloritite body).

Bulk rock compositions of the chloritites show that they underwent very intensive metasomatism during the hydrothermal alteration. That is, severe removal in SiO2, CaO and LIL elements, and large uptake in FeO characterize the chloritites. Such types of the alteration is not known from the hydrothermal system beneath ocean ridges, but we believe that the black bodies found in the Oman ophiolite may give a new aspect on the hydrothermal system.
Partial melting of oceanic crust: Anatectites in the gabbro-dike transition of Oman ophiolite

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There are two different models for the origin of oceanic plagiogranite; 1) extreme fractional crystallization of mafic melts (Spulber and Rutherford, 1982) and 2) partial melting of crustal rocks. Furthermore, two different partial melting processes are debated: hydrous melting (Koepke et al., 2004) and dehydration melting (Beard and Lofgren, 1991). It is still unclear that which mechanism is most effective. We found numerous large blocks retaining partial melting processes from the basal part of the Suhaylah plagiogranite complex in the northern Oman ophiolite.

The Suhaylah complex, about 2.5 x 2.5 km, occurs between gabbro and sheeted dike complex. The complex shows heterogeneous occurrence and is composed of leuco gabbros-diorites, quartz diorites and tonalites.

The basal part of the complex is characterized by a frequent occurrence of metamorphosed dike blocks. The size of blocks is variable and attains about 20 x 5 m. They are traceable over 1.5 km slightly oblique to the boundary between gabbro and the Suhaylah complex. The blocks are composed of two pyroxenes, and plagioclase with variable amount of quartz. Texture is heterogeneous within one specimen and blocks to blocks. Most common textures are globular aggregates consisting of opx-cpx-oxide wrapped by quartz set in a matrix of pl-opx-cpx-oxide. Quartz occurs also as single rounded crystal, globular aggregate and irregular shaped vein. Thus, these blocks may reveal a dehydration melting as similar as the Troodos ophiolite (Gillis and Coogan, 2002).

Minor elment compositions of these anatectites show two contrastive behaviors; one group is characterized by highly depleted feature and the other group by evolved MORB signatures. The former group is composed of two-pyroxene assemblage with few quartz, and regarded as restite. While the latter group contain abundant quartz and is assumed to be melt-rich part.

References

Temporal changes of the subduction components in volcanic products from Aso area, SW Japan.

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Aso volcano is located in a critical area where Philippine Sea plates (PSP) of old age (40-115 Ma) in the south and young age (15-26 Ma) in the north and Eurasian plate meet. To investigate the temporal changes of subduction signatures, we analyzed boron (B) and other major and trace element compositions in Aso basalts and andesites which erupted since 4 Ma. Boron is a key element for evaluating the slab influence on the subjacent mantle compositions in subduction zones, because this element is enriched in altered oceanic crust and sea floor sediment.

We grouped volcanic activities of Aso area into four stages. Different geochemical types of magmas were found in all stages.

I) 4 Ma: High-magnesium andesites (HMA); II) 2-0.5 Ma: Adakitic andesites, arc-type andesites and high-alumina basalts (HAB);

III) 0.3-0.09 Ma (caldera forming stage): Arc-type andesites and HAB accompanied by large volume of dacites and rhyolites;

IV) 0.09-0 Ma (post-caldera stage): Arc-type andesites and HAB accompanied by small volume of dacites and rhyolites. The ratios of B to fluid-immobile elements are useful tracer of subduction, because they are not controlled by crustal contamination, fractional crystallization and/or partial melting processes. The ratios of B/Sm (1.0-0.4) and B/Zr (0.03-0.05) in the HMAs are lower than those of the HABs (1.3-5.0 and 0.06-0.17, respectively). B/Nb ratios in the HMAs are similar to those of the mantle values (0.05-0.5). On the other hand, B/Nb ratios (1.4-4.0) in the HABs overlap with those of basalts from cool subduction zones (Kurile and NE-Japan).

These observations suggest that the released phase has slab component beneath Aso area changed from melt derived from dehydrated slab to hydrous fluid between stage I and II. This may have resulted from the lowering of geotherm beneath Aso area caused by the change of subducted plate from young PSP to the old one. This implies that the boundary between young and old PSP moved northward crossing Aso area from 4 to 2 Ma.
Paleo-hydrochemical changes of deep groundwater in Mizunami area, Japan

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Introduction

Multilayered fracture-filling calcite mineralization was studied to assess the long-term hydrochemical changes of deep groundwater in the Mizunami area, Japan. Four generations (I to IV) of calcite precipitation can be differentiated on the basis of detailed studies using optical and cathode-luminescence microscopy, SEM, laser ablation microprobe-ICP MS, stable isotope geochemistry, and fluid inclusion analysis.

Results and Discussion

Carbon and oxygen isotopic ratios suggest that the Generation I calcite is of hydrothermal origin. On the other hand, generations II, IV and III calcite were precipitated from freshwater and marine water, respectively. Fluid inclusions could only be observed in calcite generations II and III. These fluid inclusions show no obvious change in fluid salinity between generation II and III calcite mineralization. The generation II and III calcites were possibly precipitated from mixture of freshwater and marine water. The calcite crystal morphology is sensitive to the chemistry and salinity of the groundwater. Morphological change during generations II to IV coincides with the changes of groundwater origin indicated by stable isotope and fluid inclusion composition. On the other hand, REE distribution patterns within the different generations of calcite show that no differential behaviour between REEs and Ce, which is known to be redox sensitive, and the trivalent REEs. This suggests that the redox condition of groundwater have remained relatively reducing during the different generations of calcite precipitation, even though groundwater chemistry had changed.

Conclusion

Detail analysis of multilayered calcite fracture mineralization associated with groundwater flow paths provides a valuable information to evaluate long-term palaeohydrogeological changes of groundwater chemistry.

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Fission-track thermochronology evidence on Wulonggou gold mineralization, eastern Kunlun Mountains, northern Qinghai-Tibet Plateau

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Wulonggou gold ore district is located at the eastern Kunlun Mountain, northern Qinghai-Tibet Plateau. The mineralization category belong to tectonic altered rock type. The gold mineralization is intensive and distribute mainly along construct-zone. Fission track thermochronology has been used to constrain the mineralization histories of gold ore districts in eastern Kunlun Mountains in this work.

Five zircon fission track ages for the ore and altered rock samples range from 235±4 Ma to 194±10 Ma, concording with various Rb-Sr and K-Ar isotopic ages (207.1-252.9 Ma) for the mineralization (Lu et al., 1999; Mock et al., 1999; Qian et al., 1999). Two apatite fission track ages of the ore samples are 201±7 Ma and 151±6 Ma respectively, which corrected ages are close to the zircon fission track ages and isotopic ages. Therefore, the FT age could presents the time of mineralization thermal events. Another two apatite samples collected both from selvage and faulted lens with 50±3 Ma and 45±4 Ma FT ages recorded late tectonic activities.

Mineralization thermal histories are modeled and the samples produced remarkably similar thermal paths. Polymineralization could be identified. The major mineralization period was around 240–150Ma. It is the polymineralization that not only prolongs the mineralization period, but also enhances mineralization degree. The mineralization temperature didn't exceed about 300°C after about 240 Ma according to the zircon fission track data. The mineralization thermal events were mainly relevant to the subduction along South-Kunlun sutrue and the intrasubduction along Middle-Kunlun zone at that time.

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References

In situ measurements vs. lattice strain model calculations: Distribution of REE between Grt and Cpx in garnet peridotites from Vitim (Siberia)

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We present newly determined REE-distribution coefficients between clinopyroxene (cpx) and garnet (grt), which can be used to model and understand geochemical processes such as crystallisation, differentiation and melting.

From the literature it is known that discrepancies exist between calculated REE-distribution coefficients from natural samples (whole-grain separates) and those collected from experimental run products. To address these discrepancies we measured cpx and grt of grt-peridotites xenoliths from the Vitim volcanic field in Siberia. The samples were selected because they are well studied, formed over a restricted P-T range (1050-1200°C, 2.1-2.5 GPa) and do not show evidence of metasomatism and other secondary processes. The minerals were analysed in-situ, within thin sections, by electron microprobe and secondary ion mass spectrometer (SIMS). Only samples with unzoned minerals were used for the determination of REE-distribution coefficients, which were calculated from mineral core compositions.

The cpx-grt distribution coefficients vary between 240 and 360 for La and between 0.03 and 0.07 for Yb, which is consistent with experimental data from Burgess and Harte (2004) at temperatures between 900°C and 1000°C. Compared to mineral separate data for REE from Vitim xenoliths (Ionov et al. 1993) the newly determined Kds are in good agreement, but show less scatter for the HREE between different samples. This may be explained by the ability to avoid micro-inclusions by in situ SIMS analyses.

In the original lattice strain model the physical characteristics of the cation site in grt and cpx are used to predict distribution coefficients for various trace elements in equilibrium with a melt. In our case there is no melt, and our calculations are therefore based on one measured distribution coefficient to predict the others (Yb is used here). The predicted Kd pattern agrees well for the HREE (Er to Tm) with the measured, but is less steep (hinges on Yb). The maximum differences are a factor of about 2 (La to Er). We will explore the model parameters that may contribute to this remaining discrepancy.

Age and variability of dissolved organic carbon in the St. Lawrence River

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Riverine export of dissolved organic carbon (DOC) to the global ocean represents about 0.25 x 1015gC/yr. Various studies have shown that this DOC mainly derives from terrestrial organic matter (OM). It is generally considered to be refractory and transported conservatively to the ocean. However, recent work has shown that many rivers transport a high 14C content DOC. Knowledge of the age (residence time) of both labile/refractory components of DOC and of its variability is essential for a robust assessment of the role of riverine DOC in the global carbon cycle. Here we report chemical and isotopic composition of DOC from the St. Lawrence River, with a focus on 14C ages of labile vs. total DOC fractions, and on the spatial, seasonal to interannual variability of DOC export. Alkaline CuO oxidation was used to study a refractory DOC component and to identify sources and degradation stages of terrestrial organic matter. Our results indicate some variability in total DOC from year to year, but more notably, temporal and spatial variability in 14C-activities of the refractory DOC component, which represent approximately 6 to 30% of total DOC and yielded 14C-activities ranging between 75 and 96% of modern carbon (pMC). From these values, 14C-activities of labile compound were estimated and ranged between 100 and 111pMC. Labile DOC compounds are thus very young or have a short residence time in this system. This residence time is much shorter than the one estimated for water flowing through the Great Lakes/St. Lawrence River system, thus suggesting prominent terrestrial sources for this reactive organic carbon. Although accounting for lower overall DOC fluxes, refractory material display ages that suggest aging for a significant time in soils of the watershed.
Layered granitoids; Migmatites and/or granitoids mixing zone?

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In the SW sector of the Ossa-Morena Zone (Iberian Variscides), a structurally complex and lithologically heterogeneous outcrop (Pereira & Silva, 2002) along the Almansor River was studied. This outcrop was previously considered to represent migmatization. Other works (e.g. Moita et al., 2005) in nearby areas have shown that syntectonic plutonism and migmatization have been important in the period from 330 to 320 Ma.

In this study, three main lithotypes were identified which together define a strongly layered pattern: diatexites (Dtx), weakly foliated granitoids (WFG) and leucogranitoids (LG). The Dtx are peraluminous monzogranites to quartzofeldspathic rocks with \( (\text{87Sr}/\text{86Sr}) \) from -9.32 to -8.92; the WFG are metaluminous to weakly peraluminous trondhjemitic rocks with \( (\text{87Sr}/\text{86Sr}) \) from -3.79 to -6.09. The isotopic signature and multi-element patterns of Dtx are not only internally coherent but also similar to Neoproterozoic metasedimentary rocks suggesting that they represent anatectic magmas. The WFG and LG exhibit more complex multi-element (Moita et al., 2006) and isotopic signatures which were interpreted as the result of strong magmatic differentiation from mafic magmas accompanied by interaction with crustal melts.

Therefore, the studied outcrop, rather than testifying in loco migmatization seems to correspond to complex mingling/mixing(?) of magmas, evolved through different sources and processes (crustal anatexis and magmatic differentiation), within a shear zone.

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References


Graphite + apatite in >3.83 Ga ferruginous quartz-pyroxene (supracrustal) rocks from Akilia, southern West Greenland

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Graphite associated with apatite (Fig. 1) is present in magnetite-bearing banded quartz-pyroxene units from an early Archean supracrustal succession preserved on Akilia (island), West Greenland [1]. This observation stands in contrast with some recent reports that graphite was absent in apatite crystals from these same units [2]. Sample (G91-26; ref. 1) comes from rocks of sedimentary protolith with \(^{13}C\)-enriched carbon (\( \delta^{13}C < -30\% \)) in intimate association with apatite and previously presented as evidence for life on Earth before ca. 3.83 Ga [3]. Here, we report further examples of graphite+apatite in pre-3.78 rocks of sedimentary protolith from other Akilia association enclaves on Innersuatuq island (West Greenland; ref. 4) and metasediments of the pre-3.75 Ga Nuvvuagittuq Supracrustal Belt (northern Québec, Canada; ref. 5).

Since the original description, geochemical evidence has accumulated that significantly bolsters the initial interpretation that the Akilia rocks were originally chemical sediments deposited before 3.83 Ga, and that they provide information on surface processes and biological activity on the early Earth [6].

Figure 1. TL micrograph of graphite inclusion in apatite.

References

Glacial-interglacial variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of seawater

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Many natural radiogenic isotopes in seawater show variations on glacial-interglacial timescales that can be related to either local or global changes in continental weathering and/or changes in Ocean circulation. On such timescales the long residence time of Sr necessitates very large changes in the continental flux to the Oceans to cause a measurable shift in the $^{87}\text{Sr}/^{86}\text{Sr}$ value of seawater (Richter & Turekian, 1993). Early studies reported fluctuations in marine $^{87}\text{Sr}/^{86}\text{Sr}$ over glacial-interglacial cycles (Dia et al., 1991; Clemens et al., 1993) but later work indicated that at the ±13 ppm level there was no evidence for any change (Henderson et al., 1994) However, changes of 6-9 ppm could not be ruled out, which, though small, correspond to a ~30% change in the riverine Sr flux.

Since that time a new generation of TIMS instruments, has enabled a 5-10 fold improvement in the precision of absolute isotope ratio measurement. This study presents very-high precision $^{87}\text{Sr}/^{86}\text{Sr}$ measurements for planktonic foraminifera from ODP site 758 in the Indian Ocean, that complement existing $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{187}\text{Os}/^{188}\text{Os}$ isotope data for the same samples. Repeat measurements of NBS 987 demonstrate a long term reproducability of ±3.4 ppm 2 s.d (n = 30). Size restricted samples of the species G. conglobatus and N. dutertrei were subject to oxidative-reductive cleaning and Sr separated using Echlon Sr-spec resin. Preliminary results indicate the presence of 3-9 ppm cycles over glacial-interglacial timescales, but unlike Nd and Os these cycles are not in phase with the oxygen isotope curve (as predicted by Richter & Turekian, 1993). The simplest interpretation is that these variations reflect changes in continental input accompanying climate cycles, corresponding to a ~10-30% change in the riverine Sr flux.

References

The origin of Tertiary intraplate volcanism in the Siebengebirge volcanic field, Germany

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The Miocene (~25 Ma old) Siebengebirge volcanic field, belonging to the Central European Volcanic Province (CEVP), is located at the SE end of the Northern Rhine Embayment near Bonn, Germany. For its relatively small size of ca. 900 km$^2$, mafic magma compositions are unusually diverse, ranging from basanites to alkali basalts. Differentiated rocks comprise both silica saturated (latitic to trachytic) and undersaturated compositions (phonotephritic to tephrilithic), which only occur in a small area in the central part. In contrast to other volcanic provinces in Germany, nearly all magmas appear to be subvolcanic.

In order to unravel mantle sources of the magmas, trace element and isotope compositions were determined for representative mafic and felsic samples. In mafic samples (MgO > 7 wt.%), εHf range from +6.5 to +8.0, εNd from +3.1 to +4.4, $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7034-0.7038, and Pb isotope compositions from 19.46-19.69 (207Pb/204Pb), 15.63-15.66 (206Pb/204Pb) and 39.34-39.62 (208Pb/204Pb). Together with the Hocheifel volcanic field, the mafic Siebengebirge samples display the highest Pb isotope compositions amongst all other volcanic provinces in Germany (i.e., Hessian Depression, Westerwald, West Eifel, East Eifel, Vogelsberg).

Trace element patterns show a strong enrichment of LREE compared to the HREE, indicating enriched sources in the spinel and garnet peridotite transition zone. Isotopically, the primitive samples cover a range between a “HIMU-like” endmember composition, compositions reflecting the influence of subducted sediments (“EM-2 like”) and depleted endmembers. High Zr/Hf ratios and positive Nb anomalies confirm the presence of HIMU-like domains, originating from recycled oceanic crust.

Alkali basaltic compositions reflect higher melting degrees and lower average melting depths than basanitic compositions, indicating a variable lithosphere thickness. Negative K-anomalies in primitive mantle normalized trace element diagrams reveal the influence of a volatile- and K-rich phase, most likely amphibole in the lithospheric mantle. Notably, the K anomalies are neither correlated with trace element or Pb isotope variations, suggesting a minor role of lithospheric components. Hence, the enriched signatures rather originate from locally enriched domains in the convecting asthenospheric mantle.

The silica saturated group of differentiated rocks can be shown to originate from alkali basaltic parental magmas whereas the undersaturated group crystallized from basanitic parental magmas. High $^{87}\text{Sr}/^{86}\text{Sr}$ (up to 0.7062), low εNd and εHf (as low as -2.3 and +0.4, respectively) indicate significant upper crustal contamination for both groups.
REE distribution between zircon and orthopyroxene in granulites as a link between petrology and geochronology

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Zircon has been the most versatile tool for high temperature geochronology for many decades. New trace element tools are now developed to use it also as thermometer and link it to pressure and temperature evolution of metamorphic rocks. The main focus in studies on the distribution of rare earth elements (REE) has been on garnet and zircon; with an ongoing debate about which distribution patterns constitute equilibrium under different metamorphic conditions in granulites, eclogites and migmatites. There is little data available for REE exchange with other minerals in high grade metamorphic assemblages.

We present in-situ ion microprobe data on coexisting zircon-orthopyroxene (opx) pairs from garnet-free high temperature leucosomes (tonalitic composition) as well as both garnet-absent and garnet-bearing granulites of granitic composition. The samples are from the high-temperature low-pressure granulites of Rogaland (SW Norway) and the UHT medium pressure granulites from the Brasilia fold belt. All investigated rocks without garnet yield similar patterns for orthopyroxene, with low abundances of L-MREE (La to Eu) between 0.1 to 1x chondritic values, small negative Eu anomalies and steeply increasing M-HREE to ca. 50x chondrite for Yb. Zircon in the orthopyroxene-bearing leucosome and garnet-absent granulites have steep REE patterns, including a steep rise in HREE (at variable absolute values) with Yb/Gd of 10-20. The relatively flat HREE zircon-orthopyroxene distribution patterns (10-30 for Gd to Lu) are quite similar to patterns obtained from UHT leucosomes and granulites for zircon-garnet pairs (own studies and other authors). It can be concluded that when present in equilibrium with zircon in high temperature rocks, orthopyroxene is a sink for MREE and HREE not to be overlooked. The impact on HREE abundances in zircon is thus diminished and the HREE pattern of zircon in equilibrium is steep.

As a result, we caution against overinterpretation of REE patterns from detrital zircon, i.e invoking granulate conditions for source rocks based only on flat or decreasing HREE patterns.

PGE distributions in Mesoarchean chromitites and mafic-ultramafic rocks in the Singhbhum Craton (India): Evidence for presence of a subchondritic source mantle domain

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In the Singhbhum Craton of India the layered ultramafic bodies with chromite deposits occur within the Archean greenstone sequences of Iron Ore Group mainly in the Nuasahi, Sukinda and Jojohatu areas. In many places these ultramafic bodies are closely associated with gabbroic intrusions. The massive chromitites of seams from the Nuasahi area are enriched in total platinum group element (PGE) concentrations (∑PGE=142 to 549 ppb) compared to host peridotitic (∑PGE=7 to 26 ppb) and adjacent gabbroic rocks (∑PGE=3 to 116 ppb). The PGE compositions for peridotitic rocks are near chondritic with strong Ir-depletion with a general positive slope (Pd/Ir = 3 to 10). The PGE compositions of chromitites are superchondritic with strong Pt depletion coupled with Ru enrichments. Gabbroic rocks have strong subchondritic IPGE compositions and show distinct PPGE fractionated trend with strong positive slope. The geochemical distributions of the PGEs in chromitites and silicate lithounits bear directly on the two problems (1) why PGEs fractionate and (2) why are they enriched in chromitites. The strong depletion of Ir and relative enrichments of PPGE in ultramafic suite along with high PGE concentrations in chromitites are genetically related to crystallization from a boninitic parental magma in a suprasubduction zone setting in Archean. However, it is difficult to explain the strong fractionation between IPGEs (Os/Ir and Ru/Ir) in the peridotitic rocks by the existing models. The strong subchondritic Ir pattern is perhaps related to the presence of a subchondritic source mantle domain beneath the Singhbhum Craton. The notion of the presence of a subchondritic source domain within the upper mantle beneath the Singhbhum Craton is also supported by the recent Os isotopic studies of these rocks.
The stability of calcite and aragonite
in sediments overlying zones of
basement fluid upwelling in the
eastern flank of the Juan de Fuca ridge

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Heat flow measurements and sediment porewater composition data collected on the Eastern flank of the Juan de Fuca ridge during numerous cruises have evidenced the extend and the features of the low temperature fluid circulation in ridge flanks, with the aim of quantifying the contribution of this circulation to heat and mass fluxes between the ocean and the oceanic crust. One of the questions is to know how basement fluid may react with the sediment, with the consequent modification of the composition of basement fluids discharging to the seafloor.

The Retroflux expedition (September 2000) has mapped fluid discharge zones associated with basaltic outcrops and seamounts using heat flow measurements and coring. Ninety three cores (up to 7 meters in length) were collected during this expedition. Porewaters were analyzed on board for chlorinity, Ca, Mg, pH, alkalinity, and nutrients and on shore for trace elements. In upwelling areas, porewaters display a rapid Mg depletion and Ca enrichment with depth consistent with a fluid in basement that has reacted with basalt at low temperatures. These upwelling fluids have an alkalinity that is lower than that of seawater. In contrast, porewaters from cores collected outside zones of fluid discharge have alkalinitities that increase with depth resulting from the oxidation of organic matter and the reduction of sulfate during diagenesis. Thus a variety of alkalinity depth profiles exists reflecting the competition between alkalinity production from diagenetic reactions and the transport of an alkalinity-depleted basement fluid. pH variations reflect sediment heterogeneities (local chemical reactions?) that persist even in zones of rapid fluid upwelling. Thermodynamic calculations show that equilibrium with aragonite is achieved for cores without diagenesis or flow, at in situ T and P, which excludes any sampling bias. They also reveal a variety of cases for equilibrium and/or supersaturation with respect to either aragonite or calcite, depending on the increase in alkalinity, the rate of fluid upwelling and the degree of alteration of discharging basement fluids with respect to normal seawater.

Melt segregation and melt – mantle interaction in a supra-subduction zone context: An example from the Khoy ophiolite, NW Iran

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Introduction

Petrographic and geochemical studies of residual mantle exposures in supra-subduction zone environment provide important information on partial melting, melt segregation and melt – mantle interaction processes in the oceanic mantle lithosphere. Ultramafic tectonites comprise dominantly lherzolites and cpx-harzburgites in Khoy ophiolites.

Discussion of results

These peridotites can be distinguished into three groups:
1- Peridotite type-(I) samples contain Al – rich spinels (Cr# of 0.16 – 0.26, Mg# of 0.75 – 0.68 and TiO2 = 0.01 - 0.12 Wt %) with generally smooth LREE – depleted and fairly flat MREE – HREE profiles. 2 - Peridotite type-(II) samples contain Cr – rich spinels (Cr# of 0.31 – 0.66, Mg# of 0.66 – 0.89 and TiO2 = 0.00 to 0.06 Wt %) with LREE – depleted and positive slopes MREE – HREE profiles. 3 - Particular peridotite samples contain Cr – rich spinels (Cr# of 0.45 – 0.88, Mg# of 0.63 – 0.86 and TiO2 = 0.13 to 1.03 Wt %) with U – shaped REE patterns indicative of interaction between LREE – depleted mantle peridotites and LREE – enriched extracted melt.

Conclusions

The results illustrate that the peridotite type-(I) samples resemble fertile abyssal peridotites, which has probably originated as the residue from less than 15% partial melting and MORB magma extraction in a slow – spreading back – arc basin centre. Peridotite type-(II) samples represent depleted abyssal or supra – subduction zone peridotites, which has experienced more than 15% partial melting from segregation of IAT or transitional IAT-MORB magmas. Peridotite type-(II) samples were subsequently modified to particular peridotite samples by interacting with divers types of arc magmas in a supra-subduction zone setting.

References

Magma chamber processes and geochemical aspects of megaporphyritic basic-intermediate lava in West Alborz Iran

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The studied area is in the northwest of Khalkhal (Azerbaijan, NW of Iran) and related to Alborz – Azerbaijan structural zone. The oldest stratigraphic units belong to pre-Cretaceous deposits and the youngest units are quaternary alluvial deposits. The Eocene volcanic rocks are composed of olivine basalt, trachy basalt, trachy andesite and megaporphyritic basic-intermediate lavas. The latter have few centimeters phenocrysts of plagioclase and are extended in a large area from NW to SE of Iran volcanic belt (Urumieh-Dokhtar magmatic belt). They are a good indication for Upper Eocene volcanic activity in Iran. Geochemical and isotopic data for megaphyritic lavas show that the basaltic rocks have transitional trend with sodic character and the intermediate terms belong to calc-alkaline series with sodic or potassic affinities due to different rates of crustal contamination and fractional crystallization (AFC process). The basaltic lavas are not relatively rich in plagioclase phenocrysts and have been ascended rapidly to the surface but the rich megaporphyritic intermediate lavas are the result of basic magma storing in upper crust chambers, suffering fractional crystallization and crustal contamination. These megaporphyritic lavas are also interested for Cu,Pb,Zn mineralization.

References

Rhombohedral calcite precipitation from CO2-H2O-Ca(OH)2 slurry under supercritical and gas CO2 media

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The formation of solid calcium carbonate (CaCO3) from aqueous solutions or slurries containing calcium and carbon dioxide (CO2) is a complex process of considerable importance in the ecological, geochemical and biological areas. Moreover, the demand for powdered CaCO3 is recently very important in various fields of industry. The aim of this study was then to synthesize fine particles of calcite with controlled morphology by using an original method.

The morphology of precipitated particles was identified by transmission electron microscopy (TEM/EDS) and scanning electron microscopy (SEM/EDS). In addition, the x-ray diffraction was performed to investigate on the carbonation efficiency and purity of solid product.

The carbonation of dispersed calcium hydroxide (Ca(OH)2 + CO2 → CaCO3 + H2O) in presence of supercritical or gas CO2 allowed the precipitation of sub-micrometric isolated particles (<1µm) and micrometric agglomerates (~5µm) of calcite rhombohedral-crystals. For this study, the global Ca(OH)2-CaCO3 conversion is not significantly affected by PT conditions after 24h of reaction. However, the x-ray spectra for solid products suggest a better purity for supercritical CO2 system. The use of high pressure of CO2 could be desirable for increasing the production rate of CaCO3, carbonation efficiency and purity, approximately 47.94 kg/m3h, 95% and 96.3%, respectively for this study. The dissipated heat for this exothermic reaction was estimated by calorimetry concept, -31.42 kJ/mol for supercritical CO2 system and -41.9 kJ/mol for gas CO2 system.

Keywords: Supercritical CO2; Calcite precipitation; Rhombohedral-crystals; Calcium Hydroxide; Carbonation.
The effect of LMW organic ligands on Plutonium and Uranium solubility under hyperalkaline conditions

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The chemical degradation of organic materials present in low/medium activity nuclear waste leads to the formation of LMW organic ligands that may contribute to the mobilisation of radionuclides. Among the expected ligands, isosaccharinic acid (ISA), acetate, phthalate and adipate have been identified as the most relevant compounds resulting from the degradation of polyurethane, cellulose and plastics materials. This work aims at assessing the effect of these organic ligands on the possible mobilization of Uranium and Plutonium under the hyperalkaline conditions defined by a cementitious environment.

The first step has consisted of the preparation of a complete and consistent database including complexes of U and Pu with ISA, acetate, phthalate and adipate. The sensitivity study has focused on the solubility of U and Pu under alkaline conditions and has taken into account the following parameters: a) a concentration range of organic compounds; b) a concentration range of calcium and c) a redox conditions range (from reducing to oxidant conditions).

Under the studied conditions, acetate, phthalate and adipate show almost no effect on U and Pu solubility, given both, the low affinity of these ligands toward U and Pu and the high affinity of Ca present in the system towards the studied ligands. Indeed, the presence of Ca in the system reduces the amount of available free organic ligand to radionuclide complexation showing a minor influence of organics ligands on Plutonium and Uranium solubility. Nevertheless, ISA has been shown to significantly increase the solubility of U and Pu, even when Ca is present in the system.

Using reactive transport models and chronosequence data to elucidate differences between laboratory and field mineral dissolution rates

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Silicate mineral weathering rates in soils have implications for processes including ecosystem nutrient cycling, soil formation, and groundwater quality. The orders of magnitude difference between laboratory and field dissolution rates results from factors including hydrology, proximity to chemical equilibrium, inhibition of aqueous species (e.g., aluminum), and reactive surface area. An ideal approach to quantifying the effects of such factors on differences between laboratory and field rates is to use a reactive transport code to model dissolution.

The Merced chronosequence is an ideal system for applying the reactive transport model FLOTRAN because of the large dataset collected for soils ranging in age from 40 to 3000 ka. Measured values were used for the mineral volume, porewater chemistry, flow rates, and BET surface area (SA). If the measured values were used with laboratory values for the rate constants and pH-dependence, model dissolution proceeded too quickly. The only way to achieve model results that matched the field data was to reduce the product of the rate constant and reactive SA. Laboratory rate constants were assumed to be intrinsic rates (whereas field rates can be thought of as “apparent” rates). Thus reducing the reactive SA of the parent material by 3 orders of magnitude compared to the BET SA gave results that matched field data well. Alternatively, a good model fit was achieved with a non-TST (non-linear) rate law by decreasing the reactive SA by 2 orders of magnitude. Model results did not match field data well when increased clay solubility, decreased clay precipitation, or inhibition of plagioclase dissolution by aqueous species were used as primary fitting parameters.

Mineral dissolution, including plagioclase dissolution, across the Merced chronosequence was successfully modeled by reducing the parent material reactive SA. Chronosequence data provided constraints that increased the uniqueness of model fits. For example, greater clay solubility reduced plagioclase dissolution in younger chronosequence soils, but resulted in too little K-feldspar dissolution in the oldest soil. These model results point to the usefulness of reactive transport models for understanding field weathering and corroborate other studies that point to the importance of developing techniques to measure reactive SA.
Estimating submarine groundwater discharge in the range $10^1$ to $10^8$ km$^2$ using Ra Isotopes

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The flux of submarine groundwater discharge (SGD) provides an important pathway for enriching coastal waters in nutrients, carbon, and metals. Here SGD is defined as all flow of subsurface water from the continental margin to the ocean, regardless of composition or driving force. Regional quantification of SGD is difficult because direct measurement over large temporal and spatial scales is not possible by conventional means. Measurements of naturally-occurring radionuclide tracers at the aquifer-marine interface and in the coastal ocean provide a method to produce integrated flux estimates of discharge not possible by other means. In this talk I will explore the use of four radium isotopes to quantify SGD at scales ranging from small tidal creeks to the entire Atlantic Ocean. Radium is especially useful in this regard because it has high concentrations in SGD relative to coastal waters, low reactivity in the ocean, and four isotopes with half lives ranging from 3.7 days to 1600 years.

At small and intermediate scales, the technique requires a measure of the Ra inventory in the surface water and its concentration in SGD, evaluation of other sources of Ra, and a measure of the residence time of the water body. With this information, the inventory of Ra in the water is converted to the SGD Ra flux. This Ra flux must be replaced by new inputs of Ra from SGD. Thus, Ra concentrations in SGD convert the Ra flux to the SGD flux.

On a large scale, the decay of the $^{228}$Ra inventory in the upper 1000 m of the Atlantic must be balanced by a flux from the continental margins. By evaluating other sources of $^{228}$Ra and concentrations in SGD, a total flux of SGD to the Atlantic is obtained. This flux is in the range 0.5 to 1.0 of the river flux to the Atlantic. Because SGD is generally higher than river water in nutrients, metals, and carbon, the SGD fluxes of these materials probably exceed their riverine fluxes to the Atlantic.

The evidences of magma mixing and mingling in the Aran area (central Iran zone)

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This area is located in Eurmia-Dokhtar zone. The Eocene volcanism in this area is related to the orogeny activities in middle Alp. The tectonic activities in central Iran indicate most movement in this time. There are some deep marine sedimentary within volcanic-sedimentary rocks (i.e. ash and pumice tuff). There are some magma mixing evidences in this area which contain existence three different glasses (acidic, basic and hybrid glasses) in the matrix of hyaloclastic breccias and some plagioclases and pyroxenes with sieve texture, absorption and corrosion in their rims. Existence of basic micro pillows in acidic matrix and amphiboles with opaque rims. There are some mingling evidences in this area which are result of entrance of hot basic magma into co-magmatic and differentiated acidic magma in the magma chamber like two basic glasses with different composition and reverse, oscillatory zonation in the minerals.
Hf-in-zircon perspective on crustal growth and recycling in the Arabian-Nubian Shield

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The Arabian-Nubian Shield (ANS) is a collage of Neoproterozoic (850-750 Ma) island arcs that were accreted together and then squeezed again towards 640 Ma in relation to Gondwana assembly. Arcs accretion was followed by a widespread, late-post kinematic, calc-alkaline igneous activity that culminated at ~ 630-600 Ma, and by subordinate alkaline magmatism. Isotopic evidence, mostly Sr and Nd, indicate that the ANS was formed as juvenile crust during the Neoproterozoic. The northern tip of the ANS is exposed in southern Israel (Elat area) where it displays ca. 200 m.y of crustal evolution via igneous activity and dynamo-thermal metamorphism. We analyzed zircon U-Pb and Lu-Hf isotope data from 5 representative rock units of the Elat association whose age spans the entire crustal history in the region. All calculated Epsilon Hf values are positive, and define a linear array when plotted versus age. Intersect of this line with the DM evolution line suggests crustal extraction at ca. 1000 Ma. This demonstrates that although the ANS as a whole is rightly considered juvenile, most of its Neoproterozoic evolution is characterized by crustal recycling and or differentiation processes. Detrital zircons from the Elat schist representing the oldest island arc material show a considerable spread over more than 8 Epsilon units, from the DM evolution line down towards CHUR values. This spread highlights the possible contribution from an additional source, beside the DM, to the island arc magmas. This additional source could either be an enriched mantle or a slightly older, ca. 1100-1200 Ma, juvenile crust.

Terrestrial plandes formation: Our Solar System and extra-solar Worlds

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According to our current understanding, terrestrial planets form in two steps. First, a disk of planetesimals gives origin to the rapid formation of a system of numerous planetary embryos, of masses comparable to that of the Moon or of Mars. Then, the embryos start to collide with each other, as their orbital eccentricities are excited by mutual perturbations and by the giant planets. According to N-body simulations for our Solar System, this leads to the formation of a few (3-4) terrestrial planets in the 0.5-2 AU region, and a substantially depleted asteroid belt. The problems with these simulations is that the resulting planets are typically on orbits that are too eccentric and inclined with respect to the real orbits, and the formation time exceeds 100 My.

A possible solution of the problem consists in accounting for the interaction between the growing planets and the disk of planetesimals. By a process called dynamical friction, the planetesimals damp the eccentricities and inclinations of the terrestrial planets. The most modern simulations accounting for this process have allowed to achieve, for the first time, terrestrial planets on orbits consistent with the real ones and formation timescales of order of 30-40 My, consistent with Hf/W chronology. However, these spectacular results have been achieved assuming that the giant planets at the time were already on their current orbits. Unfortunately, there is a growing consensus that Jupiter and Saturn had to have quasi-circular, less separated orbits. With this set-up, the terrestrial planets still appear to form a bit too slowly and on orbits slightly too excited. It is possible that the future generation of simulations, accounting for a larger number of planetesimals and for their regeneration during collisions among the embryos, will allow to obtain ‘good’ terrestrial planets even in the framework of circular giant planets.

All current simulations show that the accretion of terrestrial planets is heterogeneous; material is incorporated in a stochastic way from a large variety of heliocentric distances, including from the asteroid belt. Thus, water could have been accreted during the formation process from the regions where hydrated meteorites come from.

The process of terrestrial planets formation has also been explored in the context of different giant planets systems, inspired by extra-solar planets discoveries. In general, more eccentric or massive giant planets lead to the formation of a smaller number of more massive terrestrial planets. Eccentric planets also inhibit the delivery of water from the asteroid belt equivalent. More recently, it has been shown that the radial migration of a giant planet toward the central star does not abort terrestrial planets formation.
Geochemical model and temporal distribution of Ni laterites in Urals

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Nickel lateritic deposits of Urals have been forming during late Triassic – Early Jurassic and Early to Late Cretaceous. Remobilisation and redistribution of Ni is related to Tertiary processes. Blanket-like, linear and combined types of deposits have traditionally been distinguishing by Russian geologists. Presented is a model showing that all listed types represent a result of the same geochemical process.

Generalization of published materials and author’s experience point to the dual nature of Ni concentration during lateritic weathering. Within laterite and saprolite, Ni concentrates in situ due to removal of alkaline and alkaline earth elements as well as Si. Ni accommodates in oxides and hydroxides (goethite, haematite, maghemite, magnetite) within laterite zone and in layered silicates (smectites) within saprolite zone. Infiltration of Ni partly dissolved by weathering and its following precipitation leads to formation of rich quartz-garnierite ore in the zones of faults and deep karst cavities along the contacts of serpentinites and carbonate rocks. Such mineralization can be traced to the depth 400 – 500m. It seems that two described mechanisms cannot exist without each other: on the one hand, lateritic profile cannot develop without developing intensive drainage system which provides downward solution movement and leaching primary minerals; on the other hand, zones of faults and contacts with carbonate rocks play the role of such systems also being geochemical barriers for Ni precipitation.

Thus, the existence of poor residual (lateritic) or poor infiltrative (linear) deposits seems to be doubtful. These types were distinguished due to weak tectonics study of ultrabasic massifs and impossibility of proper erosion level estimations.

Preliminary Ni isotope study (δ60Ni and δ62Ni, MC-ICP-MS Neptune, Centre of Isotopic Research, VSEGEI) shows, that with respect to Ni isotope composition of parent serpentinites, samples of quartz-garnierite infiltration ore show more heavy composition, while in-situ laterite samples have more light composition. This indirectly confirms the opinion about dual nature of Ni behavior during lateritic weathering of ultrabasic rocks.

Noble gas concentrations and isotopic ratios in single chondrules using laser ablation: Constraints on the origin of noble gases in chondrites

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The question of the origin of the noble gases on Earth remains unclear. Solar wind irradiation with mass fractionation due to sputtering on parent bodies is one scenario, dissolution of a dense primordial atmosphere in a molten earth is another one. Neon and argon isotopes measured in mantle-derived rocks suggest that the irradiation scenario is strong. In order to understand how parent bodies acquired their noble gases, we have developed an ablation system coupled to a noble gas mass spectrometer allowing measurement of noble gases in situ. The ablation system is an Excimer laser (193nm), giving ablation spots of ~60µm in diameter and ~50µm in depth. It is coupled to our glassy mass spectrometer ARESIBO II.

NWA3128 is a LL3.8 ordinary chondrite that shows chondrules up to 1mm in size. A sample of 0.1mg was first heated using a 10W continuous Wave Ytterbium fiber laser in order to get bulk helium and neon compositions. 4He and 20Ne concentrations were 7 * 10^-3 and 3 * 10^-4 ccSTP/g respectively. 4He/3He ratio is 2870 (SW=2500), 20Ne/22Ne=11.44 and 21Ne/22Ne=0.0780, suggesting a solar wind implantation in this sample.

We then have performed profiles in different chondrules from NWA3128 using our ablation system. Our results clearly show that the solar gases are at the surface of the chondrules. The concentrations obtained in the rims are more than ten times higher than the interior the chondrule. Moreover, isotopic ratios are solar-like in the rim (e.g. 20Ne/22Ne=11.59±0.07) whereas the interior presents a more important cosmogenic contribution (20Ne/22Ne=8.6 and 21Ne/22Ne=0.15).

Our results show that the chondrules were formed in an environment with a strong solar wind that was implanted at the surface of chondrules before the formation of the chondrite. An important proportion of noble gases that are present in the earth’s mantle may derive from the solar wind implantation in chondrules, close to the young Sun. These chondrules will then mix to a matrix to form the different chondrite classes. Noble gases are then a mixture of these solar gases, fractionated during implantation, and gases from the matrix. Thermal metamorphism will homogenize these components to give the planetary signature.
Os isotope and PGE evidence for major disruption and addition to the lithospheric mantle: A study of peridotites from the Premier Mine, Kaapvaal craton, SA

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Determining the processes responsible for modification of sub continental lithospheric mantle (SCLM) is key to understanding early crust formation and stabilisation. The Kaapvaal SCLM, as a residue from partial melting, is characterised by depletion in basaltic melt components, but contains high silica and incompatible trace element contents indicative of a complex melt-fluid enrichment history (Griffin et al., 2003).

Tomographic studies have establish that Kaapvaal SCLM forms a thick buoyant lithospheric root except for a region in Central Kaapvaal where a marked seismic anomaly coincides with the region of a major magmatic activity that formed the Bushveld Province at 2.05Ga.

This study aims to establish the effect of this major magmatic event on the SCLM through a study of mantle xenoliths from the Premier kimberlite pipe that occurs in the centre of the seismic anomaly. The specific goal is to determine if new SCLM was formed at 2.05 Ga or if there was a major modification of existing SCLM. A combined petrology, major and trace element and Hf-Os isotope study will be reported. Peridotites range from highly depleted spinel and garnet harzburgites to garnet lherzolites. The Premier suite is characterised by two distinct PGE patterns. Group 1 is characterised by fractionated I-PGE to P-PGE patterns typical of residua from high % partial melting (PdN/IrN<0.4) while Group 2 has 0.3<PdN/IrN<1.6. Os model ages of Group 1, are generally Archaean whereas Group 2 clusters at ca. 2.0 Ga. A model will be presented to explain the observed depth vs. age of melt depletion relationships which will constrain amount of new vs. modified SCLM beneath Premier.

References

2-D diffusion modelling – extracting timescales and crystal histories from BSE images

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Modelling of diffusion profiles within phenocrysts from igneous systems has become more common in recent years. Initial modelling was conducted from linear traverses across crystals measured quantitatively by electron microprobe. Use of Back-Scattered Electron (BSE) imaging allows us to improve the spatial resolution to that of a focused electron beam, at less than a micrometre per pixel, and also to work with two-dimensional images rather than simple traverse lines. When calibrated against electron microprobe analysis, such images can, for certain elements in certain minerals, be used as high-resolution compositional maps.

Combination of imaging with other techniques such as Electron Back-Scatter Diffraction (EBSD) and U-stage measurements allows us to account for many of the geometric uncertainties that exist in diffusion, with crystal orientation (and hence diffusional anisotropy), and boundary orientation being measurable. This presentation introduces a simple finite-difference model (FINDIF) that can incorporate diffusional anisotropy, compositional dependence of both diffusion coefficients and trace element activity coefficients, and elemental partitioning between different crystal phases and liquids (modelled as infinite buffers). Initial states can be read in from TIFF files created with standard image manipulation software, allowing the direct modelling of BSE images that are frequently captured in this format. Multiple grains of multiple minerals can be considered simultaneously, allowing the modelling of polymineralic aggregates.

The program can model the degree of fit between modelled values and an input value within specific pre-defined regions of interest, allowing separate treatment of different regions of interest within the same field of view.

The results indicate that diffusion processes in phenocrysts are actually rather complex even within single crystals and are intimately tied into the dynamic processes of growth, cracking and dissolution to which a crystal is subject during magmatic residence.
**In-situ** arsenic speciation in Earth surface environments: Importance of iron oxides

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Contamination of aquifers by one of the most toxic forms of arsenic, As(III), is an important health concern in many parts of the world \(^{[1]}\). Recent studies have revealed that intimate relations exist between As and Fe cycling in Earth surface environments: microbial reduction of As(V) and Fe(III) is thought to be responsible for large-scale contamination of aquifers by As(III) in Southeast Asia \(^{[2,3,4]}\); in contrast, microbial oxidation of As(III) and Fe(II) leads to efficient water decontamination, especially in acidic environments \(^{[5]}\). Further modelling of As transformations partly suffer, however, from the scarcity of data addressing molecular-level speciation in field samples.

In this context, we have compared in situ speciation of As in natural and impacted soils, by combining XANES and EXAFS spectroscopy with selective chemical extractions. Our results indicate that As mainly occurs as surface complexes on iron oxides \(^{[6]}\). The relative importance of phyllosilicates as arsenic sorbents is generally difficult to evaluate in soils. It may, however be responsible for an increase of As(III) mobility \(^{[7]}\), especially in iron-depleted anaerobic media.

Recent investigations of acid mine drainage \(^{[5]}\) and geothermal springs \(^{[8]}\) revealed similar coupling between arsenic and iron chemistry in these acidic environments. In both contexts, microbial oxidation of Fe(II) and As(III) leads to the formation of amorphous As(V)-Fe(III) hydroxysulfate compounds with similar local environments of As(V) and Fe(III). Importantly, the solubility of these compounds decreases with increasing Fe/As ratio. Frequently associated with biological substances, such compounds could be considered as potential markers of microbial activity in acidic environments.

**References**


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**High-silica magmatism in an oceanic core complex from the Central Indian Ridge**

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**Introduction**

An oceanic core complex located at 25°S (25°S OCC) of the Central Indian Ridge (CIR) was explored by SHINKAI 6500 of the Japan Marine Technology Center. Serpentinitized peridotites and gabbros were collected with metamorphosed/ altered basalts from the OCC. Highly deformed rocks of variable origins including peridotite and gabbros were also collected on the top surface of the OCC. These characteristics support that the OCC is a tectonically exposed deep-seated rock on the sea floor. Plagiogranite was recovered from the 25°S OCC. Quartz-bearing granitic small veins crosscut a gabbro. Origin of plagiogranite is still in debate (Koepke et al., 2007). We report petrology and chemical compositions of plagiogranites in the CIR.

**Results and discussions**

The plagiogranite in this study consists of fine grains of quartz and sodic plagioclase with small amount of amphibole, epidote including allanite, apatite and zircon. Geochemical characteristics of the plagiogranite are extremely high in SiO\(_2\) content (80 wt. %) and low TiO\(_2\), FeO\(_{total}\) and P\(_2\)O\(_5\) contents. Chondrite-normalized REE pattern of the plagiogranite is characterized by high REE abundances with conspicuous negative Eu anomaly, indicative of very high degree of fractional crystallization. In addition, convex (M-type) tetrachloride effect is clearly recognized in the sample, implying unusually volatile-rich (e.g., H\(_2\)O, CO\(_2\), Li, B, F, and/or Cl) parent magma of the plagiogranite (Nakamura et al., 2007). These characteristics suggested that plagiogranite was formed by either interaction with an external fluid originated from seawater or hydrous partial melting of pre-existing rocks in the initiation of amagmatic opening related to intermediate-spreading ridge.

**References**


Formation of amorphous forsterite particles by levitating Mg$_2$SiO$_4$ melt droplets

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To simulate the evolution of amorphous Mg$_2$SiO$_4$ (forsterite) to the forsterite crystals, we need amorphous particles in the experiment as the starting materials. Although amorphous forsterite has been synthesized from vapor phase [1], these particles are too small ($\phi < 1 \mu m$) to be investigated by optical method. Therefore, we have applied a gas jet levitator method to solve this problem. A gas jet levitator method is useful to avoid heterogeneous nucleation during cooling process and thus melt droplets were very stable at large supercooling (> 1000 K) [2].

The starting materials were synthesized forsterite spherules (~ 2 mm), which was set at the top of the nozzle (1 mm in diameter) of the gas jet levitator and then levitated by introducing Ar gas. The spherule was melted by CO$_2$ laser (100 W) irradiation. The melt temperature was measured with a pyrometer. The crystallization and vitrification process from the supercooled melt were observed with a CCD camera.

The experimental results show that amorphous formation of forsterite took place at ~ 1000 K with a larger cooling rate than 300K/s (fig. 1), which was much smaller cooling rate as obtained by Tangeman et al. (2001), 700 K/s [3]. While, enstatite melts with higher SiO$_2$ content formed only amorphous material at any conditions.

The value of 300 K/s is not led only by heat radiation but by additional gas flow during cooling. If forsterite melt droplets were cooled only by radiation in space, melt droplets with less 10 μm in diameter, could become amorphous particles rather than crystalline particles. Presence of amorphous forsterite particles around AGB stars might be due to this reason.

Fig. 1 Cooling curves during formation of (a) amorphous forsterite and (b) forsterite crystal in levitation. (c) The sample was set on a graphite rod.

References

Reaction kinetics of shallow water marine carbonates: Successes and failures in bringing laboratory experiments and the ocean together

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A wide range of geochemical observations have been made of the composition and behavior of marine carbonates in shallow water carbonate-rich sediments generally found in tropical to sub-tropical waters typified by environments such as atolls and lagoons, carbonate banks and platforms, and coral reefs. The carbonates found in these environments are often a complex mixture of aragonite, high and low magnesian calcites, and, rarely, (proto) dolomite. They may have both biotic and abiotic origins, and can undergo both formation and dissolution during early diagenesis. Because they will play a significant role in the response of the ocean to its “acidification” due to rising atmospheric pCO$_2$, there has been renewed interest in understanding the reaction kinetics of their formation and dissolution.

A major question that has often been hotly debated and continues to be a major source of concern is how well laboratory measurements of factors influencing their precipitation and dissolution kinetics, and pseudo-solubility behavior are representative of their behavior in the “real world”. These concerns center around several basic factors. Perhaps foremost amongst these are the clear and potential differences between natural biogenic material and abiotic carbonate minerals. Numerous studies of the behavior of magnesian calcites, which typically comprise about 24% of shallow water marine carbonates, stand as all too clear examples of the limitations and failures that can be encountered. However, in situations where abiotic marine carbonate formation occurs, such as aragonite needles in “whitings” on the Great Bahama Bank, experimental and observed reaction rates can be brought into close agreement, but, even in these types of situations surprises can be found-e.g. the “kinetic” solubility is about twice that of aragonite.

After over half a century of trying to understand the behavior of natural marine carbonates in marine sediments from laboratory kinetic experiments there is clearly still much to learned.
Oxygen isotopes of diatom silica and their utility for palaeothermometry

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The use of the oxygen isotope composition of diatom silica ($\delta^{18}O_{\text{diatom}}$) as a palaeothermometer has found increasing attention. Two main reasons have hindered an even broader application: Firstly, substantial analytical problems with the preparation of diatom frustules, particularly from fresh diatom silica and, secondly, considerable uncertainty with respect to the temperature dependence of the oxygen isotope fractionation during silica formation. We have developed a novel technique for the determination of $\delta^{18}O_{\text{diatom}}$ which is based on inductive heating and high temperature carbon reduction (iHTR) of the silica. With the new iHTR method quantitative silica disintegration with low sample amount and high accuracy and precision is achieved in one continuous routine in a high-vacuum device. Calibration studies with marine and freshwater diatoms had provided contradictory results with published temperature coefficients varying from zero to –0.5‰/°C. Therefore, we have accomplished a calibration study using fresh diatoms grown during an annual cycle in Lake Holzmaar, a small freshwater lake (Germany). Based on identical results for three different diatom size fractions we propose a value of –0.2‰/°C as the most realistic temperature coefficient of oxygen isotope fractionation between diatom silica and lake water. However, at the sediment surface and within the surface sediment, an effect of silicon dissolution / biogenic silica maturation takes place that causes an $^{18}$O enrichment of the diatom silica and introduces a possible bias with respect to palaeothermometry.

References

Investigating empirical equations of determining concentration time of flood in Karaj river basin

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Time parameters are used mostly in hydrologic and hydraulic models. The most often used time parameter in hydrology is concentration time.

Concentration Time is the time required for a particle of water to travel from the hydrologically most distant point in the watershed to outlet or designing point. Concentration time is used for designing spillway, estimating flood volume, preparing flood hydrograph and many other hydrologic analysis.

Many methods (empirical equations) are available for estimating concentration time. the aim of this research is selecting the best method(s) for estimating concentration time in the studied basin. To achieve the said aim, a field method based on measurement of travel time by salt solution is used. In order to select the best method(s) for estimating concentration time in the basin, the difference between values obtained by using these methods and the field method are determined.

Results of this research show that In steep area, SCS Lag method is the best for estimating concentration time. In this area Ventura, Gianduti, Passini, and Carter methods provide a fairly good estimate of concentration time.

In flat area, Chow, Kirpich, Basoo, and California methods provide a fairly good estimate.
Sulphur solubility in andesitic to basaltic melts: An example of Hekla volcano

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The magmatic gas phase plays a major role at active volcanoes and the interest in studying degassing processes has been continuously increasing in modern volcanology. However, the mechanisms of volatile release and partitioning between melt and fluid phase during eruptions of andesitic to basaltic volcanoes are not yet well-understood. In fact, mainly to model the distribution of complex volatiles between volcanic gases and natural silicate melts, especially for mafic systems, are limited to a few studies.

In this work, particular attention is given to the Hekla volcanic complex (one of the most active volcanoes in Iceland), which is well characterised, both for the petrology and degassing behaviour (Sigmarsson et al., 1992, Moune et al., 2006, Moune et al., 2007). The distribution of sulphur between silicate melts and coexisting gas phase has been determined experimentally at 300 MPa, 1050°C and FMQ oxygen buffer in the systems containing H-O-S-bearing fluids. Experimental products and natural phases is used to interpret and during magma ascent. The comparison between the gas phase compositions during magmatic differentiation these experimental results show the evolution of the melt and basaltic melts of Hekla coexisting with pyrrhotite. Moreover, experimental results confirm a saturation of 2500 ppm S in the variations in sulphur during volcanic eruptions as well as eruptive mechanisms.

Further Helium isotopic evidence for a lower mantle contribution to the Cape Verde plume

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The origin of Cape Verde Islands has been intensely debated, and controversy still exists concerning the influence or not of a deep mantle plume beneath the archipelago. In order to better constrain the ultimate origin of the Cape Verde magmatism we will present and discuss He isotopic data, which has been considered one of the most powerful geochemical tools presently available to identify the contribution of the lower mantle to magmatism.

For Brava, one of the youngest Cape Verde islands, He isotopic signatures were performed on olivines, extracted from mafic silicate rocks, and on calcites and apatites occurring in sôvitic carbonatites. While apatites are strongly radiogenic, owing to their high U and Th contents, calcites and olivines are usually characterized by 4He/3He values lower than the typical value of 90,000±10,000 reported for MORB, presenting values as low as 60,711 (11.9Ra) and 53,663 (13.4Ra), respectively. Low 4He/3He was obtained for silicate rocks of S. Nicolau (45,928; 15.73Ra) and S. Vicente (58,887; 12.27Ra) (Doucelance et al., 2003). R/Ra values as low as 46,414 (15.5Ra) were also obtained for S. Vicente carbonatites. Cape Verde islands define two alignments (Northern and Southern islands), presenting distinct elemental and isotopic signatures (e.g. Doucelance et al., 2003). Our helium isotopic data for Brava are clearly distinct from those reported for other Southern Islands where the lower 4He/3He values are MORB-type. These results show that for both Northern and Southern islands, silicate and carbonatitic magmas preserve signs of the contribution from a relatively undegassed/primitive reservoir, as compared with the upper mantle sampled by MORB. We consider this a compelling evidence for a lower mantle origin of the Cape Verde plume, thus supporting the tomographic data imaging the plume down to significantly below the 670 km discontinuity (Montelli et al., 2006).

References

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Pressure induced phase transition in hydrous Sr-anorthite

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A recent survey of hydrous species and concentrations in igneous feldspars (Johnson and Rossman, 2004) shows that feldspars may contain structural OH (0-512 ppm H2O) and structural H2O (0 – 1350 ppm). However, little is known about the defect locations of the trace hydrous species, their concentrations as a function of pressure and temperature and their effect on the physical properties. In this contribution we report on OH in Sr-anorthite including in-situ FTIR experiments as a function of pressure in a diamond anvil cell (DAC) in regions of OH stretching and lattice vibrations to evaluate the effect of OH on pressure induced phase transitions.

Two syntheses were performed at 20 kbar and 700 °C in a piston cylinder apparatus. The monoclinic products (space group I2/c) consist of 100 - 300 μm large clear single crystals which were investigated by FTIR, X-ray diffraction and electron microprobe. Polarised single crystal infrared spectra in the OH stretching region showed a broad but weak band centered around 3400 cm−1 plus three sharp and intense bands: band (1) at 3628 cm−1, band (2) at 3598 cm−1 and band (3) at 3500 cm−1. We interpret the broad band to result from OH stretching vibrations of structural water and/or molecular water in inclusions. From the pleochroic behaviour we assigned band (1) to vibrations of a O3-H dipole and bands (2) and (3) to O6-H dipoles most probably bonded both to O8 oxygens but occurring in different chemical environments (Al, Si). The water content of the synthetic Sr-anorthite is with 1100 ppm twice the maximum value observed for natural anorthite.

The DAC experiments in the OH stretching region show a clear change in the behaviour of band (1) between 8 and 9 GPa which was fully reversible upon pressure release. We interpret this as an indication for a phase transition in that region. For pure monoclinic Sr-anorthite McGuinn and Redfern (1994) described only one phase transition at 3.2 GPa, i.e. from monoclinic to triclinic (I1-). For a feldspar with composition Ca0.25Sr0.6Al2Si2O8 Nestola et al. (2004) observed an additional transition at 7.3 GPa from monoclinic I 2/c to a not further specified monoclinic symmetry. Most probably the observed transition in this study corresponds to the transition described by Nestola et. al. (2004). As observed for hydrous ringwoodite (Chamorro Perez et al., 2006) the presence of structural bonded OH and/or H2O may trigger the transition and/or displace phase boundaries as compared to the dry system.

References

The δ18O of the Ocean at 3.8 Ga

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The recently discovered hydrothermally altered sheeted dike complex at Isua, Greenland provides insights into the 3.8 Ga ocean and may resolve the long standing controversy regarding the δ18O of ancient oceans and sediments. It has been argued that the very low δ18O Archean cherts (12 to 24‰ SMOW) may have precipitated from a hot Archean ocean, a conclusion incompatible with some models of atmosphere and seawater compositions. Critics of a hot ocean have invoked moderate surface temperatures but a very low δ18O ocean (-13‰). The δ18O of the ocean is held at its present value by a balance of low and high temperature water rock interactions primarily linked to plate tectonic processes. Thus as long as there is extensive hydrothermal alteration of the seafloor by seawater the δ18O of the oceans will be near 0‰. A -13‰ ocean would impose a very large 18O-depletion on any hydrothermally altered rock. The Isua dikes range in δ18O from 5.7 to 6.9‰ giving no evidence of low, but rather a slightly enriched 18O seawater at 3.8 Ga. The data from Isua as well as previous studies on pillow lavas from Pilbara and Barberton show that a very low δ18O ocean is untenable and that modern style seafloor spreading, including hydrothermal systems, may have been operating in the Archean.

The δ18O of the pillows and dikes indicate that the earliest ocean crust had already reacted chemically with seawater. This has great implications to the composition of the oceans themselves because seawater/seafloor rock reactions are known to massively affect if not control the chemical make up of seawater. The composition of seawater (as well as the inferred hydrothermal systems) may also play a role in the evolution of life.


Ar, Kr, and Xe composition of the Earth’s mantle: Implications for the formation of the atmosphere

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Establishing whether the Earth’s mantle has solar or planetary heavy noble gases is crucial for planet accretion models and understanding how volatiles were incorporated into the solid Earth. Furthermore, isotopes of Ar, Kr, and Xe that are not produced by radioactive decay, can provide a critical test for models that suggest the Earth’s atmosphere was derived from mantle degassing. Here, I report new high-precision Ar, Kr, and Xe in gas-rich basalt glasses from the Atlantic and Pacific Ocean basins that indicate the atmosphere was not primarily derived from outgassing of the mantle.

The noble gases were extracted from fresh basalt glass by step crushing and measured using the Nu multicollector noble gas mass spectrometer at Harvard. Significant improvements in the measurements of heavy noble gases have been made in the Harvard laboratory that allow detection of small isotopic anomalies, of order few per mil, in Ar, Kr, and Xe.

Compared to atmospheric ratios of $^{124,126,128}\text{Xe}^{130}\text{Xe}$, a clear excess in these ratios is observed in basalt glasses from both the Atlantic and Pacific basins. The maximum excess in $^{128}\text{Xe}^{130}\text{Xe}$ was 18‰ and correlated with excess $^{129}\text{Xe}$ and $^{136}\text{Xe}$. The $^{124,126,128}\text{Xe}^{130}\text{Xe}$ ratios are consistent with mixtures of either air-solar or air-chondritic (Q) xenon. Solar Ar and Kr are significantly different in isotopic composition compared to their chondritic counterparts. Hence, isotopes of Ar and Kr could potentially fingerprint the excess xenon to be either solar or chondritic. The excess in non-radiogenic xenon isotopes is accompanied by air-like non-radiogenic Ar and Kr isotopes. The $^{38}\text{Ar}^{36}\text{Ar}$ composition of the atmosphere is indistinguishable from chondritic, and while atmospheric Kr is isotopically heavier than chondritic, it is closer to chondritic than solar composition. It is possible that mantle Ar and Kr in the basalts were overprinted by air-contamination. While this possibility cannot be disproved, based on the excess non-radiogenic xenon isotopes and the high-precision measurements, I argue that Ar, K, Xe composition of the Earth’s mantle is closer to chondritic than solar.

A chondritic composition for heavy noble gases in the Earth’s mantle implies that degassing of the mantle followed by mass fractionation through hydrodynamic escape cannot generate the atmospheric Ne, Ar, Kr, and Xe isotopic compositions. Delivery of volatiles via late accreting planetesimals may better explain the origin of the terrestrial atmosphere. If the bulk of the present atmosphere was not derived from the mantle degassing, the excess $^{129}\text{Xe}$ in MORBs, compared to the atmosphere, cannot be used to calculate a degassing age for the mantle. Rather the excess $^{129}\text{Xe}$ simply indicates that the mantle and the atmosphere have evolved with different I/Xe ratios.

Hydrogen isotope variations in hydrated volcanic glass as tracers of late Cenozoic precipitation patterns in the western United States

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Volcanic ash deposits characterize large portions of the Miocene-to-recent sedimentary successions in the western United States. Within thousands of years after deposition at the Earth’s surface, volcanic glass in these ashes incorporates relatively large amounts of water (3-5 wt.%). This hydration process provides a hydrogen isotope record that directly reflects paleoclimate and precipitation regimes. Once correctly correlated, widely distributed ashes may then serve as excellent paleoclimatic and paleoaltimetry proxies as a) deposition and hydration are almost instantaneous on geologic timescales and can be dated with high temporal resolution and b) the chemical composition of the proxy is constant over large areas (100-100,000 km2) thus eliminating compositional uncertainties related to proxy formation. Here we present, hydrogen isotope data from volcanic glasses across the Basin and Range Province and relate the long-term changes in isotopic composition to changing surface topography and precipitation patterns. Glasses from individual ash layers found in the Central Valley (CA) strongly contrast those in the Northern and Central Basin and Range. Moreover, systematic variations in the dD of volcanic glass at various locations in the Basin and Range Province document the long-term interplay between regional changes in surface elevation, developing topography, and changing precipitation patterns.
Infrared spectroscopic identification of aqueous uranium(VI) species

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Migration of uranium(VI), the most stable form of uranium in environmental waters, is largely controlled by its geochemical reactions, both in solution and at the mineral-water interface. Current knowledge about U(VI) speciation is mainly based on thermodynamic calculations using data obtained by non-structural experiments, i.e. potentiometric titration [1]. A spectroscopic verification of the speciation of aqueous U(VI) is still insufficient. For the identification of different molecular species previous studies applied primarily EXAFS and Raman spectroscopy at very high uranyl concentrations (>100 mM) unexpectedly in an environmental context [2-4].

In this study we used Attenuated Total Reflectance Fourier-transform Infrared (ATR-FTIR) spectroscopy, that allows the direct measurement of liquid samples. Our aim was to obtain additional vibrational spectroscopic information on the U(VI) species and especially to verify the U(VI) speciation throughout a wide pH range (pH 2-10) at a micromolar concentration level. The obtained spectral information was compared to previously reported thermodynamic data [1].

ATR-FTIR spectra were recorded at UO$_2^{2+}$ concentrations ranging from 5 to 0.005 mM at pH 4. The spectroscopic results indicate distinctly that dimer and trimer hydroxo complexes become dominant upon lowering the uranyl concentration at pH 4. The obtained spectral information was compared to previously reported thermodynamic data [1].

At the micromolar concentration level the calculations predict the dominance of the uncomplexed uranyl ion until pH 5 and the formation of uranyl hydroxo complexes at neutral pH. Uranyl complexes with atmospheric carbonate in alkaline solutions are proposed above pH 6.5. However, the obtained ATR-FTIR spectra of low concentrated 0.02 mM uranyl solutions already show the coexistence of free and hydroxo complexed uranyl at pH 2.5. The appearance of carbonate complexes in solution becomes noticeable at the spectra of solutions at pH 7. Since the results are partially contradictory to previous predictions of U(VI) speciation a critical review of the present knowledge of uranium migration in the environment is required.

References

Crystal size distribution (CSD) of periclase in marbles from the southern Adamello Massif, Italy

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Crystal size distributions (CSD) of periclase are presented for two profiles near the Cima Uzza summit, located in the southern Adamello massif (Italy). The data base was combined with geochemical and petrologic information to deduce the controls that acted on the periclase forming reaction.

Contact metamorphic dolomite marbles are exposed as xenoliths surrounded by mafic intrusive rocks. Periclase was retrograded to brucite. Periclase growth is the consequence of limited high temperature fluid infiltration. Stable isotope data show depletion for $^{13}$C and $^{18}$O in a narrow region (~40cm) near the igneous contact, whereas the periclase forming reaction front extends up to 4m into the host rock. A similar median grain sizes for periclase crystals was found over the entire profiles, but a larger proportion of bigger grains with increasing distance from the contact was observed. Textural analyses are combined with geochemistry data in a qualitative model that describes the dynamic nucleation and crystallization of periclase in this infiltration driven system. We attribute variations in grain sizes to changing reaction affinities along a dispersed infiltration front. This study highlights the need to invoke disequilibrium processes for metamorphic mineral growth and expands the use of CSD’s to systems of mineral formation driven by fluid-infiltration.

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Deformation experiments on natural omphacite: A TEM study

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The rheological behaviour of eclogite is dominated by the deformational properties of omphacite which therefore are most important for the geodynamic processes of subduction and exhumation of oceanic and continental crust. The deformation mechanisms activated are obviously not the same in eclogites from different geological areas as shown by several transmission electron microscopy (TEM) studies. In order to attribute the specific microstructures of omphacite to the deformation conditions of the eclogite in its geological environment, deformation experiments on natural omphacite under conditions of high pressure metamorphism have been started. The source material was fibroblastic omphacite with the space group P2/n from Tianshan (Gao and Klemd, 2001). TEM showed that it contained small-angle grain boundaries formed by crystal growth and the common 1/2[110] antiphase domains. The experiments were conducted using a Deformation-DIA (D-DIA) high-pressure apparatus at a strain rate of 10^{-5} s^{-1}, a confining pressure of 2 GPa, and temperatures between 800 °C and 500 °C.

The omphacite deformed at 800 °C had still the space group P2/n, was well-ordered and showed in addition to the defects in the omphacite as-grown) deformation twin lamellae on (100) with widths which varied between a few nm and about 0.5 µm. Deformation twin lamellae on (100) have been repeatedly observed in omphacites from eclogites of various occurrences but not in all (Godard and Van Roermund 1995; Müller et al. 2004). Defects parallel to (100) which apparently consist of numerous dislocations lined up parallel to (100) were seen in one area of the specimen. They are interpreted as precursors of twin lamellae; these microstructures have not been reported before. In addition, planar faults parallel to (110) and (1-10) stretched between dislocations have been observed. They may be similar or identical to crystallographic shear planes parallel to (110) which were found for the first time in the ultra-high pressure metamorphic rocks of Lago di Cignana (Müller and Compagnoni 2007, unpublished). Chain multiplicity faults parallel to (010), however, which are so frequent in omphacite from the Lower Schist Cover of the Tauern Window (Müller et al. 2004), have not been observed so far in the experimentally deformed omphacite.

References

Impact of future Greenland deglaciation on global weathering fluxes and atmospheric CO2

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About 1.76x10^6 km² of Greenland are currently covered by ice. It is expected that this large ice mass will melt away over the next 3000 years if anthropogenic CO2 emissions continue to rise (Alley et al., 2006). As a result, the bedrock currently covered by ice will lie free and become subject to chemical weathering. The resulting weathering fluxes will contribute to increase both the consumption rate of atmospheric CO2 and the production rate of riverine HCO3⁻. Increasing these two fluxes will tend to decrease the atmospheric CO2 partial pressure, as a result of the modified ocean-atmosphere carbon cycle. Chemical weathering may thus possibly act as a negative feedback in the Greenhouse World. Other changes (e.g., vegetation cover and additional climate change) concomitant with the melting of the Greenland ice-sheet may either amplify or dampen, if not reverse the weathering effect.

Here we use the intermediate complexity Earth System model CLIMBER-2 to quantify and analyse the weathering flux changes that result from the projected melting of the Greenland ice sheet and the implications for atmospheric CO2. The biogeochemical module of CLIMBER-2 has been extended to account for the consumption of atmospheric CO2 and the production of riverine HCO3⁻ by continental weathering processes, as a function of geographically distributed runoff (interactively provided by the CLIMBER-2 climate module) and lithology (derived from Amiotte Suchet et al., 2003). We find that the increased weathering processes alone would lead to a sustained 0.2 ppm/kyr decrease in atmospheric pCO2. The climate change resulting from the deglaciation of Greenland reduces the magnitude of this trend to 0.1 ppm/kyr. Only in the case where the effect of freshly comminuted bedrock is taken into account (Clark et al., 2006) does the weathering feedback help to reduce atmospheric pCO2 by about 10 ppm in 5000 years.

References
The geochemical behaviour of W, Nb-Ta, and Zr-Hf during mid ocean ridge melting

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Tungsten is traditionally regarded as one of the most incompatible trace elements during mantle melting, similar to Th. However, previously reported W/Th data indicate that the Earth’s mantle has a lower W/Th (0.19) compared to the Earth’s crust (0.26), suggesting that W is more incompatible than Th. In order to assess the behaviour of W relative to Th and other HFSE during mantle melting, we analysed a suite of MORB glasses from the 7°30’S and 11°30’S section of the Mid Atlantic ridge (MAR South) for their W-Nb-Ta-Zr-Hf compositions, employing isotope dilution and MC-ICPMS. Trace element compositions of the MAR South rocks nearly cover the whole range of MORB (e.g., Zr/Nb from 9-115).

Whereas contents of highly incompatible elements in the MAR South samples vary by more than an order of magnitude (9-220 ppb W, 30-1300 ppb Th), Nb/Ta and W/Th only show little variation (14.0–16.9 and 0.16-0.21, respectively). In marked contrast, Zr/Hf ratios vary from 28-39 and are positively correlated with contents of moderately incompatible trace elements. Nb/Ta ratios decrease slightly with Zr/Nb but are decoupled from Zr/Hf, similar as found in a previous high precision study on MORB samples [2]. These findings appear to be inconsistent with results from experimental studies, predicting that for mantle melting ΔNb<ΔTa and ΔZr<ΔHf (e.g., [3]).

The contrasting behavior of W-Th-Nb-Ta with respect to Zr and Hf is explained by the different bulk partition coefficients for each element group, dominated by cpx. Zirconium and Hf are much more compatible during mantle melting (e.g., [3]), leading to a much stronger fractionation of Zr/Hf in melts, even at relatively large melting degrees. Conversely, modelled W/Th and Nb/Ta ratios approach those of the mantle sources already at melting degrees of ca. 5%, thus providing a good estimate of the average W/Th and Nb/Ta in the mantle source regions. As these source regions of the MAR South magmas are variably depleted, the partition coefficients for Th and W must be similar to within ca 10%. Alternatively, both elements might rather be hosted at grain boundaries [4] and not in the pyroxene crystal lattice. The new estimate for W/Th in the depleted upper mantle (0.18±0.3, 2σ) indicates that W/Th is not significantly fractionated during dry peridotite melting, tentatively suggesting that the fractionated W/Th in the continental crust reflects a different behaviour of the two elements during subduction zone processes.


Magmatic paragonite: Vapour saturation of hydrous arc magmas at high pressure?

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Exposed deep roots of island arcs (e.g. Kohistan arc, Pakistan; Talkeetna; Alaska) are key for understanding continental crust growth mechanisms. Igneous lower arc crust, however, is faced with high-temperature conditions prevailing for a long time, and thus apparent granulite facies ‘metamorphic’ textures often mask the igneous crystallization history of intermediate to high-pressure arc plutonic rocks. Trace element modeling cannot really discriminate between dehydration melting and high-pressure igneous crystallization when both result in the removal of a small liquid fraction at similar conditions and mineralogy. Besides thermal considerations, one of the keys is that dehydration melting leaves mostly anhydrous residues, while high-P igneous crystallization concentrates H2O in residual liquids, until (eventually) saturation and exsolution of volatiles occurs. We explore phase relations and textures in lower arc crustal rocks from the Jijal sequence of the Kohistan paleo-island arc (NE Pakistan), to constrain the dehydration melting vs igneous hypothesis.

We studied a sequence of ultramafic and mafic rocks which shows locally cyclic cumulate units (websterites, dunites, garnet clinopyroxenites), pyroxene-bearing garnet hornblendites, garnet gabbros, dissected by patches of paragonite-epidote-garnet gabbros and by garnet-bearing felsic veins. Petrography, phase relations, and thermometry are inconsistent with a dehydration melting hypothesis of the Jijal complex, because of (i) the presence of pg-epi-gar gabbros, with a very uneven distribution in the field indicating late stage localized H2O-rich melt pods, (ii) wormlike intergrowths of epi+qtz and hbl+qtz, a typical cotectic crystallization feature, (iii) the overall composition of cumulus minerals, garnet in particular, (iv) oxide, gar-hbl and gar-cpx thermometry approaching/exceeding temperatures of 1000°C. Whole rock major and trace element data demonstrate that garnet gabbros and epi-pg-gar gabbros have identical compositions indicating that the Jijal complex fractionated from low-K, hydrous, calcalkaline magma(s). However, the pg-epi-gar gabbros have lower SiO2, Na2O, Sr, and Ba, indicating loss of these elements by fluid exsolution upon final crystallization. Thus paragonite and epidote in gabbros are not indicative of retrogression but texturally and mineralogically testify local H2O saturation of hydrous arc magmas at high pressures.
Gradual rise of atmospheric oxygen between 2.5 and 2.0 Ga revealed by Fe oxidation kinetics

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The evolution of atmospheric oxygen during the Precambrian is a key to understand the co-evolution of life and environment. A change in the redox state of the atmosphere during the Paleoproterozoic has been recognized from geologic records being termed as the Great Oxidation Event. The disappearance of mass independent fractionation in sulfur isotopes confirms that oxygen increase from $\lesssim 10^{-6}$ atm to $\gtrsim 10^{-3}$ atm took place between 2.45 and 2.0 Ga indicating the timing of $P_{O_2}$ transition rather than its quantitative pattern. Despite this advancement, the precise nature of quantitative evolution of atmospheric oxygen during the Paleoproterozoic has remained elusive.

The fractions of redox sensitive elements such as Fe and Mn retained in weathering profiles should reflect the concentrations of atmospheric oxygen at the time of weathering. We calculated retention fractions of Fe and Mn (ratios of the concentrations in a paleosol relative to the parent rock on isovolumetric basis), $F_{Fe}$ and $M_{Mn}$, corrected for compaction factors using available literature data. The $F_{Fe}$ and $M_{Mn}$ increased gradually with age during the Paleoproterozoic ($M_{Mn}$ showing less steep slope than $F_{Fe}$) suggesting an almost continuous increase in the oxidation of $Fe^{2+}$ and $Mn^{2+}$ in paleosols between 2.5 and 2.0 Ga.

We, then, applied Fe oxidation kinetics (-$d[Fe^{2+}]/dt = k[Fe^{2+}][OH]^{-2}(PO_{4})^4$; $x$ is the variable) to the data set of Fe$^{2+}$ and Fe$^{3+}$ concentrations in paleosols to quantitatively model the atmospheric oxygen increase. The above equation was finally converted to:

$$\psi/\psi_A = (PO_{4})^{4-x}/(PO_{4})^4$$

where $\psi$ is the ratio of $[flowing-out Fe^{2+}]/[dissolved Fe^{2+}]$ and the parameters with subscript A are values for reference paleosol A. We also considered formation time of weathering and variation of $P_{CO_2}$ with time in our calculations. Our results suggest that the atmospheric oxygen increased linearly in the logarithmic scale from $\sim 10^{-7}$ atm at 2.5 Ga to $\sim 10^{-3}$ atm at 2.0 Ga, which is in contrast to the drastic rise at $\sim 2.3$ Ga. The gradual rise of oxygen is consistent with isotopic records of carbon and sulphur.

Influence of microbial activities on the behavior of iodine in soil

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Studies of iodine in soil are important because of the following two reasons. From the nutritional viewpoint, iodine is an essential element for human because of its role in thyroid gland. Therefore, it is necessary to know the levels and behavior of this element in the soil-vegetation system. From the radiological viewpoint, $^{129}$I (half-life: 16 million years) is released from nuclear industries into the environment. Because of its long half-life, it is important to understand the fate of iodine in the soil environment. In this study we have carried out laboratory experiments on the sorption, desorption and volatilization phenomena of iodine in soil with a special reference to the role of microorganisms. We also analyzed iodine concentrations in various soils collected in Japan.

Very high iodine concentrations (on average: ca. 40 ppm) were found in Andosols, the most common soil type in Japanese upland fields, although its parent materials such as volcanic ash contain very low iodine (ca. 0.04 ppm). This indicates that iodine evaporated from the ocean into the atmosphere was deposited on the soil surface and accumulated there. Using radiotracer experiments, we found that fresh soils had a very high sorption capacity for both iodide ($I^-$) and iodate ($IO_3^-$), whereas that of autoclaved soils was markedly small, specifically for iodide. This suggests the possibility that microorganisms or their products (e.g. enzyme) play an important role in the iodine adsorption. Desorption of iodine from soil under flooded conditions was observed, i.e. iodine associated with soil was dissolved into water due to the reducing conditions (low $E_h$) created by the effects of microbial activities. Low iodine concentrations observed in rice paddy soils can be explained by this effect.

From the soil-plant system, iodine evaporated as organic iodine. In order to investigate this mechanism, we have performed experiments by using bacteria. It was found that a wide variety of bacteria had capacities for producing methyl iodide (CH$_3$I) and they contributed to the volatilization of iodine from soils and also from seawater. Some kinds of fungi also showed a high ability in methylating iodine. We have also carried out studies on the oxidation and reduction of iodine by bacteria. Iodide-oxidizing bacteria, which oxidize iodide to molecular iodine ($I_2$), were isolated from underground brines containing very high iodide. Oxidation of iodide was found to be mediated by an oxygen-requiring enzyme. Iodate-reducing bacteria, which reduce iodate to iodide, were also found. Our results showed that microbial activities influence the chemical form of iodine, which is important to understand the fate of stable and radioactive iodine in the environment.
D/H of kerogen across the Permian/Triassic (P/Tr) boundary

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One of the most severe mass extinctions of Earth’s history occurred near to the Permian/Triassic (P/Tr) boundary approximately 251 million years ago. Nearly 90% of all marine species and 70% of all terrestrial life became extinct (Benton & Twitchett, 2003). Several stable isotope excursions (δ13Cbiomarkers, δ13Ckerogen, δ34Spyrite) occur near this boundary and suggest a global disruption to carbon and sulfur cycles (e.g. Grice et al., 2005).

Stable hydrogen isotope (δD) data from stratigraphic sequences of kerogen can provide information about changes in palaeoclimate if the kerogens are of comparable type and thermal maturity (e.g. Lis et al., 2006). We present new δD data of stratigraphic series of kerogens from 3 different localities across the P/Tr boundary from Western Australia, East Greenland and Spitsbergen. The insoluble nature of kerogen guarantees that this material reflects in situ geochemical conditions. A dramatic change in δD of kerogen (35 ‰) is evident in several of the sections. The significance of this change along with δD of biomarkers will be discussed in terms of source/facies, paleoclimate and the extinction event.

The kerogen preparation method included demineralisation of solvent-extracted and decarbonated rock samples, heavy liquid separation, a second solvent extraction and final equilibration of the kerogen with isotopically heavy and light water vapours ahead of the on-line TC/EA measurements (Robl & Davis, 1993; Schimmelmann et al., 1999).

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A field-scale study on in situ measurement of microbial activities below the sea floor, Ikeshima, Japan

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We employed the push-pull test (Istock et al., Groundwater. 35(4), 619 (1997)) to determine the possibility of developing a measurement system for studying in situ microbial activities (organic matter degradation, iron and sulfate reducing activities, etc) that result in a change in groundwater geochemistry below the sea floor, Ikeshima, JAPAN. The test solution was prepared from ca. 3000 ml of groundwater with the addition of ca. 10 mmol/l KBr as a tracer, 10 mmol/l Na-lactate, and 10 mmol/l NaNO3. The test solution was injected at a pressure of 0.6 MPa into a borehole ca. 130 m below sea surface level on the Ikeshima island, Japan. The borehole was 2-m deep and 86 mm in diameter, and the working volume was ca. 12000 ml. After the injection, the groundwater in the borehole was mixed with the test solution and extracted at a specified time. During extraction, the pH, redox potential (ORP vs Ag/AgCl), and dissolved oxygen (DO) were measured, and the concentrations of lactate, Br-, and NO3- were determined by an ion chromatogram. Prior to the injection of the test solution, the properties of the groundwater were as follows: pH, 7.8; ORP, −98 mV; DO, 0.6 mg/l; EC, 4.92 S/m; and 25.8°C. After 24 h, the concentrations of lactate and NO3- had decreased drastically, and DO had reduced slightly from 0.6 to 0.2 mg/l. These results reveal that there is a possibility of a microbial effect on the geochemistry of groundwater and the measurement of in situ microbial activities.
In situ observation of radial pyroxene chondrule formation from levitated melts

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Chondrules were crystallized from levitated melts to study the rate of crystallization during cooling. Levitation is known to reduce the heterogeneous nucleation rate considerably and thus highly supersaturated melt become stable for a long time.

The levitation experiments were done by using a gas-jet levitator (Nagashima et al., 2006). MgSiO 3 glass spherule (diameter < 3 mm) was set at the top of nozzle of the gas jet levitator and the melt temperature was kept at a given temperature by adjusting the power of CO 2 laser power. To investigate the seeding effect, enstatite (MgSiO 3) particles, ~ 5 µm in diameter, in the gas flow were forced to be impinged to the surface of the supercooled melt droplet, the nucleation process of which was observed by a high speed CCD camera.

Although we had expected easy homogeneous nucleation from the melt droplets by this seeding, this seeding experiments failed over a wide range of supercooling. Crystallization was found to be possible only at a very large supercooling temperature regime (∆T ~ 260-860K). When the ∆T is less than 260K, neither homogeneous nucleation nor heterogeneous nucleation could be detected. If ∆T is more than 860K, crystallization was impossible because of glass formation.

Typical radial textures from levitated melts (fig. 1) was obtained at ∆T ~ 800K, in which a single nucleation center at surface of the melt was observed. The fact that natural radial textures in chondrule starts from the surface might suggest the impingement of a few cosmic dust particles during the cooling.

Figure 1: (A) In-situ observation of the levitated melt during crystallization. Radial texture was formed at ∆T ~ 800 K. (B) Polarized image of (A).

Crystal chemistry of pumpellyite: Chromium distribution between the octahedral sites

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The crystal structure of a chromian pumpellyite of general formula \( \text{VI}_n \text{H}_8 \text{VI}_n \text{X}_4 \text{Y}_4 \text{Z}_4 \text{O}_{42}(\text{OH})_{13.81} \) from Sarani, Ural, Russia, was refined using X-ray single-crystal data to investigate the crystal-chemical behavior of Cr in pumpellyite.

The chemical composition of the crystal is CaO 21.9, MgO 3.6, total Fe 2O 3 0.2, V 2O 3 0.2, Cr 2O 3 14.6, Al 2O 3 16.3, and SiO 2 35.4 wt. %.

Optical spectroscopic analysis showed the oxidation state of Cr to be trivalent. The crystal structure was refined using 1297 unique reflections that converged to a \( R \) factor of 2.8%. The site populations at the \( X \) and \( Y \) sites were determined by using the observed site-scattering values. Since Mg is only located at the \( X \) site, as confirmed by TOF neutron powder diffraction analysis (Nagashima and Akasaka, in press), it was assigned to the \( X \) site. The crystal chemical formula \( \text{Ca}_6(\text{Mg}_{0.73}\text{Cr}_{1.45}\text{Al}_{0.74})_{23.00}(\text{Al}_{0.55}\text{Cr}_{2.42})_{23.00}\text{Si}_{12}\text{O}_{42.19}(\text{OH})_{13.81} \) results. The Cr amount, derived from the site-scattering values (3.87 apfu), is consistent with that obtained by EPMA analysis (3.85 apfu). Although Cr 3+ is located at both the \( X \) and \( Y \) sites, the distribution coefficient \([\text{Cr}/\text{Al}]^3\) = 4.46 indicates a stronger preference of Cr for the \( X \) site than the \( Y \) site, contrary to the proposal of Ivanov et al. (1981) that Cr 3+ prefers the \( Y \) site. The volume of the \( \text{YO}_6 \) octahedra and the mean \( Y \)-O distance increase with increasing Cr 3+ substitution for Al at the \( Y \) site, which also causes an increase in the \( a \), \( b \), and \( c \) unit-cell dimensions.

However, the volume of the \( \text{YO}_6 \) octahedra and the mean \( X \)-\( O \) distance are not correlated with the site populations of cations at the \( X \) site. Distortion parameters for the \( Y \) site tend to decrease with an increasing mean \( Y \)-\( O \) distance and volume of the \( \text{YO}_6 \) octahedra. This indicates that the \( \text{YO}_6 \) octahedra become less distorted with the expansion of the octahedra through substitution of cations larger than Al.

References


The crystal chemistry of macfallite

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The crystal structure of macfallite (ideally-
Ca₂Mn₃⁺³Si₃O₁₀(OH)₃) from the Keweenaw Peninsula, USA,
was refined by single crystal X-ray diffraction. The
distribution of cations between the three independent
octahedral sites M₁, M₂ and M₃ were determined in order to
investigate the nature of the cation substitutions and the
crystalchemical properties of macfallite and related minerals.
The chemical composition of the macfallite crystal in this
study in terms of oxide wt.% is 33.14 SiO₂, 2.49 Al₂O₃, 0.09
V₂O₃, 35.80 total Mn₂O₃, 0.45 CuO, 0.69 MgO, 20.53 CaO, 0.07 SrO, and 0.03 Na₂O. The structure 
was refined using 1717 unique reflections that converged to a
R factor of 4.2%. The site-populations at the M₁, M₂ and M₃
sites were determined in order to investigate the nature of the cation substitutions and the
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sites were determined in order to investigate the nature of the cation substitutions and the
crystalchemical properties of macfallite and related minerals.

The advantage of studying basalts from intra-transform
spreading centers is that they provide well-defined locations of
melt delivery and crustal formation. Also, magmatism in
fracture zones is not supported by long-lived magma chambers or along-axis transport of melt from other parts of the
spreading system. Thus lavas from fracture zones represent
pre-aggregated melts and their compositions provide insight
into models of melt generation and transport processes
beneath mid-ocean ridges.

Geochemistry of basalts from intra-transform spreading centers:
Implications for melt migration models

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The Quebrada/Discovery/Gofar (QDG) transform fault
system offsets the fast-spreading East Pacific Rise (3°-5°S) by
approximately 400km and is composed of 7 active intra-
transform spreading centers ranging in length from 5 to 70km.
Forty-seven dredges of young intra-transform basalts were
collected from this area and analyzed for volatiles, major and
trace elements.

QDG basalts exhibit varying degrees of differentiation,
which correlate with the estimates of crustal thickness of each
ridge segment derived from gravity models. The incompatible
trace element ratios (e.g., Th/La) of these lavas range
significantly from ultra-depleted to extremely enriched
compositions. Furthermore, the level of enrichment correlates
well with both ratios of volatiles to similarly incompatible
refractory elements (e.g., H₂O/Ce) and indicators of depth of
melt segregation (e.g., Sm/Yb). Overall, the chemical
variation of these basalts is greater than that previously found
in fracture zones (such as Siqueiros and Garrett FZ) and is
similar to the compositional range defined by northern EPR
seamounts.

Models of mantle flow and melt delivery in the QDG
study area predict significantly different compositions and
crustal thicknesses at the various intra-transform spreading
centers. We will test the validity of the different models by
comparing the observed and predicted lava compositions.
Effects of self-consistently-calculated thermodynamic properties in thermo-chemical multiphase mantle convection in a 3D spherical shell

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High pressure and temperature experiments and calculations of the properties of mantle minerals show that many different mineral phases exist as a function of pressure, temperature and composition (e.g. Irifune and Ringwood, 1987), and that these have a first-order influence on properties such as density and elastic moduli (hence seismic velocity). Numerical models of thermo-chemical mantle convection have typically used a simple approximation to treat these complex variations in material properties, such as the extended Boussinesq approximation. Some numerical models have attempted to implement multiple, composition-dependent phases into thermo-chemical mantle convection (e.g. Tackley and Xie, 2003; Nakagawa and Tackley, 2005) and to calculate seismic anomalies from mantle convection simulations based on polynomial fitting for temperature, composition and mineral phase (Nakagawa and Tackley, 2006). However, their linearised treatments are still approximations and may not adequately represent properties including effect of composition on phase transitions. In order to get closer to a realistic mineralogy, we here calculate composition-dependent mineral assemblages and their physical properties using the code PERPLEX, which minimizes free energy for a given combination of oxides as a function of temperature and pressure, and use this in a numerical model of thermo-chemical mantle convection in a three-dimensional spherical shell, to calculate three-dimensionally-varying physical properties. In this presentation we compare the results obtained with this new, self-consistently-calculated treatment, with results using the old, approximate treatment, focusing particularly on thermo-chemical-phase structures and seismic anomalies in the CMB region and the transition zone.

References

Development of chelate resin column preconcentration method for precise isotope analysis of Mo in seawater

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Mo is present nearly conservatively in the modern ocean (~10 ppb). However, Mo is depleted in reducing environments and hydrothermal systems and so on, and such fractionation should be reflected in the Mo isotope composition. In addition, because Mo is an essential element for organisms, biological activity may change the Mo isotope composition. Therefore, precise isotope analysis of Mo in seawater is expected to provide new valuable information, and to be a good tool in geochemical oceanography.

Only a few data have been reported on the isotopic composition of Mo in seawater. More than 50-fold concentration of Mo in seawater is required for isotopic measurement. An ion exchange resin method was used to purify Mo, but this method requires concentrated acid for elution, and may not be able to separate major elements of seawater completely. So, we have newly developed a chelate resin column preconcentration method.

8-hydroxyquinoline (8HQ) bonded covalently to a vinyl polymer resin, TSK-8HQ (Dierssen et al., 2001), was used in a column to concentrate Mo. The sample solution that has been adjusted to pH 2.0 by HCl was passed through the column, and then the adsorbed Mo was eluted by the back flushing of 2 M NH3. To obtain a high concentration factor, the eluate was evaporated to dryness, and Mo was then redissolved in 0.05% tetramethylammonium hydroxide. Mo isotope ratio was measured by MC-ICP-MS (Nu Plasma 500). The mass discrimination effect on Mo was internally corrected by 88Sr/86Sr to be 0.1194 using the exponential law. Individual sample uncertainties (2σ) of this element spike method are 0.03% per amu for 1 ppm Mo.

Mo in 500 mL seawater sample was collected quantitatively. The procedure blank was less than 10-3 times of Mo concentration in seawater. The residual ratio of major elements of seawater in the eluate was less than 10-2, and their matrix effects on isotope analysis of Mo were negligible.

δ88Mo in seawater collected from 697 m depth in Suruga Bay, Japan was 2.49 ± 0.10 (2σ) relative to JMC standard. We will report the vertical profiles of Mo isotope ratio from stations in the western North Pacific Ocean at the presentation.

References
Effects of hydrogen on limits of radiative emission from a planet with a saturated-water-vapor atmosphere

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It is known that there are upper limits of radiative emission from a planet covered with sufficient water (i.e., an ocean). If incoming thermal flux exceeds the limits, extra thermal energy is used to evaporate the ocean, which means that an ocean is unable to exist under such a circumstance. These limits have close relationships with the early evolution and habitability of planets. Since the energy flux from the planet’s surface decreases with time because of cooling of the planetary interior, the limits constrain the timing of ocean formation. Moreover, because the stellar radiative flux decreases with distance from the star, this limits constrain the inner edge of the habitable zone in a planetary system.

Several studies investigated these limits (Komabayashi 1967; Ingersoll 1969; Abe and Matsui 1988; Kasting et al. 1988; Nakajima et al. 1992). However, no study has evaluated the effects of hydrogen on these limits. According to recent studies of the accumulation of the Earth’s atmosphere, the initial Earth is likely to have been rich in hydrogen (e.g., Ikoma and Genda 2006). Furthermore, in extrasolar planetary systems, there might exist hydrogen-rich terrestrial planets.

In this research, we have investigated the effects of hydrogen (e.g., changes in mean molecular weight and opacity) and gravity on the limits by simulating the structure of the atmosphere in the radiative-convective equilibrium. Then we discuss the early evolution of the Earth and the location of the habitable zone in extrasolar planetary system.

References

Chemical composition and behavior of atmospheric aerosols in the mountainous and plain regions of Toyama, Central Japan

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Introduction
East Asia is one of the most troubled regions in terms of atmospheric environment due to its huge population and industrial development. The emission of anthropogenic substances in East Asia has been on the rise due to the use of fossil fuels, industrialization and due to the lack of waste control practices. In particular, it is predicted that NOx emission will increase approximately 5-fold from 1990 to 2020 (Akimoto, 2003). The excessive N loading may have several adverse effects on both ecosystem health and water quality.

The western North Pacific receives a large influx of mineral dust and pollutants from East Asia through atmospheric long-range transport. The Japan Sea is a marginal sea of the western Pacific Ocean and located in a transit zone for the continental air masses traveling to the open North Pacific. The coastal area of Japan Sea is an important area to study the transport mechanisms and modifications to chemical properties of aerosols.

Method
Chemical composition of aerosols and suspendes particle matter (SPM) measurements were conducted at Mt. Tateyama (2450 m a.s.l.) and Imizu (10 m a.s.l.) in Toyama, central Japan, simultaneously from 18 May to 8 June 2006.

The sampling period was about 24 hours and the sampled air volume was from 27.7 to 39.1 m³.

Results
During the observation period, anthropogenic plume were observed. One of these episodes were almost equal nss-SO4²⁻ levels to the urban atmosphere, even in Tateyama.

The mean concentrations of nss-SO4²⁻ and NO3⁻ in Tateyama were 5.37 and 0.59 µg m⁻³, respectively. The concentration of nss-SO4²⁻ was relatively lower than that of Imizu 8.68 µg m⁻³. However, the concentration of NO3⁻ was much lower than that of Imizu (2.93 µg m⁻³). The NO3⁻/nss-SO4²⁻ ratio in Tateyama (0.11) was lower than that of in Imizu (0.34). This is probably because NO3⁻ combined with nss-Ca²⁺ removed from the atmosphere faster than that of nss-SO4²⁻. New particulate nss-SO4²⁻ is expected to form by gas to particle conversation with time.

These pollutants will influence air quality and radiative forcing. To understand the effect of nitrogen deposition to the ecosystems, both wet and dry including gaseous matter measurements are required.

Reference
The mineralogy of Comet Wild-2 nucleus samples – What we think we know and what we do not know

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The sample return capsule of the Stardust spacecraft was successfully recovered in northern Utah on January 15, 2006, and its cargo of coma grains from Comet Wild-2 captured in aerogel tiles has now been the subject of intense investigation by approximately 200 scientists scattered across five continents. We have now performed mineralogical and petrographic analyses of particles derived directly from the Jupiter-family Comet Wild-2.

Numerous particles were collected by impact into low density aerogel. Dozens to thousands of fragments of the impacting particles are distributed along 100 m-1cm-length tracks. So far 52 of these tracks have been harvested, and samples of 26 tracks have been studied in enough detail to give first order views of their mineralogy [1]. The recovered Wild-2 samples are mixtures of crystalline and amorphous materials. However, it is unclear how much of the amorphous material was produced from the aerogel during the particle capture. Crystalline materials are abundant in Comet Wild-2 and many are "coarse-grained" (1-10 \( \mu \)m) relative to the submicrometer scales characteristic of anhydrous IDPs and interstellar dust. Of the best studied 26 tracks, eight are dominated by olivine, seven by low-Ca pyroxene, three by similar amounts of olivine and pyroxene, and the remaining eight are dominated by other minerals, mainly Fe-Ni sulfides. Our emerging model is that many of the impacting particles were very fine-grained, loosely-bound aggregates with a bulk chondritic composition. Most also contain large individual crystals (most commonly) of olivine, pyroxene and Fe-Ni sulfides, similar to chondritic IDPs. Olivine and Low-Ca Pyroxene is present in most Wild-2 particles, with grain sizes ranging from sub-\( \mu \)m to over 10 \( \mu \)m. Wild-2 olivine has an extremely wide compositional range, from Fo1.2-100, with a pronounced peak at Fo99. The wide Mg-Fe compositional range of Wild-2 olivine is similar to both anhydrous chondritic IDPs, and also to matrix minerals of the chondrites Murchison (CM2), and Orgueil (C11), which have experienced extensive, from En45.100, with a significant frequency peak centered at En85.

Reference


Rb-Sr single bed isochron dating with evidence of isotope equilibrium

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Introduction

Sedimentary rocks consist of various components, isotope ratios of which are considered to indicate different ages. If isotopic age determinations of the sedimentary rocks can be carried out, the isotopes had to equilibrate, after sources of them had deposited. It is difficult to verify the isotope equilibrium. Shibata and Mizutani (1982) reported Rb-Sr isochron age of 211 ± 4.7 Ma with initial \( {^{87}}\text{Sr}/\text{Sr}^{86} \) ratio of 0.71325 ± 0.00020 for the Triassic chert, which is younger than the fossil age. They regarded the Rb-Sr age as a diagenesis age. They collected the samples ranging 10 m in thickness. The strata of this thickness is hard to regard to be formed by a single sedimentary event. They didn’t discuss equilibrium of Sr isotopes.

In this study, we used a single layer of the Triassic bedded chert in the Mino belt, central Japan to determine a Rb-Sr isochron age. Conodont fossils, one of the components of the chert, were also separated in order to measure the \( {^{87}}\text{Sr}/\text{Sr}^{86} \) ratio.

Analytical method

The sample was cut parallel to the bedding plain into twelve slices, each of which was used as a whole rock sample. Concentration of Rb and Sr of the slices were determined by a thermal ionization quadrupole mass spectrometer, Finnigan MAT Thermoquad THQ. Sr isotope ratio was measured with a VG Sector 54-30 thermal ionization mass spectrometer at Nagoya University. In case of conodonts, a Ta emitter solution (Brick, 1986) was used to load Sr onto single Re filament with 2M-H3PO4.

Result and Discussion

Rb-Sr isochron age of the chert was 219 ± 22 Ma with the initial \( {^{87}}\text{Sr}/\text{Sr}^{86} \) ratio of 0.7125 ± 0.0020. The Rb-Sr age is indistinguishable from the depositional age (Norian: Sugiyama, 1997) indicated by the radiolarian fossils.

Conodonts in the chert consist mainly of apatite. Apatite contains extremely low content of Rb but rich in Sr. This indicates that the \( {^{87}}\text{Sr}/\text{Sr}^{86} \) ratio of conodonts would not have evolved since the conodonts were deposited. Since conodonts are part of marine organisms, the \( {^{87}}\text{Sr}/\text{Sr}^{86} \) ratio must be same as that of seawater at the time of deposition. The \( {^{87}}\text{Sr}/\text{Sr}^{86} \) ratio of the Triassic conodonts, however, is 0.712211 ± 0.00020 \((^{87}\text{Rb}/^{86}\text{Sr}=0.10) \) and higher than that of Triassic seawater (=0.708), while it is indistinguishable from the initial Sr ratio (=0.7125 ± 0.0020) of the chert. This indicates that the chert layer including conodont fossils are equilibrated in term of Sr isotopes after its deposition. Because the Rb-Sr age is consistent with the radiolarian age, the Sr isotopes were equilibrated just after the sources of chert had deposited.
Noble gases and nitrogen in the Isheyevo CH/CB chondrite
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Metal-rich CH and CB carbonaceous chondrites are known to show characteristic noble gas signatures and nitrogen isotopic compositions [e.g., 1-2]. Noble gases in CHs and CBs are characterized by Ar-rich gases and low \(^{136}\text{Xe}/^{132}\text{Xe} \) ratios (solar wind-Xe like) [1]. In addition, these chondrites have the isotopically heaviest N in chondrites (\(\delta^{15}\text{N} \sim +1000\%\); [2]). In this study, we analyzed noble gases and nitrogen in magnetic fraction (MF) and non-magnetic fraction (NMF) from Isheyevo, which is an unique meteorite consisting of CH-like and CB-like lithologies [3].

Isotopic ratios of He and Ne show that light noble gases in both fractions are dominated by solar and cosmogenic noble gases. Trapped \(^{4}\text{He}/^{20}\text{Ne} \) ratios are about 400 for MF and 170 for NMF, indicative of high retentivity of solar noble gases in MF. Trapped \(^{20}\text{Ne}/^{36}\text{Ar} \) ratio of MF (~5) is lower than that of NMF (28). This can not be explained by preferential loss of solar \(^{20}\text{Ne} \), because of higher retentivity of solar noble gases in MF. It is likely that the low \(^{20}\text{Ne}/^{36}\text{Ar} \) ratio is due to enrichment of \(^{36}\text{Ar} \), i.e., Ar-rich noble gases, which are considered to be fractionated solar wind noble gases [e.g., 4]. In the case of Isheyevo, Ar-rich gases appear to be concentrated in metallic phases (MF).

Xe isotopic ratios in NMF are almost identical to Xe-Q, whereas Xe in MF seems to be the mixture of Q-Xe and solar wind-Xe (SW-Xe). This indicates that SW-Xe is contained in MF. Since MF contains both solar and Ar-rich gases, it is not clear whether SW-Xe is associated with solar or Ar-rich gases. Nitrogen in MF (\(\delta^{15}\text{N} \sim +1230\%\)) is isotopically heavier than that in NMF (+310%). Nitrogen in NMF may be diluted with isotopically “normal” nitrogen (0±50%); [5]).

Acknowledgement
We thank M. A. Ivanova for providing magnetic and non-magnetic fractions of the Isheyevo meteorite.

References

Physicochemical speciation of trace metals during the mesoscale iron enrichment (SEEDS II) in the western North Pacific
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The mesoscale iron-enrichment experiment SEEDS II was conducted near the edge of the subarctic Western North Pacific gyre, where SEEDS I had been carried out [1, 2]. We investigated dissolved and particulate Co, Ni, Cu, Zn, Cd and Pb in seawater from both field observation for 26 days and shipboard incubation with a natural phytoplankton assemblage for 10 days. Discrete seawater samples were filtered through 0.2 µm filter and acidified to pH 2.2 for the determination of the dissolved species by ICP-MS. The filter was used to measure the particulate species by FI-ICP-MS.

Before the iron enrichment, the average concentrations for dissolved Co, Ni, Cu, Zn, Cd and Pb in the surface mixed layer (0-20 m) were 70 pM, 4.9 nM, 2.1 nM, 1.6 nM, 0.48 nM and 52 pM, respectively, and those for the particulate species were 1.7 pM, 0.052 nM, 0.094 nM, 0.46 nM, 0.037 nM and 5.2 pM, respectively. After the enrichment, there was a threefold increase in chlorophyll \(\alpha \) (~3 µg/L) by day 12. However, there was no detectable difference in the dissolved and particulate trace metals between inside and outside the patch. In the shipboard incubation, addition of 1 nM Fe caused a 30-fold increase in chlorophyll \(\alpha \) (~9 µg/L) dominated by Pseudo-nitzschia sp. and increases in the particulate trace metal fraction up to 3-45%. These results suggest that Fe was a limiting factor for the growth of phytoplankton. In addition, enhanced-grazing by mesozooplankton presumably limited the growth of phytoplankton and the transformation of trace metal speciation during the mesoscale Fe enrichment.

References
The Sept Iles mafic layered intrusion: An example of ferrobasaltic differentiation

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The Sept Iles Mafic Intrusion (SIMI) (Quebec, Canada), part of the Sept Iles Intrusive Suite (SIIS), is a 6 km-thick layered troctolite-gabbro intrusion with a funnel shape of 80 km in diameter. The SIIS has been dated at 564 ± 4 Ma [1] and supposedly results from the activity of a mantle plume related to the formation of the St-Laurent rift system. Flood basalts may have erupted before its emplacement [2]. A detailed petrologic study of the SIMI has been undertaken with the aim of better constraining the differentiation of ferrobasaltic liquids [3]. We present here the first results of this study which focus on the possible composition of the SIMI parent magma and on the main structure of this magma chamber.

The exposed part of the SIIS is surrounded by a Border zone of variable thickness made of massive and locally fine grained gabbros. These fine-grained gabbros have high FeOt (up to 15 wt. %) and TiO2 (3 wt. %) contents, moderate P2O5 content (0.35 wt. %) and no Eu anomaly (Eu/Eu* = 0.95). They are typical ferrobasalts very similar to the estimated parent magmas of the Skærgaard [4] and Newark Island intrusions [5]. The composition of liquidus phases obtained with the MELTS algorithm (plagioclase An67, olivine Fo75) perfectly matches the most primitive compositions of plagioclase (An68) and olivine (Fo75) observed in the SIMI. Moreover, the sequence of crystallization experimentally obtained by [5, 6] on samples which are very similar to the ferrobasalts from Sept Iles is in agreement with the sequence of crystallization of the SIMI (plagioclase and olivine, + Ca-rich clinopyroxene, + magnetite and ilmenite - olivine, + apatite). The fine-grained gabbros from the Border Intrusion are thus plausible compositions for the parent magma of the SIMI.

From base to top, the plagioclase composition evolves continuously from An68 to An30, then displays a significant reversal to An30 followed by a new decrease down to An25. The magnetite Cr content displays a parallel evolution. This reversal is interpreted as a new magma influx which is marked by an intraplutonic quench horizon. Other small reversals are observed throughout the Series.

References:

Zircon M257 – A new standard for SHRIMP U-Pb geochronology


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The possibility to determine U-Pb ages from micron-sized areas within single zircon crystals using the SHRIMP technique has opened up new possibilities for detailed studies of the history of crustal rocks and constraining their ages. This technique, however, depends on the availability of well-characterized, natural reference materials (Kennedy, 2000). We propose a gem-quality zircon (Univ. Mainz sample no. M257) as a future SHRIMP U-Pb zircon standard.

Zircon M257 is a pale brown, clear stone with a weight of 25.7 ct [for comparison, SHRIMP standard CZ3 (Pidgeon, 1997), which has been used for more than ten years, had a weight of only 4.5 ct]. M257 is remarkably homogeneous; no internal zoning at all was found using CL imaging, transmitted light microscopy and Raman line-scanning. Its comparably high actinide concentrations (U, 810 ppm; Th, 224 ppm) will account for high U and Pb count rates. Preliminary TIMS analyses (done in Giessen, Santa Barbara and Oslo) indicate a concordant U-Pb age of ~562 Ma. Unit cell dimensions (a0, 6.626 Å; c0, 6.030 Å) and Raman parameters {e.g., FWHM[ν3(SiO3)], 11.8 cm−1} correlate very well with the calculated time-integrated alpha dose of 1.66 × 1018 α/g (compare Nasdala et al., 2004). This and the (U+Th)/He age (419 ± 9 Ma), which is consistent with previous helium ages for zircon from Sri Lanka, allow us to exclude any heat-treatment. Further characterization of the isotopic composition of sample M257 is in progress.

References
Deficient electron microprobe totals: Discussion of potential causes

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Radiation-damaged minerals, including zircon, coffinite, thorite and monazite, are occasionally found to yield electron microprobe results whose totals (oxide sums) are deficient, i.e. appreciably below 100 wt%. Causes of the apparently too low totals are controversial; most authors have assigned the phenomenon to enhanced contents of hydrous species, other non-analyzed elements, textural peculiarities such as voids, or instability and degradation under the electron beam. It has also been observed that micro-areas yielding low totals are typically recognized from very low BSE intensities (Kempe et al., 2000), which is in apparent contradiction to their usually high degree of radiation damage and the positive correlation between radiation damage and BSE intensity (Nasdala et al., 2006).

We have studied low-totals zircon from three localities. Deficient totals and accompanying very low BSE intensities are only detected in areas affected by secondary alteration whereas primary zircon never shows these phenomena. The alteration has often, but not always, led to enhanced actinide content, which is why low-totals areas are mostly radiation-damaged. Low-totals areas were found to contain up to 5 wt% hydrous species, which explains both the deficient analysis sums and the low BSE intensity (due to decrease of the average atomic number). In the TEM, low-totals areas show a sponge-like texture with numerous sub-micron sized voids, as it was suggested by Pointer et al. (1988). We explain the formation of this texture and the water uptake by secondary, fluid-driven alteration of previously radiation-damaged and thus volume-expanded zircon.

References

The first record of allochthonous kimberlite within the Batain Nappes, Eastern Oman

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Kimberlites, carbonatites, alkaline and ultramafic lamprophyres and other alkaline ultrabasic rocks have been recently discovered within the Batain Nappes in the eastern Oman Mountains. The Kimberlite area comprises several allochthonous bodies. Most of these are carbonatite and carbonate kimberlite which contains mantle derived (altered peridotitic) xenoliths and xenocrysts. The kimberlite occurs either as breccia pipes and/or as long dykes ~ 6 km long. The kimberlites contain abundant macrocrysts of mica (phlogopite and/or biotite), chromite, chrome diopside, pelletal lapilli and autolithic clasts in a calcite + serpentine matrix. The kimberlites are dominantly composed of ‘hapabbyssal and diatreme facies’ volcaniclastic rocks. These include pyroclastic lapilli-, carbonate-dominated tuffs, and volcaniclastic kimberlite, all of which intruding late Jurassic to Lower Cretaceous marine sedimentary rocks (cherts and shales) of the Wahra Formation, within the Allochthonous Batain Melange. Major and trace elements and isotopic composition indicate that the Omani kimberlites in this study form a compositionally cohesive group of rocks more akin geochemically to the Koidu type kimberlites of West Africa than the Group I kimberlites from South Africa. The kimberlite contained zircon, G9 garnet and chromite grains with typical kimberlitic morphologies and chemical properties similar to diamond inclusion chromite. However, there were no micro-diamonds observed.

Fifteen pinkish (‘kimberlitic’) zircon grains, 0.5 to 1.5 mm in size, were picked from the kimberlite tuff and were analyzed at GEMOC. Trace-element patterns are typical of kimberlitic to carbonatitic zircons. Their mean age of 137.5 ± 1 Ma (95 % confidence,MSWD = 0.49) is consistent with intrusion into Lower Cretaceous rocks. Their $^{176}$Hf/$^{177}$Hf (0.28286±1, $\varepsilon_{Hf}$ = 6.2) is typical of kimberlitic zircons of this age, and may represent the subcontinental lithospheric mantle.
Is the isotope composition of Reunion plume really homogeneous?

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Réunion Island, Indian Ocean, is the present signature on the Earth surface of the Réunion hotspot. The island is composed by two volcanoes: the inactive Piton des Neiges and the active Piton de la Fournaise. The isotope compositions of Réunion lavas are usually described as homogeneous. This homogeneity is remarkable compared to other hotspot volcanism. However, a fine study of the Réunion database reveals that the large majority of the available data comes from analyzed lavas produced by Piton de la Fournaise. Furthermore, the few available Pb isotope data have been published before 1972. Consequently, the apparent homogeneity of Reunion lavas is potentially due to analytical or sample bias.

With the intention of testing this homogeneity, we have recently sampled the Piton des Neiges. The sample collection (n=47) covers temporally and geographically this volcano.

Taking advantage of recent analytical development, Pb isotope compositions were measured using a MC-ICP-MS (Neptune) and mass fractionation is corrected using a Tl spike. The Pb isotope composition range from \(206\text{Pb}/\text{204Pb}: 18.79-18.90\), \(207\text{Pb}/\text{204Pb}: 15.56-15.60\) and \(208\text{Pb}/\text{204Pb}: 38.79-39.04\). These ranges overlap those given for the Piton de la Fournaise \(\text{206Pb}/\text{204Pb}: 18.55-18.91\), \(\text{207Pb}/\text{204Pb}: 15.58-15.65\) and \(\text{208Pb}/\text{204Pb}: 38.74-39.01\) from 71 samples). Based on these preliminary results, we suggest that lavas from both volcanoes plot on same lines in Pb isotope spaces. However, it seems that Piton des Neiges lavas might extend Pb isotopes ranges given for Reunion plume.

Pb isotopes and trace element concentration analyses currently in progress will help further constrain the geochemical composition of the Piton des Neiges, the chemical structure of the Réunion hotspot and the influence of the Reunion hotspot on the regional magmatism.

Influence of porosity on basalt weathering rates from the clast to watershed scale

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Production of saprolite from bedrock is an important source of both mineral detritus and dissolved ions. The rates at which saprolite is produced have far reaching impacts on important processes such as global flux of dissolved material to oceans, nutrient cycling in soils, sedimentation that ultimately leads to oil and gas generation, and the fate of atmospheric CO\(_2\) over geologic time scales. Despite their importance, saprolite production rates cannot currently be predicted. In low porosity rocks, like basalt, rates of saprolite production are dependent upon the ability of water to infiltrate the parent rock. Fracturing of these rocks by either physical or chemical mechanisms is one way of increasing available water. However, not all rocks fracture during weathering and in these systems porosity can be enhanced through the dissolution of primary phases.

We are currently using weathering rinds developed on unfractured basalt clasts as a natural system where we can study processes and rates of saprolite formation over long time periods (35-250 ka). Across a weathering interface approximately 2 mm wide parent basalt weathering to form saprolite that is completely depleted in Ca, Na, Si and Mg. Associated with the weathering is an increase in porosity from 3-50%. Theoretical calculations of diffusion limited weathering predict that the weathering rind will grow as a function of the square-root of time \((t^{0.5})\). However, these calculations are for constant porosity systems and many studies of weathering rinds indicate a \(t^{0.8}\) dependence. By including dissolution enhanced porosity in reactive transport models of the basalt clasts, we are able to predict both the geometry of the weathering interface and time dependence of rind formation.

Given similar lithology and climate, the knowledge we have gained by studying saprolite production on basalt clasts should provide insight into weathering of basalt watersheds. However, making comparisons between watershed denudation rates and weathering rind advance rates is complicated due to the difference in methods used to measure surface area. We compare weathering advance rates (\(\text{mm yr}^{-1}\)) calculated from laboratory, clast, soil profile and watershed studies using fractal theory in an attempt to reconcile basalt weathering rates across scales.
**The impact of subducting sediment on the HFSE budget of arc-related igneous rocks, Banda arc, Indonesia**

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Subduction processes and associated arc volcanism play a key role in determining the chemical composition of continental crust. The contribution of subducting sediment to arc magmatism is still poorly constrained but potentially accounts to a significant extend for the HFSE budget of arc-related igneous rocks. The Banda arc in Indonesia has a unique geologic setting that allows HFSE behaviour in a subduction zone to be studied. The amount of subducting sediment being dumped into the subduction regime increases from NE-SW from 0.1 to 5 wt.% [1]. Samples collected along the arc front, well defined for their Nd-Pb-Sr-O isotopes and trace elements [2,3], are analyzed for their Hf isotopes and HFS element concentrations. Hafnium isotope data, ranging from $-3.4 \epsilon_{\text{Hf}}$ to $+13.0 \epsilon_{\text{Hf}}$, and negative-correlated Hf-O isotope co-variations support the increase in sedimentary influx. The Hf isotope data are systematically decoupled from Nd isotopes, most likely due to partially enhanced fluid-melt mobility of LREE. Zr/Hf exhibit no variation with Th/Yb, which points to no significant decoupling of Zr from Hf with elevated amounts of subducting sediment. In contrast, Nb/Yb is significantly elevated with Th/Yb, pointing to enhanced Nb concentrations with increasing sediment subduction. High precision Nb/Ta data will be used to monitor variations in HFSE caused by sediment subduction and potential residual mineral phases.

**References:**


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**Tracing Earth’s first crust with Hf isotopes in zircons from the Narryer Gneiss Complex, Australia**

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Witnesses of the infant crust on Earth are rare because no rocks that formed in the first 500 Myrs are preserved and the only remnants of Hadean material are zircon crystals that survived reworking of their host rocks. In order to unravel the evolution of the Earth’s oldest crust, Archean and Hadean detrital zircons from the Mt. Narryer Gneiss Complex were investigated for their U-Pb and Lu-Hf isotope systematics. The U-Pb systematics of six zircons from the Meeberrie Gneiss define an upper concordia intercept age of 3300 Ma and two lower intercepts at ~ 500 Ma and 700 Ma, which we interpret as the formation ages of the gneiss protolith and later thermal overprints, respectively. Corresponding $\epsilon_{\text{Hf}}$ range from -8.6 to -11.2. Eight zircons from a metasediment from Mt. Narryer show ages from 3.2 to 4.2 Ga with corresponding $\epsilon_{\text{Hf}}$ of +3.4 to -2.9. The age distribution and corresponding initial Hf isotopes indicate similar source regions for the Mt. Narryer metasediments and Meeberrie Gneiss. Older (>3.8 old) grains from Jack Hills and the Mt. Narryer metasediments origin from sources that already formed in the Hadean. The combination of these new data with published zircon data, indicate that crustal growth during the first 500 Myrs occurred more or less continuously by formation of small crustal domains.
Trace element partitioning in the granulite facies

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Granulites from Central Finland experienced pT-conditions of 800-950°C at 9-11 kbar during a major collisional event in the late Archean. Anatectic was induced by dehydration melting of amphibole leading to the formation of cpx, opx, garnet and tonalitic melts. We constrained granulite facies trace element distribution by in situ LA-ICP-MS studies of the principal mineral phases. Our analyses indicate that equilibrium was attained between most phases. Garnets grew in microdomains and only equilibrated with their immediate surrounding. Hence, garnet exerts limited control on the bulk partition coefficient. Accessory phases are important hosts of REE (apatite), HFSE (ilmenite) and transition elements (ilmenite, magnetite).

Using predictive models, comparisons with published data and relationships between minerals and observed melt compositions, we formulate $D_{\text{mineral/melt}}$ values that are applicable for trace element modelling under lower crustal conditions; these are broadly similar to magmatic values for intermediate melt compositions. Uniform $D_{\text{mineral/cpx}}$ for the REE were integrated into the set of $D$-values so that

$$D_{\text{mineral/melt}} = 3 \times D_{\text{amph/cpx}}$$

We provide the first self-consistent set of $D$-values for Sc, V, Cr and Ni between cpx, amph, grt, opx, bt and ilm:

<table>
<thead>
<tr>
<th></th>
<th>$D_{\text{mineral/cpx}}$</th>
<th>$D_{\text{mineral/melt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cpx</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>grt</td>
<td>0.8-1.2</td>
<td>11-12</td>
</tr>
<tr>
<td>amph</td>
<td>0.15-0.25</td>
<td>1.0-3.0</td>
</tr>
<tr>
<td>opx</td>
<td>0.15-0.25</td>
<td>1.0-3.0</td>
</tr>
<tr>
<td>bt</td>
<td>0.15-0.25</td>
<td>1.0-3.0</td>
</tr>
<tr>
<td>ilm</td>
<td>0.15-0.25</td>
<td>1.0-3.0</td>
</tr>
</tbody>
</table>

Ilmenite was found to strongly influence the distribution of Nb and Ta and has partition coefficients an order of magnitude higher than amphibole. Thus, ilmenite has to be considered in future discussions about the role of melting of amphibole-bearing source rocks as the driving mechanism for Archean crust generation.

Geochemistry of I-type granodiorite and tin-bearing S-type granites from Gouveia area, central Portugal

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The Gouveia area is located in the Iberian Massif, which is a large segment of the European Variscan Belt. Granitic rocks intruded a Cambrian schist-metagraywacke complex and predate the area. SHRIMP U-Pb zircon age for a peraluminous biotite I-type granodiorite is 481.8±5.9 Ma. So, it was emplaced during the Early Ordovician. The granodiorite has ($^{87}\text{Sr}/^{86}\text{Sr})_{\text{ Initial}}=0.7036$, $\varepsilon_{\text{Nd}}(482)=2.5$ and $\delta^{18}\text{O}=8.84\%$, which indicate that it contains a mantle component.

Seven peraluminous two-mica S-type granites are Variscan, as SHRIMP U-Th-Pb monazite ages range from 288 to 304 Ma and record granite emplacement. They have average Sn contents of 16-40 ppm. Most granites define individual fractionation trends, have REE patterns that intersect each other and distinct initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.7086 to 0.7129 and $\delta^{18}\text{O}$ values of 10.34-13.34 %o and represent different pulses of granite magma. Their zircon core ages range from ~300 to 2100 Ma suggesting that these granites were derived by partial melting of sediments having a range of sources. Granites contain zircon cores similar in age to the granite.

One of these granites and another granite define a sequence shown by fractionation trends for major and trace elements of granites and their micas, subparallel REE patterns of granites and a common whole-rock Rb-Sr isochron. Least square analysis of major elements and modelling of trace elements indicate that the younger granite is derived from the older granite by fractional crystallization of quartz, plagioclase, biotite and ilmenite. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and $\delta^{18}\text{O}$ values increase from the older to the younger granite suggesting that fractional crystallization was accompanied by assimilation of metasedimentary materials. Fractional crystallization was the mechanism responsible for the increase in Sn content in individual granites, sequence and their micas, but it is crucial that the granite melt contains at least 8 ppm Sn. Muscovite retains a higher granite tin content than biotite does.

Cooling $^{39}\text{Ar}/^{40}\text{Ar}$ plateau ages of micas through the Ar closure temperature range from 285 to 293 Ma. There is no significant difference between these ages if errors are taken into account. When the four youngest S-type granites were emplaced at 288-290 Ma, I-type granodiorite emplaced at 482 Ma and the three oldest S-type granites emplaced at 301-304 Ma were affected by the Saalian Variscan movements and their mica $^{39}\text{Ar}/^{40}\text{Ar}$ ages record recrystallization or Ar loss. Trace elements of biotite from the I-type granodiorite were affected, while trace elements of micas from the three oldest S-type granites define individual fractionation trends.
Improved U-(Th)-Pb dating of monazite by ion microprobe: Correcting for an isobaric interference of PrP04 on 204Pb

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High U and Th abundances, resistivity to diffusion and resilience to weathering make monazite one of the most important minerals for U-Th-Pb dating. Chemical characteristics (e.g. Y content, REE pattern) can be used as indicators of monazite growth reactions, and allow correlation of age data with metamorphic, magmatic or hydrothermal processes.

It has been noted that ion microprobe analysis of Th-rich monazite can yield discordant Pb-U and Pb-Th dates (e.g. Stern & Berman 2000; Zhu & O'Nions 1998), or may show excess scatter on the 207Pb/206Pb dates. Both effects compromise the analytical accuracy and the geological interpretation. These effects may be attributable to matrix effects, i.e. subtle crystallographic differences may result in different ablation and Pb/U characteristics of unknowns and the monazite inter-element fractionation standard used during SIMS analysis. In comparison to zircon, commonly occurring monazite cover a much wider range of chemical compositions.

To evaluate the effects, we have systematically studied a suite of monazite reference materials with a range of chemical compositions, from the brabantite (CaTh(PO 4)2) as well as the huttonite (ThSiO 4) solid solution series, and with varying Yttrium content. Independently determined age data exist for all these materials from TIMS measurements.

We propose that the observed excess scatter on the 207Pb/206Pb ratios results from an isobaric interference of PrP04 on 204Pb that has so far been ignored in ion microprobe data reduction and correction procedures. Using a correction based on the La/Ce counts, routinely measured in monazite analytical session on SHRIMP, and extrapolating to Pr, a correction can be applied before further corrections for Th-related “excess 204Pb are applied. Our correction routine has been built into the recent version of CONCH, a visual Basic program for processing of ion-microprobe analytical data developed by Nelson (2006).

Acknowledgements

Thanks to N. Rayner, D. Upadhyay, J.W. Boyce, A. Kennedy and P.D. Kinny for donating material, to D. Rhede and E. Thern & A. Frew expert help on the EPMA and SHRIMP, respectively.

References

Heterogeneity of MORB composition along the eastern part of the Southwest Indian Ridge

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Regional variations of basalt compositions from the eastern part of the Southwest Indian Ridge (SWIR) were shown by Natland (1991), Meyzen et al. (2003) and Robinson et al. (1996). However, the definitions for the regional variation along the SWIR are different from each other in above studies. We have analyzed major and minor element compositions (including REE) of basalts obtained from 55E to 70E along the SWIR. In this study, We discuss for the regional variation based on our result and PETDB.

We defined from 55E to Rodriguez Triple Junction (RTJ) into 4 areas; Area I: 68E to RTJ (70E), Area II: 60E to 68E, Area III: 57E to Melville F. Z. (60E), Area IV: 55E to Atlantis II F. Z. (57E). The basaltic rocks from Areas I&IV, II and III show different trends, indicating that they were not derived by simple fractional crystallization, but also by a different degree of partial melting.

The basalts of Areas I &IV show a N-MORB-like REE pattern, while those of II show enriched pattern in LREE. However, the compositions of Area III basalts are intermediate--both in REE pattern and Na$_2$O contents.

We conclude that enriched source in terms of LREE and Na$_2$O exists under Area II. Whereas Area I & IV are underlain by N-MORB-like source. The intermediate composition in Area III may be explained by mixing between enrich source and N-MORB source. It is noted that the enriched source of Area II is completely distinct from E-MORB signature.

References

Boron influence on biochemical reactions in natural zeolites

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The special zeolitic characteristics such as cation exchange, molecular sieve capacity, open crystal framework and reversible dehydration make them interesting in many aspects. They may be used as absorbents for pollutants in the agricultural and environmental industry, fertilizers and in the treatment of nuclear wastewaters. Another use is to investigate their role as catalysts or adsorbents of organic compounds in their crystal channels, which provide a protected microenvironment for chemical reactions. Adsorbance of labile biomolecules onto the zeolite crystal tunnel walls may stabilize and therefore trigger their readiness to further react, possibly in polymerization reactions.

It has also recently been shown that borate minerals stabilize ribose, a highly thermo-labile pentose, by forming complexes. Even synthesis of pentoses is possible in the presence of borate. Thus, boron containing minerals may have been important in the development of larger biomolecules on the early Earth.

In our project, we are going to do gaseous and aqueous adsorption tests on natural zeolites, with and without boron in their crystal structure. In some of our material, boron has substituted for beryllium and possibly silica in the zeolitic crystal framework. The combination of the microenvironment given from the zeolite and the stabilizing properties of boron may be ideal for some organic reactions. Until now, most adsorption tests have been made on synthetic zeolites for industrial usage. Natural zeolites will provide a better analogue to actual earthly systems than synthetic ones.

Reference
Mo isotopes in modern euxinic environments: Water column and sediment data

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The present study investigates the pathways of molybdenum (Mo) scavenging under euxinic conditions following the fractionation of stable Mo isotopes in three modern settings: The Black Sea, the largest permanently euxinic basin, and two anoxic troughs of the Baltic Sea. Water column profiles, as well as surface sediment samples, were recovered from different water depths and analyzed for the concentration and isotopic composition of Mo, besides other geochemical parameters.

Mo is a redox-sensitive trace metal which is soluble as the molybdate oxyanion in oxic seawater with a residence time of about 800 ka. The isotope signature of Mo is a relatively new proxy used to reconstruct the paleo-redox conditions of the Earth’s atmosphere and the oceanic system. The Mo isotope composition in seawater is homogeneous, as shown by [1]. Scavenging of Mo under euxinic conditions is related to the amount of free H2S. Near total removal of Mo from the water column is reached at a H2Saq concentration of 11±3 µM [2]. In the Black Sea this corresponds to a water depth of about 400 m. Sediment samples of the Black Sea from more than 400 m water depth show seawater isotopic composition, agreeing completely with the assumption of bulk Mo removal. However, shallower sediments deposited under lower H2S concentrations show significant Mo isotope fractionation.

Brackish Baltic Sea surface sediment samples are taken from two separate basins, the Gotland Deep and the Landsort Deep which have maximum water depths of 248 m and 459 m, respectively. The Baltic Sea oceanographic conditions, including temporary bottom water oxygenation due to sporadic North Sea water inflows, are more complex than in the Black Sea. The dissolved sulfide concentrations in the water column are less than 50 µM and the salinity is less than 22 PSU. In the anoxic part, Mo isotope signatures are shifted towards heavier values indicating in-situ fractionation upon scavenging under euxinic conditions. The surface sediments are the sink for reduced Mo and show Mo fractionation similar to the oxic to slightly euxinic sediments of the Black Sea. Intra-basinal differences and downcore variations can be explained by changes in the bottom water redox conditions due to episodes with different inflow intensities and reflect varying concentrations of dissolved sulfide in the water column.

References

Extremely refractory oceanic lithospheric mantle and its implications for geochemical mass balance

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In several ocean islands (e.g. the Canary Islands, Kerguelen, Cape Verde and Savai‘i) the mantle xenoliths population is dominated by extremely refractory spinel harzburgites. These harzburgites (OI1) show no petrographic evidence of metasomatism, and carry no primary clinopyroxene. However, minor metasomatism may be reflected in the incompatible trace elements and radiogenic isotopes. The major element and modal compositions of the OI1 harzburgites correspond to residual mantle formed from a primordial source after 25-30% partial melting, leaving a clinopyroxene- and garnet-free residue. These peridotites are, on average, significantly more refractory than MOR peridotites. Estimated P-T conditions (850-1200°C and 0.7-1.3 GPa) indicate that the OI1 peridotites last equilibrated within the abyssal mantle lithosphere. Their textures and high solidus temperatures imply that their strongly refractory nature cannot be the result of processes (“additional” partial melting or melt – wall-rock reactions) associated with the present plumes. Although interaction with plume melts has caused minor enrichment in radiogenic isotopic ratios and the most strongly incompatible elements, their original (pre-ocean-island) compositions are preserved in the most abundant major elements and in the modal relationships. Highly refractory OI1 spinel-harzburgites have higher solubility than more fertile, clinopyroxene-bearing peridotites, and are likely to be resistant to further partial melting. We interpret the OI1 peridotites as fragments of recycled, “sterile” asthenospheric material that have been trapped in the abyssal mantle lithosphere. These peridotites imply that the convecting mantle includes material that is significantly more refractory than MOR peridotites. The OI1 peridotites are buoyant relative to less refractory, denser mantle material and may preferentially accumulate at the top of the convecting mantle, where they freeze to the base of newly formed abyssal lithosphere.
Distribution and redox status of Arsenic in framboidal pyrite from estuarine sediments


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Synchrotron μXRF measurements of 106 μm-sized pyrite framboids from anoxic sediments of the Achterwasser lagoon, a part of the estuarine system of the river Oder, SW Baltic Sea, show highly variable As concentrations ranging from 6 to 1140 μg/g within the uppermost 50 cm of the sediment column. Even within a single depth layer, the As concentration of different framboids vary greatly with no clear depth trend visible. Median values calculated from μXRF data for each depth layer are similar to the chemical extraction data (28 to 143 μg As per g pyrite), suggesting that the applied extraction procedure yields realistic average As concentrations in pyrite from bulk sediment. Pyrite can account for 9 to 55% (average 22%) of the total As budget of the sediments indicating that authigenic pyrite plays an important role in the geochemical cycling of As in coastal sediments.

High-resolution μXRF mapping of single pyrite grains shows that As is distributed inhomogeneously within larger framboids, and more regularly in the smaller pyrite grains. This may be due to changing pore water composition during pyrite growth, with larger and older framboids being subjected to more frequent changes in the pore water composition as compared to the smaller and younger framboids from the same depth layer.

XANES spectra indicate that a considerably part of As is present in higher valence state (+III+/V) in samples from near the sediment/water interface. This can be explained by frequently occurring resuspension of the surficial sediments to the oxic water column due to wave action and subsequent re-deposition. This process might be responsible for adsorption of As(V) oxyanions onto pyrite. Reduced As(-I) species become more important in the deeper samples, reflecting decreasing redox potential and increased time since deposition. This suggests that adsorbed As(V) and As(III) species will be reduced by the sulfidic pore waters prior incorporation during pyrite growth.

Degassing of oceanic H2S and its delivery to terrestrial ecosystems during the Permo-Triassic extinction

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Evidence is growing that drastic changes in the oceanic sulfur cycle were intimately linked with the greatest extinction of the Phanerozoic at the Permo-Triassic boundary. Isotopic changes in proxies for seawater-sulfate suggest the transformation of a significant portion of the marine sulfate reservoir to dissolved sulfide by bacterial sulfate reduction during the late Permian (Newton et al., 2004). Rapid return to 34S depleted sulfite at the extinction level can be explained by ocean overturn and re-oxidation of this sulfide, providing a kill mechanism in the form of H2S poisoning. Modelling using end-Permian boundary conditions permits the escape of this sulfide from the surface of the ocean (Kump et al., 2005), so ocean overturn and sulfide release could therefore link the marine and terrestrial extinctions which are closely spaced in time. Here we present new results from lacustrine sediments from north-west China, and re-interpret existing results from South Africa (Maruoka et al., 2003). Sulfate concentrations in freshwater lake systems are low when compared to supplies of reactive Fe and organic matter. Hence, sulfate is often quantitatively reduced and preserved as pyrite in lake sediments, recording the isotopic composition of the original sulfate.

Isotope data from both localities record relatively stable backgrounds (δ34S between -4 to +5‰, China, and 0 to +5‰, South Africa), within the normal range for weathered sulfate from large geologically diverse catchments. Close to the P-Tr boundary these stable records are interrupted by rapid negative shifts to around -12%δ34SVPDB (both locations).

These excursions could not be caused by inputs of volcanogenic sulfur (δ34S -5 to +5‰), and provide the first direct evidence of transfers of oceanic derived H2S to terrestrial ecosystems. The exact role of H2S in the terrestrial extinction is unclear. Possible mechanisms include direct poisoning, acidification, or as part of an ozone depletion scenario, leading to radiation exposure (Lamarque et al., 2007).

References
Isotopic evidence for Uranium retardation in zeolitic rocks at Yucca Mountain, Nevada

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Retardation of radionuclides by sorption in the nonwelded tuffs below the proposed high-level nuclear waste repository in the unsaturated zone at Yucca Mountain, Nevada, is a positive attribute of the natural barrier. Alteration of volcanic glass in these tuffs produced thick, widespread zones of zeolite- and clay-rich rocks with high sorptive capacities. The alteration of glass to zeolites, however, was accompanied by reduction in the matrix porosity and permeability causing most flow to occur through fractures, which may have decreased the overall effectiveness of radionuclide retardation in the zeolitic rock matrix.

Chemical and uranium-series isotopic compositions were measured in samples of unfractured and rubble rock from core, surfaces of natural fractures in the core, and in rock leachates and pore water extracted from these core samples. Uranium concentrations in sodium acetate leachates indicate that the mobile $^{238}$U is 0.3 to 1.7 percent of total $^{238}$U in rock samples and allow estimates of the time-integrated in situ U distribution coefficient $K_d$ ($K_d=C_{\text{solid}}/C_{\text{water}}$, where C is concentration). Use of median U concentrations in pore water that the mobile $^{238}$U is 0.3 to 1.7 percent of total $^{238}$U in rock matrix.

Samples of rock from unfractured core, rubble core, and fracture surfaces have similar $^{234}$U/$^{238}$U activity ratios (AR) ranging from 0.92 to 1.16, indicating both enrichments and depletions in the daughter $^{234}$U relative to the parent $^{238}$U. In contrast to the rock, all pore water and rock leachate samples have elevated $^{234}$U/$^{238}$U AR ranging from 1.1 to 5.2. The chemical and isotopic data indicate that the matrix in zeolite- and clay-rich rocks is capable of exchanging uranium with $^{234}$U-enriched percolating water and that retardation of radionuclides can occur in altered rocks below the proposed repository.

Weathering of Ca- and P-bearing minerals by fungi in a northern hardwood forest

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In many ecosystems, mineral weathering is the initial source of calcium and phosphorus, both of which are essential nutrients for plants. Mycorrhizal fungi are symbiotically associated with tree roots and exude organic acids that enhance mineral dissolution and transfer nutrients to trees (e.g., Jongman et al., 1997). Understanding this process in forests of the northeastern USA is important because acid deposition has increased Ca leaching from Ca-poor soils such as those with granitic parent material.

To test the role of fungi in weathering of Ca- and/or P-bearing minerals, mesh bags containing quartz (as a control), quartz plus 1% wollastonite (CaSiO₃), or quartz plus 1% apatite (Ca₅(PO₄)₃(F) were buried in mineral soil beneath American beech (Fagus grandifolia Ehrh.), sugar maple (Acer saccharum Marsh.), and mixed spruce and basalm fir stands (Picea rubens Sarg. and Abies balsamea L.) at the Hubbard Brook Experimental Forest, New Hampshire, USA. A 50-µm mesh size was chosen to exclude roots but allow fungal hyphae to enter the bags.

Microbial community composition and biomass in the mesh bags and surrounding soil were characterized and quantified using phospholipid fatty acid (PLFA) analysis. Fungal biomass (estimated as moles of fungi-specific PLFA 18:2ω6 and 18:1ω9c) in the soil and control bags did not differ significantly among stand types. In contrast, the degree of fungal colonization in apatite- and wollastonite-amended bags varied significantly with stand type. In the beech stands, fungal biomass was significantly greater in the apatite-amended bags, suggesting that apatite dissolution stimulated fungal colonization. In the spruce-fir stands, the fungal biomass did not vary as a function of the mineral assemblage, suggesting that the natural supply of Ca and P in these stands is high enough to meet nutrient demands. In the sugar maple stands, fungal biomass was significantly lower in the wollastonite-amended bags relative to the control and apatite-amended bags. The different response in each stand type appears to be related to the type of fungi present as well as the nutrient status of the soils. These results are important for evaluating nutrient demands of vegetation, and the effects of microbial community composition on the mineral dissolution of Ca and P-bearing minerals.

Reference
H$_2$O diffusion in rhyolite at 1-2 GPa

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Water diffusion in silicate melts is crucial for understanding various volcanic processes, including bubble formation and growth, magma degassing, and magma fragmentation. H$_2$O diffusivity in rhyolite were previously measured at 0.1-810 MPa (Zhang et al., 1991; Zhang and Behrens, 2000). To better constrain the pressure effect on H$_2$O diffusion, we conducted diffusion-couple experiments at 407-1629°C and 1-2 GPa in piston-cylinder apparatus. After experiments, samples are doubly polished to ~200 µm thickness, and H$_2$O concentration profile along the centerline is measured using FTIR microscope.

Compared to Zhang and Behrens (2000), H$_2$O diffusivity at 1-2 GPa increases less rapidly with water content. H$_2$O diffusivity in rhyolite melt decreases from one atmosphere to 2 GPa, and such negative pressure effect is more remarkable as the temperature decreases, which leads to a larger activation energy at higher pressure. If the model of Zhang and Behrens (2000) at <2 wt.% water content is extrapolated to 2 GPa, the prediction results in roughly the same activation energy, but the predicted diffusivity is systematically lower than our measurements by a factor of about 3, which suggests a smaller pressure effect and therefore a smaller activation volume. By combining previous data and our measurements and assuming total H$_2$O diffusivity is proportional to total H$_2$O concentration, a new H$_2$O diffusivity model at <2 wt.% water contents and 0.1-2000 MPa has been constructed, which better constrains the pressure dependence. We are also developing a general H$_2$O diffusivity model applicable to higher water contents and 0.1-2000 MPa.

References

The accuracy of $\delta^{11}$B measurements of foraminifera

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The pH of seawater reflects the speciation of dissolved carbon and hence also, in part, the extent of the partitioning of carbon dioxide between the oceans and atmosphere. Reconstructions of past seawater pH therefore allow investigations of, for example, the concentration of CO$_2$ in the past and the mechanisms of glacial-interglacial CO$_2$ change.

A number of contributions have demonstrated that the boron isotopic composition of marine carbonates, such as foraminifera, record the pH of the seawater in which they grew. Sample size requirements have led to most workers measuring the small amounts of boron in foraminifera by negative-ion thermal ionisation mass spectrometry (NTIMS), which has very high ion yields. What is more, this technique uses the Ca (plus trace metals) of the dissolved marine carbonate as an activator, requiring no additional purification and/or concentration of boron, which greatly simplifies the approach. We show here, by a comparison between the $\delta^{11}$B of samples and solutions measured by both total evaporation NTIMS and multicollector inductively coupled plasma mass spectrometry (MC-ICPMS), that this latter feature, although seemingly advantageous, results in a significant bias in the $\delta^{11}$B measurement by NTIMS.

We conclude that organic carbon, probably hosted within the foraminiferal shell and hence inadequately oxidised during cleaning, has a detrimental and variable effect on the thermal ionisation of boron. This effect does not necessarily relate to the presence of CN$^-$ molecules and results in the TE-NTIMS $\delta^{11}$B measurements being shifted to heavier not lighter values as would be expected from CNO- interference at mass 42. This matrix effect may go some way to explaining the reported large $\delta^{11}$B differences between laboratories for similar foraminiferal samples (up to 6 ‰ disagreement by NTIMS). With careful treatment, reliable $\delta^{11}$B data can be generated by NTIMS. However, we hope that this realisation, along with a modified loading technique outlined here, makes $\delta^{11}$B isotope measurements by negative thermal ionisation techniques more routine and accurate.
Root zone of sheeted dike complex in Oman ophiolite-dynamical model

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As in many other ophiolites, there is in Oman an horizon called the root zone of the sheeted dike complex (RZSDC) located below the volcanics and the diabase sheeted dike complex and above the gabbro unit. This RZSDC is described here based on structural and petrological observations carried during the extensive mapping of this ophiolite (Nicolas et al., 2000) and on a new fine-scale mapping in a selected area. The Oman ophiolite is derived from a fast spreading ridge where a melt lens is located above the main gabbro unit and just below the RZSDC. With a few exceptions, the RZSDC thickness is rather constant, in the 100 m range, with a crude internal stratigraphy.

The base of RZSDC is a level of isotropic doleritic gabbros interpreted as a thermal boundary layer transitional between the magmatic system of the melt lens convecting at 1200°C, and a high temperature (HT) hydrothermal system convecting within the RZSDC at <1100°C. In this field of very sharp thermal gradient (~7°C/m), increasing seawater flux locally generates near total hydrous melting at the expense of these isotropic gabbros, at ~1100°C (companion abstract). The upper part of the RZSDC is richer in vari-textured doleritic and pegmatitic gabbros, with trondhjemitic intrusions, formed by a similar process at temperatures below 1000°C. The latter formations constitute screens between the lower dikes of the sheeted dike complex. At the very base of this complex a new boundary layer, with HT diabase dikes, separates the preceding HT convective system from the well known LT (T<450°C) hydrothermal system operating throughout the sheeted dike complex, to the seafloor.

Intruding the isotropic gabbros near the base of the RZSDC, protodikes with a distinctive microgranular border and a doleritic center testify that the RZSDC was generated by melt conduits issued from the melt lens. Each dike of the sheeted dike complex is thus fed by one protodike. However, protodike swarms are exceptional because, crystallizing ~1100°C, they are largely destroyed by dike-in-dike intrusions and by hydrous remelting.

Reference

Generation and emplacement of granitic magmas at the Paleocene Rum Igneous Complex, northwest Scotland

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The Isle of Rum is one of several igneous complexes within the British-Irish Paleocene Igneous Province that formed prior to the opening of the North Atlantic Ocean during a period of crustal stretching and thinning. An elliptical ring fault, 12km across, bounds the igneous centre enclosing remnants of an early granitic phase of intrusive and eruptive activity that is cross-cut by basic and ultrabasic intrusions. This activity consists of intra-caldera rhodacitic ignimbrites and microgranitic to granitic shallow-level intrusive bodies that are all located within, and in close proximity to the Main Ring Fault.

These early granitic magmas show a strong involvement and interaction with crustal materials. Isotopic data implies 40-90% contamination of mantle-derived magmas by upper crustal Lewisian amphibolite-facies gneiss. Some of these felsic intrusions are intimately associated with mafic magmas. 87Sr/86Sr isotope data from basaltic margins and lobate inclusions, to and within the granitic rocks, indicate that very few of these mafic components have uncontaminated mantle-like values. Most of them also show varying degrees of crustal contamination (87Sr/86Sr 0.7029 - 0.7140) by both Lewisian amphibolite-facies material and a component that is similar in isotopic composition to Lewisian granulate-facies gneiss.

This isotopic information provides a unique window into the crustal structure beneath the Rum Igneous Complex and combined with detailed field investigations allow for an integrated approach to interpreting the generation, emplacement and eruption of anorogenic granitic magmas. We propose that basic and ultrabasic intrusions at depth, migrating towards the surface, heated and partially melted the more felsic components of the surrounding crust which gave rise to a voluminous, but ultimately short-lived, episode of granitic magmatism on Rum.
Assessing the relative production rates of cosmogenic $^3$He and $^{21}$Ne in olivine, pyroxene and quartz

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Currently used methods to derive cosmogenic $^3$He and $^{21}$Ne production rates ($P_3$ and $P_{21}$) for pyroxenes based on their major element composition yield inconsistent exposure ages by up to 40% (Niedermann et al., 2007), indicating a substantial flaw in our knowledge on production systematics of the noble gas isotopes, in spite of a general agreement of the models with experimental determinations of $P_3$ in olivine and $P_{21}$ in quartz. However, $P_3$(ol) has never been directly experimentally determined. Our exposure geometry may have changed during degradation of a sample is not from a well-defined surface location (the well as olivine and pyroxene phenocrysts. Although the sample is not from a well-defined surface location (the exposure geometry may have changed during degradation of a lava tube), it provides the opportunity to study the ratios of $P_3$ and $P_{21}$ in olivine, pyroxene and quartz. The resulting $P_3$(ol)/$P_{21}$(qz)=$7.80\pm0.55$ and $P_3$(px)/$P_{21}$(qz)=$8.00\pm0.62$ are $\approx30\%$ higher than the value obtained by comparing the experimental $P_3$ in olivine ($\approx116$ at g$^{-1}$ a$^{-1}$) to the experimental $P_{21}$ in quartz ($\approx19$ at g$^{-1}$ a$^{-1}$). The difference is similar to that resulting from different methods to calculate $P_3$ and $P_{21}$ from major element composition. A difference of $10\%$ at most might be assigned to unfavorable irradiation conditions, if the quartz xenocryst was located at the very bottom of the sampled rock during most of the exposure. But still the results would imply $P_3$(ol) $\approx20\%$ higher or $P_{21}$(qz) $\approx20\%$ lower than the values usually assumed. The determinations of cosmogenic $^3$He and $^{21}$Ne in our sample are robust since they are based on a value of 7.9 $R_\alpha$ for the magmatic $^3$He/$^4$He ratio and an atmospheric trapped Ne composition. Any reasonable different assumption could only increase the $P_3/P_{21}$ ratios.

The comparison of cosmogenic $^{21}$Ne in olivine (Mg-rich) and pyroxene (Mg-poor) may, in principle, be used for an experimental determination of the $P_{21}$(Mg)/$P_{21}$(Si) ratio. Our present data indicate a value of $\approx3.4$, but with a large uncertainty of 30-50% which critically depends on the uncertainty of the $^{21}$Ne(ol)/$^{21}$Ne(px) ratio. We hope to obtain a more accurate result by analyzing Ne in olivine and pyroxene from a well-defined surface sample.

Reference

Hydrothermal alkali and oxygen-isotope exchange in alkali feldspars controlled by dissolution reprecipitation mechanisms

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The re-equilibration mechanisms of solid phases in hydrothermal fluids are only poorly understood. Depending on the prevailing conditions a sequence of fluid-induced dissolution-reprecipitation or solid state processes may take place. In the present study, we have investigated the re-equilibration of albite in the presence of a fluid phase. For this, we have experimentally treated a natural albite crystal in an aqueous KCl solution at 600°C and 2 kbars. To trace the exchange between mineral and fluid, the aqueous KCl solution was enriched with $^{18}$O (95 atom %). The major aim of this study was the characterization of the chemical and physical properties of the K-feldspar reaction rim that is known to form during the interaction of albite with an aqueous KCl-rich fluid under the chosen conditions (Labotka et al. 2004). Transmission electron microscopic investigations have shown that the interface between the pristine albite and the K-feldspar product phase is sharp on a nano-scale, with a strong diffraction contrast difference between both phases, suggesting a defect-rich K-feldspar product. A porous zone also evolved near the interface. Existing crystallographic orientation as well as twinning in the albite is preserved in the K-feldspar reaction rim. Powder X-ray diffraction analyses revealed a change from triclinic Al$_2$SiO$_5$ ordered albite structure to an Al$_2$Si disordered monoclinic structure in the K-feldspar. Furthermore, Raman spectroscopy has been applied to map the mass frequency shift of the Si-O-Si bending vibration near 476 cm$^{-1}$ in the K-feldspar due to the incorporation of $^{18}$O. The frequency of this mode shifts to about 457 cm$^{-1}$ in K-feldspar formed in $^{18}$O-enriched solution, reflecting a high enrichment of $^{18}$O in the K-feldspar lattice. In the K-feldspar formed in $^{18}$O-enriched solution the highest frequency shift was found close to the interface, which coincides with an enrichment of the orthoclase component close to the interface, as revealed by electron microprobe measurements. This indicates that the higher frequency shift close to the interface results from chemical changes rather than from a higher $^{18}$O content. An important observation is that there is no gradient in the frequency shift that could be related to diffusion of $^{18}$O.

We propose that the new data are fully consistent with an interface-controlled dissolution-reprecipitation mechanism that operates at an inward moving replacement front.

Reference
Systematic thallium isotope variation in Fe-Mn crusts: A proxy for changes in ocean chemistry?
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We have measured the thallium (Tl) isotope composition of samples from the Pacific Fe -Mn crust CD29-2, which have recently been dated using Os isotope stratigraphy [1]. The samples have a spatial resolution of about 1mm which equates to about 0.5 Ma. Thus far we have investigated the time interval spanning 60 to 30 Ma and large systematic Tl isotope variations ranging between $\varepsilon^{205}\text{Tl} = +6.8$ and $\varepsilon^{205}\text{Tl} = +11.4$ are apparent (where $\varepsilon^{205}\text{Tl} = 10^4 \times (^{205}\text{Tl}/^{203}\text{Tl}_{\text{sample}} - ^{205}\text{Tl}/^{203}\text{Tl}_{\text{NIST 997}})/^{205}\text{Tl}/^{203}\text{Tl}_{\text{NIST 997}}$). The most striking feature is a systematic increase from $\varepsilon^{205}\text{Tl} = +6.5$ to $+10.5$ occurring in the time interval 58 to 50 Ma. A small number of previous analyses at various depths in CD29-2 [2] are fully consistent with our more detailed investigation.

Rehkämp er et al [2] argued that these variations most likely reflected a change in the Tl isotope composition of seawater and this remains a firm possibility. However, recent theoretical calculations of the mechanism controlling Tl isotope fractionation have shown that there is a large equilibrium isotope fractionation between Tl$^{1+}$ and Tl$^{3+}$ [3]. Published Tl isotope compositions of modern Fe-Mn crusts [4] and altered mid ocean ridge basalts [5] are consistent with these two reservoirs exclusively incorporating Tl$^{3+}$ and Tl$^{1+}$, respectively. Hence, changes in the speciation of Tl in seawater may also be responsible for the observed Tl isotope variation recorded in Fe-Mn crusts. This proposition appears to be in agreement with the fact that the timing of Tl isotope change in CD29-2 coincides exactly with the massive change in atmospheric CO2 inferred from boron isotope compositions of planktic foraminifera [6].

We are currently performing thermodynamic calculations aimed at determining the speciation of Tl in seawater in order to investigate the potential for Tl isotopes to be used as a proxy for changes in the chemical and physical conditions of seawater.

References
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Geochemical analysis of obsidian and the pattern recognition of sites spatial distribution in the chalcolithic of the Eastern Lake Urmia, Northwestern, Iran

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Results presented here are the chemical analysis of significant numbers of obsidians from several Chalcolithic sites in the eastern shores of Lake Urmia, Northwestern Iran, as part of a large and most comprehensive study of obsidian sources in this region. In this study, XRF is used to generate trace element data for some elements. A number of analytical methods such as Bivariate plots of the incompatible trace elements were used to separate the obsidian sources in study area and source separation was confirmed by using linear Discriminant analysis. The existence of multiple sites containing obsidian artifacts in the area of Urmia and on some of the other nearby regions, however, has enabled the study of specific spatial patterns of source exploitation and the trade mechanisms which resulted in the distribution of obsidian hundreds of kilometers away during the Chalcolithic period (ca. 5000-3000 BC).
Extreme Pb-isotope diversity in the sources of K-rich magmas in Italy: Evidence from melt inclusions

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We present 170 SIMS (Cameca 1270) analyses of Pb-isotope ratios of homogenized melt inclusions in Fo-rich (Fo92-88) olivines from primitive lavas in Central-Southern Italy. The samples cover the entire compositional spectrum of potassium-rich magma series erupted from major Pliocene-Quaternary volcanic centres in peninsular Italy.

The inclusions contain 1-140 ppm Pb. For inclusions with > 5 ppm Pb (80% of the population) in-run precision was 0.5-0.05% (2σ) for 207,208Pb/206Pb, and 1.5-0.15% (2σ) for 206,207,208Pb/204Pb.

Our results significantly extend the existing bulk-rock data towards more extreme compositions. A second key observation is the strong isotopic variability that appears to exist within individual volcanic centres, within magma series, and even within individual lava samples, testifying that widespread mixing in magmatic systems involved melts derived from mantle columns that are isotopically heterogeneous on small volume scales. The Pb-isotope systematics confirm that magmas were derived from mantle sources that are largely binary mixtures between components with low- and high-radiogenic 206,207,208Pb/204Pb ratios, respectively. However, extrapolation of mixing trends points to isotopic variability in each of these end-members, both in the original mantle component and in the metasomatic component that is inferred to be of upper crustal/sedimentary origin. The nature of the ‘pre-metasomatic’ mantle of the Roman and Campanian Provinces is distinct, the former being MORB-type, the latter showing a modest contribution of the FOZO-HIMU signature seen at Vulture and Etna. The Pb-isotopic signatures further indicate that in a transition zone (Roccamonfina-Ernici) the High-K-series melts are derived from the ‘Roman’ mantle, but K-series melts from the ‘Campanian’ mantle. Variations in the metasomatic agent are inferred to be related to (former) subduction, and reflect along-strike isotopic changes between Adriatic and Ionian domains of the plate. In conjunction with trace-element signatures of the melt inclusions, source mixing scenarios and implications for the regional geodynamic controls will be discussed.

Volcanic arc development due to intraoceanic subduction: Numerical model

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We have created a new 2D coupled geochemical-petrological-thermomechanical numerical model of retreating intraoceanic subduction associated with volcanic arc development. The model includes spontaneous slab bending, subducted crust dehydration, aqueous fluid transport, mantle wedge melting and melt extraction resulting in crustal growth. This model allows us to study influence of melt extraction intensity on the dynamics of subduction, mantle wedge plumes development and magmatic arc growth and displacement. In our numerical experiments subduction nucleates across the weak transform fault separating two oceanic plates different age. Subduction rate strongly varies with time. In all studied cases there is a deceleration period of a few Myr after the beginning of subduction, during this period subduction rates decrease from ~ 7 cm/yr to ~ 4 cm/yr. Subsequently, two scenarios can be distinguished: (1) decay and, ultimately, the cessation of subduction, (2) increase in subduction rate (to up to ~12 cm/yr) and stabilization of subduction. In scenario 1 the magmatic arc crust includes large amounts of rocks formed by melting of subducted crust atop the thermally relaxing slab. In contrast, in case of stable subduction, magmatic rocks produced by partial melting of hydrated mantle wedge clearly dominate the crust. In several numerical experiments an intra-arc extension is observed during subduction. This process results in splitting of previously formed magmatic arc crust by a newly formed spreading center. The loci of magmatic activity and intensity of crustal growth is strongly dependent on the dynamics of hydrous partially molten upwellings (cold plumes) rising from the slab.
Three kinds of superstructures of wollastonite whose compositions were Ca(Ge0.65, Si0.35)O3, Ca(Ge0.50, Si0.50)O3 and Ca(Ge0.15, Si0.85)O3 were synthesized. In this abstract, they are called 65Wo, 50Wo and 15Wo. The lattice constants of 65Wo, 50Wo and 15Wo are: (angstrom, degree) a=2X8.038(4), 2X7.995(2), 4X7.949(5), b=7.451(1), 7.400(1), 7.352(1), c=7.194(2), 7.148(2), 7.093(1), alpha=89.93(2), 90.05(2), 90.06(2), beta=94.85(2), 94.97(2), 95.11(1), gamma=103.34(2), 103.43(1), 103.39(1), respectively.

65Wo consists of the neighbouring two units of the basic-wollastonite along the a-axis. The X-ray diffraction pattern showed a pseudo-C lattice. Therefore, the stacking sequence of 65Wo can be represented as AB, where A is the unit cell of the basic-wollastonite and B is the unit cell of the basic-wollastonite with b/2 displacement. The final R-value was 12%.

50Wo consists of the neighbouring two units of the basic-wollastonite along the a-axis, too. However, the X-ray diffraction pattern was different from 65Wo. Judging from the characteristics of the X-ray diffraction, the stacking sequence of 50Wo is represented as AA. The final R-value was 13%.

15Wo consists of the four units of the basic-wollastonite along the a-axis. There were four possible stacking sequences described as AAAA, ABAB, AABB and AAAB. The structure having the sequence AAAA will show the strong intensity on the h=4n diffraction. The structure ABAB will show the strong intensity on the h=2n diffraction. The structure AABB will show the extinction rule of the pseudo-C lattice. The last structure AAAB will not show any characteristic rules on the X-ray diffraction. As the result of the observation of the X-ray diffraction of 15Wo, it was clear that the stacking sequence AAAA was most reasonable. The final R-value was 14%.

In common with 65Wo, 50Wo and 15Wo, each tetrahedral site has the statistical distribution of Ge and Si atoms.

**References**


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**Temporal change of a layer sequence in reaction zones in the system dolomite – quartz – H2O**

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**From an initial transient state to a steady state**

Hydrothermal experiments at 0.1GPa and 600°C were carried out with two kinds of configurations for starting materials: one is dolomite single crystal + quartz powder + H2O and the other is quartz single crystal + dolomite powder + H2O. We got the following results. (i) Reactions were incomplete in all runs and the reaction zone developed only locally on the dolomite crystal. (ii) In short duration (45 – 71h) runs metastable layer sequences involving wollastonite and talc occur in the reaction zones, whereas they disappear in longer duration (168 – 336 h) runs. (iii) The layer sequence of the reaction zones in short duration runs differ from place to place on the dolomite crystal even in the same run. (iv) The diversity of layer sequences in the short duration runs merges into a unique layer sequence of Qtz / Di / Fo + Cal / Dol + Cal / Dol in the longer duration runs. (v) No reaction zone was observed on quartz crystals. These lines of evidence show that the system evolves from an initial transient state to a steady state and that the kinetic effect is important in the development of reaction zones. This part of the work has been recently published (Nishiyama et al., 2007).

**Temporal change of a layer sequence at 800°C**

We carried out additional experiments in the same system at 0.1GPa and 800°C with run durations of 48, 109 and 357 h. In these higher temperature runs reactions were complete in all runs such that the dolomite crystal was completely surrounded by a reaction zone with a definite layer sequence. Observed conspicuous features are as follows. (i) The layer sequence Dol / Dol + Cal / Fo + Cal / Fo / Mon (Monticellite) / Di / WO / Qtz is common in all runs. (ii) The thickest layer is Di in 48 h run, Mon in 109 h run and Fo (or Fo + Cal) in 357 run. (iii) A void layer formed between Dol + Cal and Fo + Cal layers in all runs, and it becomes thicker as the duration. (iv) Reaction zones have never formed on the quartz crystal, although the quartz shows resorption after the run. These results show little change of the layer sequence but a considerable temporal change in the growth mode of the reaction zone. A steady diffusion modelling was applied to the representative layer sequence to discuss this temporal change.

**Reference**

Varying Ni in OIB olivines – Product of process not source

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The source of ocean island basalts (OIB) has been widely accepted as resulting from ancient recycled oceanic crust (ROC) [1] although there are many more difficulties than certainties in this model [2]. Sobolev et al. [3] concluded that Ni content in olivines of Hawaiian shield basalts is too high, precluding basalt origin by partial melting of mantle peridotite, asserting that this can only be explained by melting of an olivine-free pyroxenite. This pyroxenite originated by reacting mantle peridotite with a SiO$_2$-rich melt derived from partial melting of recycled oceanic crust in the form of “SiO$_2$-oversaturated eclogite”. This is a revised version of the ROC model, but the complex behavior of Ni makes the interpretation non-unique. Sobolev et al. [4] show that while Ni content in olivines of basalts varies widely, it is conspicuously higher in basalts erupted on thick (> 70 km) lithosphere (THICK, including Hawaii) than on thin (< 70 km) lithosphere (THIN, including Iceland), and is still higher than in MORB. For primitive olivines with Fo > 89, $N_{\text{THICK}}$ (3417±452 ppm, 1937; mean±1σ, n > $N_{\text{THIN}}$ (2477±263 ppm, 746) > $N_{\text{MORB}}$ (2324±296 ppm, 1700). This lithospheric thickness control (lid effect) poses the question why recycled oceanic crust prefers to exist and participate in magmatism beneath thickened lithosphere relative to beneath thin lithosphere and ocean ridges. Melting beneath thick (> 70 km) lithosphere is largely in the garnet peridotite facies: $a_{\text{Cpx}} + b_{\text{Gnt}} + c_{\text{Ol}} = 1.0_{\text{Melt}} + d_{\text{Opx}}$, where olivine, the primary Ni host, contributes to the melt. Melting beneath thin lithosphere occurs mostly in the spinel peridotite facies: $a_{\text{Cpx}} + b_{\text{Opx}} + c_{\text{Spl}} = 1.0_{\text{Melt}} + d_{\text{Ol}}$, where olivine crystallizes and demands Ni from the melt. A common peridotite source Ni = 1900 ppm, and ~10% melting, can yield ~400 ppm and > 560 ppm Ni in melts parental to MORB and those erupted on thick lithosphere respectively. With these results and realistic magma chamber process models [5], the observed $N_{\text{THICK}}$, $N_{\text{THIN}}$ and $N_{\text{MORB}}$ in olivines can be explained without invoking the revised ROC model which still has to address the difficulties noted in [2].

References

Dissolution, nucleation and growth of mineral phases in aqueous solutions

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In order to take into account the initial stages of formation of mineral nanoparticles in water-rock interaction models, we have developed a theoretical approach of nucleation, growth and ageing processes, relevant for precipitation in solution. It is based on the classical nucleation theory, on a size-dependent (algebraic) growth law allowing growth, resorption and ripening of particles simultaneously, and on conservation laws akin to a thermodynamically closed system.

We will apply it to the formation of silicate phases, and particularly kaolinite-type minerals, from aqueous solutions resulting from rock alteration processes, through the geochemical code NANOKIN that we have elaborated. The nanoparticle formation is simulated versus time in terms of populations of particles appearing successively, surviving and growing or disappearing depending on the evolution of the resulting saturation state of the solution with respect to the corresponding mineral phase.

We will show that two very different scenario may take place, depending upon whether an initial supersaturation is provoked in the solution (i.e. in an experimental approach), or whether it progressively appears as a consequence of rock dissolution. The time dependence of the supersaturation, the size evolution of the particles and the crystal size distribution functions present very specific features in these two cases.

The simultaneous precipitation of competitive secondary phases has also been tested taking into account their specific solubilities, surface energies, geometric shapes and growth rates. This allows to predict the surviving phase in long-term processes.

Work is currently under progress to include chemical variability of the produced particles in the model.

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References

Stabilisation of continental crust by dehydration melting: An example from the Västervik area, SE-Sweden

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The Palaeoproterozoic Västervik area (Baltic shield, SE-Sweden) is located at one major terrane boundary on the Baltic Shield. To the south lies the Transscandinavian igneous belt and to the north follows the Svecofennian domain. In addition, the Västervik area is known for lp-lH amphibolite metamorphism in combination with intensive metasomatism.

From field relationships at least three different granitoid generations can be identified that discriminate in their geochemical and isotope signatures as well. Primitive granitoides (QMD) of quartzmonzodioritic and granodioritic composition, metagranitoides (MG) of quartzmonzonotic (MGf = non fluid) and alkali-granitic composition (MGf = fluid) as well as anatectic monzogranites (AG). QMD and MGf seem to represent “normal” crust-building granitoides with geochemical signatures of rather typical continental crust. The above mentioned metasomatic fluids seem to have affected the MGf and AG as for example initial Sr isotope ratios are as high as 1.5, respectively. Such increased ratios are observed in the surrounding metasedimentary Västervik Formation as well indicating a genetic relation with the anatectically created AG. Further, geochemical signatures and fluid classifications show that both MG-groups probably share the same petrogenetic evolution with the sole difference of a fluidchemical imprint in the MGf granitoides.

Based on the results, a geotectonic model for the evolution of the different granitoides was developed. We postulate an active subduction zone beneath the svecofennian continental margin. This subduction zone was blocked leading to the evolution of a new subduction zone further southwest building up an island arc of which rocks of the Oskarshamn-Jönköping belt belong to. Our geotectonic model relates the evolution of the QMD and MGf to this maturing island arc. The accretion of this mature island arc on the continental margin of the Svecofennian terrane caused compression and folding leading to crustal thickening. Subsequently, intruding melts show higher SiO₂ contents and are more differentiated (MGf).

Pressure increase due to crustal thickening and heat input by the ascending melts finally resulted in mica breakdown. Resulting dehydration melting is thus the trigger for the crustal anatexis event that produced the AG and led to fluids that percolated through some of the MG.

Results of mineral nanoparticles in water-rock interaction models, we have developed a theoretical approach of nucleation, growth and ageing processes, relevant for precipitation in solution. It is based on the classical nucleation theory, on a size-

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Radiation damage, internal textures and post-growth history of the Plešovice zircon standard

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We have studied internal textures and the post-growth history of accessory zircon crystals from a granulate near Plešovice, southern Czech Republic. This zircon has recently been proposed as a new reference material for determination of U-Pb ages using the laser-ablation inductively coupled plasma mass-spectrometry (LA-ICP-MS) technique (Slama et al., 2006). Extraordinary properties of the Plešovice zircon include its uniform, concordant U-Pb age, relatively high U concentrations (>600 ppm), homogeneous Hf isotopic composition, and its availability in a large quantity.

In spite of its isotopic homogeneity, the Plešovice zircon shows heterogeneous incorporation of trace elements. Typically there is strong primary zonation, including both oscillatory growth zoning and sector zoning. About 10% of the grains show sectors (corresponding to the growth of pyramid faces) that are particularly rich in actinides; here U content may be as high as 3000 ppm. Those sectors are easily recognized, e.g., from particularly high BSE intensities. The Plešovice zircon is in general moderately radiation-damaged whereas the high-U sectors are strongly metamict. All areas are roughly as radiation-damaged as it would correspond to U and Th concentrations and an assumed accumulation of material. Consequently, these areas need to be avoided in using the Plešovice zircon as a U-Pb standard material.

References


Geochemical meddling, microbing, Marsing, and mitigating mine drainage

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Acid mine drainage (AMD) and acid pit lakes, for all their ugliness and environmental damage, provide opportunities for scientists and engineers to test their skills, push the frontiers of their research, and make a contribution to the remediation. Extreme environments such as the Rio Tinto mining district, Spain, have become favorite sites for both researchers and tourists because of the presumed analogy to the Martian surface. Rio Tinto and Iron Mountain, California, USA have also been a major focus of microbial research. The production of AMD is a complex hydrobiogeochemical process that is much better understood today because of sustained research in the fields of geology, hydrology, geochemistry, and microbiology. Mine-site remediation cannot proceed effectively without the combined expertise from these fields. Further, the most cost-effective remediation benefits from an independent technical oversight committee with such expertise.

We now know that pyrite oxidation can create waters of negative pH, that mine plugging is often an ineffective remediation method, that microbial catalysis of pyrite oxidation involves a community structure including, but not limited to, Acidithiobacillus, Leptospirillum, Ferroplasma, and heterotrophs, that surface-water contaminants are attenuated and can be modeled, that dynamic rainstorm events can cause increases in concentration destroying aquatic life, that remediation scenarios can be evaluated before executing, and that the collaboration of scientists and engineers working together on remediation is far better than just engineers working alone. Research papers on sulfide mineral oxidation to mine-site characterization have proliferated over the last two decades. We also know much more about the processes (dissolution rate, solubility, sorption) controlling mine drainage (cf. Nasdala et al., 2001), which excludes any major thermal annealing event. Heterogeneous metamicitization has resulted in zoned fracturing; fractures have been filled with secondary phases such as Fe hydroxides. First LA-ICP-MS U-Pb analyses of high-actinoid micro-areas turned out to be most difficult and unreliable. Consequently, these areas need to be avoided in using the Plešovice zircon as a U-Pb standard material.
Differentiating fluid boiling from condensation

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Fluid inclusion petrography cannot differentiate boiling from condensation. Inclusions formed during boiling and condensation may have liquid- and vapour-dominant types that show approximately the same Th. During boiling a vapour phase develops in response to changes in liquid P or T. Condensation occurs when a liquid is subject to a vapour flux. This may occur at any depth in geothermal systems. At shallow depths this process generates steam-heated waters. At greater depths vapour from magmatic bodies can flux through circulating meteor waters.

Modelling demonstrates that boiling and condensation changes the concentrations of gaseous species in different manners. Boiling strips dissolved gaseous species from liquids and low solubility species such as H₂, CH₄ and N₂ more strongly partition into the vapour phase. Hence a ratio of soluble species like CO₂ to N₂ increases during boiling. Condensation increases liquid concentration of soluble gaseous species (see fig.). Gas ratios from the USGS Cerro Prieto data set show positive correlations between total gas and CO₂/N₂ ratios. Sequential fluid inclusion gas analyses shows negative correlations at Guanajuato where there is other evidence of boiling and positive correlations in geothermal systems were condensation is predicted.

We know that gaseous components and liquids commonly decouple and recombine in geothermal systems. We find evidence in active geothermal systems and in fluid inclusions that both processes operate. Condensation may be an import process in the production and localization of high grade sulphide ore bodies by locally producing high fluid concentrations of H₂S.

Quantifying accelerated surface denudation as a result of external forcing

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The evolution of mountain belts is a balance between forces that build topography and those that destroy topography. This study focuses on the destructive forces, weathering and mass wasting, fluvial or eolian erosion, glaciers, etc., that are inherently surfacial processes. In order to understand how orogens change through time, we need to identify and quantify the processes responsible for denudation.

We apply a combination of novel and proven techniques to address the question of how these forces modify the landsurface. Morphometric analysis based on high resolution LIDAR data is used to identify transient landscapes. These geomorphic data are then combined with cosmogenic nuclides, ⁹⁰⁰⁰Be from quartz in sediments specifically, in order to quantify process rates.

In a case study in the Alpine Foreland, we identified two adjacent drainage basins which have responded differently to the same forcing event, a fall in stream base-level at 16,000±3,000 yrs BP. One of the watersheds has a coupled hillslope-channel system, while the other is decoupled. Denudation rates in the coupled system, 380±50 mm ky⁻¹, are equal to those in the headwaters of the decoupled system, 380±50 mm ky⁻¹. However denudation rates in the decoupled system increase downstream to 540±100 mm ky⁻¹, with denudation in the incised region occurring at extremely high rates, ~1800 mm ky⁻¹. The denudation rates show that within 16,000 yrs, only the channels themselves have responded, and spatially extensive erosion occurs only after a significantly longer lag time.

The advantage of this approach is that the geomorphic response of a landscape to external forces can be identified by morphometric analysis, and the process rates that are measured with cosmogenic nuclides can be used to quantify landscape response times on the time scale of climate change or fault movement.
**Sulfur in tree rings in Central Europe: A negative $\delta^{34}S$ shift relative to regional pollution sources**

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Sulfur isotope composition in tree rings of 50-year old Norway spruce was compared with $\delta^{34}S$ values of local coal and atmospheric deposition in the Black Triangle region of Central Europe. For this purpose we have analyzed soft coal from two East German Basins (Espenheim near Leipzig, and Lausitzer region near the German-Polish border) and two Bohemian basins (Sokolov and Most, northern Czech Republic). In all, 150 soft coal samples from all stratigraphic levels of these Tertiary deposits were analyzed for $\delta^{34}S$. Sulfur isotope composition of air-borne SO$_2$ was based on 170 monthly samples (Novak et al., 2001), $\delta^{34}S$ of rainfall sulfate was based on 200 monthly samples (Novak et al., 2000). The studied spruce was one of the few surviving trees in an area affected by pollution-related spruce die-back of the Erzgebirge Mts. The tree was harvested in 2005, while most other trees at the research site died back between 1975 and 1995 due to acidification. Bedrock orthogneiss was S-deficient, and its $\delta^{34}S$ was 5.8 ‰. The $\delta^{34}S$ values systematically decreased in the order Espenheim coal (mean of 12.0 ‰) > Sokolov coal (11.7 ‰) > Lausitzer coal (9.6 ‰) > rainfall sulfate (5.4 ‰) > air-borne SO$_2$ (2.5 ‰) > Most coal (1.6 ‰) > Erzgebirge tree rings (0.4 ‰). Three of the coal basins had isotopically relatively heavy sulfur, one coal basin (Most, Czech Republic), had isotopically light sulfur. Most of the emissions from the coal-fired power plants were in the form of SO$_2$, which was partly oxidized to sulfate in the atmosphere before reaching the receptor site. The resulting sulfur became isotopically somewhat heavier than the residual SO$_2$. The spruce tree rings contained the isotopically lightest S of all studied S reservoirs. Our data indicate that (i) German coal S did not significantly influence trees on the Czech side of the Erzgebirge Mts., and (ii) assimilation of S by Norway spruce is associated with a negative isotope shift relative to ambient S.

References


**Quantification of stable strontium isotope variability in nature by MC-ICP-MS**

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There is growing evidence that high-temperature processes, such as diffusion, condensation and evaporation can generate significant stable-isotope fractionation. Recent observations of stable isotope fractionation in elements as heavy as Tl (Z=81) raises the possibility that there may also be natural Sr isotope variation. With conventional $^{87}$Sr/$^{86}$Sr measurements, the $^{86}$Sr/$^{88}$Sr ratio is used to correct instrumental fractionation, and although the absolute value used for this correction is unimportant, implicit in its use is the assumption that $^{86}$Sr/$^{88}$Sr ratio remains constant in all analysed materials. This ‘internal’ correction for instrumental mass fractionation thereby masks the existence of any natural mass dependent fractionation of $^{86}$Sr/$^{88}$Sr. In this study, we present a new technique that allows simultaneous measurement of both radiogenic Sr isotope variations ($^{87}$Sr/$^{86}$Sr) and possible small-scale mass dependent isotopic fractionation of the $^{86}$Sr/$^{88}$Sr ratio. Radiogenic and stable Sr isotope ratios are measured on a Thermo-Finnigan Neptune MC-ICP-MS and are corrected for mass bias ‘externally’ using admixed Zr. We present $^{86}$Sr/$^{88}$Sr data for NBS 987, a range of natural rock standards and extraterrestrial samples (for which $^{86}$Sr/$^{88}$Sr fractionation has already been documented using double spike TIMS). Incomplete recovery of Sr during column separation can significantly fractionate Sr isotopes, which implies that excluding overlapping Rb and Sr tails during column procedures will introduce inaccuracies. We demonstrate that NBS987 is fractionated relative to high-T magmatic rocks (possibly resulting from the manufacturing process), and establish a precise ‘high-T’ reference line. Due to documented variation in low-T and biological samples we suggest that this high-T reference should be adopted for Sr isotope work.
3-D colloidal crystals of magnetite in the Tagish Lake carbonaceous chondrite

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Tagish Lake carbonaceous chondrite (fallen on 2000) is known as a primitive meteorite in chemical composition but the meteorite heavily suffered aqueous alteration. In the matrix, magnetite (Fe3O4) particles were reported to be present in between tiny forsterite crystals [1]. However no detailed observation of morphology from these particles has been done, though the morphology of crystals possess the growth conditions precisely in which these crystals have been growing [2].

The chondrite with a few mm, in diameter, were cleaved, so that fine crystalline particles would expose on the fractured surface. These crystal surfaces were investigated employing field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM).

Magnetite crystals (Fd3m, cubic) usually exhibit an octahedron shape surrounded by the {111} faces. In this meteorite, however, magnetite fine particles, which are result of reaction of other silicate minerals with water or ice in the early stage of solar system, exhibit varieties of shapes, e.g. octahedron, rhombic dodecahedron with {110} face (Fig. 1), trisoctahedron with {211} face, 100-1000 nm in diameter (peak size, 200 nm). It is surprising to find that these fine magnetite particles form 3D colloidal crystals with varieties of structures, f.c.c. (Fig. 1), b.c.c, and h.c.p. In this colloidal system, not only the size but also the morphology of these particles determined the lattice structure of the colloidal crystal. It is very interesting to note that only the rhombic dodecahedron particles exhibit multiple twinning.

Figure 1: FE-SEM image, magnetite colloidal crystals formed by multiple-twin particles. Twin-boundaries are indicated by white arrows.

References

The nature of the Arabian lithospheric mantle beneath Aritain Volcano, NE Jordan

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The mantle xenolith-bearing Jabel Aritain volcano in NE Jordan belongs to the As Shamah Cenozoic lava field, which is the largest in the W part of the Arabian plate extending from S Syria through Jordan into NW Saudi Arabia.

Most Jabel Aritain mantle xenoliths are spinel lherzolites but herzogites, dunites, websterites and wehrlites are also present. Calculated equilibrium P,T conditions range from 900 to 1000 °C and 12-17 kbar, respectively, and are consistent with estimations made for peridotites from other localities in this area of the Arabian platform, indicating that xenoliths were extracted from shallow depths of 40 to 60 km (Medaris and Syada, 1998).

Glasses from melt pockets present in a number of xenoliths have an unusually high mg# of 75 and secondary olivines with Fo94.5, which suggests that the metasomatic melt was probably picritic.

LA-ICP-MS analyses of cpx show that xenoliths experienced cryptic metasomatism. Three groups of xenoliths have been recognized according to REE and other incompatible trace element patterns in cpx: group 1 has depleted LREE abundances, group 2 is highly enriched in LREE (80 x chondritic) and group 3 has moderate LREE enrichments. The REE patterns in group 3 indicate that for some reason equilibrium conditions for trace elements has non been achieved as some cpx have higher LREE abundances than others within the same sample. In this group, the common Zr depletion relative to Nd and Sm implies that it is not associated to partial melting processes but rather to metasomatic processes and that the cpx was originally not depleted in Zr. Evidently, the metasomatic agent was a H2O-rich fluid (high LREE and Sr) with carbonatitic components (depletion of Zr and Ti).

The Jabel Aritain mantle xenoliths are in terms of PT equilibrium conditions similar to xenoliths from Jabel El Arab (ca. 100 km N of Aritain) and other Arabian plate peridotites suggesting a common thermal regime.

The metasomatic fluids/melts affected variably the trace element but not the major element abundances. Apparently, the metasomatic processes were interrupted before equilibration could be achieved indicating a pre-eruption metasomatic front rising from lower levels of the local upper mantle.

Reference
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Geochemical mapping of the Collahuasi District, N. Chile: A pilot study for a geochemical atlas of the Andes

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A geochemical baseline survey of the Collahuasi District, N. Chile has been completed based on systematic regional rock and soil sampling. The Collahuasi district hosts 3 major Cu porphyry centres, Rosaria, Ujina and Quebrada Blanca which are now being mined for Cu and Mo. Approximately 1100 lithogeochemical whole rock samples were collected on a grid averaging 1-2 sq. kms. over an area of 1500 sq. km and about 250 soil samples were collected over part of the grid, centred on Rosario and covering about 650 sq. km. Approximately 74 chemical elements were determined on whole rock samples by ICPMS and ICPOES and 65 elements on soil samples after aqua regia extraction. All the methods used were those specified by the global geochemical baseline programme for mountainous terrains.

The data are shown to be of value for exploration, lithogeochemical mapping and understanding the geochemical and metallogenic evolution of the district as well as for environmental purposes. For example high field strength elements can be used to prepare lithological maps in areas where the bedrock geology is poorly known while large ion lithophile elements can be used to map regional hydrothermal alteration. The rock and soil data have been compared to international soil guideline values for chemical elements from N. America and Europe and the ratio of the concentration in soils has been compared to that in rocks for all elements. The results show that even in rock samples away from mineralisation values for several elements exceed all guidelines for part of or the entire district. This observation is critically important in setting guideline values which should more fully take account of bedrock geology.

The results show that a lithogeochemical atlas of the Andes would define the chemistry of mineralised districts, and the potential for new exploration targets as well as providing an environmental baseline against which to study human health and environmental impacts, including from future mining.

Constraints on the exhumation history of the Torres del Paine

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During field investigation on the contact metamorphism and intrusion emplacement on the Torres del Paine laccolith we found samples of suspiciously fresh scoria. These scoria were only found in two distinct steep gullies in the Eastern part of the Torres del Paine laccolith. They occur in the side valleys of Valle Ascencio, Northeast of Monte Almirante in Valle del Mirador as well as North of the Torre del Paine peaks in Valle del Silencio. The two localities relate to each other by a NW-SE running fault system. In Valle del Silencio the scoria is found close to a dike that can be followed from the southern side moraine in the valley running steeply upwards to form a steep cut just north of Torre Monzino. The same holds true for the Valle del Mirador. A dike is running into a notch giving access to the east crest of Monte Almirante. Samples can only be found along the dike gullies above the moraine deposits and below an altitude of 1760 m. At both sampling locations this altitude corresponds roughly to a position in the middle of the intrusion. Since we find scoriae this altitude marks a paleosurface and thus allows using the age constraints by Ar/Ar dating of the scoria in combination with data on age and the depth of intrusion of the Paine laccolith to constrain the exhumation history of the Paine laccolith. The finding of scoria indicates a surface that must be discussed in the light of the glaciation history.
Driekop platinum pipe, Bushveld Complex, South Africa: New insights

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The genesis of the platiniferous pipes of the eastern Bushveld Complex is still enigmatic. Orthomagmatic, metasomatic replacement, and hydrothermal models were proposed (Scoon and Mitchell 2004), however, advance on the understanding of the pipes is hampered by the fact that these orebodies were mined out early in the last century and limited material is available from museum collections only.

Our interest in the pipes was sparked off by investigations of detrital PGM in the Bushveld river systems (Oberthür et al. 2004). The present paper reports on a sample from the Driekop Pipe (Wilhelmskopje) collected in 1926 (TU Berlin) and highlights the impact of using novel methods of ore treatment on investigations especially of noble metal ores.

The greenish-greyish, dense sample is a medium-grained dunite with accessory disseminated chromite and has an ore grade of 34.9 ppm Pt. Contents of the other PGE and gold are all ≤1 ppm. Ten polished sections investigated by ore microscopy and SEM yielded a disappointing number of only 5 PGM grains (＞50 µm), underlining theoretical data (Ney 1977) on comparable gold ores that, at an average grain size of 100 µm and at a grade of 100 ppm, about 5-10 polished sections are needed to detect one discrete grain of gold.

Therefore, a combination of novel methods was tested on a slab of the sample weighing 676 grams, namely electric pulse disaggregation (EPD), hydoseparation (HS) and preparation of monolayer polished sections (5 size fractions between <63 and >400 µm) for further studies. The results were compelling: At least 500 PGM grains were found in the fractions. Grain sizes range from ~10-330 µm (most common around 100 µm). Many grains are composite. Sperrylite is the dominant PGM (ca. 90%), followed by Pt-Fe alloy and another twelve rarer PGM species. Notably, geversite (c.f. Melcher and Lodziak 2007) is absent. Analytical procedures and new data from our ongoing studies will be presented.

References

Testing the hotspot record for evidence of broad melting anomalies

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The notion of a mantle plume has long been that of a mushroom-like ‘head’ (LIP) and thin ‘tail’ structure (hotspot chain) rising from a deep thermal boundary layer, generally depicted as the core-mantle boundary. Drifting of tectonic plates over the narrow, presumably fixed, hotspots created by such plume ‘tails’ has long provided an elegant explanation for time-progressive lines of islands, seamounts and ridges. But a major problem cited for this ‘standard’ plume model is a lack of evidence in the volcanic record for head-and-tail upwellings.

New evidence from direct dating of the oceanic hotspot record is also suggesting that hotspot melting anomalies might be much broader than commonly inferred from the ‘head-tail’ plume model and the dimensions of individual seamount chains and aseismic ridges. For example, new age data show that the Galapagos volcanic Province developed via the progression of broad regions of concurrent dispersed volcanism that we link to a correspondingly broad mantle melting anomaly (O’Connor et al., submitted, 2007). Moreover, recent thermo-chemical numerical modelling is exploring scenarios where upwelling structures are more irregular in shape and behaviour compared to a classic thermal plume ‘head-tail’ (e.g., Farnetani and Samuel, 2006).

New strategies are therefore needed for investigating the hotspot volcanic record in order to better test the ‘fixity’ of hotspots and the mantle plume hypothesis. To this end we have recently sampled multiple seamount chains and ridges scattered across a broad region of the southern South Atlantic. Our focus is on investigating multiple hotspot chains and ridges stretching across a very broad region of the South Atlantic seafloor as a potentially useful way of testing 1) the new thinking that plume upwellings may differ from the classic ‘head-tail’ structure and 2) our evolving hypothesis that hotspot melting anomalies are much broader than suggested by regions of active volcanism marking the young ends of individual hotspot trails. A key component of this strategy is our IODP proposal to drill Walvis Ridge once we have developed a fuller understanding of how Walvis Ridge fits with the predictions of the fixed hotspot and mantle plume hypotheses.
Mineralogical and geochemical study of airborne particulates (PM$_{10}$) in an urban environment

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Airborne particulate matter (PM) is known to affect human health significantly. Especially the fine PM, with sizes $<10$ µm (PM$_{10}$), poses a considerable health threat, due to its ability to enter human lungs. Sources of anthropogenic PM$_{10}$ in the atmosphere include waste incinerators, traffic, and thermal power plants. Coal-fired power plants, for example, emit various distinct phases, including several types of crystalline metal sulphates (Gieré et al., 2006). Knowledge of the identity and composition of individual particles is essential to predict their environmental behaviour.

The study focuses on PM$_{10}$ collected in the neighboured urban environments of Strasbourg (France) and Kehl (Germany). This urban area, situated on both sides of the river, Rhine is exposed to different PM sources such as a thermal power station, waste incinerators, and a steel plant. Our interest lies in the bulk chemical and mineralogical composition of the overall PM$_{10}$ in the city centre of Strasbourg and in the specific evolution of these compositions as function of distance from the steel plant. Pb, Sr and Nd isotope ratios of these emissions are already precisely identified and allow to be traced over more than 3km along the prevailing wind pathway (Lahd Geagea et al., 2007). Thus, in this special case study we have a direct control of the origin of the PM$_{10}$ and can compare the PM$_{10}$ compositions with those of filter dust from the plant. The bulk chemical composition of PM$_{10}$ trapped on teflon filters is analyzed by using ICP-MS. Identification and characterisation of the mineral phases is performed using SEM techniques, which allow us to determine morphology and chemical composition of µm-sized individual particles. Preliminary results show that, in addition to soot and various silicate particles, metal sulphates are present in the PM.

References


Do fluids flow through or around mineral grains?

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A large body of evidence demonstrates that mineral transformation commonly occurs through a dissolution/precipitation mechanism where 1) the fluid moves into the parent phase from its original surface and 2) the crystal structure is preserved between the parent and secondary phase (Putnis and Putnis, 2007). The goal of this study is to assess if a similar dissolution/precipitation mechanism can transport fluids through mineral grains where the driving force is either a pressure or a temperature gradient.

Calculations were performed using dissolution rates (c.f. Gislon et al., 1997; Oelkers, 2001), aqueous diffusion coefficients (Oelkers and Helgeson, 1988), and mineral solubilities calculated using SUPCRT92 (Johnson et al., 1992) as a function of temperature and pressure assuming that precipitation rates are consistent with Transition State Theory and the law of detailed balancing. Results show that the degree to which fluid ‘flows’ through minerals depends on the identity of the mineral. For example the calculated logarithm of water permeability (in Darcy) through quartz, assuming fluid flow is driven by an isothermal pressure gradient, is -10 at 200°C, increasing to -5 at 600-700°C. In contrast, the corresponding log permeability through enstatite is far higher increasing from -6 to -3 over this temperature range. Note at elevated temperatures these latter values are comparable to that of sandstones in sedimentary basins. Moreover, temperature gradients are, in general, more effective at provoking fluid flow due to the relatively stronger effect of temperature on solubility.

These calculations suggest that large quantities of fluid flow can occur through mineral grains at elevated temperatures due to either pressure or temperature gradients. The consequences of this fluid flow in terms of 1) isotopic reequilibration and 2) stability of fluid inclusions will be detailed.

References


Accretion of terrestrial planets from oligarchs in a turbulent disk

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Introduction

We have investigated the final accretion stage of terrestrial planets from Mars-mass protoplanets that formed through oligarchic growth in a disk comparable to the minimum mass solar nebula (MMSN), through N-body simulation including random torques exerted by disk turbulence due to Magneto-Rotational-Instability. For the torques, we used the semi-analytical formula developed by Laughlin et al. (2004). The damping of orbital eccentricities (in all runs) and type-I migration (in some runs) due to the tidal interactions with disk gas are also included.

Without any effect of disk gas, Earth-mass planets are formed in terrestrial planet regions in a disk comparable to MMSN but with too large orbital eccentricities to be consistent with the present eccentricities of Earth and Venus in our Solar system. With the eccentricity damping caused by the tidal interaction with a remnant gas disk, Earth-mass planets with eccentricities consistent with those of Earth and Venus are formed in a limited range of disk gas surface density (~10^{-4} times MMSN). However, in this case, on average, too many planets remain in terrestrial planet regions, because the damping leads to isolation between the planets.

Results

We have carried out a series of N-body simulations including the random torques with different disk surface density and strength of turbulence.

We found that the orbital eccentricities pumped up by the turbulent torques and associated random walks in semimajor axes tend to delay isolation of planets, resulting in more coagulation of planets. The eccentricities are still damped after planets become isolated. As a result, the number of final planets decreases with increase in strength of the turbulence, while Earth-mass planets with small eccentricities are still formed. In the case of relatively strong turbulence, the number of final planets are 4-5 at 0.5-2AU, which is more consistent with Solar system, for relatively wide range of disk surface density (~10^{-4}-10^{-5} times MMSN).

References


Distribution of mercury and methylmercury in deep-sea surficial sediments of the Mediterranean Sea

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This communication presents the results of the investigation of the distribution, speciation and methylation of mercury in sediments of the Mediterranean Sea. The samples were collected at different locations in the Western and Eastern Basin of the Mediterranean during the cruise of the Italian research vessel Urania in summer 2003 as part of MERCYMS project. Total mercury (HgT) and methylmercury (MeHg) in pore water and sediments were determined down the sediment profile and coupled with other biogeochemical parameters, including organic carbon content. The diffusive fluxes of HgT and MeHg were calculated to estimate the importance of sediment-water exchange as potential sources of HgT and MeHg. In addition, the radioactive isotope 197Hg was used to determine the methylation potentials. The concentrations of HgT in sediments ranged between 0.06 and 2.23 nmol g^{-1} and vary irregularly with depth, which may reflect changes or redistribution during diagenetic processes. No correlation between HgT and organic carbon content was found, but a relatively high proportion of MeHg to HgT of approx. 2.0% was observed. The integrated flux of HgT was estimated to be 109 kmol year^{-1} and agrees well with the mass balance calculation preformed for total underwater emissions of HgT in the Mediterranean Sea of 80 kmol year^{-1} by Rajar et al., 2007. The emissions of MeHg were estimated to be 14 kmol year^{-1} and indicate that deep-sea sediments could be an important source of the MeHg content in marine biota. It was found that accumulation of MeHg in surficial sediments of the Mediterranean is not directly related to the potential rates of bacterial Hg methylation. Much of the MeHg produced in the sediments is lost to the overlying water. Our results suggest that MeHg production depends on partitioning of Hg(II) influenced by the organic carbon content in the sediment. Reduction of organic carbon in sediment could increase pore water Hg(II) and enhance bacterial production of MeHg.

These are the main results of a first study performed on Hg speciation, partitioning and methylation potential in deep sea sediments, giving a new insight into deep sea Hg biogeochemical cycling.
Contrasting surface chemistry of adsorbed ions in iron oxyhydroxide coatings on feldspar grains in soils deposited over mineralized and unaltered granite in the Big Creek Mining District, Idaho, USA (ToF-SIMS analysis)

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An existing hypothesis in applied geochemistry suggests that a variety of ions are absorbed on pre-existing iron and manganese oxyhydroxide coatings formed on mineral grains in soils, and that these ions move upward and laterally by vadose zone, vapor transport, electrochemical and biogeochemical processes to these depositional sites. Desorbants are used to selectively extract these ions from the grain coatings and the analytical results are used in conjunction with geospatial techniques to identify areas of potential mineralization. Feldspar grains from both samples were used to eliminate potential effects of confounding variables that may be associated with other minerals and surface coatings on those minerals. Elemental maps created by ToF-SIMS analysis indicate that hydrothermal trace elements associated with mineralization concentrate in iron oxyhydroxide coatings on feldspar grains in b-horizon soil developed over gold-silver mineralized and altered granite. Weathered pyrite is the probable source of iron oxyhydroxide mineral coatings in this soil. Elemental maps of arsenic, antimony, lead, and copper are variably present in coatings along flat grain surfaces, and are strongly enhanced in surface coatings located on grain corners. These elements are below detection in iron oxyhydroxide coatings on feldspar grains in b-horizon soils developed over an unmineralized granite outcrop located several kilometres from known geochemical anomalies or mineralized sites. Iron oxyhydroxide coatings on soil grains at the unmineralized site are related to weathering of biotite. These observations suggest that the depositional chemistry portion of the hypothesis is valid.

Catalytic potential of silicate, oxide and sulfide minerals for the abiotic polymerization of glycine under high pressure and temperature conditions

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Polymerization of amino acids is the essential step for the origin of life. It is still uncertain if minerals had a progressive role for polymerization of amino acids in any ancient geological environments. Polymerization experiments of glycine, catalyzed by minerals, were performed under 150°C and 100 MPa for 8 days, using a test-tube type autoclave. Various sulfides (millerite, troilite, pyrite and sphalerite), magnetite and montmorillonite were mixed with glycine monomers in order to test if these minerals behave as the catalyst to promote peptide formation. HPLC and LCMS analyses of the products showed that: (1) glycine in all the experimental runs polymerized from 2-mer to 11-mer; (2) the highest yield of oligopeptides was found in the sphalerite experiment; (3) cyclic anhydride was more abundant in the montmorillonite experiment; and (4) other minerals behaved intermediately between sphalerite and montmorillonite.

In order to examine surface processes, adsorption experiments were also performed by NH3- and CO2-TPD (temperature-programmed desorption) methods. The TPD analyses indicated that sphalerite has high adsorption capabilities both of NH3 and CO2. These results imply that sphalerite has high adsorption capabilities of amino and carboxyl groups affecting the elongation of peptides. On the other hand, montmorillonite only has the capability to adsorb NH3, thus amino group. This type of adsorption may only result in cyclization of amino acids preventing elongation of oligopeptides.
Application of compound-specific radiocarbon dating for studying West Antarctic Ice Sheet during the Late Quaternary

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Compound-specific radiocarbon dating is a powerful tool for reconstructing chronologies in high-latitudinal sediments. Since high-latitudinal sediments generally lack carbonate, total organic matter has been used to establish sediment chronologies. However, the “contamination” of reworked sediments eroded from the Antarctic Continent leads to anomalously old core-top ages or to age reversals down-core (Ohkouchi and Eglinton, 2006).

Ohkouchi et al. (2003) first reported that the radiocarbon dating of solvent-extractable, short-chain (C14, C16, and C18) fatty acids isolated from surface sediments of the Ross Sea, Antarctica, indicated them to be consistent with the modern DIC reservoir age (Pre-bomb: $\Delta^{14}C \approx -150‰$, Post-bomb: $\Delta^{14}C \approx -100‰$). Furthermore, the radiocarbon ages of these fatty acids at five down-core intervals progressively increase with the core depth. These results clearly show a utility of the compound-specific radiocarbon dating for developing sediment chronologies in Antarctic margin sediments (Ohkouchi and Eglinton, submitted).

In this study, we determined radiocarbon ages of the fatty acids from a core recovered in the NW Ross Sea to reconstruct sediment chronologies. Furthermore, we determined hydrogen isotopic compositions of sedimentary biomarkers in the core. Around 7, 6, 4.5, and 2.5 kyr ago, the reconstructed $\delta^2$D values of paleo-seawater were -200‰ or lower, suggesting a large amount of meltwater influx to the Ross Sea. We propose that recurrent massive melting of WAIS could have occurred at least four times in the Holocene.

References

Mobility and transport of Nd isotopes during weathering of till in a boreal forest

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It has been suggested that the Nd transported in the large, pristine Kalix River in northern Sweden originates from organic bound REE from the uppermost soil horizons (Öhlander et al., 2000; Andersson et al. 2001). Here we present new data of the distribution of Nd isotopes in a spodosol profile developed in a till which was deposited 8700 years ago. In addition, Nd isotopes were analysed in soil water, groundwater and stream water in a small catchment situated within the Kalix River drainage basin.

The results indicate that a large part of the Nd released by weathering in the E-horizon is trapped in the B-horizon, and that the major part of the dissolved Nd exported from the studied catchment via stream water is derived from weathering in the shallow groundwater zone within the till rather than in the top soil. Due to the very low weathering rate at that depth, there is still a relatively little altered pool of reactive minerals containing Nd. It will take a very long time ($>> 8700$ years) before the Nd leaving the catchment will have an isotopic composition different from today.

The export of Nd from a large boreal drainage basin, in this case to the Bothnian Bay, is, to a large extent, controlled by selective weathering and reactions with organic matter in the upper soil horizons, and by Nd released by slow weathering in the groundwater zone.

References
Formation of probable lateritic soils ~3.43 Ga in the Pilbara Craton, Western Australia

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An alteration zone (~20-80 m thick), characterized by the abundance of pyrophyllite (aluminum-rich clay) and the depletion of iron and most elements, is widely developed in pre-3.4 Ga submarine basalts that occur beneath the oldest-known (~3.4 Ga) erosional unconformity (i.e., oldest land surface) in the North Pole Dome region of the northern Pilbara Craton, Western Australia. Some previous researchers suggested this alteration zone as a product of hydrothermal activity ~3.4 Ga.

We have recently discovered more than 100 iron pods (each ~1 to ~6 m thick and ~1 to ~50 m long) within the iron-depleted pyrophyllite-rich zone at seven sites over a ~30 km expanse in the studied area. They typically occur as clusters at 0 - 30 m below and generally parallel to the ~3.4 Ga unconformity, rather than being parallel to the modern groundwater tables. These iron pods are mostly composed of well-crystalline hematite (~30 to ~90 wt% Fe2O3) and pyrophyllite.

The geometrical, geological, mineralogical, and geochemical characteristics of iron pods and alteration zone in the studied area (e.g., the rarity of quartz-sulfide veins; sizes and crystallinity of hematite; trends of Al/Ti, Mg/Ti, Fe/Ti, Ca/Ti, Na/Ti, and K/Ti ratios; trends of trace element ratios; REE behaviors) resemble those of “groundwater-type” laterites of the Phanerozoic and Proterozoic ages (e.g., the ~2.2 Ga Hekpoort and Hokkalampi paleolaterites). Groundwater-type laterites require the following conditions for formation: (i) distinct wet/dry seasons; (ii) the development of microbial mats/vegetation on/in soils during wet seasons, which produce abundant organic acids that leach both ferric and ferrous irons from the soils and create ferrous-rich groundwater; and (iii) an abundance of oxygen molecules supplied from the atmosphere to the soils and groundwater, mostly during dry seasons, to precipitate the aqueous ferrous iron as ferric (hydr)oxides. Therefore, if the North Pole Dome ironstones are indeed ~3.43 Ga laterites, they suggest the very early developments of the terrestrial biosphere and an oxygen-rich atmosphere.

Mass dependent isotopic fractionation of Ce and Nd in geochemical samples

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The study of naturally occurring mass dependent isotopic fractionation of rare earth elements (REEs) has a potentially significant influence in geochemical research fields. Isotopic fractionation of REEs with their chemical similarities and gradual changes of ionic radius may provide new insights about chemical weathering processes. One of the most attractiveness of REEs is anomalous behavior of Ce mainly due to the existence in not only the trivalent state but also the tetravalent state. Since the valence of Ce depends on the redox conditions, differences of isotopic fractionation between Ce and the other REEs could provide information about the redox conditions of depositional environment. Among the other REEs, Nd could play an important role in the stable isotope geochemistry of REEs as a reference compared to Ce. Moreover, radiogenic growth of 143Nd can also provide chronological constraints on a sample formation process.

In this study, we have developed a new chemical and mass spectrometric procedure for the investigation of mass dependent isotopic fractionation of Ce and Nd in geochemical samples. In order to detect the small isotopic fractionation, mass discrimination effects on Ce and Nd isotopes were externally corrected by Sm and Eu, respectively. The resulting analytical precisions for δ142/140Ce and δ146/144Nd were better than 0.01% (2SD). Isobaric interferences were eliminated by an extraction chromatography using a Ln spec. resin. We examined isotopic fractionation of Ce and Nd during the separation procedure. The result of the test demonstrated that the cumulative isotopic value of the eluent showed no detectable isotopic fractionation through a few percent loss during the chromatographic separation.

Cerium and Nd isotopic compositions of GSJ geochemical reference samples (Basalt, JB-1a; Andesite, JA-2; Manganese Nodule, JMN-1; Chert, JCh-1; Dolomite, JDo-1) have been measured in order to examine the possible isotopic fractionation of Ce and Nd. The isotopic data of Ce and Nd for the samples revealed δ142/140Ce and δ146/144Nd data for JDo-1 were different from that of the igneous rock samples. Moreover, there was positive correlation between the resulting δ142/140Ce and δ146/144Nd, implying that the isotopic variation of Ce and Nd observed in JDo-1 might be caused by non-redox reactions such as preferential precipitation or dissolution processes, rather than the redox reaction. In this presentation, Ce and Nd isotopic data on several geochemical materials and possible mechanism of isotopic fractionation will be discussed.
Interactions of heavy elements with microorganisms

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Introduction
The high capacity of microbial surfaces to bind actinides may affect the migration of actinides in the environment. However, we have only limited knowledge of the role of microorganisms in the migration of actinides in the environment. We have been conducting basic scientific research on microbial interactions with actinides in order to elucidate the environmental behavior of actinides under relevant microbial process conditions.

Pu(IV) sorption and reduction
Adsorption of Pu(IV)-desferrioxamine B (DFO) on bacteria indicate that Pu(IV) is dissociated by contact with cells, after which Pu(IV) is adsorbed, and that pH dependence of adsorption density of Pu(IV) on cells is dominated by the stability of Pu(IV)-DFO complexes. Study on reduction of Pu(IV) in the presence of citric acid at pH 7.0 suggested that Pu(IV) is reduced to Pu(III) by the activity of sulphate reducing bacteria.

U(VI) mineralization
Uranium mineralization by the yeast Saccharomyces cerevisiae was examined by batch experiment at pH 3.2. Analysis of the U(VI)-bearing precipitates by FESEM-EDS, TEM, and visible diffuse reflectance spectrometry demonstrated the presence of H-autunite, UO3PO4·4H2O and thermodynamic calculations suggest that the chemical compositions of the solutions were undersaturated with respect to H-autunite, but were supersaturated with ten-times more U(VI) and P than were actually observed. These findings indicate that the yeast’s cell surfaces, rather than the bulk solution, offer the specific conditions for this geochemical process.

A combined terrestrial and marine geochemical mapping project in Japan

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Spatial distribution patterns of elemental concentrations on land, geochemical maps, are effective for mineral exploration and environmental assessment. In Japan, the Geological Survey of Japan, AIST conducted a nationwide geochemical mapping program at 1:2,000,000 scale using fine stream sediments for these purpose (Imai et al., 2004). Japan is, however surrounded by a vast expanse of sea, so that examination of geochemical baseline in coastal-open sea is also essential for environmental assessment. Approximately 3000 surface marine sediments around Japan were collected for this purpose and analyzed for 51 elements including heavy metals (e.g. Cu, Zn, Cd, Hg, and Pb). This project is intended: 1) to elucidate background of elemental abundance in terrestrial and marine areas of young island arc; 2) to find mass transport from land to sea; and 3) to estimate diffusion processes of pollutants.

The elemental concentrations of marine sediments are determined primarily by grain size. Most elemental concentrations increase with decreasing grain size and eventually become constant. Overall, marine sediments and stream sediments show similar elemental abundance patterns, but marine sediments have lower elemental abundance than stream sediments because of dilution effects imparted by calcareous sediments and organic materials. These results suggest that marine sediments in coastal seas originate mainly from terrestial materials. However, a few examples of direct mass transport from terrestrial area to marine environment are apparent. The spatial distribution patterns of K and Cr concentrations, which are good examples of mass transport, suggest two types of high-concentration area extending continuously from land to sea: high concentration area proximal to a river mouth (20-30km) and high concentration area extending over 60 km offshore along a deep-valley.

These results suggest that sediments deposit by fanning out near shore and a part of them are further conveyed along the deep-valley by gravity movement. Diffusion of heavy metals such as Cu, Zn, Cd, Sn, Pb, and Bi is observed in coastal bays surrounded by urban and industrial areas, from which the stream sediments are extremely abundant in those elements. It is noteworthy that the materials with heavy metals seem to remain in the bay without diffusing to the outer sea. The sediments with heavy metals might not diffuse readily to the outer sea because of a strong bottom current (estuary circulation) that flows from outer sea to the inner part of the bay.

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The effect of iron spin transition on electrical conductivity of perovskite and magnesiowüstite
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The electrical conductivity is one of the observable physical properties of the Earth’s mantle. The pyrolitic lower mantle mainly consists of Al-bearing (Mg,Fe)SiO3 perovskite and (Mg,Fe)O magnesiowüstite, and the electrical conduction occurs through these two iron-bearing phases. The electrical conductivity profile in the lower mantle has been estimated by extrapolating the data from 40 GPa [Shankland et al., 1993]. Recently, Badro et al. [2003, 2004] discovered a pressure-induced electronic spin transition of iron in both magnesiowüstite and perovskite. The spin transition of iron may have significant effect on electrical conductivity, but it has not been examined yet.

Here we measured the electrical conductivity of Mg0.81Fe0.19O magnesiowüstite and Mg0.91Fe0.09SiO3 perovskite at high pressures up to 135 GPa and 300 K in a diamond-anvil cell (DAC). The results demonstrate that the electrical conductivity of magnesiowüstite increases with increasing pressure to about 60 GPa and exhibits anomalous behavior at higher pressures; it conversely decreases to around 80 GPa and again increases very mildly with pressure to 130 GPa. Perovskite shows similar profile to that of magnesiowüstite; it increases to 60-70 GPa and decreases to 80 GPa, then again increases mildly with pressure up to 135 GPa.

This observed reduction in electrical conductivity may be explained by the high-spin to low-spin transition of iron in magnesiowüstite and perovskite. A smaller pressure effect on the electrical conductivity of magnesiowüstite above 80 GPa suggests that a dominant conduction mechanism changes by the electronic spin transition. The electrical conductivity of perovskite becomes higher than that of magnesiowüstite above 90 GPa. Therefore, perovskite can be a main conductor, at least in the deep lower mantle. The electrical conductivity below 2000-km depth in the mantle may be much smaller than previous estimates due to the effect of electronic iron spin transition.

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Geochemistry and TEM observation of graphite in 3.8 Ga metasedimentary rocks in Isua Supracrustal Belt
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The remnant of oldest life was reported only from one outcrop at the 3.8Ga Isua Supracrustal Belt (ISB), West Greenland [1], although graphite-bearing rocks are located at several spots in the Isua area. New outcrops of graphitic schist, which graphitic contents are up to 8.8 wt %, were found through the course of this study. The graphitic schist is interbedded with banded iron formation and extended for approximately 500m from NW to SE. Major and trace element were determined on graphitic schist samples. Carbon isotope compositions of graphite were determined using the laser micro probe system. TEM analyses were also performed on the extracted graphite samples.

CI chondrite-normalized REE patterns of the new graphitic schist are similar to other Archean shales or banded iron formation. Therefore, new graphitic schist has characteristics of marine clastic to chemical sediments.

Carbon isotope compositions of graphite were determined on 50 samples. Their compositions range from –22.4 per mil to –13.2 per mil. The carbon isotope compositions change systematically, correlated to geological occurrence. Lightest carbon isotope composition was found in the most western area where complicated nano-scale textures of graphite were observed by TEM. The heaviest carbon isotope composition was found in the most eastern area. This carbon isotope shift is probably due to the more metasomatic effect compared to the western samples. Considering those all geochemical data, graphite in new graphitic schist also gives another evidence of 3.8Ga marine biota.

References
Wilhemine copper mine, Spessart, Bavaria: A Kupferschiefer-related, hydrothermal mineralization

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The vein-type copper mineralization in the abandoned Wilhelmine copper mine at Sommerkahl is hosted by orthogneisses of the Spessart Crystalline Complex. These are covered by sedimentary rocks of Permo-Triassic age, including the stratabound base-metal mineralization of the Kupferschiefer. Ore textures in the sulfide veins testify to three stages of mineralization:

(i) An early stage is characterized by colloform textures, documented by spherical, garland-shaped or cockade-like aggregates of tennantite I, enargite I, pyrite I, chalcopyrite I, bornite I and digenite I.

(ii) During a subsequent recrystallization stage, these were overgrown by, or enclosed in, tennantite II, enargite II, bornite II, digenite II, pyrite II and chalcopyrite II. Fine-grained to submicroscopic digenite-bornite intergrowths, exsolved from an initial 1a-solid solution, contain up to 55 mole-% of bornite, indicating a minimum temperature of 175°C for this stage.

(iii) A late alteration stage led to the replacement of primary sulfides by yarrowite, spioncopite and rare covellite, together with goethite.

The close spatial association of the vein-type Cu mineralization with the overlying Kupferschiefer suggests a genetic relationship. In situ sulfur isotope analyses of sulfide minerals yielded negative δ²⁸S values of −12.8 to −23.9 ‰, indicating a derivation from the Kupferschiefer, presumably by hydrothermal leaching. By contrast, we assume that the metals were derived from deep-seated sources, transported upwards by hydrothermal fluids and precipitated by thermochemical sulfate reduction, due to interaction with the Kupferschiefer. Formation of the sulfide ore veins is related to a hydrothermal activity in Middle Jurassic to Early Cretaceous times.

Micro-Raman and cathodoluminescence characterization of shocked quartz from impact craters

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Introduction
Evidence of shock metamorphism can be sufficiently proved by the existence of planar deformation features (PDFs) found in quartz. However, visual identification of the planar features under optical microscope should be unambiguous for clarifying PDFs. To characterize shock-induced planar microstructures such as PDFs in quartz from various impact craters, we used a combination of cathodoluminescence (CL) and micro-Raman spectroscopy with high sensitivity and high spatial resolution.

Samples and Methods
Quartz grains from Ries Crater, Barringer Meteor Crater, and Oikeyama Crater are employed for Raman and CL measurements. They were prepared as polished thin sections. PDFs are observed in several quartz grains under a petrographic microscope. Raman spectra were acquired with a confocal micro-Raman spectrometer at 20 mW using a Nd:YAG laser (532 nm) excitation system. CL imaging and spectral measurements were carried out on a SEM-CL (scanning electron microscope combined with a grating monochromator) with an accelerating voltage of 15 kV.

Results and Discussion
SEM-CL imaging of quartz grains from each crater shows non-luminescent or CL-dark lines related to PDFs, which can be clearly observed under polarized microscope. Raman spectra of shocked quartz from the Ries Crater exhibit a pronounced peak at around 459 cm⁻¹, which can be assigned to Si-O-Si stretching vibration, whereas unshocked quartz has a sharp and intense peak at 464 cm⁻¹. This frequency shift may arise by a distortion of the structural configuration (i.e., formation of high density silica) caused by shock-metamorphism. The Raman imaging of shocked quartz from each impact crater shows a stripe pattern suggesting layers comprised of high and low crystalline parts corresponding to the optical image of PDFs. Our results show that shock-induced amorphization might effect an alteration of electronic transition processes in defect centers that are correlated to CL emission.
Hydrogen isotope geochemistry of basalts from Samoa

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Hydrogen is present at low concentrations (tens to hundreds of ppm H₂O) throughout the upper mantle but exerts a strong influence on the melting behavior and rheologic properties of peridotite. The distribution of hydrogen in the entire mantle is a key constraint on mantle convection that remains unquantified. The D/H ratio of hydrogen in fluids and in silicate materials can be fractionated by tens of per mil under mantle conditions and offer an opportunity to identify and describe hydrogen storage and transport processes within the mantle. To pursue this goal we examined the hydrogen isotope composition of submarine ocean island basalt glasses collected from Malumalu, Vailu’lu, and Ta’u in the Samoan island chain. Lavas from the Samoan islands contain extreme trace element and radiogenic isotope enrichments that define the EM 2 (enriched mantle 2) mantle endmember [1]. The D/H composition of Samoan lavas vary between -79 and -37 per mil, a similar range to what is found in other ocean island basalt localities and in back-arc basin basalts that are influenced by fluids released from subducting ocean crust. The lowest δD values of Samoan glasses (-79 per mil) are close to the mode of values for mid-ocean ridge basalts (-75 per mil) while the highest value is similar to the isotopic composition of serpentine in equilibrium with seawater. This range in hydrogen isotope composition suggests that the mantle source region of Samoan basalts may contain fluid derived from ancient subducted ocean crust that has retained a distinct hydrogen isotopic composition over the timescale of mantle mixing.

Correlations between La, ⁸⁷Sr/⁸⁶Sr, and water content in Samoan lavas are attributed to equilibration of initially water rich subducted materials with the ambient mantle water content [2]. Equilibration is possible due to rapid diffusion of hydrogen in mantle minerals [3]. The preservation of D-rich compositions in the source of Samoan basalts suggests that hydrogen isotopic anomalies are not diffusively lost, possibly due to high concentrations of D-rich hydrogen in subducted materials that result in large regions of the mantle with high D/H ratio.

References

The model structure of kaolinite in relation to surface complexation

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Methods

Surface complexation modelling using the FITEQL software was applied to explain the surface acidity of kaolinite. In this context, a number of different models and modelling approaches were tested. Further, a density functional method, CASTEP (Accelrys, 2001), was used to investigate the crystal and surface structures of kaolinite, and to calculate surface charge densities.

Results and discussion

To enable the interpretation of adsorption results with surface complexation modelling, an adequate characterization of the surface charging of the adsorbent is needed. In general, titration experiments are capable of providing this information for ionisable interfaces. However, results based on experimental data give only average values of surface charge densities. Therefore, in this study, molecular modelling was used to calculate surface charge densities of likely the most reactive kaolinite crystal faces separately (see Figure 1 for the (010) surface). Based on this information, an attempt will be made to constrain the number of surface sites and magnitude of surface hydrolysis constants, often considered as adjustable parameters devoid of deeper understanding, in surface complexation models.

Figure 1: Model (010) surface of kaolinite and its surface charge density.

Conclusions

The molecular-level modelling produced invaluable background information of the kaolinite surface for further development of surface complexation models in terms of the surface charging and the adsorption of metal cations.

References

Chemostratigraphy and lead isotopic composition of a sediment core profile from a small pond in a remote equatorial island

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A 72-cm long core was collected from Lagoa da Viração (LV), a small pond in the Fernando de Noronha island, northern Brazil, in order to study vertical changes in major, trace and Pb isotopes concentrations with depth. Sediments from the lower section of the core (20-70 cm) contains essentially mineral matter, while in the upper section (0-20 cm) mineral matter is mixed with organic matter, which is increasingly more abundant toward the top. Lithogenic conservative elements – Si, Al, Fe, Ti, Co, Cr, Cu, Ga, Hf, Nb, Ni, Y, Zn, Zr and REE – exhibit remarkably constant values along the core, with concentrations similar or moderately higher than those of the bedrock. The vertical distribution of soluble elements – Ca, Mg, Na, K, P and Mn – is also homogeneous, but these elements are systematically depleted in relation to the bedrock. LOI, TOC, Br, Se, Hg and Pb, although showing nearly constant values in the lower section of the core, are significantly enriched in the upper section. Pb isotopic ratios are nearly constant and very similar to those of the bedrock in the lower section of the core, but are increasingly less radiogenic in the upper section. Ti-normalization allowed the separation of natural and anthropogenic Pb, indicating that the latter was restricted to the upper section of the core, and was probably added to the sediments via atmospheric transport. Se and Br appears to be originated from seawater sprays. The source of Hg seems more uncertain, but at least partially it might have been accumulated via atmospheric deposition. Whatever the source of Pb, Br, Se and Hg, their close association with TOC suggests that organic matter has played an important role in their accumulation in the surface sediments.

Molecular markers and trace-metals as proxis of biomass combustion in Central Amazon sediments

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Large scale forest fires occur in the region denominated “deforestation arc” circumscribing the southern area of the Amazon Region. Under certain meteorological conditions like in the dry season of 2005 clouds of particulate matter reached Manaus and the Central Amazon. The goal of the present work was to search for indicators of combustion in sediments of the Solimões River and associated lakes. For this sediments were sampled in the wet and dry seasons in 2005 and were analysed for 39 PAHs, molecular markers and trace-metals. Among other approaches, to verify the contribution of biomass combustion to the PAH pool in the sediments the diagnostic ratio Fl/(Fl+Py) was plotted versus 1.7/(1.7+2.6)DMPh, which was used as a proxy for combustion sources. The cross evaluation shows PAH in sediments deriving predominantly from mixed combustion sources. Evidently the traffic of ships along the river contributes for the pool of PAH in the sediments. Significant correlation (p<<<0.05) of perilene, the major PAH, with BbFl, BkFl, BaPy and several metals were found. These and additional correlations were confirmed in the factorial analysis in which the correlation coefficients in factor 1 were: 0.79 for Fl, 0.76 for BaA, 0.83 for BbFl, 0.66 for BkFl, 0.82 for BaPy, 0.83 for Cd, 0.77 for Pb, 0.79 for Cu and 0.73 for Zn. The association of perilene with combustion derived PAH and metals, which can also be produced in forest burning, is an indication that combustion is one of the relevant sources of this compound to the sediments. For the dry season samples, strong correlations were found between 1.7/(1.7+2.6)DMPh and trace metals (Cu, V, Zn, Pb, Cd) which confirm the contribution of forest fires for the pool of trace metals in sediments, especially in such occasions of intense combustion as in late 2005. The same approach applied to a dated core showed that biomass combustion imprint is present in sediments deposited since the end of the 19th century. In general the high values for the ratio Σ3-6 ring PAH/Σ5 Alk PAH series sustain the evidence that combustion is a major source of PAH in the examined sediments.
Seasonal variations of physical and chemical erosion: A three-years survey of the Rhône river (France)

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For obvious logistical reasons, most previous studies on the main world rivers were based on wide scale investigations carried out on short timescales. By comparison, much less effort has been devoted at long term monitoring, as a mean to verify the temporal variability of the average characteristics, temporal trends, and representativity of short-term investigations. Here we report the results of a three years survey (November 2000 to December 2003) of the geochemical composition of major and trace elements in dissolved and suspended matter in the lower Rhône River (France), the largest river of the Mediterranean area. Subsurface water samples were collected in Arles, 40 Km upstream of the estuary, twice a month routinely, and at high frequency during flood events.

We show that the annual average SPM flux of the Rhône River to the Mediterranean Sea (7.25 x 10^6 tons/yr) was largely controlled by the flood events (83% of the solid discharge occurred in less than 12% of the time), and that the precision on the total output flux depends strongly on the precise monitoring of SPM variations during the floods. Chemical budgets have been calculated to discriminate the respective contributions of marine aerosols in rain water, carbonate, silicate and evaporite weathering, as well as anthropogenic inputs.

Our data corroborate previous studies suggesting a strong coupling between chemical and physical erosion fluxes, during the Rhone hydrological seasonal cycle. However, the correlation observed between physical and chemical transport rates is clearly different from that reported on global compilations of annual averages in the largest world rivers.

The steady state model of Gaillardet et al. (1995) has been applied to the chemical composition of dissolved and solid products. We show that the Rhône River exports currently much less material than produced at steady-state by weathering in its watershed. The sediment flux inferred from the steady-state calculation (20 x 10^6 t yr^-1) is on the same order as those estimated in the literature for the nineteenth and the beginning of the twentieth centuries. This unbalance may suggest that the Rhône is under a transient erosion regime following climate change (i.e. significant decrease of the floods frequency). On the other hand, the unbalance may also be due to the trapping of alluvion by the numerous dams on the river and its tributaries.

Abiotic hydrolysis of glucose-1-phosphate adsorbed at the water-goethite interface

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Phosphorus is essential to organisms. In the environment it occurs mainly as inorganic phosphates or as organophosphates. Due to the high reactivity of the phosphate group, these interact strongly with environmental particles. In order to make the phosphate in organophosphates available for uptake by organisms, hydrolysis is usually required. This process may be mineral-surface-mediated (abiotic) or enzymatic (biotic).

Glucose phosphate is one of the dominant components of the natural organophosphate pool [1]. The aim of the present work is to study the interactions between glucose-1-phosphate and goethite, with respect to adsorption characteristics and the role of the mineral surface in the abiotic hydrolytic process. The work was done in series of batch experiments, measuring ligand adsorption as a function of pH and time. The concentrations of the hydrolytic products glucose and phosphate were also measured. ATR-FTIR spectroscopy was used to evaluate the surface speciation of glucose-1-phosphate. Kinetic data will be presented which show the pH dependent surface-promoted hydrolysis, and these will be discussed in combination with molecular-level results obtained by ATR-FTIR spectroscopy.

References
As(V)-bearing lepidocrocite and green rust reduction by *Shewanella putrefaciens*: Evidence for Fe(II) carbonate hydroxide formation

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Arsenic is a toxic metalloid involved in important health issues due to the contamination of water resources. High arsenic concentrations typically derive from the breakdown of As-bearing Fe-oxides, particularly under anaerobic conditions. A variety of microorganisms influences arsenic mobility using oxidation, reduction, and methylation reactions that strongly control arsenic speciation in the environment. In the present study, *Shewanella putrefaciens* strain ATCC 12099, an iron-respiring bacterium, was incubated under anaerobic conditions with As(V) ions, As(V)-bearing lepidocrocite, or a lepidocrocite without arsenic. Results show that strain ATCC 12099 is capable of reduction of HAs(V)O₄²⁻ to H₃As(III)O₃ when the former oxoanion is dissolved in solution (at pH 7.8), or when it is adsorbed onto the surface of lepidocrocite. Cultures in which lepidocrocite was used as the sole electron acceptor led to the formation of biogenic hydroxy carbonate green rust prior to ferrous carbonate hydroxide. In contrast, when the electron acceptor was As(V)-bearing lepidocrocite, XRD analysis revealed ferrous carbonate hydroxide to be the dominant reaction product; no green rust formation was observed in this case. As K-edge XANES spectroscopy indicated that all As(V) (K-edge(max) = 11875eV) was reduced to As(III) (K-edge(max) = 11871.3eV). These results suggest the presence of As(III) either on the surface of ferrous carbonate hydroxide, and/or in another ferrous-solid phase, and they show for the first time bacterial reduction of hydroxy carbonate green rust.

Nd Isotopic Constraints from the 3.8 Ga Nuvvuagittuq Greenstone Belt for the Degree of Depletion of the Early Earth’s Mantle

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Rare occurrences of Eoarchean mantle-derived crust provide the only compositional and isotopic constraints on the early crust-mantle differentiation of the Earth. There is currently considerable debate about the implications of the Nd isotopic compositions of such early Archean mantle-derived rocks. The relatively high positive initial εNd values obtained on Eoarchean rocks (Nulliak Assemblage, Labrador, Canada; Amitsok Gneisses, Akilia and Isua supracrustal assemblages, SW Greenland) are interpreted to indicate derivation from a mantle source already strongly depleted in the Eoarchean, implying that significant volumes of continental crust had formed early in the Earth’s evolution. Here we present the Nd isotope data of the newly discovered ca. 3.8 Ga Nuvvuagittuq greenstone belt (Northern Québec, Canada), and discuss their implications for early mantle depletion.

The Nuvvuagittuq greenstone belt contains numerous ultramafic and gabbroic sills. Most of the gabbro and ultramafic samples display positive εNd (3.8Ga) values ranging from -1.8 to +3.9, with an average of +1.3 ± 0.2 in 29 samples. The few samples that yield εNd (3.8Ga) values > +3 (up to +3.9) suggest that they may have been derived from a mantle source that had already experienced an extensive trace element depletion well before 3.8 Ga, equivalent to that seen in the present-day MORB source. Such a degree of depletion of the early Archean mantle, however, is not supported by the flat to slightly LREE-depleted profiles of the gabbros. Furthermore, whole rock analyses for a series of samples from an ultramafic sill and a second series of samples from a gabbroic sill fall along ~3.8 Ga isochrons with initial εNd values of +1.3 and +2 respectively, values which are similar to the mean of all the individual sample values. This suggests that the few higher εNd (3.8Ga) values are either anomalous or indicate heterogeneity of the mantle source of Nuvvuagittuq’s rocks. Nevertheless, the Nd isotopic compositions of these mantle-derived rocks suggest that the degree of depletion of the mantle recorded in the Nuvvuagittuq greenstone belt is not as extreme as that indicated by the Nd isotopic compositions of the 3.8 Ga SW Greenland rocks.
Using $\delta^{30}{\text{Si}}$ to follow the soil-plant Si cycling in a weathering sequence of volcanic ash soils, Cameroon

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Plants take up Si as silicic acid and form phytoliths, a biogenic opal (BSi). This Si bicycling affects the availability of Si for clay formation, and for Si export through waterstreams. Si stable isotopes measurement provides a tool to quantify present and past impacts of plants on the continental Si cycle.

In order to calibrate this proxy, we report on detailed $\delta^{30}{\text{Si}}$ of plants, sand ($>50\mu$m), silt (2-50$\mu$m) and clay fractions ($<2\mu$m), and amorphous Si (ASI) in a weathering sequence of andesitic ash soils from the Mungo area (Cameroon). Plant communities consist of 50 years old banana stands. The soil sequence involves an increasing clay content from young (Y) to old (O) volcanic soils (vs). The $\delta^{30}{\text{Si}}$ values were measured by MC-ICP-MS Nu Plasma in medium resolution, operating in dry plasma with Mg doping: $\delta^{30}{\text{Si}}$ vs NBS28 $\pm 0.07‰$ ($\pm 1σ$).

Compared to fresh andesitic ash (-0.39‰), clay fractions displayed a gradient from -1.19‰ in Yvs to -1.62‰ in Ovs, thus confirming the trend of lighter isotopic compositions with increased weathering. The isotopic signatures of silts fractions (-0.44‰ in Ovs, -0.03‰ in Yvs) compared to clay fractions support that $\delta^{30}{\text{Si}}$ may reflect the ratio between primary and secondary minerals. ASI fractions (involving phytolith-rich BSi, volcanic glasses, and allophane constituents) were heavier in surface horizons than at depth ($\Delta^{30}{\text{Si}} = +0.34‰$), in agreement with the surface accumulation of phytoliths. Indeed, banana plant isotopic compositions were +0.10 and +0.55‰ respectively in Yvs and Ovs. Moreover, ASI were lighter in Yvs (-0.38‰) than in other soils (+0.44‰) pointing to a larger effect of phytoliths in ASI of weathered soils, devoid of volcanic glasses. Surrounding river waters in this area were very heavy (+1.20‰).

Our $\delta^{30}{\text{Si}}$ data thus support that plants can induce a strong isotopic imprint by rejecting phytoliths to soil surface. Numerous and successive plant cycles leading to phytolith accumulation would gradually produce a heavier signature in dissolved Si export. This plant impact was underestimated until now. It may have considerable implications on the understanding of the Si continental cycle and the quantitative assessment of Si transfer from land to sea and ocean.
Influence of acid mine drainage on aquatic life at Sar Cheshmeh copper mine

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Introduction
Investigations on impact of waste dumps on producing of acid mine drainage at Sarcheshmeh copper mine showed a pH range of 3 - 5.5, which increase the concentration of some toxic heavy metals (Cu, Zn, Pb, As, Cd, Se, Sb …) higher than the permitted standard limits (WHO). In such degraded water some of dominant microorganisms are able to survive. The fungi (Geotrichum sp. & Aspergillus sp.), bacteria (Pseudomonas sp. & Tiobacillus sp.) and non-bacterial microorganisms (green algae) were recognized in some of acidic drainages. A kind of filamentous green algae, tolerant to acid and high dissolved elements observed. The genus of mentioned algae is Ulothrix and species is Gigas, without antimicrobial and antifungal properties. These algae are present in drainages with high total dissolved solids (TDS≈1800 ppm) and acid conditions to pH 3.

Discussion of results
This research suggest the level of acidity, type of dissolved elements and the secondary minerals formed on substrate, all are important factors in distribution of these algae. Field data show the prolific growth of Ulothrix between pH 3 – 4.5. The colloidal conditions, in particular the presence of suspended iron and aluminium, prevent the growth of them. Sampling and Chemical analysis of algae for some heavy metals (Cu, Zn, Pb, As, Sb, Cd, Se, Mo) showed the high absorption of some heavy metals (Cu 3500ppm, As 5000ppm…) to manifold in compare with soil and water samples, against their less tendency to absorption of Cd (10ppm). The bacteria especially Pseudomonas may strongly impact environmental conditions in acid mine drainages.

Conclusions
The natural presence of these algae in acid mine drainage is a factor to remove heavy metals in this mine. Further works to determine natural contributions of these algae and bacteria to mitigation of poor water quality is under investigation.

References

Nanometric jarosite/alunite in carbonaceous matter rich cherts: Marble bar drill core (#1 ABDP):
Indications for acid-sulfate conditions in a hydrothermal system

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Jarosite/alunite are observed in superegen (sulfate zone of gossans) or in hydrothermal environments [1,2]. These hydroxysulfates, which were also detected on the Martian surface, can be formed abiotically [1,3] or biotically [4]. In the light of this discussion, carbonaceous matter (CM)-rich Archean cherts (0.5wt Corg., 3.5 Ga) from Marble Bar Drill core #1 (~75m depth) were studied. They represent a silt to fine sand-sized volcanoclastic silificed sediments crosscut by micro-quartz veins. CM occurs diffuse or as aggregates in the micro-quartz matrix, in pyrite, associated to Fe-oxides or as patches in quartz veins. The Raman spectra of CM show a crystallinity compatible with a temperature of at least 300°C. The black cherts, S (~3.8 wt.%) and Fe 2O3 (4.8 wt.%) rich, contain pyrite, but also sphalerite, galena, chalcopyrite, Ni-Fe-arsenides and Fe-oxides. Large pyrite grains (~100 µm) have irregular rims often characterized by nanometric pyrite spherules. When showing euhedr al grain boundaries, pyrite is rimmed by muscovite. FIB-TEM investigations show that these pyrites are composed of nano-poly- and single crystals, containing traces of Ni, As, Pb and variable Si contents. A nanofilm of amorphous carbon occurs at the interface between pyrite and muscovite. Muscovites contain N (550 ppm) and C (250 ppm) and are non-stoichiometric. The non stoichiometry is related to the presence of nanometric Fe-(K-Na)-sulfates (jarosite/alunite) indicating local acidic-oxic conditions. A hydrothermal origin and temperatures of about 300°C for these sulfates is favoured as shown by low-angle boundaries at nanoscale in micro-quartz grains and the maturity of CM.

References
Hercynian gabbroic intrusions from the Spanish Central System: Constraints on mantle composition under central Spain

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Small basic to intermediate intrusions are scarce within the Spanish Central System (SCS), outcropping among abundant coeval peraluminous granitoids. Although mixing with granite magmas is very common, in this study we only deal with the most primitive basic rocks. They range from norites to olivine gabbro-norites, with some Amph-Phl-rich varieties.

Major and trace element composition suggests a low degree of magma differentiation (Mg# = 0.52-0.75; Cr = 96-1170 ppm), though some Cr-Spl + Ol fractionation might have occurred. K2O content is in the range 0.73-2.82 wt% and a medium-K to high-K calc-alkaline affinity is observed. Their sub-alkaline nature argues against their inclusion in the appinite suite, as previously suggested.

Although two groups of gabbros may be distinguished according to LILE-U-Th concentrations, these rocks show high LREE and LILE concentrations in general, indicative of an enrichment event in the mantle source. Their chondrite and primitive mantle normalised multielement plots show negative Nb, Ta and Ti anomalies and positive Pb anomalies, suggesting involvement of subduction-related fluids or crustal recycling. These patterns resemble those of continental arc-related gabbros, but with lower Ba-Sr contents.

Their Sr-Nd isotopic signatures display a slightly enriched composition close to BSE (εNd = -2.6 to 0.7; 87Sr/86Sr = 0.7045-0.7063). This is also shown by other SCS gabbroic intrusions (e.g. Bea et al., 1999). The short isotopic compositional range suggests the lack of significant crustal assimilation during emplacement. Pb isotope ratios of gabbros also define a small compositional field, similar to SCS granitic rocks. The presence of two gabbro types might be related to variable mineral modes in the mantle sources.

The late-Hercynian mantle under central Spain has been proved to show an heterogeneous composition (Villaseca et al., 2004). This new dataset reinforces that conclusion and points to the involvement of a recycled crustal component into their mantle sources.

References
Breaching the North African watershed: Driver for Mediterranean anoxia?

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Quaternary climate change in North Africa appears to drive periodic changes in the redox chemistry of the Eastern Mediterranean, and such interactions may also be of importance for the interpretation of wider ocean anoxia. Deep Mediterranean anoxia is associated with negative oxygen isotope anomalies and the timing has been linked with northward shifts of the Inter Tropical Convergence Zone (ITCZ) and intensification of the African monsoon during Northern Hemisphere insolation maxima [e.g. 1]. These observations have led to the hypothesis that an increased flux of freshwater to the Eastern Mediterranean was a major contributing factor to the changes in deep ocean chemistry. Nd isotopes have previously been used to support a distinct increase in Nile discharge during the central periods of sapropel S1 (~9-6 ka BP) and S5 [2]. However, a Nile source alone cannot account for the entire duration of S1 and S5 (~125 ka BP) deposition. We present new evidence of a wider North African margin source of freshwater at the time of S5 from Nd isotopes in the Western Levantine and from Quaternary lake deposits in Libya.

A large oxygen anomaly of ~ -4‰ is observed across S5 in ODP core 971A from the western Ionian Sea [3]. This anomaly is much greater than that recorded in cores from close to the Nile outflow (~ -2‰) [3]. Our data from 971A show a distinct change in the εNd of planktonic foraminifera (G. ruber) towards more radiogenic values across S5. Analyses of gastropod fossils from Quaternary lake deposits in Libya also give a radiogenic Nd signal (εNd ~-2), as expected of waters rising in the range of basaltic mountains comprising the North African watershed at ~ 21°N.

These data support the hypothesis that a northward movement of the ITCZ breached the North African watershed during Northern Hemisphere insolation maxima and contributed freshwater to the Mediterranean basin. Further investigation is needed to determine the importance of this contribution in the development of anoxia, relative to Nile inputs.

References


Oligomerization of amino acid on mineral surface under the pH controlled conditions

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The role of mineral surfaces as a catalyst on the oligomerization of the amino acid, glycine, during wetting and drying cycles was investigated. Several types of montmorillonite with different interlayer cations (H, Ca, Na) and silica (quartz type) powder (10 mg) were suspended with 10 mM amino acid solution (1 ml) under pH controlled conditions. The suspensions were dried at 95°C to simulate the drying step, while addition of distilled water represents the wetting step. These wetting and drying steps were performed in several repetitions.

Amino acid oligomerization proceeded more favourably in silica as a catalyst at its point of zero charge (PZC) near pH 2.6 (Figure 1). The peptide yield was subsequently reduced under more acidic condition (i.e. pH 2) due to excess positive charges of both silica surface and amino acid ions – exerting an inhibiting effect on amino acid adsorption. At the PZC of montmorillonite and glycine (pH 6.0), the catalytic efficiency of minerals was reduced due to zwitterions forming which has a low reactivity for glycine (Zamaraev et al., 1997). The catalytic influence of minerals on amino acid oligomerization is largely influenced by the surface charge of the minerals.

Figure 1: Peptide yield from glycine in different mineral systems at pH 2.6. Glycine anhydride (■), Gly-Gly (▲), Gly-Gly-Gly (▲), Gly-Gly-Gly-Gly (▲)

Reference

Mechanism of Cr\(^{6+}\) immobilization in different soils

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We carried out experimental studies on the changes of Cr\(^{6+}\) concentration in the solutions with different pH which were reacted with different soils containing large amount of Cr\(^{6+}\) (1,000ppm) at room temperature. Soils used for the experiments include Kanto loam (weathered basaltic soil), weathered acidic soil and kaolinite bearing soil derived from weathered granitic rocks. The results obtained from the study indicated that Cr\(^{6+}\) released within a very short period (three minutes), but it decreased rapidly with time when the Kanto loam soil was used in the experiment and in this case the Cr\(^{6+}\) concentration in the solution (after 3 minutes) was 0.36 µg mL\(^{-1}\). This decrease may be due to the reduction of Cr\(^{6+}\) by Fe\(^{3+}\) in the soil. Therefore, this study suggests that the basaltic weathered soil (Kanto loam soil) is very useful material for the immobilization of Cr\(^{6+}\) from the soils and sediments.

Noble gases in Frontier Mountain ureilites

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Introduction. We report results from noble gas analyses of four ureilites from the Frontier Mountains area, Antarctica. These noble gas data complement cosmogenic radionuclide data obtained by [1] thus shedding light on the cosmic ray exposure history of these meteorites. Of interest are also the trapped noble gases, since ureilites represent a unique class of achondritic meteorites with high abundances of carbon and trapped noble gases.

Cosmogenic noble gases. Results are summarized in Table 1. FRO 90036 and FRO 90054 may be paired, with a common GCR exposure age of ~ 9 Ma. They may belong to an extensive shower as indicated by radionuclides of additional FRO ureilites [1]. FRO 97013 and FRO 01030 are separate falls. While the latter has an exposure age of ~ 4 Ma, the former was irradiated under high shielding and possibly received the bulk of its exposure on the parent body.

<table>
<thead>
<tr>
<th>meteorite</th>
<th>(^3^{})He</th>
<th>(^{21}^{})Ne</th>
<th>(^{38}^{})Ar</th>
<th>(^{22}^{})Ne/(^{21}^{})Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRO 90036</td>
<td>15.4</td>
<td>2.64</td>
<td>--</td>
<td>1.171</td>
</tr>
<tr>
<td>FRO 90054</td>
<td>15.1</td>
<td>2.12 ~0.33</td>
<td>1.225</td>
<td></td>
</tr>
<tr>
<td>FRO 97013</td>
<td>2.88</td>
<td>0.731</td>
<td>--</td>
<td>1.052</td>
</tr>
<tr>
<td>FRO 01030</td>
<td>9.64</td>
<td>1.022 ~0.9</td>
<td>1.224</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Abundances of cosmogenic nuclides (units: 10\(^{-8}\) cc STP/g) and shielding parameter (\(^{22}^{}\)Ne/\(^{21}^{}\)Ne).

Trapped noble gases. Trapped Ar, Kr and Xe abundances are listed in Table 2. Most remarkable are the low (compared to other ureilites) abundances in FRO 90054 – in line with its very low reported carbon content [2] - and the very high Ar/Xe and Kr/Xe ratios of FRO 01030, which even exceed those for the previous record holder Goalpara [3].

<table>
<thead>
<tr>
<th>meteorite</th>
<th>(^{36}^{})Ar</th>
<th>(^{84}^{})Kr</th>
<th>(^{132}^{})Xe</th>
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</thead>
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<tr>
<td>FRO 90036</td>
<td>190</td>
<td>1.78</td>
<td>0.601</td>
</tr>
<tr>
<td>FRO 90054</td>
<td>9.46</td>
<td>0.0415</td>
<td>0.0252</td>
</tr>
<tr>
<td>FRO 97013</td>
<td>508</td>
<td>2.65</td>
<td>0.295</td>
</tr>
<tr>
<td>FRO 01030</td>
<td>66.8</td>
<td>0.866</td>
<td>0.233</td>
</tr>
</tbody>
</table>

Table 2: Trapped Ar, Kr and Xe (units: 10\(^{-8}\) cc STP/g).

Acknowledgments. Luigi Folco (U. Siena) provided the FRO 97013 and FRO 01030 samples while FRO 90036 / 90054 were obtained from Euromet.

References
Evolution of anoxic aquatic systems under urban environments: Case of "Lac Sud" Tunisia

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The "lac sud" of Tunis, is an anoxic confined environment evolving under the direct control of an urban environment that affects him to various degrees (Didyk, B.M., et al 1978).

The quantitative and qualitative study of the organic matter contained in surface sediments, by the determination of the total organic carbon (TOC), the free and potential hydrocarbon compounds (S1 and S2), the total hydrocarbons and specially the saturated fraction (analyzed by gas chromatography) permit to distinguish 3 principal zones in the lake characterized by various degree of anoxia.

The western zone is characterised by an advanced and irreversible anoxic state, with an exceptional rate of conservation of organic matter (TOC > 6 %) and an exceptional enrichment in hydrocarbon compounds of biogenic and anthropological origin (HT > 2033 ppm).

The zone situated in the east of salt works is characterized by anoxic state less accentuated with a rate of organic matter conservation (TOC < 3 %) and a total hydrocarbon content (HT < 820 ppm), less important. Hydrocarbons present are of mixed origin continental and marine (Jaffé R. et al 2001).

Finally, in the central and north-eastern zone the anoxic state is in way of installation, the contents in organic matter and in total hydrocarbons are the weakest.

In addition, the analysis of the lipidic fraction allowed to show that the whole system is under direct influence of the urbanization (Medeiros P.M. and Bicego M.C., 2004). The development of the anoxia in preferential zones of the lake is evolution of aquatic systems in urban environments must be considered with a lot of interest to avoid the risk of controlled by the low reactivity of organic matter of anthropological origin.reaching an irreversible state.

References


In situ geochemical data from metamorphic rocks in the active Mariana subduction zone

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The active serpentine mud volcanism of the Izu-Bonin-Mariana (IBM) forearc exposes variably serpentined harzburgites and blueschist-facies mafic fragments to the ocean floor. The latter indicate that some of the fragments are derived from depths corresponding to the slab-mantle interface (20-40 km), i.e. between the actively subducting Pacific oceanic crust and the IBM subarc mantle.

In the past, only a few blueschist-facies mafic fragments (up to several cm in diameter; [1]) were analyzed petrologically in great enough detail. For example [1] estimated that PT-metamorphic conditions for key mineral assemblages (lawsonite + quartz, aragonite, lawsonite + pumpellylite) reveal low temperatures (150-250 °C) at pressures reaching 0.5-0.6 GPa. But to date, no in-situ trace element data exist on mafic blueschist-facies clasts from any serpentine mud volcano.

We will present abundant petrological descriptions of several newly discovered mafic fragments from the South Chamorro Seamount, ODP Leg 195. The mineral assemblages of the blueschist-facies clasts include (a) Na-amphibole + chlorite ± apatite ± sphene ± spinel ± rutile, (b) Na-amphibole + chlorite ± sphene ± rutile ± epidote ± allanite ± chlorite ± spinel ± pumpellylite ± pyroxene (Acm-Di-Jad) ± zircon, (c) chlorite ± epidote ± allanite ± Na-amphibole ± sphene ± garnet ± Fe-oxide ± rutile ± apatite and (d) phengite + Na-amphibole + chlorite ± spinel. Albite and quartz are always absent.

For studying the light elements boron and lithium we used Time-of-Flight SIMS imaging capability with a µm-scale resolution. Our multi-element maps with high spatial resolution show that in the shallow subducted slab Li resides in phengite ≥ chlorite > amphibole and that boron preferentially resides in both phengite and chlorite. SIMS analyses verify the high concentration in B and Li in these phases (with ~35 µg/g B and ~80 µg/g Li in phengite). Interestingly our images also show that boron is strongly enriched in parts of chlorite, possibly due to B remobilization from circulating fluids. Thanks to the high concentration of B in phengite and chlorite, we will measure 11B by SIMS and evaluate existing models of early B-release and subsequent isotope fractionation by forearc slab fluids.

References
Topographic and hydrologic controls of spring water travel times and plagioclase weathering rates in solid rocks

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Two sets of springs, one associated with watersheds on average smaller than 10 ha (short hydraulic circuits) and discharging 10 L/min and the other linked to watersheds on average larger than 50 ha (longer circuits) and discharging 24 L/min, were selected for this weathering study in North Portugal. Using hydrograph analysis methods it could be calculated for the first set (30 springs from the Sordo river basin, characterized geologically by granites and schists), hydraulic conductivities $K = 2 \times 10^{-6}$ m/s and drainable porosities $n_e = 5 \times 10^{-2}$, which were found to be 4 and 5 times larger than the $K$ and $n_e$ values of the second set (14 springs from amphibolites of the Morais massif). Subsequently to the estimation of $K$ and $n_e$, hydrologic travel times ($t$) were determined by a numerical (finite differences) method assuming the system to be at steady-state and the transport of solutes to be advective. In the Sordo basin $t = 3.7$ yr whereas in the Morais massif $t = 13.6$ yr. The conclusion was: the longer paths in Morais conducted amphibolite water deeper into the fractured massif, where $K$ and $n_e$ were smaller, and as result longer times were necessary to complete the corresponding hydraulic circuits. The hydrograph analysis methods also produced numbers for the surface area of plagioclase ($A_{Pl}$, m$^2$) reacting with aquifer water in unit time (1 yr), while concentrations of dissolved plagioclase at spring site ($[\text{Pl}]$, mol/L) were determined by the SiB Algorithm [1]. Finally, plagioclase weathering rates ($W_{Pl}$, mol/(m$^2$.s)) were calculated by the formula: $W_{Pl} = [\text{Pl}]/t \times V/A_{Pl}$, where $V$ is the volume of groundwater with steady-state concentration $[\text{Pl}]$ that discharges at the spring site in unit time. The weathering rates span three orders of magnitude on a secular basis (Fig. 1). The drop in the rates follows a power function described by $W_{Pl} = 1.5 \times 10^{-13} \times t^{-1.37}$, suggesting control by transport-limited reaction. A similar power function was used by [2] to describe silicate weathering.

References

Solar nebular fractionation of refractory elements Y and Ho

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The geochemical twins Y and Ho are both trace elements in chondrites and most of their components. Both are highly refractory and condense at high temperatures. No or only little fractionation between Y and Ho is expected in igneous or metamorphic processes. This makes the Y/Ho-ratio a suitable tracer for chemical heterogeneity in solar nebula reservoirs. We report Y/Ho-ratios of CAIs, chondrules and bulk chondrites.

Bulk samples were fused by means of a containerless technique to small (~2 mm) sheres, which were embedded into resin for EPMA and LA-ICPMS.

Fusion in combination with LA-ICPMS allows determination of Y/Ho-ratio with a relative error $<0.5\%$ (2$\sigma$). CCs (C11, CM2, CV3, CK4) have uniform Y/Ho $= 25.94 \pm 0.08$ (2$\sigma$). LL-, L-, H- and E-chondrites have increasingly elevated Y/Ho-ratios (see figure).

CCs have a Y/Ho-ratio that is suggested to represent the ratio of the solar system. Elevated Y/Ho-ratios of OCs and ECs are interpreted as result of loss of a fractional condensate with subsolar Y/Ho. This component may have been similar to CAIs with Group-II REE patterns, which have subsolar Y/Ho. Removal of fractional condensates may also be responsible for elevated Re/Os in ECs relative to CCs. Data of terrestrial rocks (herzolite, basalt) show that partial melting fractionates Y and Ho. The bulk Earth is suggested to have a solar Y/Ho-ratio, which excludes ECs as parental material to the Earth.

Figure 1: Relation between weathering rates and time.
Atypical SHRIMP II REE data in zircons: A positive Eu anomaly

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Distribution of REE depends on some factors:
- temperature and pressure of melt
- interaction with enclosing strata
- sequence of crystallization
- crystalchemistry of the host mineral

Enrichment in HREE as well as depletion in LREE with contrast negative Eu and positive Ce anomalies are typical for zircon structure in common case (fig.1a).

Unusual REE distribution patterns were recorded in zircons at recent investigations. They show a positive Eu anomaly with portion of LREE enrichment (fig.1b).

**Figure 1:** Chondrite normalised REE patterns: a. typical for zircon; b. atypical REE distribution.

Such REE distribution patterns were observed in the following cases: 1) in zircons from low crustal eclogitic xenoliths from an eruption pipe at Elový Island (White sea), 2) in zircons form Kalaknda massif granulites (Kola peninsula), 3) in zircons from Antarctic alkaline pegmatites. The U-Pb data show the discordant ages of these zircons as well as high magnitude Th/U ratio variation. Thus, the effects of REE pattern deviations are connected with metasomatic and metamorphic processes. These influences have an effect in Eu and LREE increaseng. Hence, these REE patterns could be considered as secondary processes affecting.

References

Laser ablation study of trace elements in chromite: Thetford Mines ophiolite chromitite ores

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This study aims to identify compositional contrasts between chromitite ores from the Thetford Mines Ophiolite (TMO), Canadian Appalachians, which contains more than 30 chromitite deposits grouped into 3 principal types, and to better understand the mechanisms of their formation.

The 3 types of chromitite are: 1) podiform chromitite found in mantle peridotite, 2) stratiform chromitite from rocks formed at the base of the crust, and 3) intracrustal discordant chromitite close to, or in crustal pyroxenites. Fractional crystallization, magma mixing, country rock assimilation, melt-rock reaction, or a combination of these processes have been proposed as important in chromitite formation. There is also a relationship between chromitite deposits and platinum-group elements (PGE) deposits.

Chromitite deposits from ultramafic-mafic layered intrusions are frequently associated with high concentrations of PPGE (Rh, Pd, Pt). Ophiolite chromitite deposits contain intermediate levels of IPGE (Os, Ir, Ru) and laser ablation analysis of PGE in chromite allows us to verify that these elements are not incorporated in chromite structure (solid solution) with the exception of Ru with concentrations from 38 to 134 (± 20) ng/g. The high PGE concentrations of ophiolite chromitites are principally related to the observed platinum-group minerals (laurite – erlichmanite series) included in chromite grains.

Our trace element analysis include Mn, Ni, Co which appear to have reequilibrated with the olivine of host dunite rocks as have Fe and Mg, therefore it is difficult to determine whether fractional crystallization or contamination (magma mixing or host rock assimilation), processes trigger chromite precipitation. On the other hand, our preliminary analysis of Ti, V, Ga and Zn, which are less sensitive to reequilibration with olivine, show an evolutionary trend compatible with fractional crystallization (negative correlation with Cr#).

Our trace element analysis include Mn, Ni, Co which appear to have reequilibrated with the olivine of host dunite rocks as have Fe and Mg, therefore it is difficult to determine whether fractional crystallization or contamination (magma mixing or host rock assimilation), processes trigger chromite precipitation. On the other hand, our preliminary analysis of Ti, V, Ga and Zn, which are less sensitive to reequilibration with olivine, show an evolutionary trend compatible with fractional crystallization (negative correlation with Cr#).
Equilibration of the Earth-Moon system following the giant impact

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The energy released in the Moon-forming giant impact is sufficient to melt and partially vaporize both the Earth and the impactor. The timescale to eliminate this heat by radiation is \( \sim 10^3 \) years. Hence, the Earth and protolunar disk are expected to be molten and enveloped by a convecting silicate vapor atmosphere for the first thousand years following the giant impact.

To explain the striking similarity of the oxygen isotopic composition of the Earth and Moon [1], we have previously proposed that the terrestrial magma ocean and the protolunar magma disk underwent equilibration in the aftermath of the giant impact through exchange with the common silicate vapor atmosphere [2]. Recent support for this idea comes from precise measurements of silicon isotopes that reveal the Moon to have a composition similar to the silicate Earth, a property not shared with Mars, Vesta, and chondrites [3].

Due to the liquid/vapor partitioning of the elements [4], such a model does not imply a chemical composition for the Moon that is identical with the silicate Earth. The ability of the vapor to exchange between the Earth and lunar disk, to undergo more vigorous turbulent motions than the liquid, and to preferentially escape in a hydrodynamic outflow will effect the chemical composition of the resulting Moon. We are presently undergoing an investigation of the consequences of the equilibration hypothesis to explore the extent to which this scenario can explain the similarities and differences in the Earth-Moon system.

References
Hf-W chronometry of chondrites

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The total Fe content of chondritic meteorites is variable, reflecting separation of metallic iron in the early solar system. Such metal-silicate fractionations should be accompanied by fractionations of Hf from W and, hence, their timing can be studied using $^{182}$Hf/$^{182}$W chronometry. Here we present Hf-W and bulk chemical data of large, homogenized samples for various groups of chondrites with the ultimate goal to date the metal-silicate fractionation in the early solar nebula. Both, Hf/W and $^{182}$W/$^{184}$W ratios increase in the order of H-L-LL chondrites, as expected from the abundance of metal in these chondrites. However, there are substantial variations in the Hf/W ratios within the H and LL chondrite groups, which may indicate W mobility during parent body processes. These currently hamper precise dating of the Hf-W fractionation among the chondrites. All LL chondrites studied here (including type 3) plot below the CAI isochron [1], suggesting that the Hf-W fractionation, i.e., metal silicate separation post-dated formation of CAIs by a few Myrs. More data, particularly for the most primitive chondrites are needed to confirm this observation. An important aspect of our new data is that H chondrites, on average, have lower Hf/W ratios than carbonaceous chondrites, whereas L chondrites have Hf/W ratios indistinguishable from carbonaceous chondrites [2,3]. This is unexpected given the fact that H chondrites have Fe/Mg ratios similar to those of CI chondrites, but L chondrites have lower Fe/Mg ratios. This and the relatively low W contents in metals from type 3 ordinary chondrites [4,5] could indicate that a significant part of the W did not condense as metal. If this is true, conditions in the chondrite formation region must have been rather oxidizing.

References

Lead origin and fate in soils:
Geochemical records in buried soils over the past 3500 years

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Methods
The effect of climate fluctuations and anthropogenic impact on lead origin and fate in Chestnut soils (Low Volga region, Russia) over the past three and a half millennia has been investigated. We compared the morphology, organic matter, soluble soil, gypsum, carbonates, total lead content and Pb isotope ratios in the profiles of modern soils and soils buried under the burial mounds, dated using archaeological methods. Buried soils form a chronological sequence from XVI-XV centuries BC till nowadays.

Results and discussion
Comparison of buried soils and their modern analogues demonstrated that during the past 3500 years the cyclic reversible changes of climate took place in this region. Drought epoch had started 4500 years ago with maximum between 2000 BC and 3000 BC. The most moist climate conditions were found in XII-XIV cent.

We observed an increase of total lead concentration in upper soil horizon along soil chronological sequence probably reflecting a growing anthropogenic input of lead. However the difference in total lead content and isotope ratios between modern and buried soils is statistically significant only for soils buried before the middle ages. Lead isotope ratios in upper horizons of modern soils ($^{207}$Pb/$^{206}$Pb and $^{208}$Pb/$^{206}$Pb) fit to European Standard Pollution Line and Russian-GDR gasoline line (Haack et al., 2003), reflecting the influence of airborne Pb, deposited from a continent-wide mixing system or local sources of Pb-gasoline.

Financial support was provided by the Russian Foundation of Basic Research (grant 06-05-65307a).
Evolution of Manzanillo batholith Complex: Structural data, thermobarometry and geochronology

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The Manzanillo batholith Complex (MBC) occurring along the south-western shores of Mexico is related to the Latest-Cretaceous convergence between the Farallon and North-America plates. The MBC is composed of metalluminous granodiorite and granite, with a gabbro-diorite core, which intruded into the Cretaceous volcano-sedimentary arc sequences of the Guerrero terrane.

Structural, geochemical as well as SHRIMP U/Pb zircon geochronology data suggest that the MBC is a composite batholith and it was formed by several magmatic bodies. They were emplaced at different depths and different times ranging from 74 to 62 Ma: five Granite Complexes (GCs), a Granodiorite Complex (GrdC) and a Gabbro Complex (GbC).

i) The main rock-type is a medium grain size granite associated with minor granodiorite and porphyry dikes (GrCs). They are typically calc-alkaline and relatively K-enriched. The oldest granitic complex was emplaced 74 Ma ago and the depth emplacement ranging between 6 and 12 km.

ii) Grain coarse Granodiorite Complex (GrdC) shows a discrete internal foliation and it is compositionally homogeneous with LILE enrichment, fractionated LREE with a distinct negative Nb anomaly and flat HREE patterns. It apparently was emplaced at shallow crustal level (< 2.8 kbar) and at 62 Ma ago.

iii) Massive gabbros and minor isolated small cumulitic bodies (associated with brown Am replacing Cpx) and diorite rocks constitute the Gabbro Complex (GbC), which occurs essentially in the central part of the MBC. GbC magmatic textures are preserved apparently in place, but locally subsolids reactions and plastic deformation are observed. Near the contact between the GrdC and GbC the gabbros are affected by melt infiltrations with a growth of Bt, Qtz, Kfs. Pl presents rounded and corroded rims. GbC is slight older (68 Ma) and deeper than GrdC.

On the basis of field, geochemical and geochronological data we argue that GbC intruded at about 15 km depth and successively was affected by subsolids recrystallization and deformation before or during fast uplift. Chemical composition support a fluid slab-related contamination and a tectonic emplacement at shallow crustal levels for these bodies.

High primary productivity in stromatolitic phosphorites from the Paleoproterozoic Aravalli Supergroup

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Paleoproterozoic biogeochemical cycles were fundamentally changed by glaciations and the accumulation of atmospheric oxygen. Higher levels of seawater sulfate and atmospheric oxygen have been inferred from Paleoproterozoic interglacial sedimentary sulfides with sulfur isotope compositions characterized by large ranges of δ34S values and the absence of mass-independent fractionation (Papineau et al., 2007; Bekker et al., 2004). Carbon isotope excursions in Paleoproterozoic interglacial carbonates from the Transvaal Supergroup and in post-glacial carbonates on most continents indicate high burial rates of organic carbon and suggest a significant production of atmospheric oxygen (Bekker et al., 2001; Karhu and Holland, 1996). Because atmospheric oxygen is primarily produced by oxygenic photosynthesis, these observations suggest enhanced primary productivity during the Paleoproterozoic. This was perhaps modulated by higher nutrient availability in seawater, such as phosphate, which could have resulted from post-glacial greenhouse conditions and accelerated weathering of continental crust.

We present new carbon isotope data from dolomite, carbonate fluorapatite and organic matter in stromatolitic phosphorites from the Paleoproterozoic Jhamarkotra Formation of the Aravalli Supergroup, India. Carbonate fluorapatite from columnar stromatolites is systematically depleted in 13C (-1.8 to -0.2‰) compared to intercolumnar dolomite (-0.3 to +0.6‰). These results suggest late diagenetic substitution in carbonate fluorapatite by HCO3 from the oxidation of organic matter. Total organic carbon extracted from these two phases overlaps in ranges of abundance and δ13C values, but are characterised by unusually heavy δ13C values up to -15‰. These carbon isotope data may reflect high levels of primary productivity during phosphorite deposition in the Jhamarkotra embayment. No carbon isotope excursion was found in stratigraphically lower and higher dolomites in the embayment, but excursions up to +5% exist in contemporary carbonates from nearby localities. Ongoing work with Re and Os isotopes could provide better age constraints for this unique phosphate deposit and relate it to other events of that time. In the context of Paleoproterozoic biogeochemical evolution, these phosphorites appear to record high biological primary productivity associated with post-glacial climate change.
Origin and evolution of ultrapotassic plutonic rocks (Durbachite series, Třebíč Massif, Czech Republic): An experimental approach

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To address the question of the origin of K-rich magmatism at the end of major orogenic episodes, an experimental study was conducted to constrain the crystallization conditions of mafic durbachite from the Třebíč Massif in the Bohemian Massif, Czech Republic. Durbachites are coarse-grained, porphyric plutonic rocks, typically containing large phenocrysts of K-feldspar, with high amounts of biotite, plus plagioclase, amphibole, augite and orthopyroxene. The durbachite series are abnormally K- and Mg-rich volcanic rocks and evolve from mafic to felsic end-members (SiO₂=52-70 wt.%, K₂O=7.3-5.5 wt.%, MgO=10-2.5 wt.%).

Crystallization experiments were performed in internally heated argon pressure vessels at 200 MPa, 900-1100°C, log ƒO₂=NNO and NNO+3.6, and various water activities (XH₂O of the coexisting fluid=0.3 to 1), using the most mafic natural durbachite as starting material. At 1100°C, only olivine crystallized (close to liquidus for XH₂O=1), whereas olivine + biotite + augite crystallized at 1000°C. At 900°C, only biotite and augite (+apatite, zircon and magnetite) are stable phases in the investigated range of XH₂O and ƒO₂. K-feldspar, plagioclase, amphibole and opx are absent in all experimental products even at subsolidus conditions (~900°C and low XH₂O). Thus, the natural mineral assemblage was not reproduced for the investigated range of T, ƒO₂ and XH₂O. Only biotite (Ti-rich: TiO₂=3-5 wt.%; mg#=75-80) and augite (Wo₄₄En₄₂), present in natural sample, could be reproduced.

Our results indicate that the mineral assemblage of the mafic durbachite may not be the product of the crystallization of a melt with the investigated bulk composition at 200 MPa. If we consider that partial melting of enriched, heterogeneous subcontinental lithospheric mantle beneath the Variscan Orogen lead to the formation of the mafic durbachite (Holub, 1997; Gerdes et al., 2000), the observed mineral assemblage may indicate that (1) crystallization occurred at pressures or volatile activities significantly different from those investigated in this study (200 MPa, XH₂O in the range 0.3 to 1) and/or that (2) incongruent reactions involving olivine, biotite and augite as reactants occurred at hypersolidus and subsolidus conditions. This hypothesis is supported by the presence of scattered clots of fine-grained actinolite mantled by biotite (“pilite”) that may be interpreted as pseudomorphs of olivine (Holub, 1997) and by the presence of augite as relics in amphibole. Another explanation is that the investigated mafic sample is not an end-member composition but a hybrid composition, contaminated by crustal material.


Interaction of copper with humic-coated gibbsite

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Both humic substances and mineral oxides exert important effects on chemical speciation and the transport of nutrients and contaminants in soils and sediments. Although most of the studies regarding chemical speciation in natural systems have been developed for individual reactive surfaces (mineral oxides, humic substances, clays), a better understanding on the subject could be achieved with mixtures of these components. The aim of this study was to compare the copper adsorption on gibbsite and HA-coated gibbsite.

First, the interaction of copper with the single systems humic acid (HA) and gibbsite was studied at different HA concentrations and pH. In order to explain the experimental results, the NICA-Donnan and the CD-MUSIC models were applied for Cu-HA and Cu-Gibbsite interaction, respectively.

The gibbsite was covered with different HA concentrations to study the copper interaction in a system that resemble more to the reactive surfaces present in natural systems. The adsorption of copper on the HA-gibbsite was higher than the adsorption on the single systems individually at the different pH values studied. This result was interpreted in a linear aditivity model basis. The copper adsorption on the HA-coated gibbsite was also compared with a system consisting of HA, gibbsite and copper simultaneously added into the reaction vessel.
Mineralogical, geochemical, and microbial characteristics of marine sediments at Tempelfjorden Fjords, Svalvard, Norway

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4University of Tromso, Tromso, Norway

Svalbard fjords, affected by turbid overflow emanating from outlet glaciers, are modern analogues for Quaternary deglacial settings. To better understand the response of the discharge of glacial meltwater including suspended sediments to the mineralogy, geochemistry, and microbial community, we sampled the subsurface sediments at 8 stations along the axis of Tempelfjorden fjords. The sediment samples were obtained using a gravity core at 1 station and a giant box core at 7 stations. The sediment samples were used for geochemical and mineralogical characterizations as well as for microbial community by genomic analysis. Iron-oxidizing and -reducing bacteria were enriched from the marine sediments at 8°C and the development of bacterial and archaeal structures in the sediments of fjords was examined using cloning and denaturing gradient gel electrophoresis analysis of rRNA gene. The water mass and marine sediments are influenced by the runoff from the glaciers at the fjord head in Tempelfjorden. X-ray diffraction analysis of the sand and silt fraction of the sediments revealed the predominance of quartz, mica, calcite, and dolomite with lesser amounts of feldspars and chlorite. Their clay mineralogy was dominated with illite, kaolinite, chlorite, and dolomite with lesser amounts of quartz, feldspar, and iron oxides. Iron-oxidizing and -reducing bacteria enriched from the marine sediments at 8°C and the development of bacterial and archaeal structures in the sediments of fjords was examined using cloning and denaturing gradient gel electrophoresis analysis of rRNA gene. The water mass and marine sediments are influenced by the runoff from the glaciers at the fjord head in Tempelfjorden. X-ray diffraction analysis of the sand and silt fraction of the sediments revealed the predominance of quartz, mica, calcite, and dolomite with lesser amounts of feldspars and chlorite. Their clay mineralogy was dominated with illite, kaolinite, chlorite, and dolomite with lesser amounts of quartz, feldspar, and iron oxides. Iron-oxidizing and -reducing bacteria enriched from the marine sediments showed active Fe(II) oxidation and Fe(III) reduction at 8°C and 25°C. Iron-reducing bacteria enriched from the sediments were formed nm-sized magnetite at both 8°C and 25°C using lactate as an electron donor and a ferric iron oxide, akaganeite, as an electron acceptor. Dynamic bacterial community succession was observed at 8 stations. Although only one type of archaeal community profile was observed, archaeal community was quite distinct in the sediments and affected by deglaciation compared to control sediments. This confirms previous study that arctic sediment microorganisms participate in biogeochemical cycles remain in active at low temperatures.

Developing extraction method for mercury analysis in soils with different mineral composition

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The toxicity of elements depends not only on their total concentrations but also on their chemical forms. In real environment where mercury was considered as contaminant, we often experience difficulty in measuring mobility of mercury from constituents soils. The final goal of this project is speciation of mercury in contaminated soils and sediments. Preliminary tests for reference materials were performed to find out simple and more efficiency method to extract mercury. The reference materials with different mineral composition were selected and used. One is composed of mostly with Al-silicate minerals and another is mostly composed with calcite and ferrosilite. Same extraction method was applied to reference material of two types. The extraction efficiency for three methods was compared with certified values of reference material. The two extraction methods of three were acid digestion with aqua regia and mixed acid. The other extracted with mixture solution methanol and HCl using microwave at 40W and 80W for 20min respectively. The most high efficiency of sample including Al-silicate mineral was microwave method using methanol and HCl, while the calcite-based sample was observed that the aqua regia extraction method is good than the others. But this sample wasn’t detected with microwave method. The developing extraction method of the microwave using methanol and HCl will be possible to analysis of mercury more easily and rapidly. Also this can be applied to mercury speciation analysis in soils and sediments.
Geochemistry of basalt from the Eastern Woodlark Basin: Its implications for the mantle heterogeneity

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A section of the active spreading center in the eastern Woodlark Basin (EWLB) is subducting beneath the New Georgia Group, a volcanic arc. Basalt from the axis of EWLB were analyzed to investigate the processes in the region where ridge subduction and reversal in subduction polarity occurred in the past. They are similar to N-MORB in their major oxides, but are more depleted in incompatible elements. Incompatible element ratios such as Zr/Y and La/Sm show a large variation, which may be explained by mantle heterogeneity where an N-MORB source became mixed with or coexists with a different, mantle source that was depleted at an earlier time (Fig. 1a). The negative correlation between Ba/La and Zr/Y ratios indicates that the prior depleted end member is more enriched in the subduction component than the N-MORB mantle source and therefore may have originated from a subduction environment (Fig. 1b). The source of the subduction component remains to be explored by further studies.

Figure 1
a. Zr/Y versus La/Sm diagram.
b. Ba/La versus Zr/Y diagram.

Assessment of phosphorus and PAHs accumulation in the Suyoung river area in Busan, South Korea

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Method
Sediment samples (0-50 cm in depth) were collected from the Suyoung river and the Hoedong drinking water reservoir area in Busan, South Korea to assess the accumulation of phosphorus and PAHs. Phosphorus was analyzed by an ICP-ES and a Spectrophotometer, and PAHs were analyzed using a GC/MSD. The phosphorus results are shown in the table below.

Table 1. Phosphorus contents in the river- sediments.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Adsorbed</th>
<th>Carbonate</th>
<th>Occluded in Fe-oxide</th>
<th>Residual</th>
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<tr>
<td>83-1</td>
<td>731.8</td>
<td>4</td>
<td>1.1</td>
<td>6.4</td>
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<tr>
<td>83-2</td>
<td>503</td>
<td>3.9</td>
<td>0.8</td>
<td>4.1</td>
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<td>4.8</td>
<td>1.1</td>
<td>6.9</td>
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<td>1.6</td>
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</tr>
<tr>
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<td>689.2</td>
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<td>1.5</td>
<td>5</td>
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<td>1.3</td>
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<td>1020.3</td>
<td>2.4</td>
<td>2.1</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Discussion and Results
Most of the inorganic phosphorus was present being adsorbed onto the sediments and its concentration pattern was very similar to that of PAHs indicating the presence of phosphorus and PAHs were influenced by the geological characteristics of the area.

Concerning the source of PAHs, the upper part of Suyoung river may be influenced by pyrolytic inputs, where the middle or down part may be influenced by petroleum inputs, which can be the vehicle emission from fossil fuel combustion.

References
Geochemical and isotopic investigations of surface waters in Chuncheon, Korea

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The Han River is the largest river in South Korea in terms of the size of watershed and water discharge, and consists of two major tributaries: the North Han and South Han Rivers (NHR and SHR). The Soyang River (SR) is one of the major tributaries of the NHR, and joins the NHR at the Euiam Lake. In order to investigate geochemical and isotopic characteristics of river waters affected by a medium-sized city, Chuncheon, we have collected a total of 109 surface water samples from the NHR, the SR and the Euiam Lake. Of these surface waters, the SR is directly influenced by the city of Chuncheon, and it is characterized by much higher concentration of dissolved ions in the lower reaches relative to the NHR the Euiam Lake waters. Especially, it is observed that the concentration of dissolved ions of the SR is the highest in summer. Compared to the SR, the NHR is much lower in concentrations of dissolved solutes, indicating little contamination by anthropogenic sources. The Euiam Lake is located at the confluence point of both rivers, thus this lake waters plot between chemical compositions of both rivers indicating a mixing relation. On a plot of oxygen and hydrogen isotopic compositions, all water samples plot in a similar range near the local meteoric water line (LMWL) of Park et al. (2006), and this indicates all surface waters originate from similar sources of meteoric origin. Most samples are enriched in oxygen isotopic compositions, and thus slightly deviate from the LMWL, implying slight evaporation from reservoir surfaces.

Figure 1. Oxygen and hydrogen isotopic compositions of the surface water samples collected in the Chuncheon area.

Diel biogeochemistry of the Rio Agrio, Argentina

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Rio Agrio in Argentina is a geogenically acidic stream that derives its low-pH waters from springs on the flanks of the active Copahue Volcano. These springs are fed partially by off-gassing (SO2, HCl, HF) of the magma-chamber beneath the volcano. This study reports the results of three diel (24-h) water samplings in three different pH regimes (3.2, 4.4 and 6.3) along the river which is acidic for ~40km. Changes in the concentration and speciation of Fe dominated the diel chemical changes at all three sites. At the two lower pH sites, dissolved Fe(III) concentrations decreased during the day and increased at night, while dissolved Fe(II) showed the inverse temporal pattern. These cycles are explained by Fe(III) photoreduction, as well as a diel, temperature-dependent change in the rate of precipitation of hydrous ferric oxide (HFO). A correlation was observed between Fe(III) and As at the pH 3.2 site, most likely due to co-precipitation of As with HFO. At the downstream (pH 6.3) location, Fe(II) concentrations increased at night, as did concentrations of rare earth elements. Photoreduction does not appear to be an important process in this reach, although it may be indirectly responsible for the observed diel cycle of Fe(II) due to advection of photochemically produced Fe(II) from acidic upstream waters. These results are very similar to diel trends recently obtained from mining-impacted streams receiving acid rock drainage (Parker et al., 2007). The results help form a link between geochemistry and microbiology in acidic riverine ecosystems. For example, Fe(III) photoreduction produces chemical potential energy (in the form of metastable Fe2+) that helps support the bacterial community in this unique extreme environment.

References

Vertical tectonics in the Neoarchean: Evidence from U-Pb detrital zircon age distribution in “Timiskaming type” sedimentary rocks in the Island Lake greenstone belt, Superior Province, Canada

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Two distinct tectonic regimes have been proposed to have been operating in the Archean, vertical and horizontal (“modern style”) tectonics. Most authors see these as separate processes that would have operated exclusively from each other, although recent work has suggested that they could be contemporaneous and that the Neoarchean represents a transition from a time dominated by vertical tectonics to one dominated by horizontal tectonic processes (Lin, 2007, and references therein).

Studies on Archean greenstone belts can help to test these ideas, and this study investigates a clastic sedimentary package that is characteristic of Neoarchean greenstone belts, the “Timiskaming-Type” sediments. Traditionally these sequences are interpreted to have been deposited in strike-slip basins opened by horizontal tectonic processes. More recent studies have suggested that these sediments were deposited in inter-diapiric basins formed by vertical tectonic processes.

This study investigates the distribution of U-Pb detrital zircon ages within the Island Lake Group, a “Timiskaming type” sedimentary succession located in the Island Lake greenstone belt. The distribution of observed ages is distinct from unit to unit throughout the succession, and correspond to the ages of supracrustal and plutonic rocks in the belt. The data are consistent with a model that involves erosion down through a supracrustal pile in the early stage of basin formation and sedimentation followed by unroofing of plutons in the latter stages. The model presented here involves sagduction and diapirism processes that produce an inter-diapiric basin as a result of vertical tectonics.

Reference

A petrologic view of mantle geochemistry: Os and He evidence for ancient depleted mantle heterogeneities

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Osmium isotopes in MORB and OIB appear to give a very different picture of the chemical history of the mantle than traditional isotope systems such as Sr, Nd and Pb. In particular, Os isotopes suggest that depleted, harzburgitic heterogeneities persist in the both the OIB and MORB source for at least 2 Ga, much longer than generally suggested by Sr, Nd or Pb isotopes. Recent partitioning experiments imply that He isotopes also record ancient depleted heterogeneities in the mantle [1]. In this talk I will show that the He and Os records of mantle depletion agree very well, with both indicating large melting events at 1.2, 1.9 and 2.7 Ga, corresponding well with peaks in the age distribution of continental crust. The agreement of these two independent mantle isotopic systems with the crustal record of melting is strong evidence for large melting events in the Earth’s past.

Why don’t we see this history in Sr, Nd and Pb? One possible explanation is that the mantle is largely heterogeneous, consisting of 15-20% subducted basaltic crust (eclogite) set within a matrix of depleted olivine-orthopyroxene rich matrix (harzburgite). This is essentially the marble-cake model of Allegre and Turcotte [2], and is supported by seismic scattering results [3] showing about 17% of the mantle consists of 10 km sized heterogeneities (presumably the eclogitic components).

If so, the eclogitic components would contain nearly all of the Sr, Nd and Pb in the mantle, while the harzburgite matrix would contain most of the Os and He (and probably the other noble gases). The eclogitic components have low melting temperatures and would melt readily if brought into a mid-ocean ridge system. Those melts would form the oceanic crust, which would eventually be subducted, turn back into eclogitic heterogeneities, which would then melt in a ridge again... This is the cyclic, young history recorded by Sr-Nd-Pb, the history of enrichment. In contrast, the refractory harzburgite would not easily melt again, even if brought into a ridge system, and so should be quite persistent in the mantle. As these refractory heterogeneities are relatively inert, they should record the timing of ancient melting events more readily than isotopes in low melting temperature phases. Thus from a petrologic viewpoint, the difference in histories recorded by Sr-Nd-Pb versus Os-He may be a natural consequence of the different minerals in which they reside.

References
The hidden history of mantle depletion: Os isotopes reveal a link between mantle depletion and crustal growth

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Two recent studies [1, 2] have provided new arguments in favor of pulsed growth of the continental crust (CC), with the main growth periods at 1.2, 1.9, 2.7 and 3.3 Ga. These CC growth pulses should be recorded as melt-depletion events in the mantle, but are not seen in the isotopic systems most commonly used to study the mantle (Sr, Nd, Pb). It is likely that the depletion history of the mantle is ‘hidden’ from these systems due to the subduction of enriched oceanic crust. Osmium, on the other hand, is compatible during mantle melting, and is a robust recorder of the timing of mantle depletion [e.g. 3].

Here we present over 400 new Os isotopic analyses (by laser-ablation multi-collector inductively coupled mass spectrometry: LA-MC-ICPMS) of osmiridium grains from three locations (Urals, Tasmania and Tibet). The data show a recurring peak at a $^{187}\text{Os}/^{188}\text{Os}$ value of 0.12±0.01, corresponding to a mantle depletion age of 1.2±0.1 Ga, and matching the youngest of the proposed CC growth events. The 1.2 Ga peak is also present in published data on osmiridiums from Oregon, USA [4] and from whole rock analyses of abyssal peridotites. Mixing models confirm the position from these systems due to the subduction of enriched oceanic crust. Osmium, on the other hand, is compatible during mantle melting, and is a robust recorder of the timing of mantle depletion [e.g. 3].

The older events, at 1.9 and 2.7 Ga, also appear to be recorded in the Os data, though the number of data points is small. In sum, the Os isotopic composition of the mantle records global melting events that correspond to peaks in CC age distributions, confirming the episodic model of CC growth and planetary differentiation.

References

Irradiation of organic matter by uranium and thorium: From mineral deposits to extraterrestrial environments

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Many occurrences of solid organic matter in ore deposits are directly related to the distribution of uranium and thorium minerals. This relationship reflects a mutual precipitation: irradiation from the minerals causes polymerization and solidification of fluid hydrocarbons, and the organic matter can cause the concentration of uranium to the scale of an ore deposit. Irradiation progressively alters the organic matter, by dehydrogenation, oxidation, and increasing aromaticity, and also causes fractionation of carbon isotopes. Studies of this alteration in samples from mineral deposits are contributing to an understanding of how organic matter is processed by irradiation in a range of other environments, from hydrocarbon reservoirs to interstellar space.

Data from mineral deposits show two opposite trends of carbon isotope fractionation with irradiation. New experimental data explains this in terms of two distinct mechanisms: (1) a decrease in alkylation and increase in oxygenated compounds related to reactions of complex hydrocarbon mixtures with free radicals, and (2) increase in polyaromatic hydrocarbon (PAH) size and alkylation due to polymerization from a methane-rich source. Both processes are expected to occur similarly in hydrocarbon reservoirs. The data also support a model for extraterrestrial PAH formation due to cosmic irradiation of simple hydrocarbons in interstellar ices, and more widely an improved understanding of the response of organic matter to irradiation will help interpret the organic compositions of carbonaceous meteorites, cometary ices, and icy moons such as Titan. As irradiation can result in increased molecular complexity and the precipitation of heavy compounds, it is possible that it played a role in the prebiotic chemistry essential as a prelude to the evolution of life.

On Mars, mineral radioactivity is relatively low but would still cause long-term damage to any microbial spores. Other forms of irradiation (solar, cosmic, UV) have a greater effect in the near-surface, and would severely alter or destroy any organic matter down to 3m depth.

References
Impact of earthworms on metal mobility and availability

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It has been suggested that earthworms may be of use in enhancing phytoremediation or alternatively that earthworms may enhance metal mobility at contaminated sites thereby increasing risk of exposure for receptors. In this study earthworms were cultivated for 28 days in two different metal contaminated soils at differing earthworm number to soil mass ratios. Swaledale soil contained 16 ppm Cd, 28 ppm Cu, 5164 ppm Pb, 3433 ppm Zn, 6 % organic matter, had a pH of 6 and a sandy texture. Wisley soil contained 5 ppm Cd, 110 ppm Cu, 910 ppm Pb, 260 ppm Zn, 10 % organic matter, had a pH of 5.4 and was a loamy sand. Earthworm number to soil mass ratios ranged from 1 :200 to 1 :5. After 28 days earthworms were depurated on filter paper and metal body burden was determined. Soil solution was extracted from soils using rhizon soil solution samplers and analysed for metals and dissolved organic carbon. Cold and hot water extractable carbon were measured on the soils. Soils were extracted with K2SO4 to estimate microbial numbers. The European 3-stage sequential extraction was applied to the soils.

Earthworm metal body burden and BCR Step 1 extractable metal decreased with increasing earthworm density. Metal and organic carbon soil solution concentrations and cold and hot water extractable soil C increased with increasing earthworm density. There were no significant changes in microbial activity with earthworm density.

The data are consistent with earthworm-derived organic compounds complexing metals and bringing them into solution off soil particle sorption sites. Thus metal concentration in soil solution and therefore metal mobility increases with earthworm density. However, the metals present as organo-metal complexes are not available for uptake by the earthworms so that metal body burden is unaffected or decreases, i.e. metal bioavailability decreases.

Corroded Magnox sludge and plutonium waste cementation

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Corroded Magnox sludge waste

Corrosion of spent Magnox fuel rods in water filled storage ponds has produced magnesium-rich sludges contaminated with fuel and fission products. We have experimentally investigated the composition and evolution of an inactive corroded Magnox sludge (CMS) simulant.

Our characterisation of the sludge using infrared spectroscopy, X-ray diffraction, and environmental scanning electron microscopy (ESEM) has determined that CMS is mainly composed of brucite, Mg(OH)2, and additionally artinite, Mg2CO3(OH)2.3H2O.

Plutonium association with CMS

It has been suggested that Pu adsorption onto CMS colloids may provide a mechanism to enhance Pu mobility. Therefore, we have determined the associative behaviour of plutonium in solution with CMS in a model storage pond/effluent treatment system. Using a full-factorial design, we have quantitatively determined the effects of CMS, and other components of the storage pond and effluent treatment system, on Pu solubility. This provides an important first approximation to true Pu solubility.

The addition of carbonate in solution had the largest influence over Pu solubility, allowing >90% of the Pu to pass through a filter membrane. The presence of CMS, and polyelectrolyte increased Pu filter hold-up. Silica at 1 ppm produced no observable effect. Solution pH was also found to have a significant influence over Pu filterability. Over the pH 7 to 11.5 range examined, more Pu was held up on the filter at higher pH.

Cementation of Pu contaminated CMS

For long-term storage it is intended that the CMS waste be immobilised in a cementitious wasteform. Our current research is intended to extend our understanding of the structure and behaviour of these cemented wasteforms. Our investigation of CMS evolution is continuing, and additionally we have begun to examine the microstructure of ordinary Portland cement (OPC) based samples. Our cement samples doped with CMS, Zr, U (and later Pu) have been analysed using SEM to establish the hydrated calcium silicate (C SH) phases present and with which phases the Zr and actinide elements associate. Further work will determine the evolution of these phases and co-ordination chemistry of the actinides. Eventually this data will be included with those from actinide leaching experiments to relate the cement microstructure with immobilisation performance.
Adsorption of heavy metal in contaminated surface water onto Limestone and Coconut Coir pith

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Geo-environmental studies were conducted in Katedan Industrial Development Area, Hyderabad, India, where the industrial effluents has contaminated the fresh water lakes.

To treat the effluent through a Permeable Reactive Barrier (PRB), the contaminated lake samples were collected to carry out the column tests in the laboratory to identify the appropriate reactive material to reduce the concentration of toxic/heavy metals like Lead, Zinc, Chromium, Arsenic, Copper etc. to an environmentally acceptable limit by their adsorption on to the reactive material.

The column experiment was conducted for one week to treat the contaminants in the surface water from Katedan Industrial Area using various reactive materials such as Zero Valant Iron, Coal, Limestone and other organic materials like Coconut coir pith, Hey, Cow dung cakes and plant materials like leaves, barks and stems etc.

The contaminated water was passed through the column made of Polyvinyl Chloride (PVC). The column is 50 cm long with diameter of 10cm. It was filled with 70% (14cm) height of 2-4 grain sized limestone and 30% (6 cm) of fibrous coconut coir pith.

The flow rate of 55 rpm was kept constant through out the column experiment. The effluents from the column were quantitatively analysed using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES).

The concentration of certain heavy metals at the effluent was reduced to the environmentally acceptable limits eg. (Cr 43.52 µg/kg to 21.49 µg/kg), (Cu 30.4 µg/kg to 4.62 µg/kg), (Ni 27.44 µg/kg to 12.54 µg/kg), (Pb15.62 µg/kg to 9.92 µg/kg), (Zn 98.25 µg/kg to 0.80 µg/kg) by limestone and coconut coir pith.

The electrical resistivity of nano-crystalline geikielite decreases from 2.246 X 10^8 Ω m at room pressure to 2.0 X10^6 Ω m at 7.8 G Pa, whereas the electrical resistivity of natural geikielite decreases from1.098 X10^8 Ω m at room pressure to 1.74 X 10^5 Ω m 7.8 G Pa, indicating more compressibility of natural geikielite in the pressure range of investigations. The present shows that the geikielite does not undergo any pressure induced phase transition up to 7.8 G Pa, indicating its stability in the earth’s mantle pressure conditions [3,4].

References
Stalagmite records of tropical Pacific climate since the Last Glacial Maximum

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Long, high-resolution, well-dated paleoclimatic records from the western tropical Pacific are scarce, obscuring the response of tropical Pacific climate to changes in global boundary conditions, abrupt climate changes, and external radiative forcing. Here we present three absolutely-dated stalagmite oxygen isotopic records from Northern Borneo that track fluctuations in Western Pacific Warm Pool hydrology over the last 27,000 years. Over 70 U-series dates and 11 isochrons provide excellent chronological control for the over 1200 stable isotope measurements. Our results suggest that rainfall in northern Borneo during the Last Glacial Maximum was similar to present. However, a pronounced maximum in stalagmite δ¹⁸O values occurs ~16.3 thousand years ago, consistent with dry conditions in the WPWP during the Heinrich 1 abrupt climate change event. The deglaciation is also marked by a 1000-yr-long oxygen isotope plateau centered at 13.2 thousand years ago that coincides with the Antarctic Cold Reversal, but there is no evidence for the Younger Dryas event observed in many other deglacial records. A broad minimum 5,000 years ago reflects the sensitivity of Warm Pool hydrology to spring/fall precessional insolation forcing. The new records demonstrate dynamic linkages between northern and southern high-latitude climate and tropical Pacific convection, and highlight the sensitivity of tropical Pacific convection to external radiative forcing.

Multiple redox states in the Archean-Proterozoic hydrosphere

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The late Archean deep water environments of Western Australia’s Hamersley Group Marra Mamba Iron Formation and Mount McRae Shale are characterised by extremely light organic carbon and relatively enriched, even positive, carbonate carbon δ¹³C values consistent with the presence of methanogens (Schidlowski, 2001). Positive mass independently fractionated (MIF) sulfur isotope values are found in fine-grained pyrite disseminated throughout these organic rich mudstones, while negative sulfur MIF is seen in rare pyrite nodules. This suggests that the fine-grained pyrite was formed abiotically, whilst the formation of the nodules was microbially mediated (Farquhar and Wing, 2003).

Multiple pyrite morphologies are not common in the Hamersley Group’s late Archean shallow water Wittenoom Formation; however, positive sulfur MIF in fine-grained pyrite in these dolostones suggests the absence of sulfate reducing microbes. The lack of very light organic carbon and positive carbonate carbon δ¹³C values implies that late Archean shallow water environments were too oxic to support anaerobic metabolisms, potentially in favour of more oxygen tolerant species.

Paleoproterozoic sulfur MIF in the Dales Gorge Member and Whaleback Shale of the Brockman Iron Formation Group shows good correlation between fine-grained and nodular pyrite in the same sample, with both demonstrating either negative or zero MIF, regardless of depositional environment. Furthermore, organic and carbonate carbon δ¹³C trends toward more modern values. This suggests that after the Archean-Proterozoic boundary, both deep and shallow water environments were sufficiently oxic for sulfate reducing microbes and thus marks the transition to a more uniformly oxidised hydrosphere capable of supporting aerobic life.

References

Tailings oxidation and mineralogy of Haveri Au-Cu mine, SW Finland – Preliminary results

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The Haveri Au-Cu deposit, situated in SW Finland, composes mainly of pyrrhotite, chalcopyrite and pyrite with accessory Fe-Co-Ni sulfoarsonides, sphalerite, molybdenite, iron oxides and native gold (Mäkelä, 1980). The tailings were piled during the active mining period from 1942 to 1961 covering ca. 18.5 ha and having an average depth of 7 meters.

In May 2006, a total of 40 profiles were drilled. Three profiles, and 17 tailings samples at intervals of one meter, were selected for mineralogical feasibility study. They were studied by optical reflected-light microscopy and by scanning electron microscope (SEM-EDS). Furthermore, the samples will be examined by X-ray diffraction (XRD), and geochemical analyses from selective leachates are planned.

The tailings are exposed to air, rainwater and meltwater which oxidize the primary sulfides remaining from the ore processing. Consequently, the tailings present zoning with oxidized vadose layer closest to the surface and unoxidized water-saturated layer below 3 to 4 meters. In May 2006, a total of 40 profiles were drilled. Three profiles, and 17 tailings samples at intervals of one meter, were selected for mineralogical feasibility study. They were studied by optical reflected-light microscopy and by scanning electron microscope (SEM-EDS). Furthermore, the samples will be examined by X-ray diffraction (XRD), and geochemical analyses from selective leachates are planned.

The oxidation process will continue for decades or even hundreds of years until reaching the groundwater surface.

The research is part of the EU LIFE Environment project “Risk Assessment and Risk Management procedure for Arsenic in the Tampere region” or RAMAS (www.gtk.fi/projects/ramas).

Reference

Chemical weathering of basaltic rocks in the tropical environment

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The chemical weathering of basaltic rocks under tropical conditions was marked with the generation of moderate to highly alkaline and reducing hot spring. Only a few similar occurrences has been reported in the Philippines where most of the hot springs are highly acidic and volcanic in nature. In Sira-an hot spring along the coast of Antique province, flammable gas (i.e. CH4(g)) accompanies the hot springs waters. Its pH, redox state, temperature, and dissolved constituents are considerably different from a nearby groundwater well and seawater such that it can be considered an anomaly. The mineral assemblage of the fracture fill materials comprises calcium-aluminum-silica-hydrate (CASH) phases, zeolites, and chlorite suggesting highly alkaline conditions.

The local hydrogeology of the area is responsible in the formation of the alkaline and reducing hot spring (Figure 1). Limestones at elevated areas dissolve to form dissolved calcium and carbonate enriched groundwater which percolates through the fractured basaltic rocks. Dissolution of minerals in the basaltic rock under anoxic conditions generates a highly reduced and alkaline aqueous conditions which converts the dissolved carbonate to methane. The dissolved components (i.e. Ca, Si, Fe, Al, Mg) in turn precipitates into CASH phases, zeolites, and chlorite.

Figure 1. A schematic presentation of the alkaline and reducing Siraan hot springs, Antique, Philippines.
Arsenic and Mercury in brown and hard coals from deposits of Poland

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Problem of the environmental pollution by As and Hg emitted during coal combustion is important. The aim of the study was a determination of As and Hg concentrations in coals extracted in Poland and mostly burned there.

Material and methods

Concentration of arsenic and mercury have been determined in 250 samples of brown and hard coals from deposits of Poland. Hard coal samples were collected from Carboniferous Upper Silesian (USCB), Lower Silesian (LSCB) and Lublin Coal Basins (LCB) and brown coal samples were collected from mined deposits in Poland – Turów, Belchatów, Koźmin, Lubstów, Adamów and Kazimierz. Arsenic contents have been determined with the ICP-MS spectrometry and mercury contents by AAS method.

Results

The mean arsenic concentration in the hard coals is 16 mg/kg. Coals from LCB contain in average 47 mg/kg of arsenic, coals from LSCB – 61 mg/kg. In coals from USCB mean concentrations of As range from 2 mg/kg (NW part of the basin) to 20 mg/kg (SW part of the basin). The average As contents in brown coals is 9 mg/kg (Turów 29 mg/kg, Belchatów – 3 mg/kg, Konin-Adamów – 1 mg/kg). The average mercury content in the hard coal samples is 85 ppb. The mean Hg content in hard coal from the LSCB is 399 ppb, USCB 60 ppb and 105 ppb in coals from LCB deposit. Coals from the eastern part of USCB contain higher mercury concentration than coal from western part of basin. They might be caused by sulphide mineralization in Triassic dolomites overlying this part of USCB. The average Hg concentration in all tested brown coal samples is 322 ppb and it is four times higher than average Hg concentration in hard coals. The highest average Hg content in lignite is observed from Belchatów deposit - 416 ppb and the lowest - 199 ppb from Lubstów deposit. Coals from tectonic grabens are enriched in Hg in comparison with lenticular deposits which were not tectonically influenced.

Conclusion

Obtained results permit to estimate that about 28t/a of mercury and about 2000t/a of arsenic are excavated and emitted with hard and brown coals burned in Poland.

Melt mixing and crystallisation in the plumbing system of the 1783 Laki eruption

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The 1783 Laki fissure eruption of SE Iceland is the second largest basalt eruption in recorded history, extruding ~15 km³ of lava and minor tephra over the course of 8 months and producing a notorious ‘dry haze’ of poisonous volcanic smog, leading to famine, disease and the death of 25% of Iceland’s population [1]. Large scale basalt eruptions are common in Iceland (e.g. Eldgjá, 934 AD and Thjórsá, ~8000 yBP; 19 km³ and 21 km³ respectively) and are fed by discrete batches of magma accumulating in large crustal reservoirs. The relationship between crystallisation and mixing in the storage reservoirs that give rise to such voluminous, long-lived eruptions has been the focus of recent SIMS analysis at the University of Edinburgh.

The concentrations of REEs and selected trace elements, including Zr, Y, Nb and Sr, were measured for 90 olivine-hosted melt inclusions from Laki using a Cameca 4f ion microprobe. The range of REE concentrations measured in the melt inclusions (representing discrete batches of parental melt) is not seen in whole rock compositions, implying that this variation is destroyed by mixing in the storage reservoir prior to eruption. Olivine compositions vary from Fo₈₇ – Fo₇₃, corresponding to a 50°C drop in crystallisation temperature. The standard deviation of La/Yb in melt inclusions hosted in olivine with Fo>85 mol% is 0.75 (n=40), but only 0.25 (n=16) in olivines with Fo<78 mol%, showing that cooling, and subsequent crystallisation of less forsteritic olivine, was therefore concurrent with mixing. The variation in La/Yb reflects variation in the composition of mantle melts being supplied to the crust under SE Iceland. A similar relationship between mixing and cooling has been found in a smaller, more primitive flow from northern Iceland [2], indicating that coupled mixing and crystallisation is common in the plumbing systems of Icelandic volcanoes.

References

Organometallic complexes from Ni-Mo-PGE black shales in South China – Combination of bioactivities, hydrothermal venting and phosphate deposition during global Cambrian biological explosion

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The study of organometallic complexes in ancient geological environments can explain mechanism of accumulation of metals and provide clues for the evolution of the earth life. For example, many synthesized complexes of aryl phosphines and aryl phosphites with platinum metals proved to have important mechanistic implications for homogeneous and heterogeneous catalysis.

Anomalous metal concentrations up to ore grade were reported from black shales that occur in different geological environments throughout the geological record. Besides major ore minerals and elevated metal concentrations in base metal sulfides, many authors suggested empirical relationship between various metals and organic matter.

Using HPCL-MS analysis, we found Co-, Cu-, Ni- and Pt-organometallic compounds in chloroform extract of organic matter from Ni-Mo polyelement sulfide ore bed hosted in lower Cambrian black shales whose organic matter was derived mainly from algae and cyanobacteria and whose formation coincided with the famous Cambrian biological explosion and world phosphate deposition. Beside organometallic compounds sulfur, polycyclic aromatic hydrocarbons and free-metal porphyrines were identified.

Our results demonstrate how biological activity was important for primary metal entrapment in hydrothermally enriched marine environment around medium temperature (<300°C) hydrothermal vent in semi-restricted basin.

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Re-Os study of the Polish Kupferschiefer: Implications for source and timing of metal enrichment

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The age and genesis of world-class copper deposits of the Kupferschiefer-type have been a subject of much debate with proposed synsedimentary to postdepositional models. The 187Re-187Os isotope system has been successfully applied to generate whole rock isochrons in differently aged organic carbon-rich sediments.

Six samples of typically Cu-mineralized Upper Permian calcareous black shale and limestone of the Kupferschiefer type from the Lubin mining district (Poland) were studied for Re-Os isotopes, platinum group elements (PGE), and selected major and trace elements.

Mineralized black shales (Cu_avg. = 4.9 wt.%, Ag_avg. = 242 ppm, Pb_avg. = 138 ppm and Zn_avg. = 87 ppm) display low PGE values (Pt = <2 – 3.2 ppb, Pd = <2 – 2.8 ppb, Ru = <10 ppb, Rh = 0.4 – 5.2 ppb and Ir = <0.1 ppb) and c(Re) = 249.4 – 22174 ppb, c(Os) = 0.4831 – 1.0009 ppb and 187Os/188Os = 10.26 – 426.7. Lower base metal but comparable PGE, Re and Os values are typical for basal limestone. Calculated correlation coefficients indicate preferential Re affinity to Cu-sulfides and Os affinity to organic matter.

In a 187Os/188Os vs 187Re/188Os plot the entire data set defines an isochron corresponding to an age of 240 ± 3.8 Ma, which most likely reflect late diagenetic/epigenetic metal enrichment.

The initial 187Os/188Os ratio of 0.99 ± 0.22 is slightly less radiogenic but within the variation range of present-day seawater and excludes any significant contribution from hydrothermal/mantle or meteoritic PGE sources.

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Three decades of Hf isotope research

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Following early experiments with the Lu-Hf system in the 1950’s to 1970’s, we established routine chemistry and TIMS measurement in 1980. TIMS Hf measurement is a “brute force” technique, involving use of a Re ionizing filament at the limit of its range. Practitioners can testify to the strain that high filament temperatures and high Re ion beams place on the ion source and collectors of the mass spectrometer. Nevertheless in this period many of the important areas of Lu-Hf isotopic studies were identified and developed. These included meteorites, crust-mantle differentiation, and the use of dated zircons to determine initial Hf isotopic signatures.

The advent of MC-ICPMS allowed analysis of up to 100 times less Hf, so that samples like chondrites and komatiites became truly accessible. High precision was obtained on small rare meteorites, and oceanic tholeiites could be analyzed in large numbers. ICP techniques also allowed a reduction of chemistry and much more rapid mass spectrometry. Somewhat intricate and/or empirical corrections needed to obtain accurate Lu and Hf data in ICP measurement are manageable. The large database now existing shows that Hf isotopic data do mirror patterns from Nd in many cases, but that Hf has considerable importance where behavior differs from Nd. Examples are oceanic sedimentation and mantle partitioning, particularly in higher-pressure mineral phases.

It seems inevitable that one of the main future applications of Hf will be in determination of initial $^{176}\text{Hf}/^{177}\text{Hf}$ in zircons U-Pb dated by laser MC-ICPMS. The initial Hf data are powerful in discriminating crustal sources, and the opportunity to acquire hundreds of Hf values is tempting. However, non-specialists often do not realize that 10 to 40% of the 176 mass signal has to be subtracted to remove Yb and Lu and arrive at the abundance of $^{176}\text{Hf}$. This is an enormous correction when epsilon-unit (i.e. 0.01%) variations of $^{176}\text{Hf}/^{177}\text{Hf}$ are the target. Intricate and empirical correction procedures are needed to account for differences in mass fractionation behavior of Yb, Lu and Hf, as well as the Er sometimes employed, and the accuracy of the 10-40% interference correction is critically dependent on these. Parallel analysis of zircon Hf by solution ICP has been employed in some critical studies, but this may not be practical for groups who measure large numbers of zircons, particularly detrital zircons. Probably, many who will measure and present laser Hf data for zircon will not be even partly specialized in isotope geochemistry. We must place a high priority on establishing robust, globally-agreed standards and procedures for laser Hf analysis of zircons.

Monitoring of atmospheric particulate matter around Raipur Central India

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The concentration, variations and sources of air borne carbonaceous particulate matters: volatile organic carbons (VOC10, VOC10-2.5 and VOC2.5) nonvolatile organic carbons (OC10- OC10-2.5 and OC2.5) and black carbons ( BC10, BC10-2.5, and BC2.5) in most polluted area of chhattisgarh Raipur have been studied for one year, June 2005-May 2006. The PM2.5 and PM10 samples were collected on pre-heated quartz fiber filters with the Partisol model 2300 Sequential Speciation Sampler (Rupprecht & Patashnick Co., Inc., USA) simultaneously. The combustion method equipped with the non-dispersive infrared detector (NDIR) is used for measurement of the volatile organic carbon (VOC), nonvolatile organic carbon (OC) and elemental carbon (EC) in the terms of CO2. The annual mass concentration of PM10, PM10-2.5, and PM2.5 was ranged from 62 – 975,17-602 and 20 – 373 $\mu$g m$^{-3}$ with arithmetic mean, median and STD values of 242, 139 and103; 222, 129 and 100; and ± 164.6,100.2 and 73.4 $\mu$g m$^{-3}$, respectively. The annual mass concentration of their carbons i.e. VOC10, VOC10-2.5, VOC2.5 and OC10- OC10-2.5 and OC2.5; and EC10- EC10-2.5 and BC2.5 was ranged 2.1 – 47.9, 1.6 – 32.2, 4.1 – 80.2, 10.3-160 and 0.1 – 35.0, and1.6 – 23.1 and 2.6 – 65 and 4.6-123 $\mu$g m$^{-3}$ with arithmetic mean, median and STD values of 10.4, 48.8, 6.9, 7.9, 19.1, and 33.9, 6.7, 11.8, 25.6, 40.9, 5.0, 7.8, 17.2, and 30.7; and 9.8, 7.4, 16.5, 32.1, 7.4, 5.5, 14.0, and 25.6 respectively.

Keywords: particulate matters, carbonaceous particulate, Partisol model 2300 sequential speciation Sampler
**Chemical and isotopic (C and S) composition of groundwaters from the Mt. Vulture volcanic system**

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Mt. Vulture volcano is located in the most external part of the Apennine orogen (southern Italy), almost at the edge of the Apulian foreland. The volcanic activity occurred up to 130 Kys ago. The volcano is formed by a main feldspar-bearing series of pyroclastic rocks and subordinate lava flows, ranging in composition from basanite and fooidite to phonolites (Schiattarella et al., 2005). Rare lava flows and dykes, with distinctly more silica-undersaturated composition melilitites, melilitite ankaratrites, and the ‘Melfi’ haüynophyre, were also emplaced. Carbonatite-melilitite magmas fed the final phase of volcanism producing maar-type craters. The large Na and S contents of the Vulture magmas (Marini et al., 1994) result in the widespread presence of sodalite-group phases among the feldespathoids (De Fino et al., 1982; Di Muro et al., 2004).

Most groundwaters are characterized by gas bubbling. In order to investigate the origin of solutes a total of 25 springs and wells were analyzed for the major and minor element contents, the isotopic composition of carbon in the total dissolved carbon (TDC) and sulfur in the aqueous sulfate. The chemical data suggest that the effects due to water-rock interaction are largely controlled by the input of CO₂. The dissolution of CO₂ in the water causes a substantial increase in its acidity, thus promoting the alteration of the rocks. Good correlations exist among alkalinity, electric conductibility and Na⁺, Ca²⁺, SO₄²⁻ concentrations. The alkaline-earth-bicarbonate and alkaline-bicarbonate compositions of the waters are in keeping with the major role played by CO₂ in the alteration processes.

The δ¹³C values of TDC corroborate the involvement of two carbon sources. The first one is biogenic CO₂, while the second one is magmatic. The δ³⁴S values of SO₄²⁻ are all positive and similar to those measured by Marini et al. (1994) in the haüynophyre magma, thus supporting for aqueous sulfate a main origin from leaching of volcanites. In few springs, however, some contribution of SO₄²⁻ from dissolution of Triassic evaporite at depth cannot be excluded.

**References**


**1⁰Be and clay mineralogical studies on lagoonal sediments from Kaluveli, Pondicherry, India: Significance to paleoclimate**

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Lacustrine and alluvial deposits of clayey sediments of 4.3-meter long core sequences from Kaluveli lagoon (N 12° 06’ 29”, E 79° 51’ 39”) situated 15 km north of Pondicherry, India, has been studied for clay minerals and ¹⁰Be abundance. This lagoon, 25 km long and 6 km wide, runs parallel to the east coast adjoining Bay of Bengal. Lake sediments contain ¹⁰Be mostly from two sources; one deposited directly from atmosphere and adsorbed to the surface of the sediments and the other is in situ produced. The adsorbed ¹⁰Be have been used to estimate rate of sedimentation in the Kaluveli Lagoon.

Upper part of the core (0 to 2.2 m) consists of gray clay unit indicating fresh water sediments, with sandy-clay horizons, quartz pebble and small amounts of calcite. Lower part of the core sequence (2.2 to 4.3 m) includes dark silty clay sediment with marine shells indicating brackish environment. Kaolinite and smectite in different proportion have been observed at various depths, which probably reflect variation in climate and/or paleogeography of this region.

Adsorbed ¹⁰Be was leached from four selected samples of this core and analyzed using newly developed AMS facility at Inter University Accelerator Center (15 UD pelletron), New Delhi, India. Concentration of ¹⁰Be varies between 3.32 x 10⁸ to 1.52 x 10⁹ atom g⁻¹ (dry sample) from 85 cm to 400 cm depth. The average sedimentation rate of 1.8 ± 0.18 x 10⁻³ mm y⁻¹ has been calculated using ¹⁰Be concentration in the sediments. Dominance of smectite over kaolinite between 40 to 50 cm depth (corresponding to age ~ 0.29 Ma) and below 220 cm (> 1.18 Ma) indicates that semiarid conditions prevailed at the time of their formation (Figure 1). Kaolinite abundance is higher in the sediments found at depth of 80 to 220 cm (0.5 to 1.18 Ma), which were possibly deposited under relatively humid climate. During this wet period laterites could have formed all along the east coast of India now preserved as discontinuous belt.

**Figure 1:** Variation of smectite / kaolinite as a function of depth and age determined using ¹⁰Be abundances.
Osmium groundwater flux from the Bengal basin: Implications for the osmium marine budget

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The osmium residence time in the oceans is currently poorly constrained, in part because the sources of Os to ocean water have not yet all been explored. One such source, potentially important, may be groundwater flux. Basu et al. [1] suggested that Bengal Basin groundwaters may provide a large flux of radiogenic Sr to the oceans. By analogy, and considering that the Ganges has the most radiogenic 187Os/188Os ratio yet measured in the world's rivers [2], groundwater of the Ganges alluvial plain may provide a significant flux of radiogenic Os to the oceans.

We present Os isotopic and concentration data for groundwaters collected along a traverse in the Bengal alluvial plain. As these waters are highly reducing, a specific method was developed (heating with CrVI in a high pressure asher, HPA-S at 250°C) to allow complete oxidation of all of the Os, and thus equilibration with the Os isotopic tracer. Oxidation at lower temperatures, in the HPA-S or in teflon vessels [3], led to underestimation of the Os concentration by as much as a factor of two.

Os concentrations are high (30-250 pg/l) and display 187Os/188Os ratios (2.2-2.6) in agreement with those of Ganges water and sediments. Os contents correlate strongly with those of Sr and several other elements, which allows us to roughly estimate the groundwater Os flux from the Bengal alluvial plain. Assuming conservative behaviour and both the mean Sr concentration and the groundwater flux of [1], we estimate an 188Os groundwater flux of ~9 M/yr. This estimate represents more than three times the Os flux from the Ganges and a radiogenic contribution similar to that of the Amazon [2]. If realistic, this estimate would significantly reduce the estimate of the Os residence time in the ocean, and may suggest that Himalayan derived Os has had an important effect on the 188Os/189Os ratio of seawater. On the other hand, preliminary results on groundwaters from the fresh/salt water transition area show that a substantial quantity of Os could be trapped here. This may indicate non-conservative behaviour which would significantly reduce our estimate of the groundwater Os flux that reaches the ocean.

Sub-segment scale mantle heterogeneity beneath the Mid-Atlantic Ridge near Ascension Island from combined Hf-Nd-Sr isotope evidence

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The Mid-Atlantic Ridge (MAR) between 7°30’S and 11°30’S shows prominent bathymetric along-axis variations with a shallow central part (segments A2 and A3) and deeply incised segments to the north and south (segments A1 and A4). These topographic variations are mirrored by a large compositional variations spanning the entire range of Atlantic MORB analyzed so far in εHf-SrNd and εHf-87Sr/86Sr space. Ascension Island is located in the immediate vicinity (80 km west of the MAR), indicating voluminous off-axis partial melting in the mantle. We analysed near primitive samples (MgO> 5 wt%) for Hf-Sr-Nd isotope and trace element compositions and our data for the submarine and subaerial portions of Ascension Island and the different segments along the MAR show that there are systematic changes in terms of εHf, εNd, and 87Sr/86Sr characteristics. In 176Hf/177Hf vs. Lu/Hf, 143Nd/144Nd vs. Sm/Nd, and 87Sr/86Sr vs. Rb/Sr spaces, the different segments define linear arrays. These arrays do not have any age significance but are mixing lines.

The central segment (A3) shows enriched mantle characteristics (εHf ~+12.5; εNd: +7.5 to +8; 87Sr/86Sr: 0.70267 to 0.70277). Segment A2, located immediately to the north, has higher values in εNd (+10.2 to +11.7) and εHf (+13.2 to +14.5) but lower 87Sr/86Sr ratios (0.70244 to 0.70237). In contrast, the data from segments A1 and A4 define distinctive linear arrays. This involves a depleted end-member with high εNd (up to +13), high εHf (up to +22), and low 87Sr/86Sr ratios (0.70244 to 0.70237) and an enriched end-member with low εNd and εHf and high 87Sr/86Sr ratios. Since there are no consistent trends with water depth or along axis position of the samples, sub-km scale mantle heterogeneities must be present beneath segments A1 and A4. The samples representing subaerial volcanism of Ascension Island mark the isotopically enriched extension of the linear array defined by MAR segments A1 and A4 (εNd: +6.8, εHf: +9.9; 87Sr/86Sr ratio: 0.70284). Samples from the submarine stage of Ascension Island are displaced towards higher εHf (+13.1 to +13.5), indicating that the volmetrically dominant volcanic basement was fed from a distinctive, enriched mantle source. Hence, all of these observations imply that mantle material, representing the enriched end member component for segments A1 and A4, replaced the mantle domain responsible for submarine Ascension Island volcanism prior to the onset of subaerial volcanism (≤ 1 Ma). Altogether, these relationships argue against a mantle plume origin for Ascension Island.

References
Thallium in brown and hard coals of Poland

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Introduction
Main anthropogenic source of thallium in the environment is high-temperature processing of raw materials, in which it occurs at small concentrations.

Material and methods
Concentration of thallium and Ag, Cu, Pb, Rb and Zn contents have been determined in 214 samples of brown and hard coals with the ICP-MS spectrometry. Hard coal samples were collected from Carboniferous in Upper Silesia (USCB), Lower Silesia (LSCB) and Lublin Coal Basins (LCB) areas, and brown coal samples were collected from mined deposits in Poland – Turów, Belchatów, Koźmin, Lubstów, Adamów and Kazimierz.

Results
Contents of thallium in brown coals ranges from 0.2 mg/kg (detection limit) to 2.4 mg/kg. It was noticed that coals from Belchatów and small town Adamów-Konin region deposits - Koźmin, Lubstów, Adamów, and Kazimierz characterize very low concentration of thallium. In these coals Tl contents not exceed 0.4 mg/kg and average contents is <0.2 mg/kg. Turów deposit coals distinguish by increased Tl contents. Thallium concentrations in brown coals from these deposits average 0.7 mg/kg. Distinctly higher Tl contents in Turów deposit coals are caused by overall lithology of the sedimentation basin and its alimentation area and may be connected with cropping up granites and granitoids of crystalline basement and Tertiary alkali basalts. High correlation between Tl and Rb concentrations in brown coals was observed.

Contents of thallium in hard coals ranges from 0.2 mg/kg to 5.3 mg/kg. Samples of hard coals from USCB characterize higher thallium concentration in comparison to two others coal basins. Average concentrations of that element in USCB coals is 0.5 mg/kg, whereas in samples from LCB is 0.4 mg/kg and in samples from LCB is 0.3 mg/kg. Our results shows diversification of thallium contents in coals from USCB. The highest concentrations were observed in coal from upper seams of SE part of the deposit. They might be connected with Zn-Pb (and Fe sulphide) mineralization in Triassic dolomites overlying this part of USCB. In these coals the high correlation between Tl and Pb contents was observed, and somewhat smaller correlations were noticed with Ag, Cu and Rb.

Conclusion
Obtained results permit to estimate that about 60t/a of thallium are excavated with hard and brown coals in Poland.

Hydrogen abundance in the prebiotic atmosphere. Reducing or weakly reducing?

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The atmospheric hydrogen abundance was crucial for the organic synthesis on the prebiotic Earth. For decades a common assumption of the fast (diffusion-limited) hydrogen escape lead to a belief that the prebiotic atmosphere had to be weakly reducing and therefore organic synthesis should have occurred only in the special locations such as hydrothermal vents.

However, the recent study of the hydrodynamic hydrogen escape from the anoxic hydrogen-rich planetary atmospheres suggested that hydrogen could have been lost at a very slow rate and a hydrogen-rich (reducing) prebiotic atmosphere could have been maintained by a reasonable volcanic hydrogen source. This calculation was incomplete though because we did not show how the atmosphere could get to the hydrogen-rich state in the first place.

Here we will report on the atmospheric conditions under which the hydrodynamic escape had to occur. We found that the switch between the reducing and weakly reducing atmosphere was a strong non-linear function of the ancient solar ultraviolet (UV) flux.

UV fluxes > 5 times the present UV flux favor the fast diffusion-limited escape and cause the atmosphere to be weakly reducing. UV fluxes < 3 times the present UV flux always result in a slow hydrodynamic escape and the hydrogen-rich atmosphere should be expected. We conclude that the rate of the organic production on the prebiotic Earth could have been directly dependent on the evolution of the UV flux of the ancient Sun.

We will also report on how the rate of the hydrogen escape would have changed when the first biosphere would provide a significant methane source in the Archean atmosphere.
Investigating the biogenic synthesis of chalcogenide-based nanomaterials

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The future of materials science is closely linked to nanotechnology and, as such, there is a need to improve the manufacture of nanomaterials in terms of environmental and economic impact. Using the capability of microbes to manufacture potentially useful bionanominerals offers new methods of material synthesis that eliminate toxic organic solvents, minimize expensive high-temperature processing and can involve the use of industrial waste as the starting material, thereby incorporating a remediation step.

This research involves (i) identification of biomolecules associated with different bacterial strains that act as templates to direct bionanomineral nucleation and growth; (ii) investigation of enzyme-mediated electron transfer reactions resulting in precipitation of nanoparticles; (iii) harnessing and scaling up these processes for biomimetic materials synthesis.

The biotransformation of selenium and tellurium oxyanions by four diverse organisms (Veillonella atypica, Bacillus selenitireducens, Geobacter sulfurreducens and Geobacillus stearothermophilus) has been selected as a model system to study bionanomineral formation by a range of reduction processes. These organisms produce size- and shape-constrained Se/Te nanoparticles with different structural and spectral characteristics to their chemically formed counterparts (Fig. 1).[1]

Figure 1: Biogenic Se and Te nanoparticles

[Image]

The elemental Se/Te is then further reduced to form reactive selenide/telluride, which is precipitated to produce chalcogenide-based fluorescent nanoparticles, such as CdSe.

Reference

Factors controlling ¹⁴C contents of organic compounds in oceans and sediments

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Fourteen years ago, Hayes published a review entitled “Factors controlling ¹³C contents of sedimentary organic compounds: Principles and evidence” (Hayes, 1993). It described four processes governing the distribution of the stable isotopes of carbon in individual molecules: “(1) the carbon source utilized, (2) isotope effects associated with assimilation of carbon,…, (3)…effects associated with metabolism and biosynthesis, and (4) cellular carbon budgets”. To a first-order approximation, only the first of these would apply in an analogous discussion of “factors controlling ¹⁴C”. The ¹⁴C content of organic samples is reported in terms of fractionation-normalized values of Δ¹⁴C or f¹⁴C (fraction modern). This practice erases all of the biosynthetic fractionations discussed above. Compound-specific ¹⁴C (CSRA) approaches were developed in part because of this apparent simplicity: values of Δ¹⁴C for individual compounds should depend only on the ¹⁴C content at t = 0 and radioactive decay since then. Calibration records determine ¹⁴C/¹²C ratios at t = 0, in principle allowing calculation of absolute chronologies. However, this applies only to organic matter produced directly from fixation of atmospheric CO₂; biosynthetic reactions that draw upon other pools of the carbon cycle automatically begin with the imprint of a “reservoir correction”. In practice, this means that the value of Δ¹⁴C rarely = 0 at t = 0. Now, after more than ten years of CSRA, it is becoming apparent that reservoir correction is just one of several challenges facing the application of individual-compound measurements. These challenges can be classified broadly as analytical or interpretational. Problems of analysis include: (1) difficulty obtaining adequate quantities of sample, (2) tedious laboratory separations, (3) balloononing uncertainties in values of Δ¹⁴C at small sample sizes, and (4) the difficulty of obtaining authentic standards and measuring realistic processing blanks. Nearly all obstacles to interpretation are due to the problem of heterogeneous mixing: there can be (1) multiple sources of the same compound, each having a different initial reservoir age but mixed in the same terminal reservoir, (2) a single source for a compound, but scrambling of its age by post-depositional mixing, and (3) in the case of prokaryotic metabolism, uncertain contributions of presumed planktonic molecules by deep-pelagic or benthic populations. Despite the challenges, there have been numerous, successful applications of CSRA. Here I will show several recent examples from the literature and discuss how further work promises to illuminate new information about fluxes and residence times throughout the global carbon cycle.

Reference
Sr isotopic compositions of ultra-deep inclusions in diamonds: Implications for mantle chemical structure and evolution

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Recent models of mantle convection combined with seismology have caused a paradigm shift in Earth Sciences away from two-layered convection of the mantle, towards models that involve convective stirring throughout most of the mantle depth. Such models are now being supported by a variety of new geochemical data. This makes the study of our only samples of the lower mantle, ultra-high pressure inclusions in diamonds, imperative as one of the few ways of directly testing predictable outcomes of these models.

To do this we have applied ultra-low blank Sr isotope chemical techniques along with carbon isotope analyses to a suite of diamonds from the Rio Soriso, Mato Grosso, Brazil to investigate the isotopic characteristics of the lower mantle. The suite of diamonds were kindly supplied by Dr F. Kaminsky and contain inclusions of Mg-silicate perovskite (MgSiO3), Ca-silicate perovskite (Ca-Pv; CaSiO3) and ferropericlasite, among other minerals. Ca-Pv inclusions contain several hundred to >1000 ppm Sr making it possible to analyse small inclusions of this mineral for their Sr isotopic composition, hence providing the first reliable Sr isotope determinations for the lower mantle environment. Our technique also allows determination of trace element compositions, including rare earth elements.

Two Ca-Pv inclusions have Sr isotopic compositions significantly less than the model “Primitive Mantle” 87Sr/86Sr composition (~ 0.7045) suggested for the lower mantle in two-layer convection models. The values obtained overlap with the MORB compositional spectrum which is taken as reflecting the long-term depletion history of the upper mantle. We interpret the Sr isotope results to indicate that the lower mantle, at the depths sampled by inclusions within diamonds, is not distinct from the upper mantle in terms of its Sr isotope composition. Carbon isotope data for these ultra-deep diamonds will also be presented to examine differences between “shallow” mantle carbon and ultra-deep carbon.
Ni signatures from the Dales Gorge Member of the Hamersley Group, Australia: Constraints on the origin of Banded Iron Formations

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The deposition of Precambrian banded iron-formation (BIFs) has been linked to significant compositional changes in the Earth's atmosphere hydrosphere, and biosphere. Previous geochemical studies have measured the isotopic composition and the concentration of major, trace and rare earth elements in BIFs. Those studies have focused on the source of the metals (Fe, Mn, and Si) but others also have considered the role of the microbial activity and the nature of the primary precipitates. In this study we present the results of microscale geochemical analyses, coupled with high-resolution petrography, with the aim of establishing the controlling factors in the source and distribution of trace elements in BIFs.

As primary precipitates, hydrous amorphous silica would have crystallized as pure chert and cationic silica gels as siderite and greenalite, the latter entirely transformed into ferroan-talc. In addition, ferroan-talc is arguably a reaction product of siderite and chert. The presence of platy hematite is accompanied by an increase of ferroan-talc and a diminished siderite content. There is no evidence of magnetite as a primary precipitate, rather, it tends to occur as overgrowths on hematite and may have also formed at the expense of disperse platy hematite. Early diagenetic apatite and late diagenetic ankerite-ferroan dolomite crystals constitute the remaining mineral phases.

We conclude that the distribution and concentration of trace elements in different mineral phases were influenced by hydrothermal activity. Considering the high concentration and strong correlation with Fe, it is suggested that Ni represents a reliable indicator of element contribution from hydrothermal vent systems, which is consistent with previous models based on REE and Nd isotopic signatures. Furthermore, by comparing the Ni:Fe ratios of the Dales Gorge Member with other major BIF types (Algoma-, Superior-, and Rapitan-type), it appears that hydrothermal input was a major source of some trace metals to the BIF depositional setting, particularly Ni.

Comparison of δ¹³C and δD values of n-alkanes from angiosperms and gymnosperms in Western Europe

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Successful applications of stable isotopes of terrestrial plant leaf waxes in paleoclimate research depend on a thorough understanding of isotopic composition of different plant types contributing to sedimentary organic matter. The primary objective of this project is to investigate the effect of environmental conditions on δ¹³C and δD values of leaf wax n-alkanes from modern gymnosperm and angiosperm species throughout a north-south climatic gradient in Western Europe.

The initial nC₂₇-alkane data from Newcastle, UK, Bremen, Germany, and Porano, Italy (3 to 5 species per location) indicate that, overall, there is a strong negative correlation between δ¹³C and δD values. While there is a definite ¹³C-enrichment of gymnosperms in comparison with deciduous angiosperms (at least 1‰, but mostly from 2 to 6‰ in δ¹³C), a significant relative D-depletion of gymnosperm species (between c. 14 to 42‰ in δD) was observed only in Porano. Gymnosperms in Newcastle and Bremen were characterized by much more similar δD values in comparison with deciduous angiosperms, the D-depletion being only between 0 and 21‰ and 0 and 14‰, respectively.

The observed isotopic variations between angiosperm and gymnosperm species in relatively warmer and drier Porano most likely resulted from physiological differences among the species. Relative ¹³C-enrichment and D-depletion of gymnosperms may have resulted from their lower stomatal conductance and greater water use efficiency. The δD data from Newcastle and Bremen, however, suggest that differences in plant physiology were not sufficient to cause appreciable variations between angiosperm and gymnosperm species in these colder and wetter locations.

The results of this study have important implications for interpreting stable isotope data of sedimentary n-alkanes. Large shifts in δ¹³C and δD values may result not only from changes in paleoenvironmental parameters but also from shift in plant communities. The magnitude of isotopic differences between plant types may also depend on climatic conditions, so that δ¹³C and δD differences between angiosperms and gymnosperms are greater in warmer and drier locations.
Mineral chemistry of pyrochlore in residually inherited Fe-P-Nb-laterite ore bodies at Sokli carbonatite complex

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The Sokli carbonatite complex in Northern Finland has undergone extensive laterization and a vertical profile through the sequence varies from 0 to 70 metres. It contains a partially weathered saprock, saprolite, laterite covered by glacial deposits. The laterite is strongly enriched in phosphate, niobium and tantalum.

Locally the weathering profile is covered by a black Fe-P-Nb-REE enriched bed, 5 – 30 mm thick, which is situated directly beneath the glacial deposits and is interpreted to be residually inherited.

The residual bed contains pyrochlore which deviates texturally and chemically from the pyrochlores in main laterite and in fresh rock by being smaller (20µm) in diameter and by their euhedral crystal habit. These grains typically contain high density of fluid inclusions. SEM-EDS and microprobe study indicate that A-site occupancy is dominated Ca and Na of the pyrochlore structure while, along with the weathering, those two ions are detected to become partially replaced by K, Sr, Ba in laterite profile. Contradictory to the pyrochlores in fresh carbonatite-phoscorite and in laterite profile, the pyrochlore in residual bed lack uranium and has extremely low contents of thorium.

The role of Iron redox cycling for the natural acidification of ground water

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In wide areas of Western Australia (WA) springs are occurring that release acidic ground water (pH<3) into gypsum-rich playas. The origin of the acidity is related to the oxidation of Fe(II) and the subsequent precipitation of ferric (hydr)oxides (McArthur et al, 1991). The similarity of these systems to acidic mining lakes (AML) is striking. AML are forming upon oxidation of Fe(II) and sulfate-rich ground water, the pH typically ranges between 2.7 and 3.3 and is buffered by the solubility of schwertmannite (Regenspurg et al., 2004). Acidic conditions in AML are stabilized by an acidity-driven iron cycle at the sediment-water interface, where oxidation and reduction of Fe balance each other with respect to the alkalinity budget (Peine et al, 2000).

We therefore determined Fe(III) reduction rates, Fe(III) mineralogy and the Fe(III) reducing microbial community at three sites from iron-oxide rich (up to 7 % dithionite extractable Fe) soil material fully saturated with acidic ground water. The maximum Fe(III) reduction rate was 4.8 nmol g⁻¹ h⁻¹, a value similar to AML. Jarosite was the only Fe(III) XRD detectable mineral, schwertmannite appeared to be missing. The occurrence of Acidiphilium cryptum, an acidophilic Fe(III)-reducing bacteria could be proved. These observations suggest that also in the acidic ground waters an acidity driven iron cycle exists. They further imply the question how such a low pH can develop in a system that, contrary to AML, is not affected by pyrite oxidation.

Significant acidification from Fe(II) oxidation occurs only, if the corresponding anion originates from a strong acid, such as sulfate. Fe(II) in the ground waters from WA are regarded to be generated during weathering of Fe(II) bearing minerals and/or reductive dissolution of Fe(III) minerals. Both processes, however, generate HCO₃⁻ as the corresponding anion. We therefore postulate that HCO₃⁻ has been replaced by sulfate through the dissolution of gypsum and deposition of CaCO₃ as so-called calcrites:

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\text{Fe(HCO_3)_2 + CaSO_4 \rightarrow CaCO_3 + FeSO_4 + 2 H}^+ \]

References


Microbial mobilization / volatilization of selenium sorbed on soil minerals

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Selenium has major nutritional and biological function but the range between essential and toxic concentration is very small. The more toxic Se(IV) and Se(VI) are water soluble and hence bioavailable. The iron oxide and clay content of soils can affect the bioavailability through adsorption reactions, whereby Se(IV) is stronger adsorbed than Se(VI) [1]. The most reliable natural attenuation process of enriched Se in the environment is microbial methylation [2].

In order to investigate the alkylation / methylation process, Alternaria alternata, known as a Se resistant and active methylating saprophytic fungus [3], was used for incubation studies. First we observed the alkylation of dissolved inorganic selenium (SeO_3^{2-}, SeO_4^{2-}) and found different alkylated species over a wide pH range. Then, different selenium enriched minerals, e.g. goethite enriched by SeO_3 or SeO_4 adsorption, were incubated with A. alternata inoculums to study the dependence of solid selenium binding on alkylation reactions. For Se speciation studies we used different analytical tools. Volatile selenium species were measured with a cryotrappping / cryofocussing gaschromatographic system coupled with ICP-MS. Beside the dominantly occurring dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe) we found also other alkylated species like diethyl selenide (DESe) and diethyl diselenide, especially in dissolved selenium experiments. In adsorption experiments the aqueous inorganic selenium species were measured by hydride generation – atomic absorption spectroscopy. In incubation experiments we used a hyphenated HPLC-ICP-MS to separate the dissolved selenium species.

In our incubation studies we found different patterns of alkylation of dissolved and adsorbed selenium. For dissolved Se, Se(IV) were alkylated in higher amounts and we found more volatile species than for Se(VI) caused by a lacking reduction step in the methylation mechanism [4]. In the opposite we found a higher methylation for Se(VI) than for Se(IV) adsorbed on soil minerals because of different kinds of adsorption [5].

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Speciation of Cd, Cu and Pb by DPASV in unpolluted soil solutions

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The mobility and the bioavailability of trace elements in soils are largely dependent upon their interactions with various organic and mineral ligands. These interactions control trace metal concentration and speciation in complex geochemical systems. The aim of this work is to determine the chemical speciation of cadmium, copper and lead in subsurface waters circulating in an unpolluted soil (Planosol). The study area is located on the Aigurande plateau in the northern part of the Massif Central (France). The substratum is composed of Paleozoic gneiss and intrusive granitic rocks. Soil solutions were collected in a gravely and concretion-rich horizon (Fe- and Mn- oxyhydroxides) from 2004 to 2006 during the soil saturation period.

Chemical speciation of Cd, Cu and Pb was obtained by titrating the filtered water samples using differential pulse anodic stripping voltammetry. Cd, Cu and Pb have been chosen principally because of their various behaviours in the soil solutions. The aim of these experiments is to determine the apparent stability constant K and the corresponding apparent ligand concentration (i.e. complexation capacity CC) using graphic method and the linear transformation method described by Ruizic (1982). A 1:1 complexing model was applied for result interpretation. Polarographic curves of Cd and Cu show significant peaks which may be associated with metal complexes. However, the copper titration curves underline different processes (complexation, adsorption and both processes) and provide evidence for “slow” kinetic reactions (in the experimental conditions). The cadmium titration curves show complexation processes and fast kinetic reactions. Results for measurement of complexation parameters are differently discussed for both metals. To evaluate the copper potential binding in all cases, potential distribution coefficients (Kd) are calculated based on (1) the estimation of K (complexation processes) and (2) the estimation of the number of sites available for metal association using potentiometry (adsorption processes). Potential Kd indicate that copper has a stronger affinity for complexation processes on organic compounds than adsorption processes. No significant seasonal variation pattern in the potential Kd parameter is observed. For cadmium, CC and K results show seasonal evolutions which can be linked to soil solution modifications and/or presence of various ligands. Pb experiments are actually in progress.

As a conclusion, voltammetry data give evidence about relationships between trace metals, organic matter and soil compounds.
Rates of weathering rind formation from $^{238}\text{U}-^{234}\text{U}-^{230}\text{Th}$ chronometry: Application to basalt weathering

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Weathering rinds developed on fresh rocks provide an opportunity to constrain the processes and rates of weathering as a function of parameters such as lithology and climate [1]. Such information requires first to develop reliable dating methods for such materials, which have been rarely studied, up to now, by radiochronometric techniques.

In this study we propose to evaluate the potential of $^{238}\text{U}-^{234}\text{U}-^{230}\text{Th}$ chronometry to constrain the age and the formation rate of weathering rinds. We worked on a rind developed on a basaltic clast from a Costa Rican alluvial terrace, which has been extensively studied for mineralogy, geochemistry and petrology [1]. Nine subsamples of this clast were collected along a 2 cm transect, from the center of the fresh basalt core to the outer rind boundary, by drilling samples (2.5-mm in diameter and 5-mm depth) on one section of the split clast. Major and trace element concentrations, as well as Sr isotope ratios and $^{238}\text{U}/^{234}\text{U}-^{230}\text{Th}$ disequilibria have been analysed in each subsample.

The data are inconsistent with immobility of Th and removal of mobile elements such as Ca, Mg, and Sr during weathering. Additionally, the increase of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios, $^{234}\text{U}/^{238}\text{U}$ activity ratio and $\text{U}/\text{Th}$ ratios from the fresh core to the outer rind boundary implies an input of U, with $^{234}\text{U}/^{238}\text{U} \geq 1$, and an input of radiogenic Sr into the rind. These U and Sr inputs could both be ascribed to an external flux of dissolved U and Sr transported by the upper soil waters and adsorbed on or incorporated into Fe-Al oxy-hydroxides. Modelling $^{238}\text{U}-^{234}\text{U}-^{230}\text{Th}$ disequilibria in the rind by using an U gain-and-loss model classically applied for the interpretation of U-Th data in weathering profiles [2] give an advance rate of 4-mm/10ka for this 1.5cm-thick rind. This age is in close agreement with other independent methods [1]. This study highlights the potential of the U-series dating method to constrain the timescale of weathering rind formation and therefore to provide new information about the rate of bedrock conversion to saprolite.

References

Tracking mobile niobium in the boreal environment with a “multi-survey” approach

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Niobium is mainly found in weathering-resistant minerals and generally considered as an immobile element and a recent soil (Echevarria et al 2005) and hydrochemical (Lutfi et al 2007) study has not changed this view. Still very little is known about the behaviour of Nb in various soils or in continental surface- and ground water environments. Nb has one stable ($^{94}\text{Nb}$) and several unstable isotopes found in radioactive wastes, e.g. $^{95}\text{Nb}$ and $^{96}\text{Nb}$ ($t_{1/2}=350$ and 2400a).

We examined dissolved and acid-available particulate fractions of Nb in boreal stream and ground waters and “non-detrbral” Nb in sediments. The data consists of both speciation experiments and time–series of a small stream, large scale regional geochemical data sets and brackish/lacustrine environment sediments.

In streams spatial patterns, temporal trends and speciation experiments all point to dissolved humic substances and colloidal Fe as the main carriers and controls of Nb. Clay-silt and ore deposits may be responsible for producing local stream-water Nb anomalies. In groundwater in glacial till overlying Proterozoic granitoids, dissolved (0.45 µm) Nb concentrations were about an order of magnitude higher than in stream water and strongly correlated with dissolved Fe. In the brackish-water sediments, the Nb concentrations (1.3-4.2 ppm) were clearly higher than in the lacustrine ones (0.25-0.53 ppm). To explain this, we assessed the potential role of organic material, biological processes, mineralogy and input factors. However, no satisfactory explanation for the change was found.

The use of multiple surveys was a successful approach for studying the behaviour of Nb. Although this metal is relatively immobile our results show that certain conditions favour Nb enrichment in the aquatic environment which also has implications for the behaviour of radioniobium.

References
Influence of transition metal cations on the formation and reactivity of biogenic Mn oxides

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Microbial manganese oxidation is the dominant pathway for Mn oxide precipitation in many environments. Several strains of Pseudomonas putida, a common soil and freshwater bacterium, oxidize soluble Mn(II) via a multicopper oxidase enzyme, producing a poorly-crystalline layer-type Mn(IV) oxide, which is deposited in matrix of extracellular polysaccharides. These reactive nanoparticles have a remarkably high sorption capacity for metals due to their large surface areas (100 - 220 m² g⁻¹), permanent structural charge (~16% Mn(IV) vacancies), and redox activity.

Our research is directed towards understanding the formation of biogenic Mn oxide minerals in metal-contaminated environments and their capacity to immobilize metals during active microbial precipitation. We have determined the effects of varying concentrations of cobalt, nickel, copper, and zinc on rates of bacterial growth and kinetics of enzymatic Mn(II) oxidation by P. putida GB-1. In addition, we have applied X-ray absorption spectroscopy and X-ray diffraction to probe the mechanism of metal sorption to the biooxide-biofilm assemblages. The results from these experiments are interpreted in light of sorption experiments performed with freshly precipitated biogenic Mn oxides.

This work elucidates the dynamic and complex interactions between aqueous species, oxide minerals, and microorganisms encountered in natural systems. The results from this research have important implications for determining the role of biogenic manganese oxides in regulating the concentrations and distribution of trace and contaminant metals in aquatic and soil systems.

Petrology and P-T path of the Guyang mafic granulites: Implications for tectonic evolution of the Western Block of the North China Craton

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In the last few years, two Paleoproterozoic continent-continent collisional belts, named the Trans-North China Orogen and Khondalite Belt have been recognized in the North Chia Craton. The Khondalite Belt formed by the collision between the Yinshan Block and the Ordos Block to form the Western Block at ~1.92 Ga, which then collided with the Eastern Block to form the North China Craton along the Trans-North China Orogen at ~1.85 Ga. In the last few years extensive investigations have been carried on the granulite-facies rocks in the Eastern Block, Trans-North China Orogen and Khondalite Belt, but few studies have been done on the late Archean granulites in the Yinshan Block. In this study, we present detailed textural and compositional data for various symplectites or coronas observed in the mafic granulites from the Guyang Complex in the Yinshan Block.

Petrological evidence from the Guyang mafic granulites indicates four stages of metamorphic evolution (M1 to M4). The M1 assemblage is preserved as mineral inclusions within minerals of the peak assemblages, represented by hornblende + plagioclase + quartz ± biotite in the mafic granulites, with P-T conditions of ~0.6 GPa and ~750 ºC. The M2 assemblage is represented by orthopyroxene + clinopyroxene + garnet + plagioclase + quartz at 8.0-10.0 kbar and 800-900 ºC. The M3 assemblage is characterized by garnet+quartz or garnet+clinopyroxene symplectic coronas surrounding orthopyroxene, clinopyroxene and plagioclase grains, with P-T of 9.0-10.0 kbar and 700-750ºC. The M4 assemblage consists of cummingtonite + plagioclase replacing clinopyroxene and orthopyroxene. These assemblages and the estimated P-T conditions indicate that the Guyang mafic granulites underwent medium-pressure granulite-facies metamorphism with an anticlockwise P-T path involving near isobaric cooling following peak metamorphism, which reflects a metamorphic event related to the intrusion and underplating of large amounts of mantle-derived magmas rather than a continent-continent collisional environment.

Acknowledgments

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Climate fluctuations during the last 3000 years in Guizhou, China: Evidence from the TIMS-U series ages and oxygen isotope composition of stalagmite

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The TIMS-U series ages and the δ¹⁸O values of stalagmites from the Qixing Cave, Guizhou (26°35’N, 107°16’E) have been determined using the MAT-262-RPQ and Delta-S mass spectrometers. The results indicate that the stalagmite was deposited during the period of 3145-200 a B.P. and experienced four stages of the climate-environmental change.

(1) The first stage is in the range of 3145-2927 a B.P., which has δ¹⁸O values from –5.61 to –5.16‰. This stage corresponds to the late Megathermal Period (7-3 ka B.P.);
(2) The second stage is in the range of 2927-1196 a B.P., which has δ¹⁸O values from –5.51 to –4.59‰. Those values are higher than that in the first stage, indicating that the climate has become colder and dryer;
(3) The third stage is in the range of 1196-545 a B.P., which has the δ¹⁸O values from –5.98 to –3.92 ‰. This stage corresponds to the Medieval Warm Period (MWP);
(4) The fourth stage is in the range of 545-200 a B.P., which has the δ¹⁸O values from –5.39 to –3.51 ‰. It had the coldest and driest climate during the period of last 3000 years. This stage corresponds to the Little Ice Age from 1555 A.D. to 1800 A.D.

A regressive equation δ¹⁸O (‰) = −2.20 × 10⁻⁴ year (a.B.P.) - 4.54 by fitting the two data sets of the δ¹⁸O values and the age (years). It indicates that the δ¹⁸O values become higher from 3145 a B.P. to 200 a B.P. which corresponds to lower precipitation. The warm and wet climate in the late Megathermal Period changed to the cold dry climate in the Little Ice Age. It is interesting to note that on the basis of the climate records during 1951-2000 A.D. measured at the Guiyang Meteorological Observatory (26°35’E, 106°43’N), two regressive equations of the temperature values and the age (years), the precipitation values and the age (years) have the negative slopes, implying that the temperature gradually decreases with an amplitude of 0.2°C and the precipitation gradually decreases with the amplitude of ~7 cm during the last 50 years. Thus, the modern climate pattern in Guizhou Province, China, may be continuing from the last 3000 years.

This work was supported by the NSFC grant of No.40473006.

Mass-independent sulfur isotopes trace magma-wall rock interactions in the Bushveld Complex

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Abundant metasedimentary xenoliths in the Platreef, the ore horizon of the northern limb of the Bushveld Complex, South Africa, suggest significant interaction between the Bushveld magma and the surrounding country rock during emplacement. Fluid-mediated concentration of Platinum Group Metals and sulfur into the Platreef ore zone likely occurred as a result of this interaction. We use measurements of ⁳⁴S/³²S and ⁳³S/³²S to test hypotheses of material transfer between the Platreef and the surrounding country rock.

Solid-earth fractionation processes of ⁳⁴S/³²S and ⁳³S/³²S are mass-dependent, characterized by: δ⁳³S = 0.515 x δ⁳⁴S. Deviation from mass-dependent isotopic fractionation is quantified as Δ³⁴S (= δ³⁴S–1000/(1+ δ³⁴S/1000)⁰⁵¹–¹). Proxies for ‘primary’ igneous sulfur (meteorites, peridotite xenoliths) possess Δ³⁴S values near 0 ‰. Similarly, relatively pristine Bushveld igneous rocks have Δ³⁴S values ≤ 0.2 ‰. On the other hand, sedimentary country rocks surrounding the Platreef exhibit substantial non-zero Δ³⁴S values. As Δ³⁴S is a chemically-conservative tracer, non-zero Δ³⁴S values in Platreef sulfide ore minerals are an indication of material transfer from the surrounding country rock.

We have performed a S isotope study along two profiles through the Platreef into underlying metapelitic and metacarbonate country rocks. In both profiles, far-field igneous rocks have Δ³⁴S values ≤ 0.2 ‰, while far-field metasedimentary rocks have significantly mass-independent S isotope compositions (Δ³⁴S ranging up to ~0.9 per mil in the pelitic rocks and up to ~5.0 per mil in the carbonate rocks).

In the metapelitic profile, Δ³⁴S values from the country rocks show only a weak positive correlation with distance from the igneous contact while S isotope compositions within the Platreef are consistent with mass-dependent S isotope compositions (Δ³⁴S ≤ 0.2 ‰). Both features suggest little magma-wall rock interaction. In the metacarbonate profile, however, Δ³⁴S values in both the country rock and the Platreef define a classic advective-dispersive tracer geometry. This geometry is not present in the associated Δ³⁴S values, revealing their susceptibility to post-transport alteration. Displacement of the Δ³⁴S front suggests fluid advection into the country rocks; this was accompanied by back-diffusion of S isotope species into the Platreef. Counterintuitively, then, mineralization may have occurred as a by-product of fluid transport out of the Platreef ore-forming zone.
The presence of excess $^3\text{He}$, which cannot result from air contamination, is strong evidence that indigenous noble gases exist in Stardust samples. The $^3\text{He}/^4\text{He}$ ratio can in principle point to when comets acquired their noble gases, and from what volatile reservoir—the early protosolar nebula, near the evolving sun during or just after the deuterium burning that elevated the level of protosolar $^3\text{He}$, or by later implantation of solar-wind-like radiation. Jupiter’s $^3\text{He}/^4\text{He}$ ratio of $1.66 \times 10^{-4}$ (Mahaffy et al., 1998) likely reflects the protosolar value. $^3\text{He}/^4\text{He}$ is $\sim 3.6 \times 10^{-4}$ in the sun after deuterium burning (Heber et al., 2004), and $4.82 \times 10^{-4}$ in the solar wind (Heber et al., 2007). Our preliminary measured ratio of $\sim 2.7 \pm 0.3 \times 10^{-4}$ falls between the protosolar and solar D-burning values.

Production of the excess $^3\text{He}$ by galactic cosmic ray (GCR) spallation reactions is unlikely. While measured $^3\text{He}$ contents are small (< 600,000 atoms), abundances/gram are not; the minimum grain concentration is estimated to be $\sim 6 \times 10^{5}$ cm$^3$/g. GCR production rates in a fosterite/enstatite particle, on the Wild-2 surface or buried under 1 m of ice, are $\sim 7-5 \times 10^9$ cm$^3$/g per Ma, requiring GCR exposures of $\sim 1000$ Ma, in either location, to generate only 10% of the $^3\text{He}$ concentration. Estimated mass loss from Wild-2 just since its 1974 appearance is $\sim 1$ m (Brownlee et al., 2004), and was probably significantly more in the Wild-2 jet sources if they were active on previous apparitions. The collected particles were therefore likely buried until very recently at depths where GCR production is essentially nil. While ancient surfaces may be preserved on Wild-2 (Brownlee et al., 2004), only $\sim 50\%$ of the observed $^3\text{He}$ could be produced in them by GCR spallation over the 4500 Ma age of the solar system.

References

The dynamic Archean Earth
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Archean cratons stand distinct from younger orogens as a result of their refractory lithospheric keels and relatively abundant komatiite and tonalite-trondhjemite-granodiorite (TTG) rock types. Yet detailed petrogenetic and structural studies within well constrained geochronological frameworks point to the operation of plate-tectonic-like processes as far back as 3.8 Ga. Modern geodynamic settings provide a template for interpretation of igneous rock sequences based on the assumption that melt compositions are governed by mantle mineral assemblages, dependent on depth and temperature, mediated by fluid fluxes. Application of the modern template to the Phanerozoic and Precambrian record has been validated through consideration of multiple characteristics including depositional setting, and timing and duration of magmatic and structural events. The Superior Province of North America records the formation of several independent protocontinental fragments between 3.8 and 2.8 Ga. Continental margin rift sequences suggest plume-driven magmatism, which was followed by production of plateau-type juvenile basaltic crust in the early Neoarchean. Consumption of oceanic domains of undetermined extent is recorded in $\sim 2750$ Ma oceanic and continental arcs with subduction signatures including pre-orogenic boninite, calc-alkaline basalt and adakite, and syn-to post-orogenic shoshonite and sanukitoids. Five discrete collision events between 2720 and 2680 Ma united the oceanic and diverse protocontinental terranes. Evidence from the western Pilbara craton supports the operation of subduction by 3.12 Ga, whereas the 3.51-3.24 Ga sequences of the eastern Pilbara appear to have evolved in a plume setting (Smithies et al. 2005). However, evidence for even earlier sea-floor spreading within a plate-tectonic framework derives from the 3.8 Ga Isua belt (Furnes et al. 2007). It is likely that plumes were a common heat-release phenomenon early in Earth history, and once may have been dominant, but evidence for Neoarchean plume-arc interaction (Dostal and Mueller 1997) suggests that as in the modern Earth, plumes were not incompatible with organized convection. Evidence from the Hadean record is scant and views of Earth’s very early evolution are guided by thermal models and insights from planetary geology.

Many features of Archean terranes appear to be directly (komatiites, charnockites) or indirectly related to higher mantle temperatures. The highly depleted compositions of lithosphere keels may result from fluxed melting of depleted mantle in high-temperature suprasubduction-zone wedges.

References
TEM evidence for lead transport by bacteria in atmospheric deposition

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Particulate matter (PM < 5) present in atmospheric deposition and subsurface soil water has been monitored during one year in two different, polluted and non polluted environments located in France. One site is a vineyard and the other one is a forest considered as an unpolluted reference site. Coupling TEM and EDX permits single-particle characterization (composition, structure, size and morphology).

PM in rainfall, leachate and soil solution show similar characteristics for both sampling sites: among more than 10000 characterized particles, 10 to 20% of the relative surface area is of biological type. Different morphotypes of bacteria and associated amorphous organic matter are regularly and significantly concentrated in lead. Lead is always associated with phosphor forming one or several granules confined inside the bacteria cell (Figure 1).

![Figure 1. a) Bacteria with internal granules (arrow). b) EDX spectrum corresponding to arrow in figure 1.a)](image)

Such lead enrichments inside internal granules have been previously shown (Roane, 1999; Suh et al., 1999) in laboratory experiments. Our study proves for the first time such an occurrence in natural environments. The presence of bacteria in both rain water and soil water suggest an ubiquitous behaviour of microorganisms and an atmospheric origin for the lead. Even if the source of lead is not known, our result furnishes evidence for a microbial airborne lead transport.

References

Estimating geochemical impacts of uranium mining exploitation: The evaluation of the natural background in the Beiras metallogenetic province (Central Portugal)

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The evaluation of the geochemical and radiological impacts associated with uranium mining activities requires a comparison, for each environmental compartment, of data taken before and after the end of mining works. With a few exceptions, no environmental data is known for Portuguese old uranium mines regarding the natural background before exploitation. A possible way to overtake this limitation is to obtain data from areas which constitute a natural analog of those that were mined for uranium ores, but where exploitation did not occur. The Oliveira do Hospital area, located in Central Portugal, fulfil such requirements; here, late-tectonic Hercynian granites and pre-ordovician metasedimentary rocks dominate. 24 samples of surficial and groundwaters were collected in the region, as well as 14 samples of soil and 5 of stream sediments. These samples were analysed for more than 40 chemical elements, using several analytical techniques. The results obtained allowed to establish reference values for the geochemical background, taking into consideration central tendency and variability parameters. An important conclusion is that several elements are frequently concentrated by natural processes above the limits referred in the literature and/or legislation as indicating anthropogenic contamination (e.g. Ba, As, P and Be in soils, $^{226}$Ra in waters), which reinforces the interest of the evaluation of the local geochemical background, as an alternative to the use of global reference values.
Hydrogeochemistry of water resources from abandoned Freixeda gold mine (NE Portugal)

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Freixeda mine is located in NE Portugal and was exploited for Au, Ag and Pb. It belongs to the Auriferous Methalogenic Province of NW of Iberian Peninsula. The mineralization is associated with sulphide minerals in quartz veins, located in metasedimentary paleozoic formations.

Water samples were collected from a gallery with acid mine drainage (AMD), 3.5 <pH< 4.0, and from groundwater and surface water, upstream and downstream from the mine influence. Water from Ribeira de Freixeda upstream from the AMD confluence is not affected by the mineralization and has Ca-HCO₃ type, slightly basic pH with no detectable As and no significant concentration of trace metals. Downstream from the AMD, surface water becomes Ca-Mg-SO₄ type with elevated concentrations of As, Zn and Mn.

Groundwater from a spring outside the influence of the mine has a pH of 6.5 and is of Ca-Na-HCO₃ type with no anomalous trace element concentrations. Groundwater exploited from a deeper well is of Mg-SO₄ type, pH about 7 and has high concentrations of As, Zn, Mn and Fe.

Conclusions from this study are that water resources of Freixeda are affected by sulphide mineral oxidation which releases cations, SO₄²⁻ and H⁺ ions. These free H⁺ ions contribute to the dissolution of carbonates (present in cement of metasedimentary rocks) and to the hydrolysis of silicate minerals (plagioclases) promoting the alkalinity and pH increase.

Concentration of As in surface water is much lower than in groundwater probably do to adsorption of As on Fe oxyhydroxides, that precipitates in stream sediments. This suggestion is supported by the absence of dissolved iron in surface-water samples. Even so, the amount of As (190 ppb) in surface water is above the limit for human consumption or watering. In groundwater, the oxidation-reduction potencial and pH conditions that allow Fe to remain in solution could be responsible for the higher concentration of As (850 ppb).

Introduction to the CAMECA IMS 7f-GEO

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SIMS is applied to a variety of applications in Geoscience, because it offers sensitivity compatible with very local isotopic and/or elemental analysis of solid samples. Large SIMS instrument like the CAMECA IMS 1280 offers outstanding performance for the entire SIMS application range (dating experiments, stable isotopes, REE analysis) thanks to its very high transmission mass spectrometer combined to a versatile multi-collection system. However, sometimes this tool can be seen as oversized for a laboratory with a limited application range. Therefore CAMECA has introduced the IMS 7f-GEO, a compact SIMS model with new features targeted to improve performance for isotopes and trace element analysis:

- Quasi-continuous record of the primary ion current during analysis.
- Magnetic sector with a very fast peak switching capability over the full mass range (magnetic and electrostatic peak switching combination).
- Secondary ion detection equipped with an EM and a pair of Faraday cups. Double FCs configuration makes possible to run an analysis in a pseudo-bicollection mode well-suited for stable isotope analysis.
- High precision Faraday Cup electrometer.

Typical analytical performance of the IMS 7f-GEO for stable isotope analysis (18O/16O): for an analysis area of 10x10µm², a single analysis internal error of less of 0.3 per mil is reached for a total integration time < 60sec. Detailed instrumental features and experimental data will be presented.
Heavy metals content in Belgrade soils

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The main goal of the paper is to present results of researches held from 2004 to 2006 regarding heavy elements content in the Belgrade city soils. Lot of 153 soil samples from 24 different locations were taken and analyzed from 2004 to 2006 in laboratory "MOL" (Belgrade).

Methods

Samples were taken from exact localities, from the topsoil (surface soil) – 0-15 or 0-20 cm of depth. Each sample was prepared as a composite of few sub-samples using standard techniques (EPA method 3040).

Different instrumental methods were used to determine concentrations of desired elements: (EPA 213.2), (EPA 239.1), (EPA 206.2), (EPA 249.1), (EPA 220.1), (EPA 218.1), (EPA 289.1) and (EPA 245.1); spectrophotometric technique was used for determining chromium concentrations.

Discussion of results

On the most of the localities (21 out of 24) certain excess of concentration of elements, which are important for soil pollution assessment, is determined. Only in one case exceeding concentration of chromium was related to geological factors; in other 152 out of 153 cases – human activities were only source of pollution.

Nickel concentration in soil samples from Belgrade area exceeds MAC of 50 ppm in 20 of 24 samples. Concentration reaches up to 228 ppm in soils from New Belgrade.

On the localities of Ada Ciganlija excess in concentrations for six elements and in New Belgrade of four elements were determined. Samples of river mud from Ada Ciganlija lakeshore showed very high level of contamination with lead, nickel, copper and especially zinc.

References


Low water contents in minerals from Gakkel ridge abyssal peridotites, Arctic Ocean

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We report the first water contents ever measured in abyssal peridotite minerals. The analyses are made possible by the exceptionally fresh state of a few Gakkel Ridge peridotites that show almost no serpentinization. Gakkel ridge is the slowest spreading ridge on Earth (Michael et al., 2003). The three preliminary samples analyzed so far come from dredge haul PS66-238 (Snow et al., 2007) from an amagmatic region where no basalts were found, and the extent of melting is low to non-existent. FTIR spectra of olivines and pyroxenes resemble previously published ones (e.g., Miller et al., 1987, Skogby et al., 1990). Water contents in one peridotite correlate with grain size in olivines and are variable in orthopyroxenes, whereas those of the other two samples are homogeneous. No water variations are observed within individual grains.

Calculated water concentrations in H2O ppm are <1-5 for forsteritles, 25-60 for enstatites, and 130-200 for diopsides. These water contents are 2 to 3 times lower than typically found in continental spinel and garnet peridotites (e.g., Peslier et al., 2002; Peslier and Woodland, 2006). Recalculated whole-rock water contents of the abyssal peridotites are at most, 50 ppm, about half the amount calculated from MORB-glass analyses for the depleted-MORB mantle (DMM) (e.g., Dixon et al., 2002). The low water contents of the abyssal peridotites also contrast with water contents measured in MORB glasses from Gakkel Ridge which are higher than those of MORB globally (Michael et al., 2006). If the low water content of Gakkel ridge abyssal peridotites is representative of that of the Earth’s oceanic mantle, models for extents of melting, major and trace element trends and crustal thickness at mid-oceanic ridges (e.g., Asimow and Langmuir, 2003) need reassessment.

References

The chemistry of diffuse-flow vent fluids on the Galapagos Rift (86°W): Temporal variability and subseafloor phase equilibria controls

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Recent (2002, 2005) expeditions to the Galapagos Rift, 86°W have conducted integrated experiments to assess temporal/spatial changes in both the chemistry and associated biology of diffuse-flow hydrothermal vents. The chemical data adds significantly to time series observations of hydrothermal processes at the Galapagos Spreading Center (GSC), where seafloor venting was first discovered in 1977. Assuming quartz-fluid equilibria (0.55 NaCl solution), end-member values for dissolved silica in 2002/2005 indicate temperatures ~50-100°C lower than in 1977. The higher predicted temperature in 1977 is consistent with observed chloride depletion in fluids issuing from Oyster Beds vent, indicating fluid phase separation, whereas all fluid samples from 2002/2005 are at or above seawater concentration. Respective values of dissolved Mn further suggest a lower temperature hydrothermal reaction zone at 86°W relative to three decades ago. The slope of Li-Si data from 1977, however, does not depart significantly from the 2002/2005 data, suggesting temperature change has little effect on dissolved Li in the hydrothermal endmember. At some point between 1990 and 2002 a volcanic eruption covered the historical Rose Garden vent-field, ending years of biological observations. Although the precise age of the lava flow is uncertain, the lack of chloride depletion and low H2S/heat ratios of the 2002/2005 vent fluids suggest the 2002 expedition arrived well after the eruption based on observations from other diffuse-flow systems perturbed by volcanic activity. Lower dissolved silica, Mn and H2S in the 2005 vent fluids relative to 2002, however, may indicate continued cooling in the aftermath of the recent eruption. Results of geochemical modeling for evolved seawater in equilibrium with a moderately oxidizing mineral assemblage are consistent with chemistry of recent GSC fluid samples, predicting H2S/Fe > 1, with little Fe in fluids diluted to the extent typical of 86°W vents. Results from in-situ chemical sensor measurements reveal non-conservative behavior of dissolved H2S, especially at temperatures below 10°C, which may be due to microbial metabolism.

Quantification of sulphur cycling at the Mid-Atlantic Ridge

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Mid-ocean ridges and associated hydrothermal vent systems represent a unique scenario in which the interaction of hydrosphere, lithosphere and biosphere and the related element cycling can be studied. Here, we present concentration and isotope data (S, O, H, C) for hydrothermal fluids and their dissolved constituents as well as from mineral precipitates collected at the Logatchev hydrothermal field (14°45′N) and different sites at the southern MAR (4° – 11°S).

δ34S values for dissolved sulphide and metal sulphides from the emanating hot fluid itself or pieces from black smokers between +1.9 and +8.8‰ (V-CDT) suggest that sulfur represents a mixture between mantle sulfur and reduced seawater sulphate. More detailed quantifications are based on the rare sulfur isotopes (33S and 36S) suggesting a contribution from recycled seawater sulphate between 20 and 30%.

Dissolved inorganic carbon in hydrothermal fluids from both hydrothermal areas show characteristic δ13C values around -3.9‰ (V-PDB, end member corrected).

Isotope values of Δ13O = 2.2‰ and Δ2H = 6.6‰ for the hydrothermal fluids at Logatchev and southern MAR sites clearly point to intense interaction between fluid and host rock. Very high sulphide concentrations up to 8.2mmol/L (calculated end member) measured for fluids from the Turtle Pits site (5°S) indicate an early stage of hydrothermal activity and are consistent with young volcanism. This indication is supported by very high fluid temperatures up to 407°C for the black smoker “Two Boats”.

Strongly negative sulphur isotope values as low as -24.0‰ for sulphidic sediments at the Logatchev HF are clear indicators for bacterial activity and, thus, point to the participation of microbial communities in sulfur cycling at the Mid-Atlantic Ridge.

The results, so far, provide a deeper insight into element cycling at the Mid-Atlantic Ridge, including apparent differences to fast-spreading ridge systems, such as the East-Pacific Rise (EPR).

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Sequential extraction of radioactive metals in soils from Crucea uranium mine (Romania)

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ICP and XRF Spectroscopy methods were used to evaluate the metals (ppm) from soils for the mining dumps of Crucea-Botusana uranium deposit (Bistrita Mountains, Romania).

The sequential extraction has emphasized the fact that U is associated with all the mineral fractions present in the soil samples. A great percentage of U can be found in the carbonate, organic and oxides fractions. The percentage of U detected in the exchangeable fraction is rather small. The fact that 21.77\% of the total U can be found in the specifically absorbed and carbonate bound fraction, indicated the important role played by the carbonates in the retention of U; one the other hand this fraction is liable to release U if the pH should happen to change.

Th appear in high-enough concentration in the soil is scarcely available because 70.29\% is present in residual fraction, and about 21.78\% in the organic and oxides fractions. This is certainly due to the fact that this naturally occurring radionuclide can be associated with relatively insoluble mineral phases like alumino-silicates and refractory oxides. Its association with the organic matter suggests that it can form soluble organic complexes that can facilitate its removal by the stream waters.

In the case of Sr, the sequential extraction shows that it is very strongly fixed because the residual fraction concentrates the great amount of this element. What is interesting is the percentage of 2.65 \% of Sr from the exchangeable fraction because it can be easily released and transported to the surrounding environment.

Pb it is present in various relatively soluble pools (17.81\% in carbonate boud and 34.85\% in organically bound), which appears to be an efficient sink for this element. This fact may indicate a possible link between the biological activity and the Pb cycling into the soil. In addition, only 17.78\% is present in the insoluble residual fraction.

Although from our research it resulted that the radioactive metals does not concentrate in the exchangeable fraction (Th) or it concentrates very little in it (U and Sr), the isolation of the mineral fraction of soil rich in U, Th and Sr helps us in the future identification of the connections which control the cycle of the radioactive metals.

These results have important implications for remediation strategies. The thorium and uranium from Crucea mining area are in labile, not strongly retained, fractions, thus making them amendable for remediation by phytoremediation.

Phase decomposition in non-isotropic multi-component systems: The alkali feldspar example

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Phase decomposition in a multicomponent system is considered theoretically. The approach of non-linear diffusion is used and the corresponding system of Cahn-Hilliard equations is systematically derived from the expansion of the free energy. In contrast to the standard Cahn-Hilliard model the possible anisotropy of the system is taken into account. The final equations set is solved numerically using a finite element approach. Realistic approximations for the free energy are used. The numerical solutions are finally compared to observations made on naturally exsolved feldspar. Good qualitative agreement is found. The morphology of exsolution phases depends on the composition of the homogeneous precursor feldspar and on the degree of anisotropy. Host-inclusion arrangements are obtained, when the bulk composition is close to one of the spinodal points and a co-continuous morphology is obtained, if the bulk composition is half way between the respective binodal compositions. For feldspar compositions that lie close to the albite-K-feldspar binary, the anorthite component is preferentially fractionated into the albite-rich exsolutions.
Isotope-geochemical criterion in search for the Noril'sk-type massive PGE-Cu-Ni sulphide ores: Constraints from Pb, Nd and Sr isotope data

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Our study aims on isotope-geochemical speciation of main types of intrusive bodies at Noril’sk district (northern Siberia), with particular focus on isotope-geochemical estimation for the unique metallogenic potential of the Noril’sk-type intrusions that range in thickness to 360 m and length to 25 km.

This study presents the first results of a multi-technique approach, which utilized isotope systematics of Nd, Sr and Pb for rock-forming minerals (i.e. pyroxene, plagioclase and olivine) and associated sulphide minerals (disseminated ores) derived from main lithological units of various ultramafic-mafic intrusions (namely economic Noril’sk-1, Talnakh and Kharanakh, subeconomic Zub-Marksheider and Vologochan, prospective Mikchangda and none-economic Nizhny Talnakh). Initial Sr and Pb isotope ratios have been also determined in massive sulphide ore samples at Talnakh and Kharanakh.

Initial lead isotope compositions of plagioclase and sulphide (67 analyses) significantly differ from each other indicating their isotope heterogeneity. Similarly, contrasting difference in the Sr isotope composition has been observed for the rock-forming silicate minerals and sulphide ores. At Talnakh and Kharanakh, concentration of Sr in massive sulphide ore varies from 4 to 30 ppm; (87Sr/86Sr)$_i$ varies in the range 0.7085-0.7111, whereas in plagioclase and pyroxene (87Sr/86Sr)$_i$ usually not exceeds 0.7076. This implies that sulphide ore melt appeared in its location site as isotopically heterogeneous mechanical admixture, marked by specific isotopic compositions of Pb and Sr, different from that of rock-forming minerals. It is noteworthy that sulphide ores, in comparison with silicate minerals, were essentially enriched by radiogenic Sr component at time of intrusion.

In Sr-Nd isotope systematics silicate matter from economic ore-bearing intrusions (about 60 bulk rock samples, plagioclase and pyroxene extracted from the bulk rocks) in comparison with silicates from none-economic weakly mineralised intrusions (81 sample) manifest clear contamination by the component, which along with relatively constant the Nd isotope composition (epsilon Nd about +1±0.5) is enriched with the radiogenic Sr. This feature can be employed as a prospective sign for the presence of significant quantities of the ore contaminant, which has isotope signatures close to that of massive sulphide ores.

Quantifying mineral aerosol inputs and the mobility of “immobile” elements in weathering studies

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Calculations of chemical weathering fluxes rely on a complete characterization of the mass balance for a given system. This study addresses two issues that may play an important role in these calculations. The first issue is that of mineral aerosol inputs, which can be a significant contribution to the overall atmospheric flux. Appropriate spatially and temporally averaged values for mineral aerosol fluxes are not easily established. The second issue is the use of “immobile” index elements such as Ti and Zr in the calculation of weathering losses of other elements. This study focuses on an analysis of mineral aerosol inputs and mobility of a wide variety of trace elements from the Rio Icacos watershed in the Luquillo Mountains of Puerto Rico. Additionally, this study puts the findings from the Rio Icacos in a global context based on literature review.

Results of our analyses in the Rio Icacos illustrate that Sr isotopes may be used to calculate watershed-scale average mineral aerosol deposition fluxes given a situation of a monolithologic catchment, a difference in the $^{87}$Sr/$^{86}$Sr ratio between the bedrock and the mineral aerosol inputs, and Sr-bearing primary minerals weathering to completion in the regolith. Nd isotopes are used to demonstrate that mineral aerosol inputs are incorporated to a depth of >3 meters in the regolith.

Trace element and rare earth element data were analyzed in order to assess patterns on elemental mobility within Rio Icacos regolith. Of all elements, Zr indicates the least mobility in this system, yet Zr data indicate leaching losses of ~50%. Alternatively, the saprolite has expanded by a factor of 2x during formation, but volume expansion is considered highly unlikely based on textural evidence. Calculations of mass losses during chemical weathering based on normalization to trace elements therefore require careful consideration in the case of intense weathering environments.
Interaction of the hydrologic cycle with the continental crust exerts a strong influence on the chemical composition of the ocean and atmosphere. Advanced models of long-term ocean/atmosphere evolution therefore critically depend on reconstructions of the hydrologic cycle and bedrock geology in the geologic past.

Here, I argue that important aspects of past surface geology can be reconstructed from radiogenic isotope records of seawater. These reconstructions rely on linear correlations between bedrock age and lithology with the isotope composition of continental runoff (Peucker-Ehrenbrink, submitted). Global and regional bedrock lithology and ages are quantified using GIS technology and digital geologic maps at resolutions of 100 to 10,000 square kilometers per polygon, whereas chemical characterization of runoff relies on literature compilations. Inverting the marine Sr isotope record in this fashion yields average bedrock ages of the continental drainage in the geologic past. This new paleo-age record indicates older mean bedrock ages in the early Paleozoic, bedrock rejuvenation from the Paleozoic into the Mesozoic and an aging trend that started in the Cenozoic. In general, aging corresponds to greater exposure of igneous and metamorphic rocks whereas rejuvenation is driven by greater exposures of sedimentary and/or volcanic rocks.

The general validity of this bedrock-age record can be independently tested with paleo-geologic reconstructions by Ronov and coworkers (as quantified by Bluth & Kump, 1991), as well as the Nd isotope evolution of sedimentary rocks from large-scale continental drainage regions (e.g. Patchett et al., 1999). Both are suggestive of a trend towards younger bedrock from early to late Paleozoic, broadly similar to the paleo-bedrock record.

The application of this concept to the marine Os and Hf isotope records requires investigating the relationships between river isotope chemistry and drainage basin geology (Peucker-Ehrenbrink & Miller, in press). Marine paleo-records for Nd need to be spatially averaged due to the short residence time of Nd in seawater and the large isotope variability in continental Nd sources (e.g., Jeandel et al., 2007); alternatively, they may yield insights into regional changes in continental drainage geology in the geologic past.

References
High-field strength elements (Nb, Ta, Zr, Hf) in continental basalts from the CEVP – Implications for the HFSE budget of the lithospheric mantle and the global Nb budget

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Nb/Ta ratios in continental basalts from the Central European Volcanic Province (CEVP) are among the highest values measured so far in terrestrial rocks by high-precision methods. In volcanic rocks from the Rhön, Vogelsberg and Eifel regions, Nb/Ta ratios are subchondritic (<19.9) with values between 15.0 and 19.1 and on average higher than in ocean island basalts at comparable Zr/Hf ratios (see figure). This observation is investigated within the context of a potentially Nb enriched lithospheric mantle that may play a role in balancing the global Nb budget.

Crustal contamination of most samples is displayed by elevated 187Os/188Os ratios (>~0.150), but samples having low (i.e. mantle like) 187Os/188Os (~0.129-0.150) have the highest Nb/Ta ratios, indicating that the elevated Nb/Ta ratios are not imprinted by crustal assimilation.

Nb/Ta ratios are positively correlated with Lu/Hf ratios in all but the Vogelsberg tholeiites, a feature that cannot be explained by partial melting of either spinel or garnet peridotite sources, but by the mixing of asthenospheric melts from a garnet bearing source with melts produced from amphibolitic veins. High HFSE concentrations and elevated Nb/Ta ratios (~17) with respect to the asthenospheric mantle (~14) require only low amounts of such melts in the order of a few percent. Therefore, elevated Nb/Ta ratios within some of the volcanic rocks of the CEVP do not mirror elevated Nb/Ta ratios within the subcontinental lithosphere itself, but reflect the presence of HFSE enriched, amphibole rich domains from which high Nb/Ta melts are produced during magma ascent and remelting.

The reconstruction of changes in the seep activity of a pockmark site using Mg/Ca and Sr/Ca ratios in the sediments of the lower Congo Fan

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Pockmark structures of the Northern Congo Fan at a water depth of 3100 m were investigated during RV Meteor cruise M56 in November and December 2002. The data presented here were obtained by geochemical sediment and pore water sampling in a pockmark called Black Hole. No direct evidence for active fluid/gas discharge into the water column was detectable in this pockmark; however, gas hydrates were found close to the sediment surface. The depression was covered by fauna characteristic for areas of fluid/gas seepage such as vesicomyid clams and vestimentiferan tubeworms. Additionally, the sediments contain huge amounts of authigenic carbonates. In the sediments, authigenic carbonate formation occurred in the form of finely disseminated precipitates and also as massive carbonate concretions. Major and minor element contents were analysed for both, the bulk sediment and the concretions, and also in the pore water. Sr/Ca and Mg/Ca ratios determined in the concretions and in the surrounding sediment showed characteristic values which were used to distinguish between authigenic high Mg-calcite and aragonite precipitations (Bayon et al., 2007). High Mg-calcite was found at different depths in the sediment, whereas aragonite was only present close to the sediment surface. Changes in the Sr/Ca and Mg/Ca ratios determined in the pore water are characteristic for the carbonate mineral which currently precipitates from the solution. Pore water-ratios indicative for high Mg-calcite precipitation were found in the recent zone of anaerobic oxidation of methane, whereas ratios indicative for aragonite formation were only found in the surface sediment where sulphate concentrations are at seawater level. The combination of pore water and solid phase Sr/Ca and Mg/Ca ratios enables a distinction between recent carbonate mineral formation and carbonate precipitation in the past. Based on the elemental composition of the bulk sediment, we created a model for the history of past methane fluxes and seep activity for the investigated region of the pockmark.

Reference
Studies for the sorption of metals from lake water using limestone and rice bran

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Environmental research studies were carried on Noor Mohamed Lake in Katedan Industrial Development Area, Hyderabad, India. The study reveals that the lake was highly contaminated with industrial effluents. Contamination of lake water was due to release of industrial effluent containing organic and inorganic chemicals. A sorption experiment using laboratory columns was carried on lake water to reduce the concentration of heavy metals to limited extent, in this study an agricultural by-product rice bran (30%) and a geological media limestone (70%) has been successfully used for reducing the concentration of metals in lake water. The Medias are efficient in reducing metal concentration by Sorption, adsorption, precipitation, oxidation and reduction reactions involved in process which depends on the factors like pH, surface areas of reactive media and porosity.

Vertical columns open at both the ends made of polyvinyl chloride of length 50 cm / 10 cm diameter was packed with two different medias in 3:7 ratio covered with a filter paper and closed with Teflon lids fitted with Silicon tubes of 3 mm size and effluent was passed using a peristaltic pump with speed of 55 rpm / 10 ml per minute. The experiment was carried for one week and the sample was collected from outlet, analysed for pH, E.C, TDS and metals like Zn, Cu, Cr, Pb, Ni by inductively coupled plasma optical emission spectrometry (ICP-OES).

The results shows that there was no change in pH but a slight increase in total dissolvable solids from 1026 ppm to 1857 ppm, this was due to the release of dissolvable solids from the medias, concentration of metals for Cr-43.52ppb (Cr-68% removal), Zn - 98.25ppb (Zn-88% removal), Cu–30.43ppb (Cu-41% removal), Ni–27.44ppb (Ni51% removal), Pb–15.62 ppb (Pb-84% removal) with limestone and rice bran.

References

Contribution of two main smelters on urban soils pollution in northern France investigated by lead isotopes

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Introduction and objectives
The studied urban zones are located in northern France at the vicinity of two base metal smelters which are 3.5 km distant from each other. Historical Pb, Cd and Zn contamination through atmospheric emissions from both plants has been demonstrated by different authors (Frangi et al., (1997) or Sterckeman et al., (2002) on cultivated soils).

Urban (kitchen garden and lawn) soils in the studied zones present varying and sometimes higher Pb contents than the neighbouring cultivated soils (Pruvot et al., 2006). Pb isotopes have then been used to better constrain the contribution of each emitter to the observed pollution. A second aim was to look for other possible sources of contamination (manures with ashes or slag, other atmospheric inputs…) to explain the anomalous contents.

Analyses have been performed on homogenised samples from the upper 25 cm of the garden soils. Pb isotopic compositions were analysed by TIMS on a MAT-261. Pb, Cd and Zn concentrations were obtained by GFAAS.

Isotopic results and discussion
Garden soils with different lead contents and supposedly various cultural practices show a distribution into two distinct and homogeneous lead isotopic signatures. Each signature corresponds to soils located in the vicinity of one of the two plants. This supports the hypothesis of a quite exclusively airborne pollution related to one refinery activity. Furthermore, mixing of the two lead types can be observed on one soil located in between the two refineries, which displays an intermediate isotopic composition. Additionally, whatever its chemical speciation, lead obtained by single chemical extractions performed on some garden soils shows isotopic homogeneity within a specific soil, suggesting that pollution has affected all soil compartments.

References
Elemental-sulfur reducing or disproportionating organisms in a ~3.5 Myr-old seafloor setting

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We report multiple-isotope sulfur analyses (³²S, ³³S, ³⁴S) of sulfides and sulfates from a unique collection of pristine drill core samples (Pilbara Drilling Project; Van Kranendonk et al., 2006) from the 3,490 Myr old Dresser Formation at North Pole, Western Australia. We show that the strongly ³⁴S-depleted microscopic sulfides preserved in barite crystals that have been interpreted as evidence for sulfate-reducing organisms during the early Archean (Shen et al., 2001; Shen and Buick, 2004) have mass independently-fractionated sulfur isotopic anomalies (Δ³³S) different from their host barite and therefore that they cannot have been produced by sulfate reducing microbes. Instead, we interpret the combined negative δ³⁴S and positive Δ³³S signature of these microscopic sulfides as evidence for the early existence of organisms or consortia that reduce or disproportionate elemental sulfur. These results support the prediction arising from phylogenetic reconstruction that elemental sulfur reduction is among most deeply-rooted metabolic pathway in both of the prokaryotic Domains.

References

Supercontinental warming, plumes, and mantle evolution

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Large-scale magmatism is often linked to the breakup of a supercontinent, but it is not established whether it is caused by a plume head or a global temperature increase of the mantle. On the basis of convection modeling in an internally heated mantle, we have shown that continental aggregation promotes large-scale melting without requiring the involvement of plumes (Coltice et al., 2007). When only internal heat sources in the mantle are considered, the formation of a supercontinent causes the enlargement of the wavelength of the flow and subcontinental warming as large as 100 °C. We will show how plumes interact with supercontinental warming in order to better understand the evolution of melting during the opening of Pangea.

We will also describe the importance of the supercontinental warming model over the course of the evolution of the Earth’s mantle and the growth of the continental crust.
CRONUS-Earth: Half-way to the destination

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In-situ cosmogenic nuclides are widely and increasingly used for to study earth-surface processes and its recent history, but these goals have been impared by inconsistencies in the understanding of the production systematics. The CRONUS-Earth Project was funded by the U.S. National Science Foundation with the objective of reconciling these discrepancies and providing a generally accepted basis for interpreting cosmogenic nuclide data. The Project is approximately half-way through its five-year duration and has achieved significant progress toward these goals. Areas of considerable uncertainty that have seen major advances include samples for $^{36}$Cl production-rate calibration and spatial/temporal scaling of production. New paleomagnetic reconstructions have become available to complement improved scaling theory, resulting in testable predictions of global production patterns. The relation between geologically-based and neutron-monitor based scaling has been elucidated through monitoring of neutron-monitor-response physics. Calibration samples have been collected in a rigorous fashion from sites associated with the shoreline of Lake Bonneville, Younger Dryas glacial sites in Scotland, and LGM glacial sites in the Puget Lowland of Washington State, a locality of particular importance for resolving discrepancies in $^{36}$Cl production. Essential data and tools include improved production cross sections from neutron beam experiments and the release of a web-based cosmogenic calculator for the community.

Extraction of biosignatures from weathered basalts

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There is a growing interest in the bio-load in weathered volcanic rocks. The relevance extends to Mars, where there are extensive regions of weathered basalt. Any bio-load in such rocks is likely to be very low, so it is essential to maximize the extraction efficiency for analysis. Analysis of suites of regolithic Tertiary (~60 Ma) basalt from Skye, Scotland, show the importance of particle size for optimal organic recovery.

Basalt from two localities was divided into fine (<500µm)- and coarse (>1cm)-grained fractions and surface contamination removed using acetone. They were then crushed and sieved into five different grain size fractions and subsequently soxhlet-extracted for 48 hours with 93:7 DCM/methanol.

The data show that a reduction in grain size results in a higher yield of extractable organic material (EOM) (Table 1). The n-alkane odd-over-even preference (OEP) exhibited by the GC-MS trace (Fig. 1) indicates that the extract is thermally immature, consistent with a recent biological (microbial) signature.

<table>
<thead>
<tr>
<th>Glen Varradale basalt</th>
<th>Quiraing basalt</th>
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<tbody>
<tr>
<td>CG⁰</td>
<td>FG⁰</td>
</tr>
<tr>
<td>&gt;425µm</td>
<td>0.001 0.002</td>
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<tr>
<td>425-125µm</td>
<td>0.001 0.004</td>
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<tr>
<td>125-63µm</td>
<td>0.002 0.005</td>
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<tr>
<td>63-38µm</td>
<td>0.002 0.005</td>
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<tr>
<td>&lt;38µm</td>
<td>0.003 0.007</td>
</tr>
<tr>
<td>CG⁰</td>
<td>FG⁰</td>
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<tr>
<td>&gt;425µm</td>
<td>0.002 0.005</td>
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<tr>
<td>425-125µm</td>
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<td>125-63µm</td>
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<td>&lt;38µm</td>
<td>0.004 0.007</td>
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⁰Coarse-grained; ⁰Fine-grained

Figure 1: GC-MS trace of the saturate fraction m/z 85 ion from the Quiraing basalt. Note marked OEP of n-alkane peaks.

The data emphasise the importance of analysing a fine grain size during processing of samples, including future Mars missions, where volcanic rocks may be targeted.
Role of bacteria on uranium migration in a calcareous peatland

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The assessment of a polluted site is usually undertaken through its hydrogeochemical characterization and the impact of the implied conditions on pollution migration. However, in specific natural environments, such as peatlands, microbial activity can also affect, directly or indirectly, this migration.

A calcareous peatland polluted with uranium particles (about 3.5 ppb) contained high concentrations of total dissolved uranium from the surface to 0.8 m deep (up to 7.10^-6 mol.L^-1). This can be explained by the formation of the major complex Ca2UO2(CO3)3. Even though uranium particles have also been found between 0.8 and 2 m, total dissolved uranium concentrations are very low (1.10^-10 mol.L^-1). At these latter depths, where the peat remains humid (water – table from 0.25 to 0.8 m), uranium solubility can decrease due to reducing conditions. The increasing occurrences of framboidal pyrite particles at depths lower than 0.8 m suggest reducing conditions related to sulfate – reducing bacteria.

In order to study the impact of these bacteria on the physico – chemical conditions of the peat soil, batch experiments were performed. Using various types of carbon sources (ethanol, oxalate) and doping with sulfate, trimethylphosphate and uranium, at 25 °C and 5 °C, the total dissolved uranium content was followed throughout the incubation. The ethanol – doped batch incubated at 25 °C shows a significant decrease of uranium from 1.95.10^-5 to 3.93.10^-8 mol.L^-1 in 200 hours. Other parameters (pH, Eh, dissolved oxygen, [SO4^2-], [HS^-], etc.) are also followed and compared to the equation of microbially – mediated sulfate reduction:

\[ 2\text{CH}_2\text{O} + \text{SO}_4^{2-} \leftrightarrow 2\text{HCO}_3^- + \text{H}_2\text{S} \]

These batch experiments and the identification of the bacterial populations (via 16S rDNA sequence) show that sulfate – reducers in peatlands produce reducing conditions that can immobilize uranium and possibly other trace metals.

The role of solvent in the kinetics of barite nucleation

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Crystallization from a supersaturated solution is one of the fundamental geochemical processes. Although several very successful models that provide a qualitative understanding of the crystal growth process exist, in most cases the atomistic detail of crystal growth is not fully understood. Here it is shown how the combined use of computer simulations and experiments can help in understanding the kinetics of nucleation and crystal growth of barite. It is found that the solvent plays a prominent role in determining the rates of both two and three-dimensional nucleation in solution. The results of this study are expected to be valid also for other divalent ion salts, as their crystallization kinetics are often remarkably similar.

References
Seismic anti-correlation in the mantle: Is hot blue and cold invisible?
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Low levels of bulk sound velocity ($V\Phi$) variations below 2000 km depth in the mantle and a prominent anti-correlation of $V\Phi$ to shear seismic wave velocity ($VS$) near the core mantle boundary are typically used to infer the presence of compositional deep mantle heterogeneity. Using a thermodynamically self-consistent mantle mineralogy model based on Gibbs free energy minimization we show that these effects can arise from differences in the isothermal and adiabatic bulk modulus at high pressure and temperature of the Earth’s lower mantle, and that it is possible to reproduce the observed VS/$V\Phi$ anti-correlation in a chemically uniform mantle. The mineralogy model provides us with elastic constants and density for any given P,T condition.

We take this density to compute convective buoyancy forces in a simple (2-D purely bottom heated isoviscous and isochemical) compressible mantle convection model. Our approach allows us to predict a number of seismic observables from the convection model, all of which agree remarkably well with observations from a tomographic study. Our results are fully compatible with other published mantle mineralogy models, which similar to our finding predict an increase of $\partial V\Phi/\partial T$ with temperature and pressure, and a pronounced VS/$V\Phi$ anti-correlation in the lowermost mantle.

Contracting KREEP magmatism in the early evolution of the Moon
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Ages of zircons from lunar Breccias

Previous (SHRIMP) age studies of zircons from lunar granophyres and other rocks (Meyer et al. 1996) showed that zircon-forming magmatism in the lunar highlands was continuous from 4.3Ga until at least 3.88Ga. We have further investigated the distribution of lunar zircon ages by undertaking SIMS U-Pb isotopic analyses (SHRIMP II at Curtin University and CAMECA 1270 at the Swedish Museum) of zircons from breccias from the Apollo 14 and Apollo 17 landing sites.

U-Pb results
Analytical results, presented on concordia plots on Figure 1, show that Apollo 14 and 17 zircons have essentially identical age patterns in the range 4.35 to 4.20Ga, but, whereas Apollo 14 zircons have ages in the range 4.20 to 3.9 Ga, zircons from Apollo 17 samples have no ages younger than 4.20Ga.

Interpretation
Our results show that lunar zircon-forming magmatism was not continuous from 4.35 to 3.88Ga everywhere on the Moon, but has a marked regional asymmetry. We explain this by proposing that between about 4.35 and about 4.20Ga the source reservoir for zircon-forming KREEP magmatism contracted to only just include the area of the Serenitatus impact (Apollo 17) and after about 4.20Ga no zircon-forming magmatism occurred at this site. Magmatism continued at a reducing rate at the Apollo 14 site until about 3.90Ga, when it also ceased.

Reference
Chemical and isotopic variations of surface waters at a small catchment scale, lithological vs biological controls (the Strengbach case).

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The accurate determination of parameters controlling the chemical composition of surface waters is important for a correct modelling of the future evolution of the ecosystems in response to external forcing such as climate and human activities. Among these parameters, vegetation plays an important role in affecting movement, cycling and fractionation of elements.

In this general framework, a detailed study of the geochemical variability of the surface waters of the Strengbach catchment was carried out. The catchment is a small-forested watershed, about 80ha in surface area, in the Vosges Mountain, France (Observatoire Hydro-Géochimique de l'Environnement; http://ohge.u-strasbg.fr). It is located on a Hercynian granite, which was more or less hydrothermally altered.

During two hydrologic cycles (2004-2006), the stream at the outlet of the watershed, as well as all springs welling up located at different altitudes from various hillsides, were regularly sampled. Major and trace element (Sr, Rb, Ba, U) concentrations and Sr isotope ratios on the dissolved load of the water samples were determined.

The data highlight the large spatial variability of the chemical and isotopic composition of the surface waters of the Strengbach watershed. The variations of the mineralogical characteristics of bedrocks and soils, which are especially related to the more or less hydrothermalized character of the bedrock, can account for the spatial geochemical variations observed among the different springs of the watershed.

The data also outline an important time variation of the chemical and isotopic composition of water samples within each spring. It can be shown by using mixing diagrams, such as 87Sr/86Sr vs. Ca/Sr, that rain contribution is not a important parameter explaining the time variation. In addition, a simple binary mixing model between two water end-members, even with variable contribution versus time, cannot account for the observed geochemical variations. The latter imply the occurrence of specific chemical fractionations unrelated to lithological parameters, but probably induced by chemical recycling through the vegetation.

The results of our spatial and time variability study of surface waters at a small watershed scale point out how such a geochemical approach can help understanding the quantification of vegetation impact on the geochemical budget.

Processes and sources during late Variscan dioritic-tonalitic magmatism (Gęsiniec Intrusion, Bohemian Massif)

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Tonalitic–dioritic intrusions are common in orogenic settings. Two groups occur, emplaced at different stages of orogenic development: syn-collisional, pre-dating the main granite emplacement stage and post-collisional, contemporaneous with or post dating granite magmatism. Diorites and tonalites together with basaltic–andesitic volcanics are often the most mafic rocks present in orogenic and are often taken as end members that interacted with crust to produce a range of more felsic magmas and/or as the heat source for melting of the crust. However, dioritic–tonalitic intrusions are often characterised by variable isotopic and trace element compositions suggesting that they themselves underwent differentiation and contamination.

The Gęsiniec Intrusion (GI, 294-307 Ma, Bohemian Massif) represents a post collisional Variscan dioritic-tonalitic intrusion, generated during lower crust and lithospheric mantle delamination. Similar incompatible element ratios suggest a common source for the tonalite – dioritic rocks in the GI, this source is distinct from that of earlier Variscan diorite-tonalite magmatism (syn-collisional, 340-350 Ma) in the Bohemian Massif. The parental magmas for the post-collisional GI were probably tholeitic, water-undersaturated basalts derived from unmetasomatised mantle that interacted with crust. Parental magmas for 340-350 Ma dioritic-tonalitic magmatism were basalts derived from subduction-modified mantle (e.g. Janousek et al. 2000).

In situ Sr isotope and trace element analyses of the GI plagioclase yield a range of 0.7069-0.7091, greater than that of whole rocks (0.7069-0.7084). Trace element and isotopic compositions of plagioclase suggest that different samples represent different processes of magma evolution from assimilation of wall rock by crystal mush at the magma chamber boundary, to interaction with water-rich magmas. The main differentiation recorded in plagioclase is thought to have occurred in the lower crust, below the level of emplacement of the GI and was followed by decompression and extensive resorption of plagioclase. The GI represents therefore an assembly of magmas derived from similar sources, but having undergone separate differentiation processes before final emplacement.

Reference
PAHs in sediment cores from an estuary in south of Brazil

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The temporal and spatial distribution of 14 selected PAHs, amongst the 16 priority pollutants have been analysed in the estuarine system of Guaratuba Bay, Paraná State, in the south region of Brazil. Two dated sediment cores of approximately 40 cm each were collected on the inner sector and close to the mouth to the sea of the estuary, which is approximately 15 km long. The sedimentation rate is estimated to be 6.1 mm/year and 5.2 mm/year accordingly to 209Pb and 137Cs geochronologies, respectively (Sanders et al., 2006). The surrounding region is not highly industrialised, with agriculture of banana and rice being the main economic activities, followed by fishery, aquaculture and tourism, the latter suffering a rapid increase in the past years due to the scenic landscape of the region. A moderate drainage basin encompasses the estuary, consisting of 1,724 km² and two main rivers alone, Cubatão and SãO João, introduce as much as 80 m³/s of freshwater into the bay. Despite of that, it is well known that PAHs are ubiquitous contaminants in the environment and the use of marine sediments to reveal levels of environmental quality have been extensively reported in the literature, as they are a sink for such hydrophobic compounds. In order to quantify the distribution of PAHs along the sedimentary record, the following individual compounds were analysed in 21 sections of the cores: naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a]anthracene, benzo[g,h,i]perylen e and indeno-[1,2,3cd]pyrene. The analyses were carried out using a HPLC coupled with a fluorescence detector. The total PAH concentration ranged from 1.5 to 3,126.8 ng/g (mean 494.9) of dry weight, and the PAHs up to four rings were the most abundant. Among these, phenanthrene and fluoranthene showed the highest concentrations. Apparently, diagenetic processes, rather than petrogenic or pyrogenic inputs, play an important role in the distribution of phenanthrene along the sedimentary column, as proposed by Wakeham et al. (1980).

References

Pb isotope provenance study of Irish Bronze Age gold using LA-ICP-MS

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The Bronze Age is seen to represent a critical stage in European prehistory because of the widespread deployment of a range of distinctive materials (e.g. amber, jet, gold) in the construction of different social identities including strategies of status differentiation. Understanding the control of access to these materials and their trade and exchange is key to understanding the new social structures that arise. In Ireland, the deposition in lakes and bogs of large gold artefacts such as lunulae and torcs is one of the most striking features of the Bronze Age. But many of these artefacts are without context, having been found by turf cutters, or lack any associated archaeology. While it is clear gold is an important and special material, it is difficult to integrate the artefactual evidence with what is known of the archaeology and social structure of the Bronze Age.

Here we present the preliminary results of a lead isotope study of Irish Bronze Age gold artefacts using the novel technique of laser ablation ICP-MS. We show that the lead isotope variation in Ireland is sufficient to differentiate sources of gold, and that the required precision of lead isotope measurements can be attained for the necessarily small samples from artefacts using laser ablation. In Late Bronze Age artefacts, where the gold has been alloyed with copper, lead mixing lines can be obtained, which may allow the sourcing of both the copper and the gold.

These and future results will complement existing microchemical studies that have suggested changing access to gold resources through the Irish Bronze Age, and will provide the basis for models of gold procurement, trade and exchange.
Experimental constraints on the origin of alkaline basalt: Evidence for a metasomatized lithospheric source

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Due to the difficulty of explaining the high trace element and isotopic compositions of alkaline magmas from oceanic islands and alkaline massifs by simple peridotite melting, a recycled oceanic crust component is often assumed to be present in the source of these rocks. Alternatively, this component may be recycled oceanic or continental lithosphere that contains metasomatic veins. Coupled major and trace element models for the formation of alkaline lavas can provide important constraints on this debate. At present, no experimental studies have successfully reproduced the range of alkaline basalts found in ocean islands or continental massifs.

We present the results of melting experiments on natural clinopyroxene hornblendite and hornblendite lithologies from the French Pyrenees conducted at 1.5 GPa and 1150-1350°C, and explore the alternative hypothesis that OIBs result from partial melting of recycled metasomatized lithosphere. The compositions of low-degree melts in experiments on both amphibole-bearing lithologies are controlled by kaersutite breakdown and are strongly ne-normative and silica-poor. K2O/Na2O, Al2O3/TiO2 and CaO/Al2O3 ratios in the experimental partial melts are similar to silica-poor basanites found in oceanic islands and continental alkaline massifs. Moreover, the incompatible trace element patterns of the glasses overlap those of silica-poor lavas in both tectonic settings. A second set of experiments was done using a layer of hornblendite sandwiched between layers of moderately depleted peridotite (DMM1) at 1.5 GPa and 1225-1325°C, and demonstrates that the reaction of partial melts of amphibole-rich veins with surrounding peridotite can explain the observed compositional transition between basanite and alkali basalt. The higher SiO2 content (4-5 wt%) observed in melts from the sandwich experiments relative to those containing just the amphibole lithologies reflects the dissolution of orthopyroxene in the peridotite layers in the sandwich runs.

Our results support the hypothesis that partial melting of metasomatized lithosphere (i.e., peridotite-amphibole-bearing veins) generates alkaline basalts in continental settings [1] and that recycling and partial melting of such veined lithosphere can also contribute to the compositional characteristics of oceanic alkaline lavas. Further, the isotopic characteristics of both HIMU and EM-type OIBs are consistent with plausible models of amphibole-bearing vein formation and the resulting element fractionations [2]. Thus, recycling of metasomatized lithosphere should be considered as a viable, testable alternative to widely accepted models of OIB formation that invoke recycling of oceanic crust ± sediments.


AFM observations of dissolution and growth on anhydrite (100), (010) and (001) cleavage faces

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Anhydrite is a common calcium sulphate mineral which can coexist with gypsum in evaporitic and diagenetic rocks. Textural relationships between both minerals often indicate that gypsum crystals form after previously crystallised anhydrite, through a process that involves the coupling between dissolution and crystal growth reactions. In this work, we present in situ Atomic Force Microscopy observations of the interaction of anhydrite (100), (010), (001) cleavage surfaces with deionised water and CaSO4 aqueous solutions. In water, anhydrite faces dissolve at different rates and exhibit specific nanotopographic features (e.g. etch pit shapes, retreating and stabilisation of certain step directions, etc.) that can be justified on the basis of the Hartman-Perdok Theory. In contact with CaSO4 solutions, the growth of metastable monolayers (~3.5Å in height) is promoted on both anhydrite (010) and (100) faces (the growth on anhydrite (001) faces was not observed). The monolayer develops jagged edges that form defined angles with the original steps on anhydrite surfaces. Moreover, as occurs in the case of dissolution, the growth of monolayers over anhydrite (010) and (100) surfaces is highly anisotropic, revealing a strong crystallographic control. The nature of such monolayer is discussed on the basis of both crystallographic and thermodynamic arguments.
Oriented overgrowth of brushite 
(CaHPO₄·2H₂O) on gypsum 
(CaSO₄·2H₂O)

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At slightly acidic conditions and 25º C, the interaction between aqueous solutions containing dissolved P(V) and gypsum results in surface precipitation of brushite (CaHPO₄·2H₂O) crystals. These crystals grow oriented onto gypsum’s surface, forming an epitaxy. Using an A-centered unit-cell setting for both brushite (Aa) and gypsum (A₂/a), the determined epitaxial relation is (010)₆ || (010)₄, [001]₆ || [001]₄, and [100]₆ || [100]₄. In the performed experiments, the obtained morphologies of brushite consist of thin crystals elongated in the [101] direction with {010}, {111} and {111} as major forms. In the present work, both crystal morphology and epitaxial orientation are approached on the basis of the bond arrangement within the structure of both mineral phases.

Figure 1: SEM image of thin brushite crystals oriented onto gypsum’s (010) face, along [101] direction.

Sequential Metal Extraction procedure as applied to sediments in Acid Mine Drainage environments (Aljustrel, Portugal)

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Acid Mine Drainage (AMD) is a serious environmental concern caused by mining activities and presents severe consequences to surface and underground water systems. In this work we have studied the partitioning of trace metals in sediments from AMD systems in the area surrounding the Aljustrel Mines (Iberian Pyrite Belt), using a modified Sequential Metal Extraction (SME) procedure.

Authors acknowledge that SME methods are useful to study metal partitioning in sediments. However, there are several problems with these methods, including the one of Tessier et al. (1979). Among these are: trace element redistribution among phases, nonselectivity of extractants, and sulphide dissolution during organic matter oxidation steps. In order to overcome these difficulties the proposed method combines modifications from Hirner (1996) and Breward et al. (1996). The oxidation of organic matter is performed separately by first extracting it from the sediment. The six-step sequential extraction procedure was performed on streambed sediments of Ribeira de Água Forte (Aljustrel). The extractant solutions were analysed by AAS for selected trace metals (Cu, Zn, Pb, Ni, Cd, and Co).

Cu, Pb, and Zn have the highest averaged relative concentrations in the sediments (51%, 27%, and 14%, respectively). Ni, Cd and Co exhibit low values (< 4%). In contrast to these results in the sediments, water analyses show higher Zn concentrations in relation to Cu, suggesting a preferential sediment-water partitioning for Cu. Also shown is the anomalous character of an iron-rich sample in relation to the correspondent water, where a peak in all elements is observed. This sample is also exceedingly anomalous in Cu for reasons currently unknown to us. In relation to the different phases, organic matter has no important role in the adsorption processes (1.7%). Trace metals occur preferentially bound to iron oxide phases (70%), followed by non-specific adsorption (25%).

References

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Chemical compositions of zircon from an U-mine area, Portugal

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The Vale de Abrutiga U-mine consists of quartz veins containing wolframite, sulphides and secondary saléeite and metasaléeite.

One hundred thirty seven chemical analyses of zircon were obtained by electron-microprobe from unaltered and altered biotite granite, mineralized quartz veins, phyllite and quartzite of regional metamorphism and phyllite adjacent to mineralized quartz veins from the Vale de Abrutiga U-mine area, central Portugal. Chemical composition of zircon is highly variable. Zircon from altered granite is the richest in P, Y and Fe³⁺ and contains on average 0.22 wt. % UO₂, but values up to 0.50 wt. % UO₂ were found in the analyses with low totals (~84.69 wt. %). Distribution of U in some of these individual altered grains shows a chemical zonation expressed in the rim containing more U than the core. The core has a chemical composition similar to that of zircon from unaltered granite. Zircon from quartzite has the highest content in Zr and the lowest of Fe³⁺. Zircon from phyllite adjacent to quartz veins has higher U content than zircon from phyllite of regional metamorphism, which does not contain U. Zircon from mineralized quartz veins is dissolved and vacuolated. The grains have cores chemically close to the endmember [(Hf,Zr)SiO₄], but rims are hydrated, have very low totals (~82 wt.%), low SiO₂ (~14 wt.%) and ZrO₂ (~40 wt.%) contents and very high Fe₂O₃ (~8 wt.%) and UO₂ (~18 wt.%) contents. The anomalous zircon rims were lately formed from U-rich supergenic solutions. Enrichment in U is a characteristic of altered zircon from the mineralized quartz veins and from altered Variscan granite. The high U contents found in rims of the altered zircon from altered granite and mineralized quartz veins are associated to high Fe contents. It is well known that uranium sorption on Fe oxyhydroxides is an important process. Therefore the very high U-enrichment found in rims of altered zircon grains can be due to the presence of these Fe oxyhydroxides.

The Vale de Abrutiga U-mine was formed in lithological and structural traps by U-rich solutions derived from meteoric water, warmed by deep circulation, and enriched in U by the solubilisation of U-minerals from granites (uraninite, monazite). Uranium from U-rich solutions percolating through the quartz veins was later adsorbed by the most altered zircon or by Fe oxyhydroxides which formed in the most altered rims of zircon crystals.

3-D modeling of iron ore deposit in Chadormalu area in the Central Iran

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Chadormalu iron ore deposit is one of the biggest iron ore in Iran. That is located in the Central Iran and excavates iron ore in this area. Chamomile reverse fault and Kankani right lateral strike slip fault shear and deform ore deposit. Asymmetric ore deposit shape and faulting are some reasons that excavators have problems for exploration. Expansion of iron ore, distribution of contaminated ore (for example apatite) and recognized of blind faults concludes with use chemical analysis and logging boreholes data in deferent topographic levels. Deferent topographic levels data merge and design under ground 3-D models iron ore. Iron ore deposit is flattening and its strike is northwest - southeast. Iron ore massive dip is high angle and its dip direction is southwest. Stratigraphic iron ore boundaries are faulted and high angle. A lot of many strike slip fault distinguish with north - south strike into ore body. Designed 3-D models can be show best location for start of excavation. Therefore, we can subdivide ore deposit to several quality parts.
Radiogenic $^{26}$Al chronometry of evaporites

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Radiogenic production of $^{26}$Al in Na rich evaporites can potentially be used for chronometry over several million years. This can be a tool for dating paleoclimate conditions in arid environments. Measurable quantities of $^{26}$Al are present in material with either high concentrations of alpha emitters (principally U and Th) or high concentrations of target nuclei. Significant quantities of $^{26}$Al are recorded in U and Th ores, and the primary mechanism of this production is the $^{23}$Na($\alpha$, n)$^{26}$Al reaction (Sharma and Middleton, 1989). Measurable quantities of $^{26}$Al should, therefore, also be present in material with modest concentrations of U and Th, but high concentrations of Na. To test this potential geochronometer, a review of the available cross-sectional data for this reaction, as well as the U, Th, and Na composition of various evaporites was done. We will present preliminary data testing the feasibility of this method.

The $^{238}$U and $^{232}$Th decay chains are the dominant natural alpha sources, with a total of 8 alpha particles emitted in the $^{238}$U decay chain and 6 from $^{232}$Th decay. The range of alpha particles in rocks is generally less than a few tens of microns, and the alpha-emitters contained within the evaporite minerals themselves are the principal mechanism of radiogenic $^{26}$Al production. Since U is soluble in water, and Th is largely insoluble, many evaporite deposits have high U/Th. Disequilibrium in the U-series decay chain occurs in subaqueous deposits over the time range of this potential chronometer, and excess of $^{234}$U over $^{238}$U in evaporites will result in higher $^{26}$Al production.

Saline minerals, which are common in marine, lacustrine, hydrothermal, and soil deposits are high in Na and low in Al. Calculated $^{26}$Al production rates for U in secular equilibrium is ~10 atoms/gram Na/ppm U, and minerals such as halite, glauberite, and trona are 30 to 40 weight percent Na. The range of measured and previously reported U concentration in salts varies from a few ppt to several ppm. Exceptionally pure salts incorporates less U, but also contain less stable Al. Al concentrations in salts range from 1.5-150 ppm. At these concentrations, production rates are comparable to cosmogenic $^{26}$Al at the surface. A salt with 10 ppm Al and 1 ppm U should contain detectable $^{26}$Al in less than a century.

Reference

Importance of thioarsenates for arsenic redox processes along geothermal drainages, Yellowstone National Park

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Thioarsenates were found to play an important role in arsenic speciation and the mechanism of arsenic oxidation in sulfidic hot spring discharges in Yellowstone National Park. Previous studies, using hydride-generation atomic absorption spectrometry (HG-AAS) [1], reported arsenite predominance at the geothermal source, followed by rapid oxidation to arsenate in the discharge channels, however, HG-AAS is not designed to measure thioarsenates. We used anion-exchange chromatography inductively-coupled plasma-mass-spectrometry to study arsenic speciation along the drainage channel of the sulfidic Ojo Caliente hot spring (pH 8) and a near-by geyser (pH 9.1).

At the geothermal sources, we detected thioarsenates, not arsenite, as the predominant species. Its formation is presumably caused by the presence of S0-donors such as polysulfides or thiosulfate (0.6 mg/L at the source of Ojo Caliente). Along Ojo Caliente drainage channel the major initial product of thioarsenate conversion was arsenite. Arsenate only formed from arsenite as a secondary product once all thioarsenates disappeared. Compared to Ojo Caliente, the discharge at the geyser was more vigorous, the drainage channel steeper and the flow faster. Under these conditions, thioarsenate was found to transform to di- and monothioarsenate with arsenate as final end product. Arsenite concentrations did not increase significantly.

Preliminary laboratory studies show that thioarsenate converts to arsenite without significant increase of arsenate, mono- or dithioarsenate if the solution is purged with nitrogen or air and sulfide is volatilized from solution or partially oxidized to thiosulfate but the oxidation rate is too low for complete oxidation to sulfate. By adding H$_2$O$_2$, thiosulfate is oxidized to sulfate and thioarsenate undergoes ligand exchange to thioarsenate species with a successively lower number of SH-groups to finally yield arsenate without formation of significant amounts of arsenite.

Reference
Oscillatory zoning fahlores from Au-Ag epithermal deposits

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Results

Oscillatory zoning was found in tellurian fahlores (goldfieldites) \([ (Cu,Ag)_{10} (Fe,Zn)_{2} (Te,Sb,As)_{3} (S,Se)_{13} ] \) from three epithermal Au-Ag deposits: Prasolovskoe, Ozernovskoe (Kamchatka-Kuril arc, Russia), and Elshitsa (Sredna Gora zone, Bulgaria). Two types of oscillatory zoning were revealed.

(1) Multiphase (or heterophase) with successive deposition of different minerals or mineral assemblages e.g. Elshitsa where there is regular alternation of goldfieldite bands (Te 2 to 3.2 apfu) with bands (1-2 to 50-100 µm) of tellurian-tennantite (Te 1.5 to 2 apfu) with abundant inclusions of native tellurium. At Prasolovskoe there are “chains” of hessite grains that occur within goldfieldite with a period of 10-20 µm.

(2) Monophase oscillatory zoning reflects element fluctuations in the chemical composition of a mineral. At Elshitsa it is represented by variations of Te from 2.3 to 3.2 apfu and As from 1.8 to 0.7 apfu with a period of 2-3 to 10 µm. At the Ozernovskoe deposit Te ranges from 1.25 to 2.5 apfu, and Sb from 0.86 to 1.33 with a period of up to 20 µm while As increases from 0.75 to 1.63 apfu.

Discussion

The number of such zones in grains with multiphase zoning is usually the same for all crystals in the sample which means that multiphase zoning was caused by an external factor, e.g. due to fluctuation of H₂S and O₂ activities in the solution, and can be described by the equation:

\[
Cu_{12}As_{2}Te_{2}S_{13} + 2.8Te^2 + 2.6H_{2}S + 0.4H_{2}O + 2.8O_{2} = 1.2Cu_{10}Te_{4}S_{13} + 2As(OH)_{3}\]

Monophase zoning is caused by an internal factor, e.g. by the difference between velocities of absorption of any component and its diffusion in the growing zone of the crystal. Since such a zoning occurs only in non-stirred solutions and can indicate local stagnation of the fluid.

Conclusions

Oscillatory zoning can be caused by both external and internal mechanisms and contain important information on mineral forming conditions.

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Terrestrial atmospheric nitrogen in lunar soils?

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Surface-correlated N in lunar soils and breccias exhibits an obvious but mysterious effect that was evident essentially from the first analyses of samples returned by the Apollo missions: The isotopic ratio $^{15}\text{N}/^{14}\text{N}$ is variable, by up to 30%. For some time this was interpreted in terms of variation in the solar wind isotopic composition, perhaps reflecting solar nuclear processes and perhaps even reflecting a secular trend (e.g. Kerridge, 1993). This would be very difficult to understand (Geiss and Bochsler, 1982) in terms of the standard model of the Sun, however, and more recently Hashizume et al. (2000), among others, have championed an alternative interpretation that the isotopic variations reflect N in extralunar, extrasolar particle infall mixing with the solar wind N.

Most recently, Ozima et al. (2005) have suggested another interpretation: That the isotopic variations in lunar soil N reflect admixture of solar wind N with an "Earth wind" flux of atmospheric N. An Earth wind flux is quantitatively insufficient under present circumstances, but might have been quantitatively effective very early in the history of the Earth-Moon system, before the development of the global geomagnetic field. Although viable this seems a quite unlikely hypothesis, but one laden with important consequences if valid.

The Ozima et al. (2005) hypothesis is also subject to simple test: If the isotopic variations are due to a contribution of Earth wind they should be essentially absent in lunar farside samples, since the Moon is thought to have been spin-locked essentially throughout the history of the Earth-Moon system, and an Earth wind would not reach the farside. The purpose of this work is to apply this test.

There are no samples returned from documented farside locations, but there are numerous lunar meteorites, half of them presumed to originate on the farside. We analyzed N in nearly all eleven soil and fragmental breccias known among Antarctic lunar meteorites. By the Earth-wind hypothesis, half should display essentially constant isotopic composition of N, at the solar wind value. This expectation is not realized in our observations, so we conclude that the Earth-wind hypothesis for the origin of N isotopic complexity in lunar soils is not tenable.

References


The rim structure of simple craters as an indicator for an impact vector

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The rims of two simple impact craters, Wolfe Creek, Australia, and Meteor Crater, AZ, USA, were examined. New methods of analysis were devised to display structural features that may be indicative of oblique impacts. Data from the two craters are compared.

Although the majority of craters are formed by oblique impacts, crater shapes remain circular for impact angles >30° and thus normally do not give any implications for the direction of impact. However, the ejecta blanket is the most sensitive indicator for impact angle and direction, and can show a “forbidden zone” on other terrestrial bodies.

The ejecta trajectories forming asymmetric or bilaterally symmetric ejecta blankets of oblique impacts may deviate from a radial orientation with respect to the final crater center and could probably be traced at the rim and overturned flaps of simple craters, which represent the most proximal part of the ejecta. We therefore systematically analyzed strike and dip of strata in the crater rims of two young, simple impact craters, Wolfe Creek Crater and Meteor Crater.

Wolfe Creek Crater is located in Western Australia, was formed 300 ka ago and has an average diameter of 880 m. It was formed in sub-horizontal Devonian sandstones that are over lain by a layer of Miocene laterites. Meteor Crater in Arizona is 50 ka old and 1200 m in diameter. Pre-impact target rocks are sub-horizontal Permo-Triassic sandstones and limestones.

The strike data collected in both craters is translated from a geographic to an azimuthal reference scheme with the point of origin situated in the crater center. The strike of rock layers in the rim is examined for deviations from a hypothetical concentric orientation with regards to the crater center. The deviation can be expressed as an angular value for each measurement.

Results: When displayed in a polar plot, which gives a better sense of the spatial relationship, the values reveal a bilaterally symmetric orientation of the bedding and potential “forbidden zones”. These preliminary results contradict earlier propositions for an impact vector in both Wolfe Creek Crater (Shoemaker et al., 2005) and Meteor Crater (Roddy & Shoemaker 1995). We intend to compare these results with other information, e.g. distribution of dip data, stereo plots and spatial relationships of bedding in three dimensions.

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References

The influence of weathering processes on riverine Mg and Li isotopes in rivers draining basaltic terrain

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Chemical weathering of continental Ca-Mg silicates is a long-term sink of atmospheric CO2, and therefore exerts a major control on climate. However, tracing change in weathering processes through time is difficult because many traditional radiogenic isotope tracers yield ambiguous signals. The transfer of Mg from the continents to the oceans, and its subsequent removal from the oceans, plays a major role in the global carbon cycle, and has also been invoked as a dominant control on oceanic carbonate chemistry. However, the relative importance of these processes, as well as those which fractionate Mg isotopes during weathering, are not well understood. Distinguishing Mg isotope variations which arise from differences in lithology from those caused by weathering processes is difficult, because the range of δ26Mg observed in different rock types is large. However, the study of monolithological terrains offers one way of circumventing the effects from different rock types.

This study presents Li and Mg isotope data for bedload, suspended and dissolved load of rivers from basaltic catchments in Iceland. In addition, primary basaltic mineral phases and soils have also been analysed to determine the possible effects of weathering of primary minerals and the formation of secondary phases.

Li isotope (δ7Li), variations are generally thought to reflect the balance between dissolution of primary minerals and secondary mineral formation; the light isotope, 6Li, is preferentially taken up by secondary minerals. The δ7Li of the dissolved phase varies between +17 and +44‰, and generally decreases downstream.

δ26Mg values of the river sediments range from -0.83 to +0.83‰ relative to DSM-3. Basaltic soils have variable δ26Mg; those with a higher secondary mineral content are isotopically lighter. Co-variations of riverine δ26Mg with suspended load δ26Mg, as well as with pH and the fraction of Mg lost to clays appear to indicate that the isotope composition of the dissolved load is dominantly controlled by preferential uptake of 24Mg into clays, leaving the residual dissolved load isotopically heavy.

These data suggest that Mg isotopes in basaltic rivers are dominantly controlled by secondary mineral formation, and thus the degree of chemical weathering.

Carbon isotope evidence (13C and 14C) for fossil methane-derived dissolved organic carbon from gas hydrate bearing cold seeps

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Vast reservoirs of gas hydrate in continental margin sediments have the potential to influence the properties of organic matter in both sediments and the overlying water column. Natural radiocarbon and stable carbon isotopes were utilized to determine if fossil methane-derived carbon associated with gas hydrate-bearing sediments was incorporated into the dissolved organic carbon (DOC) of both sediment pore waters and overlying near-bottom waters from northern Cascadia margin cold seeps. Pore water DOC from the sulfate-methane transition (SMT) had a δ13C of -60‰ at a site with a microbial methane source and -45‰ at a site with a thermogenic methane source. In both cases, methane-derived carbon was the predominant carbon source (80-100%) for DOC associated with the SMT. Furthermore, 14C- and 13C-depleted bottom water DOC from the thermogenic gas hydrate site indicates that methane carbon constituted 30-50% of the bottom water DOC. Our results indicate that fossil-derived sources of carbon were a significant component of DOC in the cold seep systems we investigated, and suggest that fossil methane-derived DOC fluxes from cold seep sediments may contribute to the aged DOC pools of the deep open ocean.
Neon and plume – MORB mixing along the Galapagos Spreading Center

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Characterizing noble gas composition variations along plume-influenced ridges can help reveal mantle processes such as mantle flow, source mixing, degassing, fractionation and mantle heterogeneities. Lava s from Western and Southern Galapagos islands have very high $^{3}\text{He}/^{4}\text{He}$, up to 30 Ra, but the Northern Galapagos islands and Wolf-Darwin lineament have relatively low $^{3}\text{He}/^{4}\text{He}$, between ~6 and 8 Ra. Along the Galapagos Spreading Center (GSC), $^{3}\text{He}/^{4}\text{He}$ ratios are from 5.9 to 8.5. No high $^{3}\text{He}/^{4}\text{He}$ ratios resembling those of Western and Southern islands are observed along the GSC, despite many indicators of the involvement of plume-derived material [1]. Here, we use Ne isotopes to detect plume involvement in the generation of GSC basalts.

New basaltic glasses were sampled in the ridge axis of GSC between 86 and 98°W. The samples were analysed by crushing of one fragment of sample in order to release volatiles trapped in vesicules. The abundance of CO₂ was measured with a capacitance manometer and the isotopes of Ne were analysed on a Helix MC noble gas multi-collection mass spectrometer.

Preliminary results from two samples so far analysed have very low abundances of mantle Ne, with $^{4}\text{He}/^{21}\text{Ne*}$ (where * denotes corrected for atmospheric contamination) significantly higher than the mantle production ratio. Fractionation of He from Ne may result from late stage degassing (during emplacement of the lavas, for example) or could be due to contamination of the plume-derived melts by asthenospheric He (but no Ne). Analysis of more samples, as well as analysis of Ar isotopes and abundances, will allow two cases to be distinguished.

References

Significance of the mantle Fe isotope variations

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The Fe isotopic variability found among mantle xenoliths [1] is in sharp contrast with the homogeneous isotopic composition of mantle-derived rocks [2,3]. To address this issue, we have undertaken a comprehensive petrological and geochemical study of different suites of mantle xenoliths. They sample continental and oceanic lithospheric mantles of different ages, in the spinel facies and the garnet facies.

The $\delta^{57}\text{Fe}_{\text{IRMM14}}$ range measured at the bulk rock scale (0.99‰) is even larger than previously found. None of the xenolith suites studied display a homogeneous isotopic composition. Bulk-rock Fe isotope signatures were compared to bulk-rock and mineral major and trace element contents. In some cases, the observed correlations can be interpreted as resulting from the effect of different types of metasomatism whereas for other examples, they seem to reflect melt extraction. Although both of these processes affected the bulk-rock Mg#, it was possible for three of the studied xenolith suites to infer the “starting” isotopic composition of the mantle area studied. Two intracontinental suites (Cameroon and South Africa) yielded a $\delta^{57}\text{Fe}_{\text{IRMM14}}$ of 0.1‰, whereas one intraoceanic suite (Kerguelen) led to a value of 0‰ for a highly melt-depleted mantle.

These results point to an “initial” lithospheric mantle, prior to multiple episodes of metasomatism and melt extraction, having a mean $\delta^{57}\text{Fe}_{\text{IRMM14}}$ indistinguishable from that of mantle-derived basalt. This inference is consistent with [4].

These findings also illustrate that Fe isotopes are a sensitive tracer of mantle metasomatic processes despite the high temperatures involved and the usually small Fe isotopic variations observed in igneous rocks. The mechanisms responsible for this peculiar behaviour of Fe isotopes has yet to be fully understood.

References
Plagiogranitic ocelli in the pillow lavas of the Eoarchean (3.7-3.8 Ga) Isua greenstone belt, SW Greenland

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Pillow basalts in the 3.8-3.7 Ga Isua greenstone belt, West Greenland, contain randomly-distributed white ocelli structures. The ocelli are composed predominantly of polycrystalline Na-plagioclase and quartz, with minor hornblende and biotite. They are devoid of any radial and concentric internal structures and display all stages of coalescence. Compositionally, the ocelli are calc-alkaline dacites, whereas the surrounding matrix is a tholeiitic ferrobasalt, suggesting that ocelli melts were not derived from the melts of basaltic matrix by fractional crystallization. Similarly, transition metal and REE abundances cannot be explained by simple closed-system crystal fractionation of mafic liquids. High concentrations of Ni (120-270 ppm in ocelli; 105-160 ppm in matrix), Cr (395-570 ppm in ocelli, 330-590 ppm in matrix), and Co (25-45 ppm in ocelli, 54-64 ppm in matrix) are consistent with near-primary mantle-derived dacites, whereas the surrounding matrix is a tholeiitic ferrobasalt, suggesting that ocelli melts were not derived from the melts of basaltic matrix by fractional crystallization. Similarly, transition metal and REE abundances cannot be explained by simple closed-system crystal fractionation of mafic liquids. High concentrations of Ni (120-270 ppm in ocelli; 105-160 ppm in matrix), Cr (395-570 ppm in ocelli, 330-590 ppm in matrix), and Co (25-45 ppm in ocelli, 54-64 ppm in matrix) are consistent with near-primary mantle-derived melt compositions. On the basis of chondrite-normalized REE patterns, the ocelli are divided into two groups. Group 1 is characterized by LREE-depleted patterns, whereas Group 2 displays LREE enrichment. The trace element characteristics of the Group 1 ocelli are similar to those of the surrounding matrix. Both the ocelli and matrix are depleted in Nb relative to Th. Geochemically the Isua ocelli and host volcanic rocks closely resemble those of Phanerozoic supra-subduction zone ophiolites. Given the pronounced depletion of Nb, relative to Th and LREE in the Group 2 ocelli and picritic to basaltic host rocks, partial melting of a forearc mantle wedge, fluxed with subduction-derived LREE-rich hydrous fluids or melts, is favoured for the source of the Isua ocelli and host volcanic rocks. The ocelli-bearing island arc picrites are structurally juxtaposed against a boninitic volcanic association [1]. Recently, the presence of a relict sheeted dyke complex has been reported within the picritic to basaltic island arc volcanic association, indicating that the Isua greenstone belt was formed by sea-floor spreading in a supra-subduction zone setting [2]. The presence of plagiogranitic ocelli is also consistent with an ophiolitic origin of the Isua greenstone belt.

References

Cathodoluminescence behaviour of Mn-rich carbonates

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It is well known that manganese is the most important cathodoluminescence activator in carbonates (Pagel et al., 2000). However, the CL method is rarely applied in the petrological investigation of Mn-carbonate-bearing rocks and mineralizations due to the commonly accepted effect of concentration quenching or self-quenching, which occurs at elevated Mn concentrations. A comprehensive knowledge about the luminescence behaviour of Mn-rich carbonates still does not exist. The purpose of our study was to determine the effect of Mn concentration on self-quenching.

The cathodoluminescence behaviour of Mn-rich carbonates (rhodochrosite, Ca-kutnohorite, Mn-rich calcite) from hydrothermal and volcano-sedimentary systems was preliminarily studied by CL microscopy and spectroscopy. Chemical composition of carbonates was investigated by X-ray diffraction and FTIR spectroscopy methods. Most of the samples showed bright orange-red CL. The brightest CL occurred in the 5 to 14 wt% range of Mn content. A strong decrease of CL intensity was observed between cca. 14 and 18 wt% Mn, but the rhodochrosite samples with 37 to 45 wt% Mn are still dull luminescent. The study by CL spectroscopy indicated a 620 nm maximum peak position for calcite, 640 nm for rhodochrosite and 630 nm for a Ca-kutnohorite with 9 wt% Mn (Fig. 1).

Figure 1. CL spectra of rhodochrosite, Mn-rich calcite and Ca-kutnohorite with 9 wt% Mn

Our results show the existence of cathodoluminescence in carbonates characterized by elevated Mn concentration (5 to 45 wt% Mn). It seems that self-quenching is not complete even in the case of rhodochrosite.

References
Did hydrothermal fluids contribute to the huge Úrkút Manganese ore body?

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Deposition of the black shale-hosted Úrkút Mn carbonate deposit in Hungary occurred in the Early Jurassic. The ore body formed in a structurally controlled marine basin via bacterially mediated, early diagenetic formation of Mn carbonates. It has been proposed that hydrothermal fluids venting into the depositional basin was involved in the mineralization, but this idea is controversial. A hydrothermal origin may be supported by several lines of evidence such as the fractionation of Mn and Fe, the in situ precipitation of celadonite and other clay minerals, and the accumulation of huge amounts of Mn, Fe, Si. However, none of this evidence alone or together for that matter are conclusive and the aim of this study is to look for evidence for a hydrothermal plumbing system by study of the underlying Mn- and Fe-oxide mineralization. Analysis of 12 samples show a wide range of Mn and Fe contents, with mean values of 35.9% Mn and 10.3% Fe. Si (4.9%), Sr (mean 0.6%), P (0.3%), Ba (0.3%) and Co (0.07%) are enriched in the Fe-Mn oxides. The Fe/Mn mineralogy of the samples is cryptomelane, todorokite, manganite, goethite, hematite, goutite. Polished thin sections show signs of bacterial activity and the precipitation of Mn oxides within soft carbonate sediment, sediment that was later partly to completely replaced by a later stage of Mn oxides. Sr and P enrichments reflect input from leaching of carbonates and organic matter. Mn oxide and Mn carbonate mineralization occur above a thick carbonate basement cut by deep fracture zones. Our data suggests that the Fe and Mn oxides were deposited from deep-sourced fluids circulating through basement rocks. Circulation along zones of structural weakness was likely driven by high geothermal gradients. Sr isotopes are being measured on these samples to confirm this idea.

Textural and microstructural analysis of rapidly grown omphacite from eclogite facies pseudotachylites

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Rapidly grown omphacite (Jd40) has been formed in melt domains of an eclogitized gabbro from central Zambia by frictional melting during pseudotachylyte formation [1]. Omphacite occurs as an extremely fine-grained matrix (grain size of 2-3 µm) and form partly spherulites with diameters ranging from 100 to 300 µm. The textures point to fast mineral growth with local differences in nucleation and growth rate due to heterogeneous cooling. Here, omphacites within melt domains have been studied using electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM) to relate mineral growth texture with deformation (dislocation) microstructure under eclogite facies conditions.

EBSD analyses of a single spherulite show a common b plane for all omphacite grains within the spherulite, while there is no lattice preferred orientation for matrix omphacite. The grains within the spherulite are significantly larger than in the matrix and form radially oriented needles. TEM revealed a strong deformation microstructure with subgrain boundaries, dislocation networks and nodes as well as stacking faults and associated partial dislocations. Grain boundaries of adjacent omphacites are often interlocked and wave-like curved. The spherulitic texture is obviously formed during growth. The distinct dislocation microstructure may have originated from the differential stress developing during rapid growth. Growth related deformation microstructures are barely studied yet and will be discussed in connection with eclogite facies pseudotachylyte formation.

References
Evaluating magnetic susceptibility as a rapid scoping tool for assessing trace metal contaminated soils

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The widespread association in many soils of various trace metals with nano- or micro-particulate grains of magnetic Fe-O-H phases has led to the proposal (Bityukova et al., 1999) that the magnetic susceptibility, \(\chi\), of soils might be used as a proxy for trace metal concentrations, particularly concentrations of bioavailable trace metals, in contaminated soils. The utility of such measurements in areas of trace metal contamination has been tested here using field and laboratory magnetic susceptibility measurements and a variety of chemical and mineralogical analyses: ICP-AES, XAS, sequential extraction, EPMA, XRD and XRF. Three contaminated sites, two in Greece (Kozani – a disused power station, Thessaloniki – the site of a tannery) and one in the UK (Potters Hill, Bolton – site of a former chromate works) were selected for study.

Good correlation of Zn and Cu with field-based \(\chi\) data was found, however a very poor correlation was found between Fe and Cr and field-based \(\chi\) data. This suggests that whilst Zn and Cu are predominately associated with phases contributing to \(\chi\), Fe and Cr occur in substantial proportions in phases with contrasting magnetic susceptibilities. EPMA mapping confirmed the existence of all of Fe-rich, Cr-rich and Fe+Cr-phases. XANES and EXAFS data were consistent with the occurrence in the soils of the Cr(III) phases with the following stoichiometries: \(\text{Cr}_2\text{O}_3\), \(\text{Cr(OH)}_2\) and \(\text{FeCr}_2\text{O}_4\).

Whilst field-based \(\chi\) measurements are both cheaper and faster than chemical analysis of bulk soil or soil extracts and thereby have the potential to be a useful scoping tool, the relationship between \(\chi\) and metal concentrations may be critically dependent on the solid phase speciation of the trace metals of interest, necessitating careful consideration of data on a site-by-site basis.

Novel corresponding - states principle approach for calculating the isotopic properties of water under elevated temperatures and pressures

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The isotopic properties of geologic fluids under geologic conditions are of geochemical interest. For this reason, we developed a corresponding-state principal (CSP) formulation for expressing the equation of state (EOS) of isotopologues of molecular fluids in terms of the dimensionless three-parameter equation (Polyakov et al., 2007):

\[
Z(\tau, \delta, \omega) = Z_0(\tau, \delta, \omega) + \frac{\partial Z_0(\tau, \delta, \omega)}{\partial \omega} (\omega - \omega_0)
\]

where \(Z\) is the compressibility factor; \(\tau\) and \(\delta\) are dimensionless temperature and pressure, respectively; \(\omega\) is the Pitzer acentric factor; subscript “0” refers to the major isotopologue. Using this CSP formulation for minor isotopologues, we further developed a general EOS-based approach for calculating the reduced isotope partition function ratio (RIPFR) for “real-gas” fluids under elevated temperatures and pressures presented by Polyaakov et al. (2006).

This novel approach was applied to the isotopologues of water (HDO and \(H_2^{18}O\)), using experimental data (e.g. liquid-vapor fractionation and molar volume isotope effects). The RIPFR of water calculated from our approach show contrasting behaviors for HDO and \(H_2^{18}O\). The D/H exhibits an overall decrease of 5‰ with increasing pressure to 1 kb, which is in agreement with experimental results for brucite - water system (Horita et al., 2002). In contrast, the RIPFR for \(H_2^{18}O\) increases by 1% with pressure to 1 kb. The significant pressure effects on the isotopic properties of water obtained from this study have important geochemical implications.

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References
Modelling of contact metamorphism and metasomatism near the Talnakh intrusion: Effect of fluid convection versus conductive heat transfer

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As was shown for a number of geological and theoretical models, convective heat-and-mass transfer near magmatic bodies is of great importance. The country rocks of intrusions in the Noril’sk ore district at the northwestern margin of the Siberian Craton are one such case. In this communication, mathematical modelling is used to describe the heat redistribution and fluid convection in the volcanosedimentary sequence at the contact with the Talnakh ore-bearing intrusion.

The problem of modeling of heat transfer and convective flows of a two-phase fluid is solved in the 2D setting in the Cartesian coordinate system on the basis of time-dependent equations of nonisothermal hydrodynamics with account of vapor-liquid phase transition (USGS HYDROTHERM code).

Patterns of fluid flow in the hydrothermal system with a permeable vertical zone that crosscuts the intrusion were obtained from the modeling results. The suggested mechanism of mixing of magmatic fluid with formation water may be efficient only at sufficiently high permeability of the rocks (fig. 1).

As the modeling results show, metasomatic zoning may arise at the postmagmatic stage within a zone 150-200 m thick above the intrusion and no more than 30-40 m thick below the lower contact.

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Temporal distribution and cyclicity in formation of porphyry Cu-Mo deposits

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The recent increased applicability of global paleo-reconstructions, coupled with improved geochronology from most of the world’s investigated Cu–Mo porphyry deposits, allows for an improved understanding of the distribution pattern of orogenic copper and molybdenum in space and time, as well as the relation between the resources of deposits and time of their formation. Geochronological data compiled for about 350 known large to medium (with resources > 0.05 mln. t) porphyry Cu–Mo deposits from all over the world including Asian part of Russia (Sora, Zhirkeen, Schakhtama, Aksug and others) and Mongolia (Khamagtau, Tsagan-Suburga, Erdenetuin-Obo) are represented on the diagram in the time of deposit formation vs resources coordinates (Fig. 1).

Figure 1: Geochronological density of copper resources

1) there is an irregularity in geochronological density of Cu-Mo resources; 2) discreteness in phases of maximum ore-forming activity (28-39; 50-60; 66-73; 75-82; 235-245 Ma) with duration up to 10 Ma; 3) in time, not every significant plume correlates with the epochs of intense ore formation; 4) spectral and wavelet-analysis of geochronological data reveals quasi-periodic cycles of 120-100, 69-60, 36-28, 20-15, 12-10, 8-7 Ma alternating at different time intervals. The latter two factors indicate the formation of porphyry Cu-Mo deposits is related not only with plumes but also with tectonic plate reorganization.

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**Raman-Spectroscopy – A powerful tool for life- and material-sciences**

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Raman spectroscopy has emerged in the last years as an extremely powerful method in almost all natural science disciplines. This renaissance of Raman spectroscopy was mainly triggered by the latest achievements in laser technology, by the design of very efficient filter to suppress the elastically scattered Rayleigh light, and by the development of extremely sensitive detectors. The advantages of Raman spectroscopy are its unprecedented high specificity and its versatility. Raman spectroscopy is a non destructive technique and does in general, require only minimal or no sample preparation. Solid, liquid, and gaseous samples can be measured as well as transparent or non transparent samples or samples with different surface textures i.e. Raman spectroscopy can be applied to any optical accessible sample, where a pre-treatment of the sample is not necessary.

In this presentation a report on a Raman spectroscopic characterization of a broad variety of biological probes will be given. Raman spectroscopy is an extremely capable, suitable and prominent method for probing the relationship between structure, dynamics and function of biomolecules. In this context micro-Raman imaging, the surface enhanced Raman scattering (SERS) technique and resonance Raman spectroscopy are commonly applied. These Raman techniques allow one to characterize the structure of e.g. isolated pharmacological relevant substances and the investigation of pharmaceutical relevant substances in plants and especially the localization of pharmaceutical relevant substances in tissues. Not only the localisation but also the investigation of the mode of action of drugs against infectious diseases on a molecular level will be presented. In addition Raman spectroscopy also allows the identification of microorganisms on a single cell level.

The main focus within the second major topic material photonics is concerned with the derivation of structure-property as well as structure dynamics relationships by means of Raman spectroscopy. In particular the characterization of mineralogical samples like e.g. extraterrestrial material (meteorites) and the derivation of structure-activity and dynamic relationships in artificial light harvesting systems or photocatalysts based on Ruthenium-polypyridyl complexes by means of resonance Raman spectroscopy will be presented.

In summary the presented examples convincingly demonstrate the great capabilities of Raman spectroscopy for life and material sciences making this technique to one of the most essential laser spectroscopical methods.

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**Experimental evidence for rapid re-equilibration of water between melt inclusions in olivine and host magma**

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Here we report the results of pilot experimental study aimed at evaluating the ability of olivine to protect melt inclusions at changable external conditions, which may readily take place in long-living magmatic systems.

For the experimental study, natural olivines containing glassy inclusions were picked from olivine-plagioclase-pyroxene phric submarine tholeiitic basalts from the Galapagos Plateau (sample PLO2-24-33 provided by D.Christie). Ninety six inclusions from this sample were preliminarily studied for major and trace elements. Water content in natural inclusions measured by ion probe ranged from 0.37 to 0.67 wt % (n=20) and was similar to matrix glass (0.43 wt %). Selected olivine grains (0.5-1 mm) with inclusions inside were loaded in Fe-presturated Au$_{80}$Pd$_{20}$ capsule together with reduced (QFM-1) powder of depleted synthetic MORB. The mixture was dopped with ~ 3 wt % of distilled water. Experiments were conducted in internally heated pressure vessel at 200 MPa and 1140 °C using Ar as pressure medium. The run duration was 48 hours.

Experimental products were studied optically, with electron and ion probe. Surprisingly, all of seven inclusions analysed after experimental treatment had high water content (2.0-2.7 wt%), close to the matrix glass (2.3 wt%) and ~5 times higher than in starting compositions and exhibited high MgO (8.1-8.9 wt% vs. 4.0-6.7 wt % prior experiment) corresponding olivine-melt inclusion equilibria at hydrous conditions. Incompatible trace elements, S, F and Cl content in the melt inclusions decreased only slightly after the experiment (due to host olivine dissolution), remaining within the range of natural Galapagos inclusions and ~10 times higher than in depleted synthetic matrix.

We conclude from this study that melt inclusions in olivine behave as semi-closed system at changing external conditions. Complete re-equilibration of water between inclusions in large olivines (up to 1mm in size) and matrix melt is achieved during 2 days or less, whereas incompatible trace elements and other volatile components (S, Cl, F and likely CO$_2$) behave as immobile. Rapid water (hydrogen) exchange between inclusions in olivine and host magma, which is faster than Fe-Mg diffusion in olivine, implies that those inclusions experienced detectable Fe-Mg re-equilibration with olivine can unlikely preserve initial water concentrations and most likely reflect water content in surrounding magma prior eruption.
Weathering of Bronze Age potsherds in a Mediterranean climate (Cres Island, Croatia)

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The aim of this study was to study the causes of well preserved status of potsherds in bronze age hill forts on Cres island (Northern Adriatic Sea) exposed to Mediterranean climate and their buried equivalents in colluvial deposits. The island of Cres has a long history of settlement and hosts some very important Mesolithic, Neolithic and Bronze age sites. Due to erosion large areas are bare karst lacking soil cover and prehistoric potsherds can be found in stonewalls of hill forts or caves.

The potsherds were analyzed by microscopy methods as well as geochemistry to study the weathering process in both exposed and buried potsherds. The colluvial soil containing potsherds was dated at Beta Analytic AMS facility (Beta-199264) and a calibrated $^{14}$C date ranging from 2030 to 1870 BC was obtained. Under the optical microscope, the potsherds are texturally homogeneous and display inclusions of similar type, abundance, and grain size.

The enrichment of Ca in exposed potsherd rims is accompanied by depletion of light REE’s and enrichment of heavy REE’s.

The results show that potsherds exposed to the Mediterranean climate for four thousand years have an improved durability due to calcite re-crystallization and notable change in the chemical composition of potsherd rims which have to be considered when using bulk geochemistry for provenance studies.

Constraining the role of anoxygenic phototrophic Fe(II)-oxidizing bacteria in the deposition of BIFs

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Banded Iron Formations (BIFs) are Precambrian sedimentary deposits of alternating iron oxide and silica mineral layers. Their presence in the rock record ca.3.8-2.2 Ga makes them particularly intriguing formations for the debate over when oxygen became dominant on Earth. The mechanism(s) of BIF deposition is still unclear and suggestions include both abiotic and biotic processes. We are interested in constraining one of these proposed mechanisms; the direct biological oxidation of Fe(II) via anoxygenic Fe(II)-oxidizing photoautotrophs.

In order to find the limitations of photoferrotrophic BIF deposition, we take a holistic approach, investigating the oxidation of Fe(II) by modern Fe(II)-oxidizing phototrophs, the precipitation of Fe(III) (hydr)oxides, and the fate of the cell-mineral aggregates in the water column and at the basin floor.

Specifically, physiology experiments with Fe(II)-oxidizing phototrophs under various conditions of light intensity, pH, Fe(II) concentration and temperature allow us to determine the environmental limits of such organisms. We carry out precipitation experiments to characterize the sedimentation rates, aggregate size and composition in order to resolve the effect of reactions in the water column. Finally, we simulate the diagenetic fate of these aggregates on the basin floor by placing them in gold capsules under temperature and pressure conditions relevant for the Transvaal Supergroup BIFs of South Africa. Recently, we have developed a tank simulating the Archean ocean in which the strains grow in continuous culture and collect the aggregates formed under various geochemical conditions.

We aim to model the extent of and limitations to photoferrotrophs in BIF deposition. This information will help constrain whether biotic processes were dominant in the Archean ocean and will offer insight to the evolution of the early biogosphere.
Trace element and Nd-Sr isotope systematics of phonolite and other rocks of the Chico Sill Complex, Northeast New Mexico

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Alkaline igneous rocks of Chico Sill Complex in northeastern New Mexico fall on the trend of the Jemez Lineament, an alignment of igneous centers that obliquely crosses the Rio Grande Rift. These 37 – 20 Ma intrusive rocks are spatially associated with younger rocks of the Raton-Clayton volcanic field, but clearly sample a different source. The sills were emplaced prior to rift extension. A subset of the spectrum of intrusive rocks (including phonolite, phonotephrite, trachyte, and lamprophyre dike rocks) is included in this study.

Phonolite is the most common rock type in the southeastern half of the sill complex and is the product of extreme fractional crystallization of a more mafic parent, but may not have evolved from the other lithologies studied. Trace element ratios and normalized-element plots suggest that at least two distinct differentiation trends produced phonolite, titanite fractionation played a role in differentiation, and a subduction component is absent from the phonolite source but may have contributed to other rock compositions. One odd feature is the enrichment of Zr as compared to other continental alkaline rock suites, in one phonolite trend relative to the other.

The subset of rocks studied shows initial Sr and Nd isotope ratios that are close to bulk-earth values, with epsilon Nd in the narrow range of 2.1 to –1.5 (144Nd/148Nd between 0.51275 and 0.51256), and initial 87Sr/86Sr ratios in the slightly broader, but still clustered range of 0.7042 to 0.7053. These isotope ranges are similar to many ocean-island basalts. The trail of the data toward higher 87Sr/86Sr values suggests a probable mixing curve with granitic or sedimentary rocks of the upper crust, although the degree of contamination must have been small and the contaminant is poorly defined.

Tracing global fallout using $^{210}$Pb and artificial radionuclides inventories in mountainous area

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Inventories of unsupported $^{210}$Pb in soils is used here as a tracer to estimate the effect of parameters such altitude, mean annual rainfall, vegetation on the long term input of atmospheric pollutants over mountainous area. Thus we examine exhaustively the magnitude and extent of soil inventories of unsupported $^{210}$Pb in French mountainous areas. In addition, we combine artificial radionuclides from global fallout (mainly $^{137}$Cs and Plutonium) with $^{210}$Pb to compare deposition mechanisms of artificial and anthropogenic radionuclides. With this view, soils were sampled between 2000 and 2006 along transects of increasing altitude and subsequently increasing annual precipitation rate, in different mountainous areas.

Data shows that $^{210}$Pb soil inventories are coarsely proportional to the mean annual precipitation occurring on each massif. Additionnaly in high-altitude sites, higher $^{210}$Pb inventories than expected are explained by orographic effects. At last, climatic parameters, such as the intensity of rain episodes in Mediterranean regions probably induce specific deposition processes of $^{210}$Pb explaining the relationship observed between soil inventories and rainfall. In addition to altitude and rain amount, the vegetation accounts for the intensity and the extent of $^{210}$Pb deposition, since the excess $^{210}$Pb in woodland soils reachs 30% with respect to grassland. Although the inventory of $^{137}$Cs and plutonium from atmospheric nuclear weapons in soil also increases with mean annual rainfall, a significant decrease of $^{137}$Cs/$^{210}$Pb ratios is observed in studied massifs from lowland to highland sites. This shows that at least two main tropospheric reservoirs with distinct $^{137}$Cs/$^{210}$Pb ratios contribute to the mountainous soil inventory of atmospheric pollutants.
Extracting sequentially Ra, Nd, Pa, Th and U from a unique natural sample, on the same column

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Multi-proxy approach is very promising for modern and past marine process investigation. However, extracting simultaneously several tracers from the same sample using the same column remains a challenge. Measuring any natural tracer requires sample collection, pre-concentration or mineralization, chemical extraction and spectrometric analysis. Natural concentrations being very low, when each tracer requires its own collection, huge volumes of water have to be taken from the rosette and/or filtered with in-situ pumps, which is time and money consuming. Since the GEOTRACES program objective is to analyse numerous tracers and isotopes along oceanographic sections, there is an urgent need to find ways to analyse as many elements as possible on the same sample. In addition, collecting more samples on the same marine cast will enhance the homogeneity of the final data, and improve the sampling resolution, therefore improving the data set quality.

A new procedure is presented, allowing the simultaneous extraction of 5 tracers (Ra, Nd, Th, Pa and U) from the same natural sample. In addition to isotopic ratios ($^{143}\text{Nd}/^{144}\text{Nd}$, $^{230}\text{Th}/^{232}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$) concentrations of $^{226}\text{Ra}$, $^{230}\text{Th}$ and $^{233}\text{Pa}$ are investigated requiring spike addition, i.e. $^{228}\text{Ra}$, $^{230}\text{Th}$ and $^{233}\text{Pa}/^{236}\text{U}$ respectively. Accuracy and precision of the analytical methods were evaluated using artificial standards and natural samples (marine suspended particles and rocks). Satisfactory purifications of Th, Pa and U were obtained from this unique column, whereas Nd and Ra extraction require light additional steps.

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New productivity in the Eastern Arabian Sea during winter Monsoon

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The biogeochemistry of the Arabian Sea is driven by seasonally reversing southwest and northeast monsoons. Although both the monsoons trigger high primary production, the underlying mechanisms are different. Recent observations on the basis of ocean color studies have shown contradicting trends in ocean productivity for the western and eastern Arabian Sea; it has increased in the western Arabian Sea over last 6 years whereas no such trend is seen in the eastern Arabian Sea [1]. In this context, it would be interesting to know about the export production taking place in this part of the world’s ocean. Measurement of new production using $^{15}\text{N}$ tracer technique [2] provides an avenue to estimate the export production; integrated over an annual time scale new productivity is equal to the export of carbon out of the surface ocean i.e., the export production. We have carried out new productivity measurements in the eastern Arabian Sea during early and late winter monsoon. Our results suggest that during the early winter, though the column N-uptake is low (~8.91mmolN/m$^2$/d) over a large area of the eastern Arabian Sea the f-ratio (new production/total production) is relatively high (~0.66). Results from the late winter, in conjunction with the earlier reported results [3], reveal consistent high column N-uptake rate (~20.1mmol N m$^{-2}$ d$^{-1}$), particularly when the bloom (dominated by heterotrophic Noctiluca Scintillans) develops in the northeastern part. During this period the f-ratio is also very high (~0.86) suggesting enhanced downward transport of newly formed organic matter implying increased sequestration of carbon to the deeper ocean.

References
Stable isotopic trends in Neoproterozoic oceans: A record of global Snowballs, global Slushballs, global methane, global diagenesis, and/or palaeogeography?


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The Neoproterozoic (1000 – 543 Ma) is a period of extraordinary Earth System change marked by extreme climatic fluctuations and hallmark biological innovations (advent of metazoans). Stable isotopic trends (C-O-B) associated with Neoproterozoic marine carbonate rocks display large amplitude fluctuations which many studies have shown are broadly reproducible worldwide and stratigraphically systematic. Amongst the most intriguing of these are from cap carbonates (carbonate rocks which rest directly on glaciogenic rocks, and/or the surface representing palaeo-glacial episodes) which show sharp negative C isotopic excursions (in many localities down to -6‰) followed by recovery to more positive values and concomitant B-isotopic excursions (about 9‰); these have generated lively debate and timing.

We have amassed a C-O-B dataset on cap carbonates from Namibia, North America and northern Europe that shows that δ13Ccarbonate trends can be distinguished based on location and inferred palaeobathymetric position within an individual basin. Along individual craton margins trends are systematic and variations can be reasonably attributed to varying palaeoenvironmental setting, i.e., they are self-consistent and compatible with the geology. However, inter-cratonal comparisons show that stratigraphic (temporal) patterns and amplitudes differ between basins. Although the duration of cap carbonate precipitation remains contentious, it is likely that deposition was relatively rapid (i.e., 10^3-4 years rather than 10^6 years). Our data can be used to imply that the isotopic composition of water masses varied from place to place in Neoproterozoic oceans. This suggests that cap carbonates and their isotopic signatures were a likely product of a dynamic interplay between palaeogeography and palaeooceanic circulation.

Adsorption and dynamics of ions at rutile and cassiterite surfaces

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The interface between aqueous solutions of ions (mostly Rb⁺, Na⁺, Sr²⁺, Cl⁻, Br⁻, F⁻) and metal oxide surfaces, represented by rutile and cassiterite, is studied using molecular dynamics computer simulations. The previously published results for adsorption of these ions at negatively charged surfaces at 25°C are extended to cover higher temperatures up to 150°C and the effect of pH-dependent surface charge density. The effect of the temperature and pH on occupancy of different types of adsorption sites will be compared with predictions of Multi Site Complexation models (MUSIC). The competition between adsorption of several cationic species present in mixed solutions used in titration experiments (e.g. Rb⁺ and Sr²⁺) and the adsorption dynamics of ions will be also discussed.

References


No need for involvement of a hidden mantle reservoir in the origin of lamproites from Mediterranean

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Recent discussion about Hf-Nd isotope geochemistry focused on the composition of lamproites and kimberlites as possible evidence for the existence of a hitherto unrecognized ‘hidden’ terrestrial reservoir. This was triggered by the discovery of an apparent discrepancy between terrestrial Hf-Nd isotopes and the BSE chondritic reference value, which could be resolved by the existence of a new geochemical reservoir with Hf-Nd isotopic values below the terrestrial array. Most lamproites do not follow the Hf-Nd array defined by other terrestrial samples, but have variable Nd at almost constant Hf isotopic values. This triggered an attractive hypothesis about their role in the evolution of the Earth and their potential to sample the ‘hidden’ reservoir. Here, we present Hf, Sr, Nd and Pb isotope results on Mediterranean lamproites that can be used to further test this possibility.

Mediterranean lamproites are derived from multi-component melts, which combine depleted and enriched end-members(s). The extremely variable radiogenic isotope composition of lamproites points to the importance of mixing relations between three contrasting geochemical components which appear in 206Pb/204Pb, 87Sr/86Sr and 143Nd/144Nd space: a crustal component, an ultra-depleted mantle component originating component. It is the third component which is the most relevant for the deflection of lamproites from the terrestrial Hf-Nd array.

Our modelling shows that the convective-mantle derived component has high Sr and Nb contents, low HFSE relative to LREE, significantly higher Nb/Ta and Zr/HF ratios, and lower Zr/Nb and Zr/Ta ratios relative to OIB and chondrite, whereas isotopic compositions are similar to OIB. This geochemical signature is considered as a “hallmark” of mantle carbonatite. In Hf-Nd isotopic space, this component is responsible for the shift of the lamproite values from terrestrial array. We interpret this shift as a mixing hyperbola between carbonatitic melts derived from sublithospheric mantle and lamproitic melts. The deviation from the array is due to the large range in Hf/Nd ratios that vary from up to 0.20 in lamproitic melts to <0.01 in asthenospheric melts, caused by extremely high Zr and Hf concentrations in lamproites (up to 1000 and 30 ppm, respectively), and very low Hf contents in carbonatitic melts. We discuss a geodynamic scenario which provides a suitable environment for the interaction of coeval asthenosphere-derived and lamproitic melts throughout the Mediterranean region.

REE in the oldest zircons, Okhotsk terrane

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For accurate definition of genetic characteristic of zircons from mafic granulites and gneisses and to find a solution of gneisses and granite-gneisses correlation, REE distribution in zircons had been studied, using SIMS SHRIMPII.

Hyp-Plag granite schist displays two oldest zircon generations: 1 (3.6-3.7Ga) with volcanic and 2 (3.5Ga) with magmatic inclusions. Volcanic zircons contain max concentrations of REE and (Lu6/Sm6=104-198, Eu/Eu*=0.2-0.39). Ultra-metamorphic zircons (2) and recrystallized grains (3) contain less REE, especially LREE, REE pattern is steeper (Lu6/Sm6=370-1305, Eu/Eu*=0.15-0.27).

Some zircons (4) correspond to Proterozoic metamorphic and metasomatic events are represented by altered discordant grains of high U contents and positive Eu anomalies (Lu6/Sm6=120-129, Eu/Eu*=2.1-2.9). Its REE concentrations are close to that of zircon 1, but REE pattern for most altered grains is flat (Lu6/Sm6=40, Eu/Eu*=1.16). Granite-gneisses zircons displays two types of REE distribution: for ultra-metamorphic cores (3.3Ga) (Lu6/Sm6=27-117, Eu/Eu*=0.1) and for metamorphic rims (2.7 Ga) (Lu6/Sm6=165-428, Eu/Eu*=0.2-0.5). Cores in zircons of granite-host gneisses (3.28 Ga) show REE pattern (Lu6/Sm6=45-166, Eu/Eu*=0.1-0.2) similar to that for cores of granite-gneisse zircons.

1. Chondritic normalised REE patterns of zircons with volcanic inclusions from Hyp-Plag granite schist are similar to that of zircons from gabбро (Hoskin, 2000) and correspond to magmatic pattern. It conforms to geochemical data and verifies belonging of such zircons to mafic volcanic protolith.

II. REE patterns of zircons with magmatic inclusions show distribution similar to zircons from leucosome of garnet-free granulites (Rubatto, 2002). III. Cores of zircons from gneisses and granite-gneisses show similar REE patterns, that indicate their origin from common protolith.

References
Contrasting behaviour of arsenic, iron, manganese and uranium during anaerobic incubation of aquifer sediments from Nadia, West Bengal

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The critical role of indigenous metal-reducing bacteria in mediating the mobilisation of arsenic from shallow sediments in Bengal has been widely muted, however, there remains debate over the mechanistic details of the mobilisation processes, including the relative importance of enzymatic and abiotic processes. Observing, in suitable microcosm experiments, the behaviour of trace elements with contrasting biogeochemistries might provide some further insight.

Using sediment from 20 m depth from Chakdaha Block, Nadia, West Bengal, we conducted microcosm experiments under anaerobic conditions with 15 g sediment / 30 mL synthetic model Bengali groundwater (after Islam et al., 2004) amended with sodium acetate (as a proxy electron donor) to 0, 0.1, 1 or 10 mM at an initial pH of 7.0, 20°C & 1 atm. Triplicate microcosms were sampled after 1, 3, 7, 10, 14, 22 and 29 days. Trace elements were determined by HR-ICP-MS, As speciation by IC-ICP-QMS, Fe(II) by the UV-Vis based ferrozine method and H₂ by GC-RCD.

Reduction of As(V) to As(III) was observed within 7 days, followed by the mobilisation of As, Fe and Mn and the immobilisation of U mostly within 14 days suggesting increasingly reducing conditions. Release of Mg, Ca, Sr and Ba may be due to dissolution of carbonate phases consistent with increasingly acidic conditions that would be expected. Amendment with acetate made no systematic significant difference to the rate or magnitude of As, Fe or Mn release – this is consistent with large amounts of H₂ generated during the microcosms and the presence of highly reactive organic matter within the sediments. Null results from sterile controls confirmed the overall critical role of microbes. Work is ongoing to characterise the bacterial communities and the nature of the reactive organic components in the sediments.

Magmatic processes and the evolution of crust: Insights from the New Zealand/Kermadec subduction system

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It is now well established that andesitic magmas have an ultimate origin in the mantle wedge but the extent to which erupted compositions are modified through crustal interaction is still being defined. Subduction-related volcanic rocks are commonly identified by their textures and by specific trace element characteristics. The textures reflect complex crustal level processes that include assimilation and crystal fractionation (ACF) and magma mixing or mingling. Although commonly interpreted to reflect slab fluid influences, the trace element characteristics are also specific to continental crust. Detailed studies (stratigraphy, major and trace element chemistry, Sr-Nd-Pb isotopes, U-series disequilibria) of andesitic eruptive sequences in New Zealand’s North Island indicate that they represent magmas that evolved through ACF processes operating on variable time scales in complex storage and feeder systems dispersed throughout the crust. Contrasts between individual volcanoes arise because of variations in storage and feeder systems and because, in the more extreme cases, for example Ruapehu and Taranaki, both mantle sources and the crustal assimilants are compositionally different. In the Taupo Volcanic Zone, the principal locus of volcanic activity in the North Island, rhyolitic magmatism marks the onset of rapid extension and high heat flow and is preceded by andesitic volcanism. The change from andesitic to dominantly rhyolitic eruptives reflects progressive thermal evolution of the lithosphere and a shift from mantle and lower crustal dominated genetic and evolutionary processes to those dominated by crustal melting and lower pressure crystal fractionation. These processes occur in both continental and oceanic segments of the New Zealand-Kermadec system demonstrating that it is the thermal evolution of the crust rather than its thickness or composition that controls the mix of lithologies in arc-type volcanoes.
Non-hydrocarbon compounds in oil and gas accumulations: Deep influx constrained by noble gases

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Recent oil and gas exploration demands deeper drilling and more complex targets. It is clear that fluids from a sedimentary basin cannot be considered isolated anymore from deeper fluids (metamorphic zones, continental basement, mantle). This induces negative consequences (occurrence of non hydrocarbon gases contaminating the hydrocarbon accumulations as carbon dioxide and nitrogen) and potential positive ones (high concentrations of helium as an economic resource, possible extra-generation of hydrocarbon gases through non organic processes). Different natural tracers allow us to quantify the importance of such deep fluids contaminants. Among them, the chemical and isotopic compositions of associated noble gases (from helium to xenon) give evidence, according to different oil fields, of mantle contributions from 0 to almost 100%. Very recent direct measurements of lead isotopes in associated liquid hydrocarbons confirm that mantle compounds may be associated both as inert gas molecules and heavy metals chemically associated with large organic molecules.

We present two examples of mantle-contaminated petroleum systems, where the noble gas chemical and isotopic patterns indicate a clear mantle contamination. Moreover, an excess of radiogenic 4He is sometimes present, due to a leaching of crustal rocks through the migration of deeper carbon dioxide and/or nitrogen carrier gas, coming from deeper sources. This implies that the usual 3He/4He ratio, used commonly as an indicator of mantle contamination, may be useless, whereas the use of 3He, associated with other gases (CH4, CO2, N2, etc...), indicates clearly a mantle signature for deeper sources. This implies that the usual 3He/4He ratio, used commonly as an indicator of mantle contamination, may be useless, whereas the use of 3He, associated with other gases (CH4, CO2, N2, etc...), indicates clearly a mantle signature for deeper sources.

U-Th-Ra fractionation in soil horizons of forested ecosystem (Strengbach catchment, France)

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The 238U series nuclides 238U, 234U, 230Th and 226Ra are recognized as tracers and chronometers of weathering processes. Using these tracers requires to understand the parameters and processes controlling their fractionation in soils surface horizons. In order to constrain these processes, the different compartments (soil profile, soil solutions and vegetation : wood, leaves, branches and roots of beeches) of a experimental plot, situated in the Strengbach catchment (OHGE http://ohge.u-strasbg.fr, Vosges, France) have been sampled and analysed for major-trace elements and U-Th-Ra isotopes.

The shallower horizons of the soils have highest (226Ra/230Th) and lowest (230Th/234 U) activity ratios (a.r.), respectively 1.41 and 1.12 compared to the other horizons of the soil profile. The analytical data of the different compartments of the vegetation suggest that the plants are characterized by very high (226Ra/230Th) ranging from 20 to 164 and low (230Th/234 U) ranging from 0.84 to 0.97. Based on these results, we suggest that the geochemical signatures of the soils surface horizons (<40 cm) are influenced by litter recycling which could provide 226Ra and 234U excess in these horizons.

The (226Ra/238U) a.r. of the soil solutions (1.88-4.75) are higher than those of the corresponding soils (≈ 1.5). They decrease from the top of the profile to 30 cm depth and then increase weakly until 60 cm depth. The vegetation, which is responsible of both the litter recycling and the root uptake displays very high (226Ra/238U) ranging from 100 to 300. We propose that litter recycling influences the isotopic characteristics of the shallower soil solutions. The fractionation induced by root uptake, which mainly operate between 30 and 40 cm depth, could explain the lower (226Ra/238U) in soil solutions at these depths.

Therefore U series disequilibria allow to constrain the dynamics of a soil system. Moreover, the data point to the important role of the vegetation in controlling the geochemical/isotopic signatures of the soils surface horizons and soil solutions (<30 cm) by litter recycling and root uptake.

Reference
Chabaux et al. (2003), Reviews in Mineralogy and Geochemistry 52, 533-569.
TiO$_2$ in OIB and the preservation of extreme isotopic signatures
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We have examined liquid lines of descent for a large set of ocean island basalts (OIB) using a compilation of major element data from the GEOROC database. We focus on the moderately incompatible element titanium and identify a ‘reference’ TiO$_2$ value for each OIB, to reflect approximate primitive lava compositions before significant fractional crystallization or crystal accumulation. High reference values are observed in OIB with low inferred degrees of melt lying above thick lithosphere, whereas low reference values are seen in OIB with larger inferred degrees of melt, atop thinner lithosphere. We find that the reference abundances are in most cases too high to be produced by melting of any plausible peridotitic mantle composition. Therefore, an additional Ti-rich component is required in the source of virtually all OIB. Recycled mafic crust appears to be the most geochemically consistent source for the extra Ti.

The OIB we investigated cover the full range of radiogenic isotopic mantle endmembers. Notably, OIB with low reference TiO$_2$ values plot in restricted, depleted ranges in Sr-Nd isotopic space, whereas OIB with higher reference TiO$_2$ values exhibit enriched isotopic signatures and expansive ranges in Sr and Nd isotopic ratios. Since higher reference TiO$_2$ values likely result from smaller degrees of melting, they may preserve extreme isotopic ratios. Larger degrees of melting may dilute enriched isotopic signatures. Therefore, degree of melting in OIB may be a dominant control on both the observed range of isotopic ratios and the ability to preserve extreme signatures. However, recycled crust does not generally produce extreme isotopic signatures seen in endmembers such as EMI and EMII, making other components necessary to explain the full breadth of isotopic data.

Pt-Re-Os isotope and HSE systematics of Belingwe komatiites
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Studies of the origin and evolution of the relative and absolute abundances of the highly siderophile elements (HSE) in the mantle provide information regarding the late accretionary history of the Earth, oceanic crustal recycling, timing of melt extraction from the mantle, and possibly the mechanisms and the extent of core-mantle exchange. We present high-precision data for HSE abundances and Pt-Re-Os isotope systematics for twenty drill-core whole-rock samples and olivine and chromite separates from the ~10-m thick Tony’s komatiite flow, which is among the freshest Archean komatiites on Earth. The emplaced lava contained 24% MgO, was depleted in LILE and had εNd(T) = +2.5. Re-Os data for two whole-rock samples and corresponding mineral separates define an internal isochron with an age of 268±11 Ma and a γ$^{187}$Os(T) = 0.13±0.08. Regression of the data for all samples yields an isochron with an age of 2674±44 Ma and a γ$^{187}$Os(T) = -0.22±0.48. A single B$_2$ sample analyzed for Pt-Os has an initial 186Os/188Os = 0.119832±8 determined earlier for the contemporary Pyke Hill komatiite source. Both sources have similar ε$^{186}$Os(T) = 0.05±0.11 and 0.05±0.07, respectively, relative to the bulk solar system initial 186Os/188Os = 0.1198269. The Belingwe source, thus, evolved with long-term 186Re/188Os = 0.400±4 and Pt/0s = 1.7±0.2, which are indistinguishable from those in chondritic meteorites. The IPGEs (Os, Ir, Ru) in the whole-rock samples are strongly positively correlated with MgO identifying the Belingwe komatiite as belonging to the Munro-type flows. The PPGEs (Pd, Pt) and Re show strong negative correlations with MgO, coincident with olivine-control lines. The HSE composition of the Belingwe source was calculated from the regressions of HSE abundance data vs. MgO for the whole-rock samples and the Pt-Re-Os isotopic data. The source contained (ppb): Re 0.23, Os 2.6, Ir 2.3, Ru 5.2, and Pd and Pt 4.3. The Ru/Ir = 2.3±0.3 and Pd/Ir = 1.9±0.2 in this source are higher than those in any known groups of chondrites, but match the recent estimates for the Earth’s primitive upper mantle derived from analyses of mantle xenoliths worldwide, or the recently obtained HSE data for some lunar impact melt breccias “fingerprinting” the composition of late accreted materials to the Moon and the Earth. The new data provide further constraints on the evolution of PUM in the Archean and stimulate additional studies of the composition of materials added to the silicate Earth in the form of the “late veneer”, as well as chondritic meteorites.
Noble gases composition of palaeo Archaean atmosphere and mantle

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Several models of the noble gas evolution of the Archaean atmosphere-mantle exist [1, 2, 3], with implications on our understanding of the development of the early Earth and the appearance of life.

Pristine drill core samples (Pilbara Drilling Project) from the 3.525 Ga chert-barite of the Dresser Formation (North Pole, Western Australia) allowed fresh samples preserving primary fluid inclusions unaffected by surface weathering to be directly analysed using synchrotron and mass spectrometer methods. The Dresser formation has been interpreted as a shallow basin strongly affected by hydrothermalism practically during formation of the basin and prior to early diagenesis [4, 5]. This chronology permitted primary fluids from different origins (marine, hydrothermal) to be trapped within the volcanic-sedimentary sequence.

Two studies, one of intrapillow quartz pods overlying chert-barite deposits [6], and the other of the same formation but 100 m deeper, have been carried out. Synchrotron X-ray microfluorescence shows the presence of three fluid endmembers (in different proportions) in fluid inclusions in quartz. Two of them, enriched in Ba and/or Fe, are likely to originate from the hydrothermalism while the third, metal-depleted, fluid is the North Pole seawater endmember. Primary fluid inclusions from the bottom of the Dresser formation are dominated by hydrothermal fluids, which allow us to constrain the noble gases hydrothermal signature.

Inclusion-trapped fluids were analysed by mass spectrometry (using a Helix Multicollector) following extraction of the fluids by in vacuo crushing. Neon isotopes, 36Ar and 40Ar, 84Kr, 129Xe, 132Xe and 136Xe were measured in fluid inclusions and in the host matrix. The results show mixing between two fluids, confirming previous studies. The Seawater pole reveals the composition of the palaeo atmosphere thus it is possible to determine the composition of palaeo archaean mantle within the signature of hydrothermal fluid.

References

Constituting groundwater residence times in a fractured aquifer using noble gas isotopes

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In fractured rock aquifers, groundwater ages obtained with environmental tracers usually do not represent the hydraulic age of the water. Solutes in the water have diffusive access to the micro pores of the rock matrix and are therefore retarded compared to the water flux in the fractures. In a system of parallel fissures, the ratio between the apparent tracer age and the water age depends on the extend of diffusive penetration between the fractures and the matrix. Visa versa is the penetration depth in transient conditions a function of the groundwater residence time in the fractures (Maloszewski and Zuber, 1994). This intrinsic dilemma for groundwater dating can only be reduced by the use of multiple tracers with different decay constants and input histories. In the present study 85Kr (T 1/2: 10.76 yr, 39Ar (T 1/2: 269 yr) and 14C (T1/2: 5730 years) were used in order to constrain the groundwater residence times in a fractured aquifer in the Clare Valley Australia (Love et al., 1999). In the atmosphere 39Ar is mainly produced by cosmic ray induced 40Ar(n,2n)39Ar reactions. In this study the subsurface secular equilibrium 39Ar activity due to the 39K(n,p)39Ar reaction exceeds the atmospheric value of 1.8 mBq/L Argon (Loosli, 1983) by a factor of two. The subsurface ingrowth rate can, however, be interpreted in terms of groundwater residence time. The obtained time scales support findings from indicators of past recharge conditions. (Love and Herczeg, 2001).

References
U and Th deficit in primitive mantle xenoliths and the nature of core power activity

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The goal of this study was to check the hypothesis according to which the core energy activity is due to radioactive decay of U and Th contained in the core. The idea of such checking consisted in the following: to identify xenoliths of the geochemically closed primitive mantle (PM) material, to determine concentration of U and Th in them and using balance calculation to estimate the content of these elements in the core which is a complementary reservoir to the PM. Original analytical data for 53 mantle xenoliths together with the numerous published data were analyzed. The material of geochemically closed PM was identified on the basis of MREE and HREE concentration, Al/Mg, Ca/Al, Mg/Si, Sr/Mg ratios and isotope composition of Pb and Os. Concentration of U (13-36 ppb) and Th (37-59 ppb) in such material is similar to that in chondrites, but lower than concentration of these elements, which would take place in silicate shell formed from chondrites after segregation of the core devoid of U and Th content. This deficiency is most distinctly apparent if to compare the U and Th concentration observed in the PM xenoliths with that in the silicate shell produced from CV-chondrites. All this allows us to assume that deficient elements of the primitive mantle are located in the liquid core complementary to it. The balance calculation showed that, according to the results obtained, the U concentration in the core corresponds to 19 ppb at initial concentration of Bulk Earth like that in Cl and 25 ppb at this initial concentration like that in CV. According to the calculations [1], such U content is high enough to generate a thermal energy from 3 up to 4.5 TW out of 7 TW attributed to the core. Taking into account that the estimated U and Th concentration in the core corresponds to the minimal value (because their content in the PM may be overestimated due to some contamination of xenoliths by hosted basalt) the hypothesis of the core power activity generated by radioactive decay of U and Th looks valid.

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Reference

A mechanism of fluid transport through minerals

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Previous explanations for the movement of aqueous fluids through rocks have concentrated on the availability of pre-existing pathways, such as grain boundaries and stress fractures (Kostenko et al., 2002). Such pathways undoubtedly play a major role in allowing easy access for fluid transport. However, there is a lot of evidence that fluids migrate through minerals, which are reactive in the presence of an interfacial fluid layer (Putnis et al., 2005; Putnis and Putnis, 2007). Using time-lapse photography, fluid movement through a single crystal of a simple salt is observed at room T and P and presents a model for more complex mineral systems, showing similar textural and compositional equilibration features. The pseudomorphic replacement of one phase by another is characterised by the development of porosity in the product phase. This porosity provides the pathway for mass transport through the parent phase, which is replaced by the product at a moving interface within the mineral during an interface-coupled dissolution-reprecipitation replacement process. Replacement textures commonly occur in relation to fluid-driven regional metamorphism and large scale metasomatism e.g the gabbro - to eclogite facies transition, western Norway (John et al., 2007), serpentinitization and rodentinization of the oceanic lithosphere and scapolitization of gabbro (Austrheim et al., 2007), suggesting that dissolution-reprecipitation is an important mechanism behind large-scale metamorphic and metasomatic processes.

References
Global volcanic emissions of SO₂, halogens and trace metals, 1998 - 2005

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We have quantified annualised global volcanic emission rates based on a compilation of measurements at 60 active volcanoes, for the years 1998 – 2005. The global mean emission rate is 16 Tg SO₂/yr, of which 9 Tg/yr (56%) is emitted by non-explosive activity. Corresponding mean annualised halogen emissions are ca. 4 Tg HCl/yr; 0.3 Tg HF/yr and 0.6 Tg HBr/yr.

There is, as expected, a large interannual variability, with measured global volcanogenic SO₂ emissions varying between 13.3 Tg/yr in 1998 to 21.3 Tg/yr in 2000; most of this variability was due to sustained emissions from two persistently degassing volcanoes (Popocatepetl and Miyakejima). There were no major explosive eruptive sources (no eruptions of VEI 5 or larger; 1 eruption of VEI 4) during this period. Extrapolation to account for the un-measured emissions at a further 58 active volcanoes may extend the annual average SO₂ emission rate to ca. 20 Tg SO₂/yr for the period 1998-2005.

Using this global volcanic sulphur emissions inventory as a basis, and combined with appropriate field measurements, we can now extend the analysis to make well constrained projections of the fluxes of other important volatiles (H₂O, CO₂); volcanic nano-particles, and volatile trace metals (e.g. Hg) to the troposphere, and thereby evaluate the importance of persistent volcanic degassing to global geochemical budgets. Considerable uncertainty remains over the trace gas and trace metal emissions to the stratosphere associated with explosive volcanic eruptions, due to a lack of appropriate measurements.

Geochemistry and genesis of the Qibaoshan gold-copper deposit in Shandong Province, eastern China

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The Qibaoshan is a medium-sized Cu-Au deposit located in a caldera near the east of Yishu deep fault zone. This deposit consists of two parts, the upper part is a gold-containing breccia pipe, and the lower part is a copper-bearing stockwork.

The caldera covers an area of 10-12 km² and rocks around it are distributed in ring shape. The inner ring consists of subvolcanics, such as pyroxene monzonite, quartz monzonite porphyry, and trachyandesite porphyry; the outer ring comprises predominantly of trachyte, trachyandesite and minor rhyolite. In southeast of the central intrusive body, there is a cryptoexplosive breccia pipe which develops gold and copper mineralization.

Mineral association of this deposit displays a clear vertical zoning, i.e., from 0 to -20 m, the dominant mineral is gold-bearing specularite; main minerals are commonly specularite, manganosiderite, quartz and minor amounts of pyrite and chalcopyrite from -20 to -70 m; and pyrite and chalcopyrite from -70 to -120 m. Wall-rock alteration is widespread in the ore district. Main alteration types are phyllic alteration, silicification and carbonatization, and in the deep part of the pipe there also develops potassic alteration.

Fluid inclusion studies show that the homogenization temperatures range predominantly from 250°C to 350°C. The estimated salinities of ore-forming fluids vary between 10.6 and 32.6 wt% equiv. NaCl. The main compositions of ore-forming solutions are characterized by enriched in Ca²⁺, Na⁺, Cl⁻ and depleted in Mg²⁺, K⁺, F⁻. The F⁻/Cl⁻ ratios of hydrothermal fluids increased obviously from the main mineralization stage to late mineralization stage, indicating that the ore materials were transported predominantly as chloride complexes.

The δ³⁴S values of sulfides vary between 0.30‰ and 3.59‰, with a δ³⁴SΣS value of 2.80‰. Overall, the H, O and S isotopic data suggest that the ore-forming fluids and materials might be originated mainly from magmatic source.

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Hydrous and anhydrous metal formates – Properties and applications

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Synthesis and Results
The metal formate hydrates are synthesized by reaction of metalcarbonate, metalhydroxide or metaloxide and formic acid in an aqueous solution. The crystallisation process takes place at a temperature of 20°C.
The characterisation of the crystals was done by X-ray diffraction, thermogravimetry, scanning electron microscopy and Karl-Fischer-titration.

Figure 1: SEM image of Cu(HCOO)₂, dehydrated from Cu(HCOO)₂·4H₂O at 20°C and the crystal structure

Discussion
It is important to investigate the crystallographic properties of the formate and their stability to investigate in further experiments the effect on acceleration and retardation of formates as admixture in Ordinary Portland Cement. In addition, we investigate the dehydration and decomposition of the metal formate to produce particles in nanometer size. The metal carboxylate are suitable because of their low decomposition temperatures.

Conclusion
By using the crystallographic information of hydrous and anhydrous metal formates, theoretical predictions for applications are be obtained.

References

Molecular dynamics simulations of fission track annealing in apatite

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Our aim is to use molecular dynamics simulations to elucidate how the composition of apatite minerals Ca₁₀(PO₄)₆(F,Cl,OH)₂ affects the annealing rate of the natural fission tracks, which form in the apatites as a result of the spontaneous fission of uranium. Knowledge of the effects that the many species present in natural apatites, particularly fluoride, chloride and hydroxide, have on the annealing rate is invaluable in interpreting accurately the results of fission track data for geothermochronometry.
The fission tracks formed by uranium fission in apatite are typically 14 µm long and 50 Å in diameter. The formation of tracks in apatite can be adequately modelled using a method where atom velocities are altered perpendicular to the track, which model produces tracks which are consistent with those observed experimentally.
The simulations show that the diameters of tracks formed in two crystal directions are similar for a series of six apatites of different composition. In pure chlorapatite the simulated tracks are somewhat larger in both crystal directions, whereas in fluoride-bearing apatites small clusters of calcium fluoride are consistently formed in the track region.

Figure 1: Disrupted atoms looking down a fission track.
The apparent activation energy for biotite dissolution by in situ Atomic force microscopy (AFM) observations

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In this study we used in situ AFM imaging of biotite (001) surfaces to observe dissolution processes in oxalic acid and hydrochloric acid solutions in real time. In oxalic acid solutions at pH 2 and 1 we observe the combined dissolution processes of slow etch pit formation, followed by relatively fast etch pit growth. The etch pit depth is found to be consistent with the thickness of 1 \textit{tot} layer (~1 nm). Measurements of the fractional surface area covered by etch pits over time provide dissolution rates in the acid solutions. Experiments over a range of temperature, 10°C < T < 35 °C, in the pH 1 solution allow an estimate of the apparent activation energy, $E_a = 49 \pm 2 \text{ kJmol}^{-1}$ using the Arrhenius equation. We find that the average radius of etch pits grows linearly with time for all T, and use these growth rates to obtain a second value of $E_a = 53 \pm 3 \text{ kJmol}^{-1}$. We also find a linear relationship between the dissolution rate and the density of step edges on the surface for all values of T. However, $E_a$ is found to vary between ~ 40 kJmol\textsuperscript{-1} and >100 kJmol\textsuperscript{-1} at low and high step density, respectively. This variation may reflect the greater energy required for etch pit formation compared with etch pit growth. In an HCl solution of pH 1 we do not observe the formation of discrete etch pits, but a more general degradation over the entire biotite (001) surface. We conclude that etch pit occurrence in the oxalic acid solution proceeds through chelation of aluminium ions in the (001) surface by the oxalate ligand. This may destabilize the silicate structure, leading to the removal of the entire \textit{tot} layer, as observed. In the HCl solution the aluminium cations are less soluble due to the lack of organic ligand so the silicate structure remains intact.

Metal silicate partitioning of Ge, Mo, Ga and P: Constraints on core formation

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Siderophile element signatures in Earth’s mantle are a result of segregation of the iron rich core from the silicate mantle. It is generally argued that during the metal silicate differentiation process these elements were substantially partitioned into the core leaving behind lithophile elements in the silicate mantle. Several core formation models have been proposed to account for the observed abundance of elements in mantle rocks. A recently proposed model [1] suggests that the core formed at the base of a magma ocean which deepened with accretion and in which conditions became more oxidising with time. This also accounts for 5-7% Si in the core.

To test this hypothesis of early reducing magma ocean [1] we are studying the metal silicate partitioning behaviour of selected siderophile and nominally lithophile elements, characterizing the dependence of the metal silicate partition coefficient, D, on oxygen fugacity. We report new experimental results on the partitioning behaviour of Ga, Ge, Mo and P, and these are compared with our previous work on Si, Ta, Nb and V. All these elements can exist in variable and high oxidation states and their partitioning could also be sensitive to silicate melt composition [2]. Experiments were made at 2 GPa and 2000 K, over a range of relative oxygen fugacities from ~IW-2 to IW-6. Silicate melts range from basaltic to peridotitic in composition. The melt compositional parameter, NBO/T, is used as a proxy for silicate melt composition, and has values from 0.7 to 4. Isobaric, isothermal data for each element were regressed using the equation:

$\ln D_{\text{met/sil}} = a + b fO_2 + c(NBO/T)$. 

Regressions show that at the experimental conditions Ge has a likely valence state of +2, Ga, Nb and V exist in 3+ valence states, Si shows a valence state of +4, whereas P and Ta appear to exist in a 5+ valence state. Observing the partitioning behaviour of these elements over the redox range investigated, Si exhibits the least siderophile tendency and it appears unlikely for 5-7% Si to sequester into the core under reducing conditions without disturbing the mantle’s budget of other siderophile and refractory lithophile elements. Further experiments are in progress to provide more constraints on the influence of fO\textsubscript{2} and melt composition on the metal silicate partitioning of these elements.

References
[1] Wade & Wood (2005), \textit{EPSL} 236, 78-95
Chemical stratigraphy of UG2, Bushveld Complex, SA: Comparison of analytical methods

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The aim of the detailed investigation was to develop and to validate the EDXRF method as a fast tool to outline zones of interest regarding PGE, Ni and Cu mineralization by using these and other pathfinder elements.

Several methods were applied to obtain geochemical, mineralogical and textural information from UG2-chromitite horizons.

The fastest information was obtained by profiles along half cores using the EDXRF-geoscanner with 250µm steps at 1 to 30 sec/point for major and trace elements. Elemental maps were collected by EDXRF-microscopy in 100µm steps, at 0.5 sec/step for selected areas. Polished thin sections were optically scanned, and investigated by SEM for PGE distribution. Besides these fast methods sub-samples (0.5 to 5 cm) with a more representative sample volume were analyzed by XRF for major and trace elements. The XRF glass beads were digested and analyzed by ICP-MS for REE. Another set of glass beads was produced in graphite containers, embedded in araldite, polished and analyzed for PGE by LA-ICP_MS. For control, the rest of the glass beads was digested in nitric acid and PGE were collected by the telluride precipitation method (Evans et al., 2003). Since our observation with SEM confirmed that most of the PGE minerals occur in the interstices of the chromite, selective leaching of the PGE and silicates by nitric acid in the microwave was performed.

Conclusions
A comparison of the methods shows that EDXRF-scanning is a fast and accurate tool to highlight areas of unusual Ni, Cu, PGE pattern. EDXRF mapping provides textural patterns for hand specimen scale and reduces the amount of polished sections needed. Ni, Cu anomalies could easily be verified by other methods (e.g. SEM). PGE distribution patterns have to be treated carefully, since nugget effects might occur or diffraction peaks obliterate the distribution pattern.

Reference

Lithogeochemistry of parautochthonous Variscan metasediments (Northern Portugal). Implications of metamorphism and metassomatism

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The studied metasedimentary rocks, belonging to different lithostratigraphic units, are inserted in the lower Parautochthonous of Galiza Trás-os-Montes Zone (2GTM), in Northern Portugal Variscan belt. The studied area involve two geographic sectors separated by the Regua-Verin fault. In the western block of the fault the metasedimentary rocks are intruded by abundant pegmatite-aplite bodies and quartz veins and show higher metamorphic conditions: staurolite to biotite zone. In the western block the metamorphic condition are biotite to chlorite zone.

The metasedimentary lithologies are mainly phyllite and quartz-phyllite rocks in an imbricate structure. Lithogeochemical studies revealed a slow sedimentary sorting and high geochemical maturity in both sectors. The Th/Sc versus Zr ratios indicates, for the two sectors, a geotectonic environment ranging from an Active Continental Margin (ACM) to a Continental Insular Arc (CIA).

The normalization to upper continental crust (UCC) diagrams showed that similar lithologies present geochemical variations according to their proximity to the pegmatite-aplite veins. Next to the veins a deficit in mobile elements in fluid phases are evident, namely in, Rb, U, Th.

Figure 1: Crustal normalization of samples near and far from pegmatite-aplite veins.

So, the lithologies next to the aplite-pegmatites had been affected by fluid circulation (metassomatic effects) in a high temperature and low pressure (HT-LP) metamorphic conditions, while the lithologies in the both sectors, far from these intrusive bodies, present a isochemical metamorphism.
Nd isotope is a powerful indicator tracing the provenances of eolian materials [1]. However, Nd isotopic characteristics of different particle sizes of eolian materials are unknown in detail yet. We report here $\varepsilon_{\text{Nd}}(0)$ values in different grain sizes of eolian dust in the Duanjiapo section of Chinese Loess Plateau and eolian sand in the Mu Us Desert (Table 1 and Fig.1).

<table>
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<th>&gt;45</th>
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<th>&lt;2</th>
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</tr>
<tr>
<td>Red-clay</td>
<td>-9.1</td>
<td>-8.9</td>
<td>-8.7</td>
<td>-8.6</td>
</tr>
</tbody>
</table>

Table 1 $\varepsilon_{\text{Nd}}(0)$ in different grain sizes ($\mu$m) of eolian dust

Eolian dust in the Duanjiapo section is fine, mostly <75$\mu$m, whereas the Mu Us desert sand is coarse, mainly >75$\mu$m in diameter. $\varepsilon_{\text{Nd}}(0)$ values change little with grain sizes of eolian dust, moreover, are similar among loess, paleosol and red-clay (Table 1), suggesting a uniform source region. But, different grain size fractions of desert sand have obviously different $\varepsilon_{\text{Nd}}(0)$ values (Fig.1), implying they have different provenances. In addition, $\varepsilon_{\text{Nd}}(0)$ values of different grain-size fractions of desert sand are all more negative than those of eolian dust in the Duanjiapo section, showing the Mu Us desert is not its main source region.

As a result, the Mu Us desert sand is distinct in Nd isotope from eolian dust in the Duanjiapo section, both are probably little related in provenance.

References
Coupling crushing and laser ablation in submarine glasses provide new constraints on noble gases composition of Earth’s mantle

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Rare gases released with traditional experimental procedures in mantle-derived rocks generally display mixing trends between a mantle and an atmospheric component. The origin of atmospheric contamination is still debated and is interpreted to result from surface contamination or recycling in the mantle.

In order to examine this problem, we analyzed noble gases in single vesicles in submarine glasses, because it gives the possibility to look at the end members. Here, we compare data obtained by crushing and by measurement of in single vesicles using a laser UV ablation system on two samples: 2πD43, considered to be representative of upper mantle volatiles from the northern MAR, and one from the western Galapagos, which appears to sample one of the most primitive mantle noble gas reservoirs.

Helium isotopic ratios in single vesicles are constant for both MORB and OIB sample with a mean values of 90,500±3,500 and 32,000±1,000, respectively. The systematic Ne-Ar in single vesicles of sample 2πD43 indicates that there is only one population of vesicles, with a mantle composition (the mean value of 40Ar/36Ar is 25,000±4,000 and is associated to a 20Ne/22Ne of 11.5±0.6). This lower 20Ne/22Ne ratio compared to those measured by crushing can be explained with a small contribution of gases, with an air-like composition, dissolved in the matrix. We conclude that isotope variations observed by crushing are due to superficial contamination.

In contrast, analyses from individual vesicles of the Galapagos sample show heterogeneities on the scale of individual vesicles (40Ar/36Ar ratio vary from 3,000±500 up to 7,500±300 and being associated to a 20Ne/22Ne from 10.3±0.5 to 11.9±0.3). Such high 40Ar/36Ar values are not observed during crushing.

Application of statistical methods in geochemical anomalies identification, Baidjan area, North of IRAN

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Methods

Baidjan Exploration Area is situated in the South of Amol, North of Iran, Whose total surface area is 140 km². A total of 264 samples of the fine grained fraction of active stream sediments were collected and were analysed by ICP-MS method. Chemical variable after replaced censored data and normalized on the base of upper stream rock unit processed and mapped by means of R_mode factor, K¬_Means Cluster and Scatter plat methods.

Discussion and result

In these ways were determined three anomaly area in north, centre and west of exploration area. In the north and most important promise point, anomalies at the local scale were identified for Au (up to 37 ppb) and As (95.4 ppm). In this anomaly area, the correlation between these threshold values and silisified carbonate or carbonate hosted silisic veins is clearly shown. The second anomaly point, in central of exploration area, anomalies at a local scale were identified for Ag (up to 3 ppm), Sb (up to 5.6 ppm), Bi (up to 2.2 ppm), Zn (up to 231 ppm) and Cu (up to 72.8 ppm). This anomaly reflected mainly a local distribution of the outcropping rock type, mainly silisified andesit and basalt that malachite and azurite in the silisic zone or veins clearly shown. The west anomaly shown threshold obtained for REE, especially Ce (up to 541 ppm) and La (up to 104 ppm) and Cu (up to 70 ppm). This anomaly was correlated to altered Eocene tuffite.

Conclusion

The high grade of Ce, La and relatively Au, Cu and Zn and association with favourable geological phenomena, ambient needing further validation, gave some indicative references to the economic potential of this area for these elements mineralization.

Reference

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Detection of hydrocarbon micro-seepage using geo-microbiological method: A case study from Deccan Syncline, Maharashtra, India

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Geo-microbial method for hydrocarbon exploration is the search for surface microseeps as clue to the presence of an active petroleum system and / or to the location of possible oil and gas accumulation. It is a surface prospecting technique used to detect the anomalous population of hydrocarbon oxidizing bacteria in the surface soils, which indicate the presence of subsurface oil and gas accumulations. This method is based on vertical seepage of light hydrocarbon gases (C_1 - C_4) from the oil and gas pools to the shallow surface, and are utilized by hydrocarbon oxidizing bacteria. These bacteria utilize hydrocarbon gases as their only food source and are found enriched in the near surface soils above the hydrocarbon bearing structures. These hydrocarbon-oxidizing bacteria used as indicators of invisible hydrocarbon microseepage, and are used to evaluate subsurface hydrocarbon potential. Microbial activity profiles have indicated a good contrast between oil producing and non-oil producing areas.

This paper presents geo-microbial study carried out in Deccan Syncline areas of Maharashtra. In the present study, propane-oxidizing bacteria were considered as indicator microbes as propane gas originates from petroleum pools only. Sub-surface soil samples were collected aseptically in an interval of 5 x 5 km, and analyzed for propane oxidizing bacterial concentration. The propane oxidizing bacterial count in the soil samples of the studied area ranged from 1 x 10^2 to 6.7 x 10^5 cfu/gm of soil sample. Two microbial blooms of high concentration of propane oxidizing bacteria were identified and mapped in the study area. Microbial prospecting method has emerged as an important tool for hydrocarbon prospecting and integration of microbial data along with geological, geophysical, and geochemical data, can lead to the successful grading of exploration leads and prospects. The success rate of Microbial Prospecting for Oil and Gas is upto 90% (Wagner et al., 2002). The paper presents the details of microbial prospecting methodology developed at National Geophysical Research Institute and its importance in hydrocarbon exploration.

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Evidence for the collapse of upper water masses during ice-rafting events: a multi-species planktonic foraminiferal δ^{18}O approach

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We have measured δ^{18}O in three planktonic foraminiferal taxa Neogloboquadrina pachyderma (s), Globigerina bulloides, Globigerinoides ruber and benthic foraminifera Cibicidoides wuellerstorfi from IODP Site U1313. Concentration of the ice-rafted debris (IRD) and benthic foraminiferal assemblages were also counted. We found similar δ^{18}O values from mixed-layer and thermocline-dwelling planktonic foraminifera during the large amplitude IRD-events suggesting the collapse of upper water masses. This data suggests that the planktonic foraminifera taxa calcified their shells at similar temperatures in a homogenized upper water column. Similar collapse can be seen from the northern margin of the IRD-belt, implying that this homogenization of water masses were widespread in the region. We suggest that an increase in storminess during large IRD event intensifies vertical mixing of meltwater from ice-rafting in the upper ocean. Lighter δ^{13}C values correspond to those large IRD-events suggesting coupled perturbation of both surface and deep waters at the subtropical latitude.
Trace elements fractionation in Ca-rich and Ca-poor alkaline-ultrabasic series

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Two separate coexisting series, high-Ca melilite-bearing rocks and more common melilite-free alkaline-ultrabasic rocks, compose the alkaline-ultrabasic association in carbonatite massifs of Maimecha-Kotui Province, NW Siberian Platform [1]. Two analogous series are now known also in other complexes.

The trace element distributions (XRF and ICP data) in the above rocks, comparable in differential degree, from the different massifs, are clearly different. Their logarithmic relations in the sequential derivatives of the series, resulted due to fractionation according to the Rayleigh model, with different partition coefficients; then quite different rock-forming and trace element contents and their zoning patterns in coexisting minerals (EPMA data), dependent on their affiliation to the above series; as well as recent results of melt inclusion investigation in olivine of melilite-bearing rocks from the Guli and Kaiserstuhl complexes, suggest that two parent primary magmas do exist. The separate primitive magma, essentially richer in Ca, was preliminary carbonatised and enriched in Sr, REE, and Nb. Ca-poor magma can fractionate during its ascent from great depths. In turn, primary magma with higher Ca, parent for melilite-bearing rocks, fractionates only at shallower depths where CO₂ activity is lower and oxygen fugacity during crystallization of the melilite-bearing rocks is higher, as compared with conditions during differentiation of Ca-poor magma.

Acknowledgement
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Reference

Orbital Forcing, Timescales, and the Pacing of Global Glaciations

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Not long after Hays et al. (1976) proved that orbital variations control climate, the technique of using orbital pacing inherent in climate proxy records to improve geologic time scales was developed. Orbital-tuning of marine or terrestrial records requires assumptions about what specific component of insolation is forcing (usually indirectly) the climate proxy, as well as the magnitude of the lag between this forcing and the climate proxy. Despite these uncertainties, the time scales developed resulted in a significant improvement over paleomagnetic time scales and even led to a reassessment of the errors inherent in radiometric dating techniques. Recently, the orbital tuning of the O₂/N₂ ratio of trapped air in Antarctic ice cores (e.g. Kawamura et al., submitted) is based on a direct physical link between local summer solstice radiation and ice metamorphism; this new method may prove to be a gold standard for orbital tuning as well as make the essential point that not all orbital tuning is equally uncertain.

The extension of ice core records into the early Pleistocene, combined with O₂/N₂ time scales, should allow assessment of one of the major drawbacks of the marine δ¹⁸O record; namely, that it does not speak to where, geographically, the ice volume component of climate variance originates. Since the development of the δ¹⁸O proxy the general assumption has been that the ice volume signal of the last 3 Ma originated almost entirely in the Northern Hemisphere with little variance contributed by the Southern Hemisphere. By contrast, we have recently proposed (Raymo et al., 2006) that from ~3 to 1 Ma a terrestrial ice margin sensitive to local summer insolation may have characterized much of the East Antarctic ice sheet. Because Earth’s orbital precession is out of phase between hemispheres while obliquity is in phase, 23 kyr changes in ice volume in each hemisphere would cancel in globally integrated proxies such as ocean δ¹⁸O or sea level leaving the in-phase obliquity (41-kyr) component of insolation to dominate the record. To test this idea for the origin of the 41-kyr world, well-dated proxy records sensitive to local climate and the lateral movement of ice margins (in both the NH and SH) are needed. Would such records show precessional and obliquity pacing?

References


238U- and 232Th-decay series constraints on the timescales of generation and degassing for phonolite erupted in 2004 near Tristan da Cunha

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Phonolite pumice found floating offshore of Tristan da Cunha following intense seismic activity 20 to 30 km southeast of the island July 29-30, 2004 was analyzed for 238U- and 232Th-series nuclides including 230Th, 226Ra, 210Pb, 210Po, and 228Th. The initial (210Po/210Pb) value of 0.16 for the phonolite shows that, like most subaerial lavas, this subaqueous tephra degassed most of its 210Po upon eruption. The (230Th/232Th) and (238U/232Th) values for the phonolite are similar to those of more mafic magmas from Tristan da Cunha. However, in contrast with trachyandesites erupted in 1961 from Tristan da Cunha (Oversby and Gast, 1968), the activities of 210Pb and 230Th are both strongly enriched with respect to 226Ra in the phonolite, which is likely due to 226Ra partitioning into feldspars and hornblende in the decades leading to eruption. Moreover, the initial (230Th)/232Th) value was 0.94±0.03 (1σ), suggesting that Ra was being fractionated from Th until just before eruption. The (230Th/232Th) and (238U/232Th) values for the phonolite are similar to those of more mafic magmas from Tristan da Cunha. However, in contrast with trachyandesites erupted in 1961 from Tristan da Cunha (Oversby and Gast, 1968), the activities of 210Pb and 230Th are both strongly enriched with respect to 226Ra in the phonolite, which is likely due to 226Ra partitioning into feldspars and hornblende in the decades leading to eruption. Moreover, the initial (230Th/232Th) value was 0.94±0.03 (1σ), suggesting that Ra was being fractionated from Th until just before eruption. These disequilibria were modeled to have resulted from continuous crystal fractionation for about 2 centuries assuming that the fractionation began with a 1961-like trachyandesite and involved hornblende, anorthoclase, apatite, and sphene. The implied fractionation rates are 2-3×10⁻³ y⁻¹, which are one to several orders of magnitude faster than has been calculated for most other magmas. Nevertheless, these rates are similar to those calculated for the relatively low volume (0.1 km³) trachyte erupted from Fogo in 1563 (Snyder et al., 2007). These data imply that the 2004 magma was not the differentiated cap of a much larger magma body that remained at depth. Instead, it was likely the residue of a relatively small magma body that migrated rapidly through the crust southeast of Tristan da Cunha and underwent extensive and rapid crystal fractionation.

References

Carbon isotopes vs temperature: Contact metamorphism in graphitic metapelites at western Venezuela

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Isotopic characterization of graphitic materials associated with the metamorphic aureole of the La Soledad Granite and the non-carbonatic phyllites of Cerro Azul Association, at western Venezuela, was used to evaluate the correlation between the variations in δ¹³C with the progress of the metamorphic process.

Raman spectroscopy was used to evaluate the graphite crystallinity and the maximum metamorphic temperature reached. Additionally, petrographic determination was also applied in this work. The mineralogical assemblage and the presence of andalusite mineral indicated an intermediate metamorphism.

The intrusion process produced, at the contact zone, an increase of δ¹³C (from -28.3 to -27.5‰) which could be linked with the temperature gradient and hydrothermal fluid action. Isotopic signals showed greater dispersion in zones closer were higher hydrothermal activity was present. However, isotopic data cannot be employed in the evaluation of the metamorphic grade of the rock, because no correlation was found with the calculated temperature derived from spectroscopic parameters (528 to 510 ± 16 °C ). Just a weak correlation with %C (0.4 – 2 %C) in the bulk rock was observed, demonstrating that other aditional factors than kinetic ones could be involved.

Several parameters are affecting %C and δ¹³C in the studied zone, these are: a) temperature; b) composition of hydrothermal fluids and c) the reactions between hydrothermal fluid with the mineral assemblage present in the the rock, as well as with graphite. Results allow us to infer that, for this type of geological environment, isotopic signature of graphite must not be employed as geothermometer.

References
Dissolution of biogenic silica in the sediments of the Scheldt continuum

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The riverine fluxes of N and P have been significantly increased by human activities, while the anthropogenic input of Si to the Scheldt estuary is considered to be negligible. This excess delivery of N and P compared to Si has affected the phytoplankton speciation and succession in the Belgian coastal zone. The regeneration and retention of Si in the estuary, and particularly in the sedimentary column, is still poorly known. During the year of 2004, surface sediments and cores were collected along the Scheldt continuum. Dissolution kinetics of biogenic silica (BSi) was carried out in batch reactors for several months on sediments from different locations and depths, and the effect of salinity on the dissolution rate was investigated. Preliminary results show that the salinity effect is stronger for low salinity values, but becomes negligible for higher values. Our results also exhibit high BSi dissolution rates in the second centimetre of the sediments cores, with lower values in the first centimetre but also at depth. These results are coherent with the BSi profiles, as well as the microscopic observations of the sediments that showed a higher abundance of biogenic opal debris in the second centimetre with respect to the first centimetre. A model taking into account a two-phase dissolution was used to fit the experimental data, the two phases considered corresponding to biogenic and lithogenic silica, respectively. Overall, the dissolution rates are low and the amorphous silica saturation concentration is never reached, suggesting that the recycling of the biogenic material in the sedimentary column is very low. Part of the opal reaching the sediments probably dissolves at the surface, while the rest is rapidly incorporated within the sedimentary column where dissolution continues along with other diagenetic reactions.

Controlling and predicting subsurface calcium carbonate precipitation for capture of inorganic contaminants

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In situ manipulation of biogeochemical conditions to induce the formation of mineral phases is one approach for immobilizing metal contaminants in subsurface environments. Examples include U and Tc bioreduction, engineered precipitation of U phosphate minerals, and microbially facilitated coprecipitation of ⁹⁰Sr in calcite. Strategies for controlling the formation and distribution of precipitated minerals usually require introduction of soluble chemical amendments to the subsurface. The challenges involve not only controlling the distribution of amendments and resulting reactions, but also predicting how permeability and flowpaths evolve as solid phases are deposited (including biomass). The changing flowpaths and geochemical environment will impact the propagation of solid phases and contaminant mobility. Computational models that can account for the scale-dependent coupling between physical, chemical and biological processes over a range of spatial and temporal scales are not well developed.

Experiments in 2- and 3-dimensional packed-sand media have been conducted where calcium carbonate precipitation and co-precipitation of Sr²⁺ is induced by one of two mechanisms. The first is by propagating calcium carbonate precipitates within the fluid-fluid mixing zone between two solutions that flow in parallel. The second approach involves in situ generation of carbonate, in the presence of dissolved calcium, by enzyme catalysed hydrolysis of urea. This is an analog for a natural biological process. In both cases, within the reaction zone, a wide range of saturation indices and ion ratios can be established at the pore scale depending on the relative rates of solute transport, mixing, and precipitation. Multiple precipitation modes (e.g., homogeneous and heterogeneous nucleation and growth), different carbonate phases, and varying morphologies can occur in close proximity. The thermodynamic, kinetic and physical control of precipitate deposition influences Sr partitioning in the porous media, as well as permeability and flow paths in the porous media.

We have simulated solute mixing and flow modifications at the pore scale using the Smoothed Particle Hydrodynamics (SPH) method. Continuum-scale simulations of the experimental results were also conducted using grid-based methods. A goal is to use SPH simulations as the basis for parameterization of macroscopic finite-element multi-component reactive transport models, correlating results from the two model scales with our experimental results.
Rapid hydrogen isotopic exchange between aqueous hydrocarbons and water under hydrothermal conditions

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Numerous experimental studies have investigated D/H isotopic exchange between sedimentary organic matter (e.g., kerogen/oil) and ambient water during thermal maturation (Schimmelmann et al., 2006). However, isotopic exchange involving low molecular weight hydrocarbons and water has revealed relatively little attention. Due to its high activation energy for exchange, alkyl-bound hydrogen (H) is widely considered to be isotopically conservative and incorporation of water-derived H is assumed to be limited to cracking reactions during catagenesis.

We conducted experiments to investigate D/H exchange between aqueous n-alkanes and water using a flexible cell hydrothermal apparatus. C₃–C₅ n-alkanes were heated at 325°C and 350 bar in aqueous solutions of varying initial D/H ratio (δD) in the presence of a pyrite-pyrrhotite-redox buffer. Extensive incorporation of water-derived H into C₂–C₅ n-alkanes was observed on timescales of months. In contrast, relatively little incorporation was observed for CH₄. Isotopic exchange observed on timescales of months in reducing aqueous environments, reaction mechanisms exist involving low molecular weight hydrocarbons and water has received relatively little attention. Due to its high activation energy for exchange, alkyl-bound hydrogen (H) is widely considered to be isotopically conservative and incorporation of water-derived H is assumed to be limited to cracking reactions during catagenesis.

We conducted experiments to investigate D/H exchange between aqueous n-alkanes and water using a Au-TiO₂ flexible cell hydrothermal apparatus. C₁–C₅ n-alkanes were heated at 325°C and 350 bar in aqueous solutions of varying initial D/H ratio (δD) in the presence of a pyrite-pyrrhotite-redox buffer. Extensive incorporation of water-derived H into C₂–C₅ n-alkanes was observed on timescales of months. In contrast, relatively minor incorporation was observed for CH₄. Isotopic exchange appears to be facilitated by reversible equilibration of n-alkanes and their corresponding alkynes by the reaction:

\[ \text{C}_n\text{H}_{2n}(aq) = \text{C}_n\text{H}_{2n-2}(aq) + \text{H}_2(aq) \]  (1)

Where H₂(aq) is derived from water. The lack of substantial n-alkane decomposition on the timescale of observation, combined with an approach to steady-state isotopic composition, suggests that n-alkane δD values may reflect an approach to isotopic equilibrium rather than kinetically-controlled fractionation effects associated with degradation reactions. Substantially lower amounts of exchange were observed for ethane relative to C₃–C₅ n-alkanes, suggesting that alkene isomerization may enhance incorporation of water-derived H in these compounds. Thus, in reducing aqueous environments, reaction mechanisms exist that allow rapid D/H exchange of alkyl-H with water at elevated temperatures and pressures on timescales much shorter than previously assumed.

Reference

Nickel isotope anomalies in iron and chondritic meteorites

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⁶⁰Fe decays to ⁶⁰Ni with a half-life of 1.49 Ma, and can be used to obtain relative ages for meteorites and processes that occurred within the first ~10 Ma of the formation of the Solar System. Radiogenic ⁶⁰Ni variations of <50 ppm are expected in iron meteorites, given ⁵⁸W core formation ages of asteroids and an initial ⁶⁰Fe/⁵⁶Fe ratio of 4 x 10⁻⁷. However, previous studies have not been able to resolve the predicted variations in ⁶⁰Ni between magmatic iron groups having different Fe/Ni.

We have developed methods for high-precision Ni isotope analysis of metal and silicate samples. Ni is separated using a 3-stage ion exchange procedure, which includes dimethylglyoxime to yield a Ni fraction free of impurities, in particular Fe, Ti, Sn that potentially form interferences on Ni masses. Ni isotopic ratios are measured using a Finnigan Neptune MC-ICPMS in medium resolution mode in order to resolve ⁴⁰Ar/³⁰O from ⁵⁶Fe and correct for ⁵⁸Fe on ⁵⁸Ni (<5 ppm). ⁵⁸Ni signals of 900pA are measured on a Faraday detector equipped with a 10¹⁰ Ω resistor. Each sample was analysed a minimum of 4 times. Using this procedure we obtain a reproducibility of ~5 ppm on the ⁶⁰Ni/⁶⁰Ni ratio. Terrrestrial samples (JP-1, BHVO-2, NIST 361 steel) have Ni isotopic compositions that are identical within error of the SRM 986 standard.

Our results show that magmatic iron meteorites have variable ⁶⁰Ni/⁶⁰Ni, ranging from a terrestrial value in high Fe/Ni group IIAB, to ~15 ppm deficits of ⁶⁰Ni in low Fe/Ni group IVB samples. Although a positive Fe/Ni/⁶⁰Ni/⁶⁰Ni correlation is consistent with ⁶⁰Fe decay, we find that ⁶⁰Ni/⁶⁰Ni ratios are inversely correlated with variations in ⁶²Ni/⁶⁰Ni, which are likely to be of nucleosynthetic origin. Moreover, ordinary chondrites (LL) and volatile poor (CV) carbonaceous chondrites cover the same range in Ni isotopic composition as seen in the magmatic iron meteorites. These combined observations show that Ni isotopic heterogeneity within bulk planetary samples is widespread, but do not yield clear evidence of live ⁶⁰Fe during planetesimal core formation. Bizzarro et al. (2006) have previously noted variable ⁶²Ni/⁶⁰Ni in bulk meteoritic material but our different sample set illustrates several contrasting systematics. In particular, we find that iron meteorites have ⁶⁰Ni/⁶⁰Ni both higher and lower than terrestrial values. We suggest that Ni isotopes may provide a valuable means to link iron and chondrite groups, with IVB samples apparently derived from a CV-like parent body and IIAB from LL chondrite. Interestingly, the only meteorite group we have found to have Ni isotopic systematics identical to Earth are the enstatite chondrites.
Influence of model aggregation on the parameterization of biogeochemical reaction kinetics in ecosystem models

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Marine biogeochemical models focusing on organic matter production and consumption are compared to study the effects of complexity on model results. The various models differ in their level of spatial and biogeochemical detail. Reduction of biogeochemical complexity is performed by aggregating the highly detailed, physiologically based, MIRO model (Lancelot et al., 2005). In particular, we investigate the relevance of biogeochemical rate constants, determined in situ or through lab experiments, for ecosystem modeling. Results show that models characterized by distinct levels of spatial resolution provide different quantitative estimates of the biogeochemical rates, especially those strongly influenced by the system’s heterogeneity. An aggregation of different functional groups or the microbial loop also requires an adaptation of reaction rate constants. The rate constants of the aggregated model have to account implicitly for the processes, which are no longer explicitly included. A direct transfer of rate constants determined experimentally or by the calibration of other models is thus strongly dependent on the respective model formulation.

References

Contrasting evolutionary trends in magnetite from carbonatites and alkaline silicate rocks

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Magnetite (Mgt) is a common accessory mineral in carbonatites and associated alkaline rocks, and a sensitive petrogenetic indicator. We examined the chemical evolution of Mgt in calciocarbonatite (MCrb) and ijolite (MIj) from Kerimasi, Tanzania. MCrb is characteristically enriched in Mg (0.18-0.32 apfu), Mn (0.05-0.14 apfu) and Al (0.01-0.26 apfu), but depleted in Ti (0.04-0.11 apfu) with respect to MIj (< 0.08 apfu Mg, 0.03 apfu Mn, 0.04 apfu Al, and > 0.21 apfu Ti). MCrb has much lower levels of Cr, V, Co, Ni and, to some extent, Nb (< 16, 1210, 120, 100 and 17 ppm, respectively), but noticeably higher Zn (1310-2770 ppm) than MIj (up to 1880 ppm Cr, 1800 ppm V, 190 ppm Co, 210 ppm Ni, 46 ppm Nb and 1150 ppm Zn). The two samples are virtually identical in terms of their Ga, Zr, Hf and Ta contents. MCrb shows a trend of decreasing Ti and increasing Mn (at nearly constant Mg) from the earliest generation to crystallize (macrocryst cores) toward the latest (rims and small groundmass grains). The early generation of MCrb is also distinguished by its higher V, Nb and Nb/Zr values. In ijolite, we distinguished two varieties of magnetite differing in their Mg, Ti, V, Ga, Nb, Ta, Co and Hf contents. The two types are also characterized by very different Zr/Hf and Co/Nb ratios. Both varieties show a trend of increasing Mg, V, Zr, Nb, Hf and decreasing Ti and Ga from the earliest generation (subhedral crystals) to the later-crystallized interstitial grains. There is also a trend of increasing Ta in variety-one magnetite, whereas variety-two is Ta-free. The significant differences in major- and trace-element chemistry of the studied carbonatite and ijolite indicate that these rocks did not originate from a single magma, but are products of two distinct magmas characterized by different distribution coefficients of trace elements with respect to magnetite.
Characterizing Fe-rich dunite xenoliths as cumulates of Phanerozoic and Archaean flood basalt magmatism

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Fe-rich dunite xenoliths occur amongst a large abundance of mantle xenoliths, in the kimberlites of the Kimberley cluster, but their origin has been unclear. On the basis of texture, major and trace elements, as well as Re-Os isotope characteristics, we interpret these dunites as cumulates of flood basalt magmatism related to the ~183 Ma Karoo and the ~2.7 Ga Ventersdorp events in southern Africa.

The Fe-rich dunites mainly comprise olivine neoblasts with subordinate olivine porphyroclasts and parallel-oriented needles of ilmenite, which enclose spinel in some samples. Olivines have lower forsterite and NiO contents than mantle peridotite xenoliths (Fo87-89 versus Fo93-95 and 1300-2800 ppm versus 2200-3900 ppm, respectively), which rules out a restitic origin. Cr-rich spinels are remnants of the original cumulate mineralogy that survived a late stage metasomatic overprint related to the production of the host kimberlite, producing ilmenite and phlogopite in some samples. Olivine porphyroclasts and neoblasts have different trace element compositions, the latter having higher Ti, V, Cr and Ni and lower Zn, Zr and Nb contents, indicating contrasting origins for neoblasts and porphyroclasts. The dunites have high 18O/16O ratios (0.11-0.15) indicating young (Phanerozoic) model ages for most samples, whereas three samples show isotopic mixtures between Phanerozoic neoblasts and ancient porphyroclastic material. Most Fe-rich dunite xenoliths can be interpreted as cumulates of fractional crystallization of Karoo flood basalt magmatism, whereas the porphyroclasts are interpreted to be remnants from the much earlier Archaean Ventersdorp magmatic episode.

The calculated parental magma for olivine neoblasts in Fe-rich dunites corresponds to low-Ti Karoo basalts, whereas olivine porphyroclasts had a parental magma with higher MgO contents similar to Archaean high-Mg and komatitic rocks. Modelling the crystal fractionation of the parental magmas with pMELTS yields element fractionation trends that mirror the element variation of primitive low-Ti Karoo basalts and the basal section of the Ventersdorp Klivriviersberg Group.

Volcanic Outgassing and the Tl Isotope Composition of the Oceans

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Thallium is a conservative element in seawater with a marine residence time of ~20 kyr [1]. It is thus unsurprising that the present oceans have a nearly constant Tl isotope composition of ε205Tl = -6 ± 1 [2-4]. This uniformity is also expressed in the recent growth surfaces of hydrogenetic ferromanganese (Fe-Mn) crusts, which incorporate seawater-derived Tl by adsorption and display ε205Tl = +13 ± 1 [2].

Time-series analyses of six Fe-Mn crusts from the Atlantic, Indian and Pacific Oceans revealed nearly constant Tl isotope compositions over the last 30 Myr. In contrast, it was also shown that the ε205Tl-values of Fe-Mn crusts changed dramatically from about +6 at 60 Ma to +13 at about 30 Ma [5]. This change has been confirmed by a recent high-resolution time-series study of the Pacific Fe-Mn crust CD29-2 [6].

Given these systematics, it is not unreasonable to assume that the time-series data reflect a change in the Tl isotope composition of seawater. Of particular interest is the possibility that the trend was generated by larger fluxes of Tl derived from subaerial volcanism in the early Cenozoic. This interpretation is in accord with observations that (i) volcanic emissions presently provide ~30% of the global input flux of Tl into the oceans [1], and (ii) such emissions may display low ε205Tl from 60 to 30 Ma may furthermore be essentially synchronous with the decrease of atmospheric CO2, as inferred from B isotope data [7], and a 5‰ shift in the S isotope composition of seawater sulfate [8]. It has been proposed that both of these changes could reflect decreasing rates of volcanic outgassing during the early Cenozoic [7, 8].

Preliminary Tl isotope data show that volcanic gases have ε205Tl-values as low as -8, and this demonstrates that changes in volcanic inputs may indeed alter the Tl isotope composition of the oceans. To further investigate this possibility, we will acquire Tl isotope data for a larger suite of volcanic emanations from Etna, Kilauea, Merapi, Vulcano and White Island.

References

Heavy isotope fractionation in the solar system – A volatile perspective

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It is well recognized that most solar system bodies are significantly depleted in volatile constituents relative to primitive CI chondrites but the origin of this signature is only poorly understood. Stable isotope studies of volatile elements in meteorites are well suited for addressing this fundamental question. This conclusion is underlined by the observation that for chondritic meteorites, heavier but more volatile elements (such as Cd) typically display larger isotopic effects than lighter and less volatile constituents (e.g., Zn). This suggests that partial vaporization and condensation play an important role in generating stable isotope variations [1-3].

The isotope data acquired for a number of volatile elements indicates that stable isotope effects are generally much larger for ordinary than for carbonaceous chondrites. The large isotope variations determined for ordinary chondrites (e.g., ~25‰ for 114Cd/110Cd) are thought to reflect redistribution of volatile constituents by thermal metamorphism on the meteorite parent bodies [1,2]. In contrast, most carbonaceous chondrites display only small or no resolvable isotope effects of ≤0.15‰/amu for Ag, Zn, Cd, and Tl [1-5]. This demonstrates that the variable volatile abundances of carbonaceous chondrites reflect either partial equilibrium condensation/evaporation or mixing processes.

Refractory (CAI- & chondrule-rich) separates from Allende display light Cd and Zn isotope compositions (of about ~1‰/amu) relative to the bulk meteorite [2,3]. These signatures cannot reflect Rayleigh evaporation but are more readily explained by the interaction of refractory materials with a volatile-rich nebular gas. Such processes may also be responsible for the lack of nucleosynthetic isotope anomalies of volatile elements in CAI’s.

The short-lived 107Pd-107Ag and 205Pb-205Tl decay systems are well suited for studying the time scales of volatile loss in the early solar system. Such studies must be carried out with care, as Ag and Tl have only two isotopes, such that radiogenic and stable isotope effects may not be readily discernable. One example are the troilite inclusions of IAB irons, which appear to have Ag and Tl isotope compositions that were fractionated (~1‰/amu) by diffusion [6,7].

References

High-resolution geochemistry and lithology of laminated sediment in the Weddell Sea, Antarctica

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Methods
Sediment sites PS1789 and PS1791 from the southeastern Weddell Sea (Antarctica), were investigated for geochemical and lithological variability. We used several non-destructive means to obtain information at ultrahigh resolution (mm to sub-mm scale). An x-ray-fluorescence core scanner should reveal relative chemical composition of some selected elements. Magnetic susceptibility records were compared to counts of ice-rafted debris (IRD). We determined sediment color using both a photospectrometer, RGB readouts from a line scanner, and gray-scale images from x-radiographs. Stratigraphy relies on previously published AMS14C dates.

Results
The glacial sediment sections reveal mostly laminated sediments and rarely intercalated fine-grained turbidites. Bioturbated section occur at the top and are linked to Holocene or late-glacial times. Geochemical composition is relatively stable during the glacial; only bioturbated sediment shows elevated Fe and diminished Al and Si contents, whereas turbidites reveal the opposite.

In order to reveal whether or not the laminations is a result of an interannual (seasonal) variability, we developed tools for semi-automated layer counting of the gray-scale scans. First results indicate that the lamination is most likely an innerannual process, e.g., site PS1789 contains 4860 visually detectable layer between 199 and 1211 cm core depth, where AMS14C dates indicate an age difference of 2430 years, i.e., more than 90% of the expected layers encountered.

Future Work
More sites will have to be investigated to corroborate the preliminary stratigraphic results. Geochemical investigation will focus on the differentiation between the seasonal layers, i.e., there is a compositional difference between the darker and lighter layers documented in the gray-scale images or is the alteration caused by grain-size changes only.
In step with time: *In situ* geochronology meets microscale records of geologic processes

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The profound record of geologic phenomena at sub-millimeter scales can be revealed by *in situ* geochronology and geochemistry in the context of key textural relationships. Complementary in situ geochemical and isotopic analyses reveal, for example, fluid evolution during cementation, the evolution of low as well as high grade metamorphism, subduction and exhumation, and the nature and duration of crustal growth. The improved accuracy and precision of U-Pb dating at <50 µm by LA-ICP-MS is increasing use of this method for *in situ* dating, especially for provenance studies and reconnaissance geochronology. Efforts to develop more matrix-matched reference materials will continue to improve the accuracy of *in situ* dating and geochemistry.

Dating of igneous and environmental samples by 234U/238U and 230Th/234U disequilibria is also possible at a spatial resolution of <100 µm. Vazquez and Reid (2004) coupled in situ U-series geochronology with crystal-scale allanite chemistry to reveal a t-T-X record for heterogeneous accumulation of the voluminous Toba rhyolite. The advent of the Ti-in-zircon geothermometer (Watson and Harrison, 2005) will ensure further crystal-scale insights into magmatic processes. In situ 235U-231Pa zircon ages may augment 238U-230Th geochronology (Schmitt, 2006). For environmental samples that contain ≥1 ppm U, dating by LA-ICP-MS affords high-resolution reconnaissance studies that can cope with open systems like bones, teeth, and possibly molluscs without chemical preparation (e.g., Eggins et al., 2005). Fluctuations in initial (234U/238U) and trace element concentrations, such as those found in 2-200 µm thick opal layers in soils, can be linked to glacial-interglacial transitions by ionprobe 230Th/234U dating (Maher et al., in prep.).

Finally, extension of *in situ* laser analyses to (U–Th)/He geochronology enables dating of 25 µm domains for provenance and unroofing studies (Boyce et al., 2006).

References

Continental scale geochemical mapping and the geochemical background

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Since 1995, large domains in Northern Europe have been mapped at ever decreasing sample densities: 1 site/300 km² in the Kola Project, 1 site/1000 km² in the Barents Project and 1 site/2500 km² in the Baltic Soil Survey. The geochemical atlas of Europe, based on a sample density of 1 site/5000 km², was published in 2005 (see www.gtk.fi/publ/foregsatlas). Results demonstrate that such low-density geochemical mapping allows for the construction of robust geochemical maps of large areas at reasonable cost. The maps contain important new information and politically vital reference data about the varying levels of chemical elements in the surface environment at the continental scale.

The data demonstrate that there exist a number of natural processes that influence the regional distribution of chemical elements in the surface environment at a variety of scales. Many of the displayed large-scale patterns are surprising and unpredictable based on geological reasoning alone. The distribution of chemical elements at the earth surface has an important impact on animal and human health. Continental scale geochemical maps of a variety of sample media, reflecting different compartments of the ecosystem, are thus urgently needed.

The anthropogenic impact on the natural environment cannot be reliably judged and interpreted without continental-scale geochemical maps and sound knowledge and documentation of the geochemical background. The observed natural variation of element concentrations in all sample materials collected so far covers several orders of magnitude. The statistical definition of a geochemical background or action levels for, for example, metals in soils of Europe, is thus fraught with problems. Obviously there is no single "natural" background value that is valid for a large area. Rather background will change from area to area within a region and between regions. The inherent connections between scale and background variation are key features for understanding environmental processes.
EXAFS analysis of reactive nanoscale iron oxidation in water

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Nanoscale zerovalent iron particles rapidly degrade chlorinated solvent groundwater contaminants into non-toxic products in situ. The efficacy of this approach is partially dependent on the reactivity and longevity of the zerovalent iron, which is readily oxidized in groundwater. Oxidation on the surface of the nanoscale iron particle can passivate the particle, potentially resulting in lowered reactivity toward target contaminants. A fundamental understanding of the chemical and structural changes that occur as a result of oxidation at the nanoscale surface in aqueous systems is necessary to assess the related impacts on reactivity and to determine the ultimate utility of the particles towards remediative goals.

Nanoscale zerovalent iron particles (initially 70% Fe0/30% Fe3O4 core/shell particles) were allowed to oxidize in anaerobic water for various times ranging from a few days up to 1 year. The resulting iron particles with varying degrees of oxidation were studied using high intensity synchrotron radiation methods at Stanford Synchrotron Radiation Laboratory, beamline 11-2. Iron K-edge extended X-ray absorption fine structure (EXAFS) spectra provided element-specific information regarding the short-range structural order around iron in the nanoparticles. Fitting of the iron EXAFS spectra using model phase and amplitude functions allowed quantification of the direct relationship between oxidation time and relative amount of oxygen present in the atomic structure. Specifically, over the range of samples analyzed the average Fe-Fe coordination number declined from 8.2 ± 0.4 to 2.5 ± 0.3 while the average Fe-O coordination number increased from 1.2 ± 0.8 to 3.1 ± 0.9. The Fe-O and Fe-Fe interatomic distances and coordination numbers determined from the EXAFS fitting process were then compared to those of known crystalline iron oxides/oxyhydroxide phases in order to characterize the progressive structural transformation of the nanoparticles during their oxidation in water.

Metals from agriculture in oxic fluvial sediments: A case study in Western Iberia

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The transport of fine fluvial sediments and associated pollutants in mountainous rivers is very dynamic, in response to precipitation episodes. The present study highlights the impact of human activities, mainly farming, in a “natural” mountainous catchment in Northern Portugal, underlain by crystalline rocks, in a temperate climate. Some inferences regarding Cu, Pb, Zn and Ca concentrations, their spatial and temporal variability, and potential bioavailability in oxic fluvial sediment samples are presented.

The study was performed on the <63µm sediment fractions. The modified BCR sequential extraction procedure (Rauret et al., 1999) was used to assess metal contents in geochemical phases. The residual phase was decomposed by aqua regia. The element concentrations were obtained by ICP-AES.

The studied metals had contents in the ranges (ppm) Cu (1-99), Pb (5-154), Zn (29-448) and Ca (362-40860), showing higher contents in sampling stations located at those points draining areas with intense agriculture. These elements are common components of fertilizers, pesticides and animal manures (cow, horse, rabbit), the last widely used in the studied area. In these sites, the metals' relative contents present in the soluble, oxidisable, and organic fractions are considerably higher. However, differences in the distribution of the potential bioavailable fraction are observed, with marked increases in different phases: Cu in the organics, Zn in the soluble and oxidisable, and Pb in the oxidisable.

Calcium was also considered in this study. Although ubiquitous in natural water systems, its concentrations in the sediment samples are relatively high, considering the local geology (granites and schists). Calcium is a major component in the chemical fertilizers used in the studied area. Calcium is low in the residual fraction, owing to its geochemical behaviour, but is present in considerable amounts in the soluble fraction. The correlations between Ca and Cu, Pb and Zn are highest at the end of the dry period. The first autumn rain leads to increased transport of these elements, either by runoff or leaching of agricultural lands.

Reference

Microbially mediated formation of gold in calcrete anomalies in Australia

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Regolith carbonates (calcrete) are widely used in Au exploration in Australia, because Au, which is often finely dispersed in calcrete, and Ca are highly correlated suggesting co-precipitation. The genesis of carbonates in pedogenic environments is dominantly ascribed to microbial processes, in particular to microbially mediated carbonate precipitation via ureolysis. Contrary to a genesis model recently published by Lintern et al. (2006), Schmidt Mumm and Reith (2007) proposed a comprehensive coupled model that includes a microbial component, which may control Au and Ca co-precipitation (Fig. 1).

Figure 1: Model for the microbially mediated formation of gold in calcrete anomalies (Schmidt Mumm and Reith, 2007).

Using microcosms and microbial enrichment culture experiments to assess the ureolytic capacity of the bacterial community combined with molecular profiling (shotgun cloning and DGGE of 16S rDNA), showed that Bacilli spp. resident in calcareous materials at the Barns anomaly are capable of producing Au anomalous Ca-carbonates. Within 96 to 240 h from the start of the incubation the urea was turned over to NH4+, the pH in solution rose by approximately 1 unit to pH 9 and Ca2+aq was precipitated as Ca-carbonate crystals; in sterile the controls no carbonates were precipitated. Gold (been added as Au-aspartic acid complexes to the growth medium) was co-precipitated with Ca and uniformly dispersed in the dominantly vaterite crystals, as shown by laser ablation ICP-MS and SEM. These results suggest that microorganisms play an important role in the formation of Au anomalies in calcrete in Australia.

References

Origin of brines in the northern Gulf of Mexico

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Brines from the northern Gulf of Mexico show distinct differences with respect to element concentrations and oxygen, hydrogen, and strontium isotope signatures. Three sites at different water depth were investigated; Bush Hill, GC415 East, and GC415 West at water depths of 540, 950 and 1050 m, respectively. All three locations accommodate near-surface gas hydrates and chemosynthetic communities at the sediment surface. They are characterized by a distinct increase in salinity with depth, however, the origin of this increasing salinity is different for the GC415 sites and Bush Hill and the depth source of the brines is considerably different for all sites. The more saline brines of the GC415 sites result from the dissolution of halite (Fig. 1) by formation water. The brine of GC415 East has most likely a deeper origin and experienced elevated temperatures leading to intensive mineral/water reactions. This process is expressed by the heavier oxygen isotope values and distinct Li, Sr, and Ca enrichments. The brine of GC415 West has a shallower origin which is expressed by a smaller enrichment in Li, Sr, and Ca and lighter oxygen isotopes (Fig. 1). The brine from Bush Hill is less saline and its fluid signature indicates intensive water/mineral interaction. Oxygen (Fig. 1) and hydrogen isotope values as well as Na/Cl and Br/Cl molar ratios indicates that the salt enrichment could have been caused by phase separation under sub-critical conditions. A simple heat flow model simulation suggests sub-critical phase separation at a depth of ~1650 m at ~350°C.

Fig. 1: Cl vs. δ18O plot. Solid lines show the evaluation path of Cl vs. δ18O values for (i) evaporation at ~25°C, (ii) gas hydrate (GH) formation, (iii) illite formation, and (v) dissolution of halite; the field expected for phase separation (no fractionation) is indicated by the solid circle.
Molecular identification of the Deuterium-rich carrier in insoluble organic matter in carbonaceous chondrites


Insoluble organic matter (IOM) in primitive carbonaceous chondrites is known to be enriched in deuterium, with D/H ratios > 350×10^-6. It is also characterized by a high degree of isotopic heterogeneity, as demonstrated by the observation of D-rich “hot spots” in NanoSIMS ion microprobe images (Robert et al. 2006). Understanding the origin of this heterogeneity represents a fundamental challenge with implications for the origin and distribution of organics in the interstellar medium and in the protoplanetary disk from which our planetary system formed.

We have determined the carrier of the isotopically anomalous hydrogen in IOM isolated from the carbonaceous chondrite Orgueil. Electron Paramagnetic Resonance spectroscopy has shown that hydrogen in the benzylid bond of organic radicals has a deuterium to hydrogen (D/H) ratio of 1.25±0.75×10^-2 in Orgueil IOM, which is the highest solar system D/H ratio ever reported (Delpoux et al. 2007).

By combining these data with quantitative image analysis recorded at a high spatial resolution with the NanoSIMS, we are able to prove that the organic radicals can account for the deuterium excess in the IOM D-rich “hot spots”. Furthermore, the radicals fall on a well-defined trend between D/H ratio and C-H bond energy (Remusat et al. 2006), consistent with a new interpretation of the hydrogen isotopic variations in solar system organics according to which pre-existing organics exchange their D with highly deuterated gaseous molecules, such as H2D+ or HD2+. The distributions of these deuterated species is now being mapped in protostellar disks (Ceccarelli and Dominik 2005).

This conclusion runs contrary to previous interpretations, according to which the IOM is an interstellar product reprocessed in the protosolar gas and deuterium-rich “hot spot” relics of pristine interstellar organic matter, which escaped solar nebula or parent body processes.

References

Delpoux O. et al. (2007) 38th LPSC, #1138.

The effects of sodium and chlorine on the solubility of molybdenum in aqueous vapour

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There is growing evidence that the solubility of Mo in water vapour may be high enough for metal transport in the vapour phase to be an important mechanism in the formation of porphyry Mo deposits (Rempel et al., 2006). Molybdenum is typically considered to be transported as a hydrated oxide, but research on Mo speciation in H2O-free vapour suggests that the formation of Mo oxochlorides and sodium molybdates may be important (Hultgren and Brewer, 1956; Choudary et al., 1975). This study reports the results of experiments designed to investigate the effects of Na and Cl on Mo solubility in high-temperature water vapour.

The experiments were conducted in NaCl- and HCl-bearing aqueous vapour at 350°C and 60-160 bars. At fHCl<0.5 bars, Mo concentration appears to be independent of fHCl. However, at fugacities of HCl typical of volcanic gases (fHCl from 0.5 to 5 bars), the sum of the fugacity of Mo species increases with increasing fHCl in a ratio of ~1:2. At all fugacities of HCl, Σ/Mo species increases with increasing fH2O in a ratio of 1:2. These observations suggest that the predominant Mo species in the HCl-H2O system is a hydrated chloride or oxychloride. In the case of the former, the stoichiometry would likely be MoCl2•2H2O, whereas the latter could be MoO2Cl2•2H2O, a species that has been reported to occur in HCl gas (Hultgren and Brewer, 1956). The sum of fugacities of Mo species in NaCl-bearing vapour rises linearly with increasing Σ/Na species in a ratio of 3:4. Furthermore, Σ/Na species is about two orders of magnitude higher than predicted for the partitioning of NaCl between H2O liquid and vapour (Bischoff 1991), indicating that the dominant Na species in the vapour is not NaCl. Values of Σ/Mo also increase linearly with fH2O (in a ratio of 1:3), suggesting the formation of hydrated Na molybdates. The ratio of Σ/Mo to Σ/Na of 3:4 implies the formation of two or more hydrated Na molybdates, e.g. Na2MoO4•3H2O or NaHMoO4•3H2O.

The results of this study, in conjunction with the known elevated concentrations of Na and Cl in magmatic vapours, suggest that such vapours are more than capable of dissolving the concentrations of Mo required to form porphyry Mo deposits.

References

Status of the impact crater age database

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The Earth impact crater database (http://www.unb.ca/passc/ImpactDatabase/) includes a total of 174 confirmed impact structures. Ages listed in the database are based on dates recommended in the most recent published papers. Precise and accurate age constraints are crucial in (1) correlating causes and effects on the bio- and geosphere for these catastrophic processes, (2) better constraining the impactor flux through geological time and evaluation of potential impact periodicity, (3) calibrating the absolute chronostratigraphic time scale, and (4) calibrating the age of within-crater continental sedimentary deposits (e.g., for regional paleo-climatic analysis).

Of the 174 confirmed impact structures only a few have ages constrained precisely enough (mostly using radio-isotopic techniques, e.g. U/Pb and \textsuperscript{40}Ar/\textsuperscript{39}Ar), with 26 ages having a stated precision better than 2% and 15 ages with a precision better than 1%. Yet, even in this very restricted subset of the database the accuracy of some of these ages can be challenged and probably improved based on more detailed and statistically more rigorous interpretations. Although geochronologists are often circumspect and advise caution in accepting calculated ages, these ages tend to propagate into the literature without further critical evaluation and become “robust” and widely accepted ages. A quick review of the age data of the 26 short-listed structures suggest that 11 ages seem accurate, 13 are at best ambiguous, and 2 are not well characterized and should not be reported with any uncertainty. We report examples of misleading ages and/or age uncertainties (e.g., poor stratigraphic constraints, data over-interpretations, ambiguity due to inconsistent results) and highlight the robustness of 11 well defined ages. We also provide some suggestions (see also \cite{1}) based on observations and modeling, in order to obtain better ages. This brief review should be interpreted as a call for drastic qualitative and quantitative improvements of the crater age database in the near future.

\cite{1} Jourdan \textit{et al.}, this volume

Arsenic uptake and release on sulfide nanoparticles

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Descriptions of molecular-level processes that control the uptake and release of As on sulfide nanoparticle surfaces were obtained from microbeam, spectroscopic, and quantum mechanical modeling techniques.

The precipitation of As-sulfide phases on nanoparticulate mackinawite (FeS) is identified as a possible mechanism for As(III) immobilization under anoxic conditions (Gallegos \textit{et al.} 2007). A major challenge in identifying As-sulfide growth phases is their nanoscale dimensions. High-angle annular dark field scanning-TEM and energy-dispersive X-ray spectrometry were used to identify amorphous AsS phases precipitating on FeS nanoparticles after As(III) adsorption at pH 5. The oxidation state of As in the surface As-sulfide precipitates was determined to be “realgar-like” from X-ray photoelectron spectroscopy results showing an As 3d binding energy of 43.0 eV.

The reverse process, the oxidative dissolution of realgar (As\textsubscript{4}S\textsubscript{4}) and orpiment (As\textsubscript{2}S\textsubscript{3}) nanoparticles, is a mechanism by which As is released back into natural waters. \textit{Ab initio} quantum mechanical methods were employed to describe indirect electronic perturbations (proximity effects) between surface adsorbates on As\textsubscript{4}S\textsubscript{4} nanoclusters. Proximity effects between O and (OH)\textsuperscript{-} ion adsorbed on a single As\textsubscript{4}S\textsubscript{4} cluster were determined to be on the order of 1 eV, depending on the O-(OH)\textsuperscript{-} distance. Calculations also show that adsorption of (OH)\textsuperscript{-} to As\textsubscript{4}S\textsubscript{4} could affect the adsorption energy of O to a neighboring As\textsubscript{4}S\textsubscript{4} separated from the former by a van der Waals gap (as is the case in As\textsubscript{4}S\textsubscript{4} molecular crystals). The findings suggest that As\textsubscript{4}S\textsubscript{4} is more susceptible to oxidative attack with the co-adsorption of (OH)\textsuperscript{-} ions.

The results of this study can be used to improve adsorption isotherms and surface complexation models that describe the factors that control As concentrations in natural waters.

Reference

Volcán de Colima, an andesitic volcano fed by a dacitic reservoir. Is that typical of continental arc magmatism?

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Volcán de Colima, Mexico is the archetype of an andesitic arc stratovolcano and is one of the most active volcanoes in North America. All historically erupted magmas have bulk andesitic compositions, yet the melt inclusion and phenocryst assemblages indicate that the melt crystallizing in the subvolcanic system is consistently dacitic in composition. Similar mismatches between whole rock and melt inclusion records are documented for several other andesitic volcanoes, which raises questions about the abundance of true liquids with andesitic composition.

Melt inclusions (MI) in phenocrysts of pyroxenes from Volcán de Colima magmas are distinctly more silicic than whole rock compositions (64-75 and 57-62 wt% SiO₂ respectively). A significant proportion of the melt inclusions have “exotic” compositions thought to be produced by grain boundary melting of co-genetic crystal-clots. The other MI show trends consistent with crystallization of the phenocryst assemblage observed in the magmas. Volatile content of these melt inclusions are distinctly low (<2.5 wt% H₂O, ≤360 ppm CO₂) and indicate crystallization in a volatile-saturated system between 90 and 0 MPa (<7 km in depth). The magmas contain ubiquitous gabbroic fragments up to few mm in size. The whole-rock compositions of the andesites systematically lie on mixing lines between the gabbroic fragments and the less evolved melt inclusions, indicating that entrainment of these gabbroic fragments is the primary factor controlling the bulk andesitic composition and, importantly, that the melt inclusions effectively record the composition of the crystallizing melt. Overall, this implies that despite the monotonous andesitic composition of the erupted magmas, the magmatic system that feeds Volcán de Colima comprise a shallow, variably crystallized dacitic magma reservoir and a pre-existing gabbroic plutonic body. It is therefore bimodal in composition, with no andesitic melt.

A compilation of published melt inclusion data for several other continental arc andesite volcanoes also shows a bimodal distribution with a marked minimum at andesite. This implies that andesitic melts are typically minor components of the upper crustal magmatic reservoir feeding arc volcanoes and that the abundance of erupted andesitic magmas reflects in large part effective mixing of these two components within the subvolcanic reservoir and/or on the way to the surface.

The building stones of the Khmer-temple at Angkor/Cambodia: A petrological and geochemical approach towards a conservation oriented characterisation of the inventory

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The Angkor Park / Cambodia, as a prominent member of the Unesco world heritage, is one of the outstanding cultural relics on earth. Countless Khmer temples were successively built between 9th – 13th century.

During the preparation of interventions in individual temples the building stones were investigated concerning their most important properties in regard to conservation strategies. It turned out that there are considerable differences in weathering behavior between the sandstones used at different temples and that the composition and texture of the building stones are determining factors for the degree and the type of decay. The study presented aims at a detailed geochemical and mineralogical characterisation of the building stones starting with samples from some of the most prominent temples. Together with petrophysical data this shall provide a material oriented database for future conservation conceptions.

The material was characterised petrographically by optical microscopy, the components were analysed by electron microprobe and whole rock chemistry of main and some trace elements that were determined by XRF-analysis. X-ray diffraction was used for determining clay minerals in selected rocks.

On a petrographic base most of the rocks can be classified as feldspathic greywackes (according to Pettijohn et al. 1972), in one, the Banteay Srei temple, lithic greywackes were found. Inspite of this similarity the rocks display a distinct variability in regard to their chemical composition and texture. The combinations of the methods show clear accordances in the observed variability of the temples building stones. On the other hand the building stones from the Ta Keo (feldspathic greywackes) and the Banteay Srei temple (lithic greywackes) are distinctly different from the others. They also show no correlation with the samples of the ancient quarries.

Future investigations extend to temples (also smaller ones) and ancient quarries in the wider surrounding of the Angkor Park aiming at the set-up of a database on the variability and historical variations in the building stones used during the five centuries of construction.
Aerogels – A kind of ceramic? Properties and applications
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Aerogels are nanostructured materials, containing until 99 wt.-% air. They are manufactured by a sol-gel process [1]. After formation of a 3D network of colloidal particles, the wet gel has to be dried without shrinkage to avoid destruction of the network by capillary forces. The drying process can be supercritical or subcritical, depending on the kind of aerogel. Because of their very special properties (extremely low density, extremely low thermal conductivity,....), aerogels are very interesting for different applications [2]. Aerogels can be classified into organic and inorganic aerogels.

The first aerogels (organic, silica aerogels) were manufactured already in 1931/32 by Kistler [3]. Inorganic aerogels are inert against metal liquids and cannot be wetted by them. We use them as crucible material for solidification of metal alloys. It is possible to watch the solidification process directly or by CCD-camera, because these kinds of aerogels are often transparent in a wide range of 350-2700 nm.

In the past few years, there has been a great deal of interest in the synthesis of hybrid materials with nonlinear optical properties, especially second harmonic generation (SHG). We prepare ferroelectric aerogels, like LiTaO₃ and LiNbO₃, and silica/titania aerogels loaded with ferroelectric nano -and microparticles, like BaTiO₃ or KNbO₃. Whenever an infrared laser light wave (e.g. 1064nm) penetrates these materials, the aerogel generates green light (532nm).

In recent years, organic aerogels were presented as a new, nanostructured material with possible applications like binding material for sand cores and moulds in the foundry industry [5] or in its pyrolyzed carbon form as a material for supercapacitors. The well investigated Resorcinol-Formaldehyde (RF) aerogels [6,7] are typically catalyzed with weak bases like sodiumcabronate. Instead of base catalysis it was recently considered to use acid catalysts, especially sodium hydroxide, for the drying of RF aerogels [8].

References

Opal records of abrupt changes in the Southern Ocean over Termination II
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Diatoms sequester CO₂ and other nutrients into their organic matter, as well as forming biogenic silica (opal), and can account for over half of the world’s primary productivity in the surface oceans. Silicon (Si) is an important oceanic nutrient for their growth and primary production in surface waters, especially at high-latitudes. Opal bio-mineralization leads to a mass-dependent Si isotope fractionation, such that the Si isotope composition (expressed as δ²⁹Si) of seawater and biogenic opal reflect the degree of Si utilization in ocean surface waters by siliceous algae, analogous to variation in carbon isotopes, but linked only to diatom productivity.

An unprecedented high temporal-resolution Si-isotope record has been measured from the South Atlantic from ODP site 1094 over the penultimate deglaciation. The qualitative trends observe a very large shift from low glacial values to high interglacial values over Termination II. These large changes are in accordance with a record from the Antarctic zone of the South Atlantic (Core RC13-259, [1]). The high temporal-resolution of this study allows us to ascertain two important features which have hitherto not been demonstrated:

Firstly, we can compare the time of changes in δ⁴₀Siopal to changes in the other stable isotope proxy of seawater, namely δ³⁴S and δ¹₃C [2], secondly, we can demonstrate that δ⁴₀Siopal changed by 1‰ in less than 2 kyr.

The changes in diatom productivity estimated from both δ⁴₀Siopal and δ¹₃C records, actually occur significantly prior to the change in δ³₀Siopal (~1 kyr). This also suggests that change in the N utilization do not occur at the same time as change in Si utilization. Overall, the degree of change (1.3‰) is greater than the isotope enrichment factor during the utilization of Si by diatoms (~1.1‰), so cannot be explained as only changes in the degree of utilization (this cannot be more than 100%). Secondly, the rate of change is similar to the mixing time of the oceans (~1500 years) and many times less than the residence time of Si in the oceans (~15 kyr), so cannot be related to changes in marine inputs to the oceans. The observed shift in δ³₀Siopal must be caused by a dramatic switch in provenance of waters coming into the Antarctic Sector of the Southern Ocean with distinctly different Si isotope compositions as well as any potential change in diatom productivity.

References
The FE-EMPA – Applications for the sub-micron analysis in geosciences

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The use of a thermal field-emission cathode in an electron microprobe (JEOL Hyperprobe JXA-8500F) has opened a new window in the analysis of structures in the sub-micron range. Small electron-probe beam size (< 50 nm) with variable probe current (5–200 nA) at low accelerating voltage (5–10 keV) allow a sub-micron spatial resolution for single spot analyses and detailed X-ray mapping of composition contrast in the range of 100 nm. The results are afflicted by reduced intensities of the X-rays (high energy K-lines are not excited, demanding the use of L- and M-lines), peak overlapping, a higher current density, and contamination. The quality of the sample polish and the thickness of the coating layer are essential. New measurement strategies and unconventional approaches are required to overcome these problems.

A selection of examples should demonstrate the improved possibilities of the FE-EMP as a tool between conventional EMP and TEM:
- Measurement of the chemical composition and the internal zoning of exsolution lamellae and symplectite in feldspars.
- Characterization of small reaction rims in natural samples in order to study the transport mechanism for the rutile-titanite transformation via a fluid phase.
- Study of the complex, diffusion-controlled growth of orthopyroxene reaction rims (zonation of Fe and Mg).
- Investigation of inclusions in minerals (unaffected by their host) down to 500 nm size, depending on composition and density.
- “Chemical” age dating of Th–U-containing minerals occurring as microinclusions in other minerals.
- Characterization of complex zoning patterns of small areas in accessory minerals (zircon, monazite, xenotime, etc.).

Preliminary characterization of São Jorge island mantle source (Azores)

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The Azores archipelago, formed by nine islands spread along the Azores Plateau, is situated in a complex tectonic setting, containing the junction of three tectonic plates, the American, Euroasiatic and Nubia plates. East of the MAR is located the central group island where São Jorge island developed (38°46' – 38°33'N and 28°20' – 27°45'W). This is an elongated shape island (WNW-ESE) with aligned volcanic cones and dikes unveiling the importance of the regional tectonic setting during volcanic activity. Stratigraphically, the island developed during three main volcanic phases (Forjaz & Fernandes, 1975), giving place to Topo complex in the SE, Rosais complex in the NW and to Manadas complex that covered the centre of the island.

São Jorge lavas are dominantly alkaline with Y/Nb ≤ 1.0, and experience some degree of differentiation extending from basanite and tephrite to basaltic trachyandesite composition. The analyses of REE and incompatible elements of the more primitive samples (Mg# ≥ 0.44 and Ni ≥ 110 ppm) can be good indicators of the petrogenesis of the three complexes.

The REE diagram shows LREE enrichment, relative to HREE, as is common in ocean island where garnet is present in the source. We also found, in Topo complex, differences between Caldeira and Cubres sequences as for instance REE ratios [(Tb/Yb)n] and incompatible elements patterns. Primitive lavas from Rosais, when compared with other lavas, are relatively enrich in La, Rh, Ba and Th contrasting with only a small K anomaly and relatively high Ba/Ce ratio. This could be explain if during partial melting Rosais lavas sampled a slightly different compositional source, constituted by a K enriched phase as reported in other Azores islands as Corvo (França et al., 2006) and Atlantic islands (Halliday et al., 1995, Ribeiro, 2001).

The question is how source composition and partial melting affected magma composition in these continuous lava sequences and the relation with the remaining Azores islands and seamounts in the Azores region.

References
Comparative study of geospeedometry methods
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Limitations of classical geospeedometry
The natural cooling rate of natural glasses is an important parameter in the assessment of volcanic hazards because it influences the degassing and flow behavior of lava. Relaxation of enthalpy (ΔH) has been successfully used to estimate cooling rates of natural glasses. This method consists of heating and cooling a glassy sample at various rates and using the Tool-Narayanaswamy model (1971) to obtain a natural cooling rate. It is however challenging to apply this technique to some glasses where the heat capacity (ΔH/ΔT) curves are not reproducible due to possible degassing and/or the ΔH/ΔT peaks are too small to be modelled.

An advanced dilatometric method
A method recently developed by Helo et al. (2006) considers the volume relaxation of multiphase samples during heating at a fixed rate, with the advantage of measuring samples containing only small amounts of glass. This method allows us to (1) estimate the calorimetric glass transition temperature (Tg_cal) and (2) measure the dilatometric glass transition temperature (Tg_dil), which corresponds to the softening point of the material. A pantellerite from Pantelleria, Italy, was heated through the glass transition. From length changes, we estimated a Tg_dil of 521°C, and from enthalpy changes measured with a scanning differential calorimeter, we obtained a Tg_cal of 524°C. These temperatures are identical within the precision of the instruments.

An alternative to classical geospeedometry
Moreover, repeated dilatometric heating at 10 K/min and cooling at 15 K/min revealed a gradual exponential increase in the Tg_dil from 625°C to 649°C, possibly due to water degassing. The first heating of the sample produced a Tg_dil of 611°C, which plotted below the trend produced by the subsequent measurements. We attribute this gap to the natural cooling rate, which we estimate to be about 10 K/min. This is the first time that a geospeedometry method considers changes in material properties to estimate a natural cooling rate. Classical geospeedometry assumes that Tg does not change through a series of cooling and heating treatments. However, we show that for some glasses, another method is required because Tg may change due to a number of processes such as degassing.

References

A thermodynamic model of uranium reduction by organic matter in the Proterozoic hydrothermal systems of Oklo (Gabon)
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Numerous geological, mineralogical, and geochemical studies have been carried out at and around Oklo (southeastern Gabon) over the last four decades, which have contributed to a better understanding of the reactions involved in the formation of these uranium deposits (e.g. Gauthier-Lafaye and Weber, 1989; Nagy et al., 1991; Cuney and Mathieu, 2000). The Oklo deposits represent one of the best examples of associations between uranium and organic matter, which raises the question of the role played by hydrocarbons in the reduction of uranium-VI to uraninite. The observation of uraninite crystals entrapped within solid bitumens in the Oklo uranium deposits led Nagy et al. (1991) to propose that a liquid, aliphatic-rich bitumen may have acted as a reductant to precipitate uraninite from hydrothermal solutions. Advances in theoretical organic geochemistry have led to the constitution of an extensive set of thermodynamic properties for solid and liquid organic compounds of geochemical interest (Helgeson et al., 1998; Richard and Helgeson, 1998), which makes it possible to investigate organic/inorganic interactions in geological processes.

A thermodynamic analysis has been made as a function of temperature, pressure, and oxygen fugacity of the reactions responsible for the formation of the uranium deposits at Oklo (southeastern Gabon). The generation of liquid hydrocarbons at 150°C as a result of the maturation of Proterozoic kerogens in the FB shales has been characterized and quantified with the aid of activity diagrams. Mass transfer calculations have been carried out to describe the alteration of U-bearing monazites and the mobilization of uranium by oxidizing hydrothermal fluids circulating in the FA sandstones, as well as the reduction of aqueous uranyl by the liquid hydrocarbons as a result of the mixing between the hydrothermal fluids and the petroleum. The latter calculations resulted in the simultaneous precipitation of uraninite and pyrobitumen, in agreement with the petrographical observations.

References
A reappraisal of the petrology and origins of the Lherz peridotite
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The massifs of the eastern Pyrenees have been the focus of a number of extensive studies and have made a significant contribution to our understanding of mantle composition and evolution. Specific problems remain, in particular the relationship between adjacent harzburgites and lherzolites, which have been proposed to be either; (1) melt depletion of an original lherzolite [2, 3] or, (2) refertilisation of a primary harzburgite by basaltic melt [1, 4].

Whole rock and clinopyroxene compositions of the peridotites and associated pyroxenites offer a means of resolving the nature of the relationship between harzburgites and lherzolites. Whole rock major and trace element analyses show that the lherzolites have a range of compositions while the harzburgites are relatively uniform. Laser ablation analyses of individual clinopyroxenes indicate some variation of lherzolite sample composition whilst harzburgites alone display marked LREE enrichment.

Whole rock 187Os-188Os values define a broad positive correlation with 186Re-188Os and indices of melt depletion (Al2O3 and S). Model ages derived from these correlations range from ~1.4Ga to ~1.5Ga. Re-Os isotope systematics alone define an errorchron corresponding to an age of ~1.7Ga. These model ages are all younger than those reported in the literature [3, 5], which previously suggested a melt depletion event across the Pyrenean suite at 1.9-2.4Ga.

References

U(VI) sorption on sandstone: Experiments and modeling
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Experimental
The sorption of U(VI) on natural and synthetic sandstone was investigated in batch sorption experiments (air atmosphere, 0.1M NaClO4, pH 3-11, [U(VI)] 10^-9-10^-4M. The synthetic sandstone was a mixture of quartz with muscovite and hematite. The surface area (N2-BET) of quartz was 0.047 m2/g, of muscovite 0.88 m2/g, of hematite 0.89 m2/g and of natural sandstone (mainly quartz) 0.69 m2/g.

Results and discussion
The pH dependence shows a maximal sorption between pH 5.5-7.5. The U(VI) sorption varied between 95% (10^-9M) and 7% (10^-4) on natural sandstone, and between 80% (10^-9M) and 2% (10^-4M) on synthetic sandstone. Fig. 1 shows the comparison of sandstone with pure components (at similar conditions) quartz, muscovite, and hematite. More U(VI) was adsorbed on natural and on synthetic sandstone, than on quartz. The higher sorption are caused by the other components muscovite and hematite, and by the higher surface area.

Acknowledgement
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References
I will discuss three types of mass transport related isotope fractionations. 1. Isotope fractionation by evaporation of silicate liquids. 2. Isotope fractionation by chemical diffusion in liquids. 3. Isotope fractionation by thermal diffusion in molten basalt.

We (Richter et al., 2002 and work in progress) have carried out a large number of experiments on isotope fractionation during evaporation and find that it follows a Rayleigh fractionation law of the form \( R_i/R_{10} = f_i^{0.1} \) where \( R_i \) is the ratio of isotopes i and j when a fraction \( f_j \) of isotope j remains in the condensed phase and \( R_{10} \) is the original isotope ratio of the of the condensed phase. The fractionation parameter \( \alpha \) is the ratio of the isotopic composition of the evaporation flux to that of the substrate. In the case of magnesium evaporating from silicate liquid at 1400°C, (relevant to the evaporation history of Ca-Al-rich inclusions found in primitive meteorites), we find \( \alpha = 0.9910 \), which is significantly different from the often assumed value of \( \alpha = (24/25) = 0.9798 \) for the fractionation of \( ^{25}\text{Mg}/^{24}\text{Mg} \) in the evaporation residue.

We (Richter et al., 1999, 2003) reported the results of experiments for the isotopic fractionation of Li, Ca, and Ge (used as a Si analogue) during diffusion between molten basalt and rhyolite, and now have new data on the isotopic fractionation of Mg is this system. We have also carried out experiments on the isotopic fractionation of Li, Mg, and Cl during diffusion in water (Richter et al., 2006). The results are reported in terms of the exponent \( \beta \) in \( D_i/D_f = (m_j/m_i)^\beta \), where the \( D_i \) is the self diffusion coefficients of isotope k and \( m_j \) is its atomic mass. For molten silicate we found \( \beta_{^{7}\text{Li}/^{6}\text{Li}} = 0.215, \beta_{^{44}\text{Ca}/^{40}\text{Ca}} = 0.075, \beta_{^{26}\text{Mg}/^{24}\text{Mg}} = 0.05, \beta_{^{7}\text{Li}/^{7}\text{Li}} \leq 0 \). In water \( \beta_{^{7}\text{Li}/^{6}\text{Li}} = 0.015, \beta_{^{37}\text{Cl}/^{35}\text{Cl}} = 0.025, \beta_{^{26}\text{Mg}/^{24}\text{Mg}} = 0 \). Note the very much smaller fractionations in water.

Our most recent experiments involve isotopic fractionations by thermal diffusion (often also called Soret diffusion). We are finding surprisingly large isotopic fractionations (~8‰ for \( ^{26}\text{Mg}/^{24}\text{Mg} \)) associated with a change of only about 150°C across molten basalt. We are in the process of determining the thermal isotopic fractionation factors of the other major elements in molten basalt.

**References**


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**Deglacial rearrangement of carbon and nutrients in surface and intermediate depth waters**

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Changes in the pattern of conveyor circulation, reconstructed from the combined nutrient proxies Cd/Ca and \( \delta^{13}\text{C} \), have been implicated in abrupt climatic events of the last deglaci. But, the assumption that characteristic endmember water mass signatures derived from southern nutrient rich surface waters close to sea ice, and northern nutrient depleted ice free surface waters, have remained invariant in time, has recently been called into question. We contrast new deglacial planktonic and benthic foraminiferal histories from intermediate depths in the high latitude North and Equatorial Atlantic with records from the South Atlantic and Pacific. The timing and amplitude of the deglacial minimum in \( \delta^{13}\text{C} \) of atmospheric CO\(_2\) from Taylor Dome, is captured by the surface \( \delta^{13}\text{C} \) records. The surface \( \delta^{13}\text{C} \) minimum is paralleled at intermediate depths in the high northern latitudes throughout the early deglacial. This may indicate continued northern sourced ventilation with an altered endmember \( \delta^{13}\text{C} \) signature, which can account for the early deglacial warming documented in the North Atlantic. Globally, intermediate depth signatures converge to the same value at the start of the deglaciation. Our data are consistent with vertical fractionation of carbon and nutrients into a poorly mixed deep reservoir during the last glacial, which is reventilated at the deglaciation and the sequestered carbon mixed via the intermediate waters to the surface and atmosphere. Divergence between the surface and intermediate depth chemical signatures occur only during the Younger Dryas. Our results confirm that endmember water mass signatures change significantly on a glacial-interglacial cycle.
Seasonal variation of oxygen and organic carbon isotopes and skeletal aragonite from *Unionidae* in the Rhine river

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Seasonal variations in the oxygen and carbon isotopic composition of Rhine River water were compared with the isotopic record from recent and historical specimens of freshwater bivalves (*Unionidae*). The purpose of this study was to investigate these aragonitic bivalves as proxies for climate change. Seasonal variations in the river water δ¹⁸O are on the order of 1 to 2 ‰. During the summer, the run-off is dominated by Alpine melt-water, resulting in average values of -10 to -10.5 ‰, whereas the non-Alpine contribution is higher during winter, as indicated by mean δ¹⁸O values of -8.5 to -9 ‰. The δ¹⁸O of growth increments in the prismatic shell layer of *Unio crassus nanus* corresponds perfectly to what is predicted by known fractionation of ¹⁸O between water and aragonite. Variations in δ¹⁸O and the river water temperature are faithfully recorded by relatively large growth increments during summer. The isotopic signatures of individual flood events are also recorded in the shells. In summer, snowmelt-related Alpine waters with low DIC contents and heavy δ¹³C lake productivity signals (-9 ‰) were observed at Cologne. In winter, however, the components of the non-Alpine Rhine dominate the discharge at Cologne. Waters had light δ¹³CDIC signals of –11‰ soil respiration in the non-Alpine zone. Sampling of Lake Constance waters showed the effect of bioproductivity in the summer surface water. Bioproductivity is related to the withdrawal of light organic carbon and has a positive δ¹³CDIC increase of 2 ‰ in the surface waters.

Speciation of Cu and Zn in natural hydrothermal boiling systems: Evidence from fluid inclusion studies by X-ray absorption techniques

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Metal speciations in fluids are responsible for the partitioning of metals into the liquid and vapour phase during fluid phase separation and can lead to major changes in fluid compositions of hydrothermal systems. Here we present data for the partitioning behaviour of Cu and Zn in coexisting liquid and vapour phase fluid inclusions formed by sub-critical phase separation. Synchrotron-radiation induced micro X-ray fluorescence analysis (SR-XRF) and temperature-dependant X-ray absorption near edge structure (XANES) experiments were performed on individual inclusions. The studied fluid inclusion boiling assemblages are hosted in quartz from miarolitic cavities of the Torres del Paine granite complex (Chile). The formation temperatures of hydrothermal quartz in vugs range between 280°C and 340°C.

SR-XRF element maps revealed that Cu and Zn show a contrasting partitioning behaviour: while Cu is dominantly detected in vapour-rich inclusions, zinc is more abundant in brine-type inclusions.

XANES experiments were performed at temperatures up to 460°C using a Linkam THMSG-600 heating-stage. Measurements were carried out at ID22 and FAME, ESRF with spot sizes of 4 and 15 µm, respectively. In vapour-rich inclusions, most of the Cu is concentrated in daughter crystals. During heating runs, the daughter crystals dissolve and Cu oxidation state changes between 190°C and 280°C from Cu²⁺ to Cu¹⁺. While Cu²⁺ seems to be coordinated with water ligands forming the complex Cu[H₂O]₆²⁺, Cu¹⁺ is coordinated by two chlorine ions forming Cu[Cl₂]⁻. In brine-type inclusions, Cu is contained in the liquid phase. XANES-spectra show that Cu dissolved in brines has an oxidation state of 2⁺ between 25°C and 460°C. These findings are in accordance with the interpretation that at temperatures of phase separation Cu¹⁺ species is more stable and responsible for the concentration of Cu in the vapour phase.

XANES spectra indicate that Zn is most probably complexed as ZnCl₄⁻ in the temperature range 25 –370°C for both, liquid and vapour rich inclusions. This shows that in contrast to Cu, changes in speciation are not responsible for the partitioning of Zn into the liquid and the vapour phase.
Numerous studies have documented the sources and behaviour of Nd in the present day ocean providing a background for paleoceanographic interpretations. In contrast, much less information is available on Hf isotopes. As a consequence, there is still an ongoing debate on the sources of Hf in seawater.

We present isotopic compositions for the dissolved Hf and Nd in seawater samples taken on a transect from the Bay of Biscay to Cape Town (RV Polarstern cruise ANXXIII/1 in 2005). Hafnium and Nd were pre-concentrated by iron co-precipitation from 70 to 140 liters of filtered (0.45 µm) seawater. Separation of Hf and Nd followed previously established ion chromatographic procedures. Hafnium and Nd isotopic compositions were measured by MC-ICPMS (Nu Plasma) with a 2σ external reproducibility of 0.65 and 0.3 ε - units, respectively. Sample sizes varied but were typically in the range of 5 to 7 nanograms of Hf.

Surface seawater as well as deep water samples extending to ~5,000 m, plot on the “seawater array” defined previously from measurements of ferromanganese crusts and nodules. Surface seawater isotopic compositions are rather uniform for Hf and Nd at most sampling locations ranging from +0.1 to +1.7 in εHf and from -12.1 to -11.5 in εNd. Two locations at 22.5°N and 10.5°N show less radiogenic compositions in the subsurface (εNd down to -12.9 and εHf down to -0.8).

Deep water compositions range from +0.8 to +4.2 εHf. The εHf variations with depth in the different profiles generally follow the patterns observed for εNd. The overall variations in deep water Nd isotopes in our data set is twice as large as that of Hf isotopes (εNd between -13.9 and -7.9) but the spread in Hf isotopes of some depth profiles is significantly larger than for Nd.

Particularly unradiogenic Nd signatures are found in the Angola Basin, where εNd is as low as -15.4. This may reflect inputs from the Congo River or sediment seawater exchange within the basin. Hafnium isotopes, however, do not show such a shift.

Neodymium isotopes are in general agreement with the results of earlier studies. Antarctic Intermediate Water, however, has been sampled at three locations where it is clearly less radiogenic (εNd = -11.1, -13.9 and -11.4) than reported before (εNd = -8.9 to -6.2).
Greenhouse gas driven hyperthermals of the Paleogene: How much carbon, how fast?

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Terrestrial and marine deposits from the early Cenozoic record a 55 million year old transient warming of the Earth’s surface, dubbed the ‘Paleocene/Eocene Thermal Maximum’ (PETM). The occurrence of a prominent carbon isotopic excursion indicates massive release to the ocean and atmosphere of CO2 and/or CH4, thought to be similar in magnitude to current fossil fuel reserves. The PETM thus represents a potentially compelling analogue candidate for future greenhouse gas driven global change. In particular, understanding this event could provide us with invaluable insights into key mechanisms of feedback between climate and global carbon cycling as well as what the long-term impacts on calcifying plankton and animals of surface ocean ‘acidification’ might be. However, the parallels that can be drawn with anthropogenic climate change hinge critically on the magnitude and time-scale of the greenhouse gas forcing of this hyperthermal event.

Here we apply an Earth system model (GENIE-1) to the interpretation of the marine geologic record of the PETM and tackle the question of what the rate and total input of carbon to the ocean and atmosphere might have been.

Surface structural modeling at the solid-solution interface of nanocrystalline anatase

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To begin to assess the effects of particle size on the surface reactivity and charging of metal-oxide nanoparticles in aqueous solutions comprehensive experimental and characterization studies were completed. Commercially available crystalline anatase (TiO2) particles were used in the study. Particle size ranged from 200 to 3 nm diameter, with corresponding BET surface areas of 10 to 350 m²/g, respectively. Potentiometric and electrophoretic mobility titrations of the anatase samples were performed in NaCl media at ionic strengths from 0.005 to 0.3 molality, at 25ºC. All samples were characterized extensively; using electron microscopy and aberration corrected electron microscopy (ACEM), neutron and X-ray small-angle scattering, and laser diffraction techniques.

A principle parameter obtained from the surface titration studies was the pH_{zpc} value. The pH_{zpc} of 40 nm diameter anatase particles (pH_{zpc} = 6.22) corresponded closely to previously published values; whereas, the pH_{zpc} value of 3 nm particles was higher (pH_{zpc} = 6.90). Furthermore, the development of positive surface charge was enhanced for larger anatase nanoparticles (>20 nm) over 3 nm diameter particles; in spite of this, the overall development of negative surface charge, relative to the respective pH_{zpc} values, was approximately the same for all particles sizes studied. At high ionic strengths the apparent pH_{zpc} value of the 3 nm particles was offset slightly toward lower pH values, which suggests some specific adsorption of the Na+ electrolyte ions.

Surface complexation modeling (SCM) was completed to rationalize the bulk surface titration data. The SCM’s incorporate all available molecular information (e.g., Ti-O bond lengths), with crystallographic information acquired from the ACEM. ACEM imaging revealed that the [100] face predominates on the 20 nm particles, and edges/facets include [010], [001], and [0-11]. A MUSIC model description of surface protonation permitted rationalization of the decrease in pH_{zpc} values with increasing particle size. Additionally, a Stern-layer representation of the EDL, and inner-sphere adsorption geometry of the electrolyte cation were also accounted for.
Fluid influence on retrograde assemblages in UHP eclogites

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This study is a combination of modelling the phase stability, fluid availability and observations in ultra high pressure (UHP) rocks from the Chinese Continental Scientific Drilling (CCSD) project. We investigate the origin of the fluid and its influence on the mineral chemistry and (re-)equilibration processes for a better understanding of the retrograde PT-path. All investigated sample lithologies (eclogites, ortho- and paragneisses and schists) have been influenced by fluids to varying degrees. The main evidence for these fluids are different types of fluid inclusions, healed cracks, pro-and retrograde formation of hydrous minerals and late crosscutting veins. Retrograde assemblages in the eclogites range from UHP to greenschist facies. These form in centimetre wide zones that can be subdivided into a transition zone and a strongly altered inner part. While the fluid inclusion bearing assemblage garnet-omphacite-coesite-phengite-rutile reflects UHP conditions, albite-clinopyroxene symplectites appear in the first stage of retrogression as a response to post peak decompression. Garnet in the transition zone is cracked and rimmed by pargasitic amphibole, signaling fluid influence in the amphibolite facies. Fluid also triggers the breakdown of garnet and omphacite to an amphibole bearing symplectite and intergrowth of rutile and newly formed ilmenite. Phengite adjacent to omphacite breaks down to biotite, albite and white mica. The inner part of the retrograde zone is a greenschist facies assemblage with a new white mica generation, which contains fluid inclusions. Quartz and calcite veins crosscut the rock in a late stage of retrogression. These different stages of metamorphic reactions influenced by fluids allow new PT estimates for the retrograde path. This evolution indicates the influence of various fluids during the exhumation history that have a significant effect on (re-)equilibration.

Cd/Ca ratios of in situ sampled planktonic foraminifera

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The Cd/Ca ratios of fossil planktonic foraminiferal tests are of particular interest to paleoceanographers as they can be used to reconstruct past surface water nutrient utilization [1]. The reliability of this proxy has hitherto not been comprehensively studied, however. In order to fill this gap, we performed Cd/Ca analyses of planktonic foraminifera (G. ruber, G. sacculifer and G. bulloides) collected from the water column and from surface sediment samples at approximately the same locations. These analyses utilized an isotope dilution technique and a MC-ICPMS instrument equipped with a multiple ion counting system.

The Cd/Ca ratios obtained for G. ruber sampled from the natural habitat in the upper 80 m of the water column generally display a correlation with seawater phosphate content. No such trend, however, was observed for G. sacculifer and this indicates that vital effects may be responsible for the different Cd/Ca systematics of these species. Moreover, the results reveal differences in Cd/Ca between (i) specimens collected from their habitat (live specimens), (ii) settling shells (deceased specimens) and (iii) tests from surface sediments. SETTING TESTS OF G. RUBER EXHIBIT ABOUT 2-5 TIMES LOWER Cd/Ca VALUES THAN LIVE SPECIMENS. THIS SUGGESTS THAT Cd IS PREFERENTIALLY RELEASED DURING PARTIALLY DOLLS OF CALCIUM DURING SETTLING OF THE TESTS THROUGH THE WATER COLUMN. FOSSIL SHELLS OF G. RUBER DISPLAY Cd/Ca RATIOS THAT ARE UP TO 15 TIMES LARGER COMPARED TO RESULTS OBTAINED FOR SETTLING SHELLS FROM THE SAME SPECIES. THIS OBSERVATION IS MOST EASILY EXPLAINED, IF SEDIMENTARY TESTS ARE DEPOSITED IN MASS SINKING EVENTS THAT ARE ASSOCIATED WITH MUCH HIGHER SINKING VELOCITIES IN COMPARISON TO THOSE EXPERIENCED BY SINGLE SETTLING SHELLS. FURTHERMORE, THE Cd/Ca RATIOS OF G. RUBER, G. SACCUFILTER AND G. BULLOIDES FROM SURFACE SEDIMENTS ARE CONSIDERABLY HIGHER THAN THOSE OBTAINED FROM LIVE COLLECTED SPECIMENS FROM THE NATURAL HABITAT. POST-DEPOSITIONAL ALTERATION OF THE TESTS IS UNLIKELY TO BE RESPONSIBLE FOR THIS DISCREPANCY. A NUMBER OF ALTERNATIVE EXPLANATIONS ARE POSSIBLE BUT THESE REMAIN SPECULATIVE AT PRESENT.

References
Tracing the sources of carbon in the rivers of Lesser Antilles

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At long timescales, the continental weathering of volcanic areas is one of the processes that control the atmospheric CO2 (e.g. Louvat, 1997, Dessert et al., 2003). However, the nature of the links between CO2 cycle and the chemical weathering of volcanic rocks is poorly known.

The CO2 consumption by chemical weathering can be estimated with the concentration of Dissolved Inorganic Carbon (DIC ≈ HCO3-) in the rivers. Nevertheless, some processes are likely to modify the DIC concentration in the river (e.g. equilibration with the atmosphere, precipitation of calcite, photosynthesis, respiration).

The processes governing the CO2 consumption by chemical weathering were studied in three volcanic islands in Lesser Antilles (Guadeloupe, Martinique and Dominica). The Lesser Antilles are ideal sites for the study of weathering due to their tropical climate and high relieves, inducing high weathering rates (Rad et al., 2006). Carbon stable isotopes of DIC and major elements chemistry were studied in streams, springs and soil solutions of these three islands during dry and wet season.

The δ13C of DIC and major elements concentrations, highly variable, allowed us to identify the origin of DIC as a mixing between soil CO2 (average value of δ13C = -29.1 ± 2.0‰) and volcanic CO2 (δ13C = -3.25 ± 0.25‰, Agrinier et al., 2002). In addition, we observed an equilibration process of the riverine DIC with the atmospheric CO2. Finally, as highlighted by Rad et al. (2006) for major elements, this isotopic study of the DIC cycling in the river demonstrates the importance of the volcanic fluids on chemical weathering processes.

References

Sedimentary 232-Th as a tracer of dissolved detrital inputs to the ocean

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This study uses long lived thorium isotopes as a tracer for dissolved detrital inputs to seawater. 232Th is derived exclusively from the partial dissolution of detritus. 230Th is produced at a predictable rate by the decay of uranium, and its subsequent removal by efficient adsorption onto settling particles provides a method to quantify dissolved 232-Th fluxes to the seafloor. Ten core-top sediment samples were treated with up to eight leaching techniques and a total digestion to determine the best method for the separating adsorbed from lattice-bound thorium. Adsorbed (and total) ratios giving high dissolved (and total) 232-Th fluxes were measured in sediments from locations with high expected detrital inputs. These fluxes are reasonable by comparison to global estimates of detrital inputs to the ocean. The half-lives of both thorium isotopes are long enough to allow us to apply this technique to sediments that span several glacial-interglacial cycles. Coupled with total sedimentary 232-Th fluxes this data has the potential to evaluate various proposed linkages between ocean and atmospheric processes in the past. Preliminary downcore results display higher 232-Th/230-Th ratios that are consistent with enhanced ice-age dust deposition in the central Atlantic, North Pacific and three out of four Southern Ocean sites. However the two- to four-fold glacial increases indicated by the thorium isotope proxy are smaller than the order of magnitude changes recorded in high latitude ice cores.
Crustal contamination of the upper mantle: Evidence from ophiolites

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Our studies of podiform chromitites in the Luobusa ophiolite, Tibet and the Semail ophiolite, Oman provide evidence that their mantle sources were contaminated by crustal minerals. The chromitites contain rounded, reworked grains of zircon, corundum, quartz, feldspar, diopside and amphibole(?). These are associated with moissanite (SiC), graphite, PGE minerals, rutile, Fe, Ti and Si alloys and native elements. Careful sample collection and preparation, and duplication of results in several laboratories rule out natural or anthropogenic contamination.

The zircon grains range from 20 to 300 µ across, are typically well rounded and have complex internal zonation. Rare grains are subhedral and have regular, concentric zoning. Some contain inclusions of quartz, rutile, orthoclase, mica, ilmenite or apatite. In situ ²⁰⁶Pb/²³⁸U dates by SIMS for the Luobusa zircons are very heterogeneous and range from 1657-549 Ma, far older than the ophiolite (~120 Ma), clearly indicating a mixed population of crustal protoliths.

The grains of quartz, corundum, feldspar and diopside range from 0.1 - 0.5 mm and are moderately to well rounded.

The morphology, composition and age of these minerals strongly suggest that they were originally derived from reworked sedimentary or metamorphic material transported into the mantle by subduction and later incorporated into the chromitites. Their occurrence with ultrahigh pressure minerals such as diamond, and coesite in the Luobusa ophiolite suggests derivation from depths of at least 100 km.

Olmec serpentinitic pieces from La Merced: isotopic and geochemical constraints

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Geoarcheology and petrological methods

The olmec (1,200 B.C. to 400 B.C.) was the first mesoamerican culture, characterized by extensive use of serpentinites (Heizer, 1961; Rodríguez and Ortiz, 2001). To know the geological provenance were performed XRF, ICP-MS, EM-WDS, and thermal ionization MS (Rb-Sr and Sm-Nd isotopic systems) on 17 archeological samples (SAO) from La Merced and 15 geological (GS) from Mexico and Guatemala.

Discussion of results

Mineralogy and geochemical composition (V, Zr, Zn, Cr, Ti; REE series) show a better correlation among SAO and GS from south Mexico. Likewise, Sr isotopic ratios for SAO ⁸⁷Sr/⁸⁶Sr (0.70567-0.71258) and the Nd isotopic system displays ε-Nd values from -5.4 to +6.6.

Conclusions

Petrological information indicate that only the Sierra de Juárez geological samples have affinities to the SAO objects from La Merced; near Vista Hermosa fault.

References

A depleted lithosphere component in the Hawaiian plume: Noble gas evidence from plume-related mantle xenoliths

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Garnet pyroxenite (GPX) xenoliths from Salt Lake Crater, Oahu, are interpreted as high-P cumulates (60-90 kbars depth) of Hawaiian plume-derived basaltic melts [e.g. 1,2]. Two generations of secondary melt/ fluid inclusions document two distinct episodes of metasomatic overprint: (1) Young, immature and irregularly shaped “type-A” inclusions represent nephelinitic host magma, trapped along poorly sealed cracks during eruption some 0.3 Myrs ago. (2) Old, mature and polygonal “type-B” inclusions aligned along well-sealed cracks document pre-eruptive metasomatism of the mantle. LA ICP-MS analyses of “type-B” inclusions indicate high contents in siderophile and chalcophile trace elements including the PGEs. TEM and spectroscopic evidence shows that, after trapping, a highly reducing C-O-H-S-Cl-rich melt differentiated into a CO2-rich gas phase, “basaltic” glass and nm-sized “exotic” minerals including nano-diamond, native Fe and Cu, PGE minerals, and corundum [3]. Combined step-heating, TEM and isotope data reveal a distinct degassing behaviour of both inclusion types. Highly “depleted” [e.g. 4] noble gas signatures of type-B inclusions (40Ar/36Ar ≈ 12000, 3He/4He ≈ 7 R/Ra, 21Ne/22Ne ≈ 0.05, 20Ne/22Ne ≈ 12) indicate generation of the trapped melts within a depleted MORB-type mantle and are compatible with the presence of old, recycled, depleted lithosphere intrinsic to the Hawaiian plume, as also suggested by the Hf-Nd-Sr isotope systematics of the GPX host [1] which the melts infiltrated. Alternatively, the melts may have originated from upper mantle material incorporated into (or enveloping) the Hawaiian plume.

References

Interaction of gypsum and As(V)aq at different pH ranges

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This research is focused on the study of As(V)-gypsum interactions in aqueous solution within different ranges of pH and concentration. The main goals of this study are: 1) to evaluate the capacity of gypsum to remove arsenic from aqueous solutions; 2) to understand the nature of the processes by which the removal takes place and, 3) to characterize the solid phases derived from these interactions. Although the mobility and toxicity of arsenic in the environment has been abundantly studied, the crystal-chemistry, thermodynamic properties and solubility products of arsenates continue to be poorly known. This lack of data is an important handicap because an in-depth study of arsenate mobility in natural systems requires a precise knowledge of the solid phases that may or may not precipitate, as well as their crystal-chemistry, and their solubility.

The study has been carried out at different pH ranges using batch experiments. The aqueous solutions were characterized by AAS, ion chromatography, and ICP-AES. The solids were characterized using SEM-EDS, powder, grazing incidence, and single-crystal XRD.

Figure 1: pharmacolite (CaHAsO4·2H2O) overgrowth on gypsum.

The results show that at high pH (>10.5) there is a virtually complete removal of As(V) due to the surface precipitation of amorphous Ca₈(AsO₄)₂·nH₂O and crystalline NaCaAsO₄·7.5H₂O. In contrast, the effectiveness of the uptake process is very low at lower pHs, as it involves the surface precipitation of different calcium arsenates (guerinite, sainfeldite, pharmacolite, ferrarisite). The study included determinations of solubility products, growth morphologies, and epitaxial relationships. In addition, structural characterization by single crystal XRD has been carried out for NaCa₂H(AsO₄)₂·6H₂O and NaCaAsO₄·7.5H₂O.
Modelling transfer of elements from the continent to the ocean at the large watershed scale in a tropical environment

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Continental weathering of silicate rocks has been recognized as a major driver of climatic changes at the geological timescale. New evidences and preliminary modelling works [1] show that the impact of continental weathering on the geochemical cycles and climate might be non negligible at shorter time scales, from $10^2$ to $10^4$ years, with for instance an increase in total continental weathering by 12% from the LGM towards the present day [2].

Continental weathering at large scale ($10^6$ km$^2$) is generally described through parametric laws (see for instance [3]), linking weathering rates to mean annual air temperature and continental runoff. These laws are masking numerous other parameters, implicitly included, such as the role of vegetation and physical erosion. These laws generally overestimate weathering rates in tropical area, because of high local temperature and runoff. It was indeed stressed by Edmond et al. and others [4] that chemical weathering in tropical environment might be extremely low due to the development of thick soils undergoing weak physical erosion.

A coupled model of biospheric and weathering processes has been developed to estimate the transfer of elements to the ocean originating from tropical watersheds. The BERNI model is the result of the coupling of LPJ – dynamic global vegetation model [5] with the WITCH model [6] that estimates dissolution/precipitation of minerals in the soil environment from kinetic laboratory laws.

Here we present results obtained for the Orinoco watershed. Output of the coupled model includes major ion concentrations that are compared to available data, and CO$_2$ consumption through weathering for a tropical environment. We emphasize the need for the development of mechanistic numerical models of weathering processes working at the continental scale.

References

Microbial leaching of iron from magnetite under aerobic and anaerobic environments

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It is in its infancy to use bacteria as a novel biotechnology for leaching precious and heavy metals from raw materials. The objective of this study was to investigate biogeochemical processes of iron leaching from magnetite reduction by iron-reducing bacteria isolated from intertidal flat sediments, southwestern part of Korea. Microbial leaching experiments were performed using both Aldrich magnetite and magnetite ore, in well-defined media with and without bacteria under aerobic and anaerobic environments. Water soluble Fe production was determined by Inductively Coupled Plasma Spectroscopy (ICP) analysis of bioleached samples in comparison to uninoculated controls, and the resulting precipitated solids were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The pH typically decreased from 7.3 to 5.5 during 4-week incubations. The Eh of the initial medium decreased from ~ 40 mV to -550 mV under anaerobic environments upon incubation with the metal reducing microorganisms. Measured pH and Eh are consistent with the thermodynamic stability of ferrous iron formation. The decrease in pH is due to glucose fermentation producing organic acids and CO$_2$. The extent of iron leaching from magnetite in the aerobic conditions (Fe = 107 ppm) was higher than that in the anaerobic environments (Fe = 94 ppm). In the anaerobic conditions, Fe(III) in the magnetite was also reduced to Fe(II), but no secondary mineral phases were observed. Amorphous iron oxides formed in the medium under aerobic conditions where there was sufficient supply of oxygen from the atmosphere. This study suggests that the reduction processes involve dissolution-precipitation mechanisms as opposed to solid state conversion of magnetite to amorphous iron oxides. The ability of bacteria to leach soluble iron and precipitate amorphous iron oxides from crystalline magnetite could have significant implications for biogeochemical processes in sediments where Fe(III) in magnetite plays an important role in the largest pool of electron acceptor as well as the tool as a novel biotechnology for leaching precious and heavy metals from raw materials.
Provenance of Lower Cretaceous sediments from Svalbard and NE Greenland: A detrital zircon study

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Upper Jurassic – Lower Cretaceous sedimentary successions in the Wandel Sea Basin of North Greenland have previously been shown to correlate stratigraphically with similar aged formations on Svalbard, including the mainly fluvial Helvetiafjellet Fm (Dypvik et al., 2002). Detrital zircons from Lower Cretaceous sedimentary formations from the Wandel Sea Basin (Kilen and Peary Land) and Svalbard (the Helvetiafjellet Fm.) have been dated by U-Pb and analysed for Lu-Hf isotopes by laser ablation plasma source mass spectrometry (LAM-ICPMS). Samples from all three areas display a similar range of U/Pb ages, with significant zircon populations at 1.0 – 1.2, 1.8 – 2.0 and 2.6 – 2.8 Ga. Major hiatus occur between 2.1 and 2.4 and from 0.48 to 0.91 Ga. Low initial 176Hf/177Hf ratios indicative of recycled older crust are predominant in Caledonian-aged zircons, in the Palaeoproterozoic 1.8 – 2.0 Ga populations, and among late Archean zircons. Other U/Pb age populations in the studied samples are dominated by zircons with positive εHf values, indicating a significant contribution of mantle-derived material. There is commonly a narrow range of εHf values seen within the various U/Pb age population, and the values seen in the different samples are in general correlated with the different age populations. One exception is the 1.8 – 2.0 Ga population where variatations suggest variable sources for this age group. The U/Pb data indicate that Greenland could be the sole source of the studied sandstones, which to a large extent is supported by Lu/Hf data. However, concordant ages in the range 1.0 – 1.1 Ga are generally infrequent in the published record from Greenland, and no large terrane of this age have as yet been discovered in Greenland. This mismatch suggests the presence of a source outside the Greenland subcontinent.

The sedimentological link between Mesozoic sediments on Svalbard and North Greenland has been known for some time. This work demonstrates that the two areas most likely had the same areas of provenance, documented by near identical U/Pb age and Lu/Hf isotope signatures of detrital zircons.

References

Metal saturation in the upper mantle

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The uppermost mantle represented by samples and partial melts appears to be quite oxidized at oxygen fugacities (fO2) around the FMQ equilibrium. However, whether the oxidation states found in shallow mantle regions are representative for the entire upper mantle remains unclear. There is evidence for reduction with depth. Thermodynamic model calculations and analyses of natural garnet peridotite samples indicate that Fq2 in the upper mantle decreases with increasing pressure [1]. In addition, experiments have shown that phases stable in the transition zone (400 to 670 km) and the lower mantle (670 to 2900 km) can incorporate so much Fe3+ that an Fe–rich metal phase is likely to be stable [2,3].

To simulate redox controls in the upper mantle experimentally, we have equilibrated Fe2O3-free synthetic fertile mantle material in metallic Fe capsules between 1 and 14 GPa and 1220 to 1650°C. fO2 at run conditions, approximated from the FeO content of the silicates, are IW – 0.5 to –1.2. Analyses of pyroxene and garnet with Electron Energy Loss Spectroscopy (EELS) show that above 7 GPa, subcalcic pyroxenes and majoritic garnets incorporate so much ferric iron that a mantle composition with 8 wt.% FeO and 2000 ppm Fe2O3 will be within metal saturation. Hence, the earth’s upper mantle at > 250 km depth is likely to be saturated with an (Fe,Ni) metal phase.

It was proposed [3] that the high ferric iron concentrations noted in experimental transition zone and lower mantle phases may be derived by disproportionation of ferrous iron components in silicates, according to 3FeO = Fe° + Fe2O3. If this was the case for the upper mantle, the Fe°–Fe2O3–Fe3O4 triple point in the Fe–O system (at ~ 570°C at 10^5 Pa) should be shifted to higher temperature with increasing depth. An in–situ determination of the wuestite–magnetite phase transition between 0.5 and 5 GPa in the presence of metallic Fe in the MAX80 high pressure device, using white synchrotron radiation, shows that the disproportionation reaction has a negative slope in P–T space. Therefore, to relate the high ferric iron concentrations in upper mantle pyroxene and garnet to pressure–induced FeO disproportionation alone seems a simplistic view.

References
Oxygen isotopic composition in deep-sea coral, Lophelia pertusa
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The deep-sea coral Lophelia pertusa is a scleractinian coral (azooidaellate) found mainly in Atlantic Ocean. The stable isotopic compositions of their skeleton are frequently used to reconstruct paleocceanographic conditions, including seawater temperature. However, microanalytical techniques, i.e. microdrill and SIMS, have shown that the $\delta^{18}O$ in lines of centres of calcification (LCC) are strongly depleted relative to the surrounding fibrous skeleton. These large amplitude, small length scale isotopic variations cannot be driven by changes in environmental parameters. Several models have been proposed to explain the observed variations, including models based on pH variations of the hypothetical extracellular calcifying fluid (Adkins et al., 2003, Rollion-Bard et al., 2003).

To document clearly the oxygen isotopic behaviour against the structure and the pH, we have performed ion microprobe $\delta^{11}B$ and $\delta^{18}O$ profiles cross-cutting the two main structures of Lophelia pertusa (the $\delta^{11}B$ values are discussed in an abstract by Blamart et al. (this conference)). The $\delta^{18}O$ data range from -2.61 to 3.41 ‰, which is in the range of variation obtained by microsampling. The LCC $\delta^{18}O$ values range from -2.61 to -1.17 ‰, with a mean value of -1.93 ‰ (n=13). The $\delta^{18}O$ values for the surrounding fibres are systematically heavier, ranging from 0.45 to 3.37 ‰, with a mean value at 2.41 ‰ (n=19). So the $\delta^{18}O$ values appear strongly correlated to the microstructure of the coral skeleton.

It was thought that this different behaviour of the $\delta^{18}O$ between fibres and COC was principally driven by variations of pH. The $\delta^{11}B$ data performed in parallel profiles demonstrate that there is no correlation between $\delta^{18}O$ and $\delta^{11}B$, and therefore no correlation with pH. Moreover, it was presumed from $\delta^{16}O$ data that LCC should have a higher pH than surrounding fibres and it is the contrary. This implies that the LCC and surrounding fibres do not derive from the same calcifying fluid. Therefore LCC and surrounding fibres are precipitated by different mechanisms, most likely which are controlled by specialized domains of the calciclastic layer.

References

Lamproite-hosted xenoliths of Vestfjella: Implications for lithospheric architecture in western Dronning Maud Land, Antarctica
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Lamproite-hosted xenoliths from Kjakebeinet (73º47’ S, 14º53’ W), south Vestfjella, represent unique samples of the unexposed continental crust at the rifted margin of western Dronning Maud Land. The xenolith suite indicates 1) heterogeneity of the crust, 2) granulite facies metamorphic conditions, and 3) mainly igneous protoliths. Two leucocratic tonalite gneiss samples yielded U-Pb SHRIMP zircon ages of ~1.0–1.3 Ga (J. Jacobs, personal communication, 2006). Interpretation of mineral–whole-rock Sm-Nd isotope data on mafic granulites is complicated by lamproite overprint. The results imply compositional affinity to Proterozoic lower crustal xenoliths from Lesotho, South Africa (Rogers and Hawkesworth, 1982) and equilibrium of the Sm-Nd system during Grenvillian and Jurassic magmatic events. Overall, the lamproite-hosted xenoliths indicate extension of the Proterozoic Maud Belt crust to Vestfjella. These results and the presence of basalt-hosted Archean xenoliths at the nearby Muren (Luttinen & Furnes, 2000) imply that the Kjakebeinet lamproites erupted probably just at the Archean-Proterozoic lithospheric boundary.

References
Experimental study of REE behaviour during apatite dissolution in presence of iron and organic matter

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The absolute concentration and distribution of Rare Earth Elements (REE) in many natural aquatic systems is controlled by 1) the dissolution/precipitation rates and 2) the solubility of phosphate minerals (c.f. Poitrasson et al., 2004), which themselves may be influenced by the presence of iron colloids and aqueous organic acids. Taking account of the results of Kohler et al. (2005) the effect of iron colloids and dissolved organic acids on the behaviour of REE in natural fluids were determined by the dissolution of natural apatite (Ca₅(PO₄)₃F) in the presence of a variety of selected aqueous fluids. To best replicate natural system, experiments were performed in closed-system reactors at 25°C and pH 4 and 6. After a short initial period due to the presence of REE in the initial apatite, the reactive solutions become supersaturated with respect to rhabdophane (REE(PO₄)₆H₂O), which buffers total REE concentration and alters the REE spectra. Complimentary synthetic lanthanum rhabdophane (La(PO₄)₆H₂O) dissolution/precipitation experiments were used to determine the steady-state rates of this reaction and to determine aid in the interpretation of the apatite dissolution experiments.

Results to be presented will be used to assess the role of rhabdophane precipitation and the presence of iron colloids and dissolved organic acids during the chemical evolution of surface and near-surface waters. Further analysis of these results is used to access the applicability of aqueous REE speciation models to predict the composition of REE in natural waters.

References


Hydrochemical characteristics of surface water in two boreal granitoidic settings, Eastern Sweden

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The Baltic Sea and its terrestrial surroundings consist of a unique environment due to the brackish water and still active land uplift (up to 8-9 mm/year). Consequently, the near-coastal catchment areas are characterised by young and unweathered soils. The overall aim of this study was to increase the understanding of the chemical dynamics that control water chemistry in small natural catchments in this region, with focus on spatial and temporal trends. The work was done within the Swedish nuclear waste programme and two different areas were studied: Forsmark which has a carbonate-rich till and Laxemar with a carbonate-poor till. One of these will be selected as a deep repository for spent nuclear fuel.

Surface water (lake and stream water) were collected and analysed for major elements, nutrients and trace elements (U and REEs). The water sampling period lasted for nearly four years and continuous flow measurement were carried out over the last two years. Repetitive seasonal cycles in surface water chemistry have been observed each year along with seasonal cycles in stream discharge. The major findings were: (1) the concentrations of elements derived from rock weathering increased in stream water during flow, (2) sporadic intrusions of brackish water from the Baltic Sea resulted in strong increase in salinity (Na, Cl-, Br-, SO₄²⁻), (3) a huge increase in biological activity during summer months resulted in decreased concentrations of NH₄⁺, NO₃⁻ and Si and increased pH and concentrations of chlorophyll a, O₂, DON, POC, PON and POP, (4) the U concentrations were high at both areas and a possible source is reduced U-minerals in the overburden due to the young and unweathered soil and (5) the REE concentrations were low and characterised either by an increase in relative concentrations throughout the lanthanide series (Forsmark) or flat patterns (Simpevarp), and were by speciation modelling predicted to be carried as organic complexes.
Surface charge, ion adsorption and molecular dynamics at the \(\alpha\text{-SnO}_2\)/water interface

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Introduction

It has been hypothesized that the bulk dielectric constant (\(\varepsilon\)) of the oxide solid influences the structure of interfacial water as well as the nature of ion sorption at the interface.\(^1\) To investigate this, we have studied cassiterite (\(\alpha\text{-SnO}_2\), with \(\varepsilon=9\)) using potentiometric titrations, quasielastic neutron scattering (QENS) and molecular dynamics (MD) simulations; and compare the results to previously obtained results for isostructural rutile (\(\alpha\text{-TiO}_2\), with \(\varepsilon=121\)).

Results and discussion

QENS experiments performed on nanosized powders of cassiterite and rutile, predominantly showing the 110 crystal face, indicated considerable differences in the dynamics of water molecules at the interface. Our MD simulation results showed excellent agreement with the measured relaxation times of interfacial water on the 1–100 ps time scale.

Titration showed that the charging of the cassiterite surface is of the same magnitude as for rutile. However, for cassiterite we obtained virtually identical charging curves in RbCl and NaCl media, whereas charging on rutile is clearly different in the different media. Results from MD simulations indicate that the distribution of Rb\(^+\)/Na\(^+\) on the two surfaces is quite different, thus providing an explanation for the observed differences. Significant differences are also observed for Sr\(^2+\) adsorption, while Zn\(^2+\) adsorption is similar on the two mineral surfaces.

Using O-H bond distances obtained in ab initio and MD simulations together with hydrogen bonding schemes obtained from MD, we constructed a surface complexation model based on the MUSIC model\(^2\) that was able to predict the observed charging and distribution of ions.

References


Phase and melting relations of a residual garnet clinopyroxene

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Melting behaviour and high pressure phase relations of refertilised mantle comprised of mixed lithologies (e.g. discrete bodies of mafic eclogite or pyroxenites and diverse types of metasomatised, re-fertilised or depleted mantle) are poorly constrained, yet this information is essential for understanding the observed geochemical diversity of primitive magmas on Earth.

Our project is designed to explore the melting behaviour of subducted crust in an inhomogeneous, buoyant, upwelling mantle. We track a sequential process in which melts are redistributed from the (initially) low temperature melting of average oceanic crust, and then from the residues (garnet pyroxenite) until the solidus of the latter equals or exceeds the solidus of refertilised peridotite.

Composition Res-2 is the melting residue of an anhydrous altered MORB composition (GA2 of Spandler \textit{et al.}, submitted) at 5 GPa near the point of coesite out, and hence is a model for recycled eclogite which has lost a siliceous melt component during mantle upwelling. It is therefore depleted in incompatible minor elements, with 2.2 wt% Na\(_2\)O and a CaO/Na\(_2\)O ratio of 4.9. Res-3 is identical but has higher CaO/Na\(_2\)O ratio of 12.1.

The subsolidus phases of Res-2 & 3 are grt and cpx with accessory coesite/quartz. The solidus of Res-2 is at 1275°C at 3 GPa, 1400°C at 4 GPa, 1425°C at 5 GPa, and <1450°C? at 6 GPa. The solidus of Res-3 behaves similarly, but is at slightly higher T than that of Res-2 (1300°C at 3 GPa).

Low-degree melting (<10%) is eutectic-like. Once coesite is melted out, the grt-cpx cotectics control melt compositions and proportions with cpx>grt. However, with increasing degree of melting, cpx/grt ratios decrease until cpx is exhausted, leaving grt as the sole liquidus phase. In contrast, coesite-out for Res-3 remains approximately constant at ~50°C above solidus at all pressures. In residues of Res-3 the proportion of grt increases with P, and always exceeds that of cpx.

Melt compositions vary with increasing degree of melting from dacitic to basaltic for Res-2 at 3 GPa. However, at higher P, melts of Res-2 are generally much less silica rich, varying from andesitic to basaltic. This is similar to Res-3 at all pressures.

For both Res-2 & 3, Ti behaves incompletely in cpx at all P-T conditions, but D\(^{30}\)cpx/melt decreases toward higher temperature. Na however, is incompatible at 3 GPa, but compatible at higher pressures.

Reference

Late-stage removal of chalcophile elements from the mantle by sulfide liquid extraction to the core

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The U-Pb chronometer reveals a more protracted age of Earth core formation (65-85 Myr; Halliday, 2003) compared to the Hf-W chronometer (30-50 Myr; Kleine et al., 2005). These long-lived isotopic systems are ideal for determining the timescale of core formation because the parent-daughter ratios are fractionated by metal-silicate segregation, with moderately siderophile W and slightly siderophile Pb following metallic liquid into the core. The discrepant timescales suggest that a strong U/Pb fractionation took place sometime during the accretionary history of the Earth, that did not affect the Hf-W system (Wood and Halliday, 2005).

Under reducing conditions in the early Earth, liquid Fe metal separated from liquid silicate to form the core. With oxidation of the lower mantle and the continued accretion of volatile-rich material, it is likely that the later stages of Earth differentiation involved the formation of a FeNi-sulfide liquid (O’Neill, 1991). It has been suggested that because Pb displays chalcophile behaviour (Jones et al., 1993), contrary to W (Chabot and Jones, 2005; Jana and Walker, 1997), removal of a small portion of this sulfide ‘Hadean matte’ to the core may have depleted Pb from the mantle, disrupting the U-Pb chronometer (Hart and Gaetani, 2006). The abundance of other chalcophile elements in the mantle would also have been altered by this process, such as Te and Se, useful in evaluating Earth differentiation processes.

Partitioning of Pb, Te, and Se between liquid metal and liquid silicate are presented at 3 GPa and 2233 K, in which the S content and O₂ are gradually increased. At IW-2, the partition coefficients (D) for Te and Se show a 3-fold increase with the addition of ~10 wt% S to the metallic liquid, with D₂g increasing from 104±18 to 324±68, and D₆e from 30±6 to 90±13. A marked increase in D₆e was observed by Ballhaus et al. (2006) with the addition of S at low pressure. Similar to Se and Te, higher pressures may increase the magnitude of D₆e, suggesting that segregation of some ‘Hadean matte’ equilibrated at high P-T conditions in a magma ocean, may have been a significant factor in disrupting the U-Pb age of core formation on the Earth.

Constraints on atmospheric H₂ from banded iron formations

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Quartz-magnetite banded iron formations are ubiquitous throughout the Archaean geologic record. Models for the composition of the Archaean atmosphere and ocean must therefore be compatible with the widespread precipitation of magnetite from the ocean. At 25°C magnetite is stable relative to siderite only when the partial pressures of H₂ and CO₂ are so low that their reaction to form methane cannot sustain reproduction by methanogenic organisms (Sleep and Bird, 2007).

If we assume ocean temperatures ~ 25°C and a partial pressure of CO₂ in the atmosphere ~ present value, magnetite stability is only possible at H₂ pressures below ~0.0001 bar. At the maximum CO₂ pressures allowed by Precambrian palaeosols (Rye et al., 1995), the hydrogen pressure would be further 5 orders of magnitude lower.

The common presence of magnetite in Archaean sediments is therefore not compatible with models that favour an early Archaean atmosphere characterized by high hydrogen mixing ratios (Tian et al., 2005) or with suggestions that H₂ nourished an extensive biosphere prior to the evolution of oxygenic photosynthesis (e.g. Tice and Lowe, 2004).

References

Mississippian microbial carbonates: Test for the validation as proxy for marine REE geochemistry

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First results suggested that recent microbial carbonates are so far the best proxy material for the record of marine REE-patterns (Webb & Kamber 2000). The results were confirmed by further tests on Archean (Kamber & Webb, 2001, Kamber et al., 2004) and Devonian (Northdurft et al., 2003) microbial carbonates.

To further validate this proxy, REE and some additional trace elements of microbial carbonates were analysed from several locations from the upper Visean (Carboniferous) of England, Morocco, and Spain. Very clean microbial material was chosen by thin-section studies and analysed by ICP-MS. All samples show very smooth REE-patterns that perfectly display the REE-geochemistry characteristics of modern seawater as e.g. LREE depletion, positive La- and Gd- and negative Ce-anomalies. The nearly marine Y/Ho-Ratio as well as the contents of Zr, Sc, Hf and Th suggest very low terrigenous contamination.

While accompanying non-microbial carbonates show the same REE-pattern as the microbial ones, they have a significantly lower absolute REE content and are therefore less readily accessible for analysis.

Slight differences exist in REE content of the different locations. Potential interrelation with the local paleogeographic situation, e.g. by incorporation of variable degrees of terrigenous input require further examination.

Our data confirm the results by Webb & Kamber (2000) that microbial carbonates are so far the most reliable and additionally easiest accessible proxy for fossil marine REE-geochemistry. They do not show the fractionation problems of skeletal carbonates, incorporate high REE content and are overall relatively resistive to diagenetic overprint.

Further investigations to elucidate the possibilities of application to paleogeographic and paleooceanographic reconstructions are necessary.

Carbonate and anhydrite veins from altered gabbroic oceanic crust (Atlantis Massif, MAR 30°N)

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Atlantis Massif is an Oceanic Core Complex (OCC) that formed in the past 1.5-2.0 Myr at the intersection of the Mid-Atlantic Ridge and the Atlantis fracture zone. IODP Hole U1309D, drilled in the central part of the Atlantis Massif OCC, is the third-deepest hole in oceanic lithosphere with a core recovery of 75%. Gabbros and troctolites are the dominant rock types (92%), followed by ultramafic (~5%) and basicitic (~3%) rocks. The magmatic sequence is metamorphosed and fractured, and fluid flow during uplift resulted in the formation of several generations of late-stage veins that record sub-seafloor water-rock interactions. Below the diabase-dominated top section of U1309D carbonate veins are the most abundant late-stage vein type. Macroscopic anhydrite veins occur only at about 740 mbsf.

Carbon, O and Sr isotope compositions of the calcites do not vary systematically down-hole. The 87Sr/86Sr ratios are relatively unradiogenic and span a limited range between 0.7043 and 0.7051. Oxygen and C isotope ratios are both isotopically light displaying δ18O (VSMOW) values of about 10‰ and δ13C (VPDB) values of about -4‰. Oxygen isotope compositions of calcites yield minimum precipitation temperatures between 150° and 220°C (assuming seawater δ18O for the fluid). The temperature could have been significantly higher, if the fluid had exchanged oxygen with basement. For instance, if the δ18O value of the precipitating fluid was 2‰, like in the Rainbow hydrothermal fluids, calculated formation temperatures would be 30° to 50°C higher. In fact, Sr isotope ratios of the carbonate veins approach values for high-temperature hydrothermal systems such as Rainbow or Logatchev. Unlike in the calcites from detachment fault rocks from the 15°20'N Fracture Zone area, however, the calcites from Site U1309D lack carbon isotope signatures for thermal methanogenesis. Hence, temperatures were likely not higher than 300°-350°C.

Two massive cm-wide single anhydrite veins were recovered at about 740 mbsf at Site U1309D. For the anhydrite veins we obtained 87Sr/86Sr ratios of 0.70774 for core 150R3 and 0.70631 for core 153R3. As the Sr isotope composition of anhydrites from 1309D and 504B are similar we infer that 1309D anhydrites may also have formed in the down-flow limb of a hydrothermal convection cell, from seawater that has been heated to about 150°C and has had limited opportunity to exchange Sr with the basement.
Seismic constraints on deep Earth structure and mantle melts

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Seismic results of recent years characterize Earth’s lowermost mantle to be highly heterogeneous on many scale lengths. Structures found using seismic means include sharp horizontal discontinuities (although strong topography on these might be present), thin ultra-low velocity zones (thin regions of strongly reduced seismic velocities), anisotropy and large anomalously slow regions with sharp vertical boundaries. Therefore, the lowermost mantle and core-mantle boundary region is a likely location of untapped, “hidden” reservoirs in the Earth which might be detectable by seismic means.

The scales of these heterogeneities span several magnitudes from 1000’s of km to the smallest detected structures with scalelengths of only a few 10’s of km. Smaller structures are likely and their detection depends on increased seismic resolution.

These results indicate a highly dynamic and complicated region that can only be understood by combining seismological, geochemical, geodynamical and mineral-physical results. Current models of the lowermost mantle, the D” region and the core-mantle boundary include the post-perovskite phase transition to explain the D” discontinuity and possibly other regional layers, partial melts to explain ultra-low velocity zones and chemically distinct regions to both explain large-scale and small-scale structures.

This presentation will highlight recent seismological results of the structure of the D” discontinuity focussing on the structure of the structure of the post-perovskite phase transition beneath the Cocos plate (central America). The second part of the presentation will focus on the fine scale structure of ultra-low velocity zones. The seismic data sampling ultra-low velocity zones can be well explained by the existence of dense partial melts in thin layers. Geodynamic modeling shows that ultra-low velocity zones could be the dominant structures at the edges of large-scale thermochemical piles as have been detected beneath the Pacific and Africa. These partial melts could be iron enriched and might be connected to plume genesis.

The Italian contribution to stardust

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We report combined micro-infrared, micro-Raman, and Field Emission Scanning Electron Microscope analyses of five particles collected by the Stardust spacecraft during its fly-by of comet 81P/Wild2 on 2 January 2004 and returned back to Earth on January 2006.

The CH2/CH3 ratios inferred from the infrared data are greater than those seen in organics in the diffuse interstellar medium, possibly indicating the presence of longer or less branched aliphatic chains. The micro-Raman data offer insights on the state of order of the carbonaceous component present in the particles. A comparison with spectra of Interplanetary Dust Particles (IDPs) and meteorites yields for most of the particles analyzed that the cometary carbonaceous material span a similar range to those of IDPs and the most primitive meteorites (see Figure 1).

Hydrated minerals seem to be present in one particle which seem to contain also carbonates, but further investigations with other techniques need to be performed to confirm these findings. Analyses interpretation is difficult because of the presence of aerogel mixed with the grain.

The analysed grains result to be: 1) rich in complex organic compounds; 2) compositionally and structurally heterogeneous. Suggesting that cometary particles consist of a mixture of subgrains of various sizes and compositions.

Figure 1: FWHM versus peak position for the G band measured for Stardust particles and IDPs (circles and triangles, LANDS team) compared to several IDPs (Wopenka 1988; Raynal et al. 2001) and Meteorites (Raynal et al. 2001).

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The analysed grains result to be: 1) rich in complex organic compounds; 2) compositionally and structurally heterogeneous. Suggesting that cometary particles consist of a mixture of subgrains of various sizes and compositions.

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Diagenetic evolution of the Hooggenoeg Formation: Implication for Archean seawater composition

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The reconstruction of the composition of the Archean atmosphere and ocean relies on scarce data and much theoretical modeling. We provide new constraints on this issue by studying the mineralogy and geochemistry of Archean sediments. The low-grade metamorphic Hooggenoeg Formation (HFm) of the Barberton greenstone belt is an extensive low-grade Palearchean volcano-sedimentary sequence, ideal for studying primitive diagenetic processes. The 3.45 Ga Upper HFm comprises a rhyodacitic volcanic complex with associated volcaniclastic sediments that locally overlie pillow basalts and hydrothermal orthochemical carbonaceous cherts. Detrital material was mainly derived from rhyodacites that were affected by an event of K-Si metasomatism prior to erosion. Phenocrysts, matrix and glass fragments were replaced by quartz-sericite-orthoclase and Ti-oxides still co-existing with primary apatite and zircon. After deposition, the detritus was cemented by early diagenetic microquartz. Silicification mainly resulted in SiO₂ dilution, as the trace element signatures (REE, HFSE) of the sedimentary source rocks were preserved.

Sandstones and conglomerates were affected by carbonatization (up to 40% vol.), as carbonate minerals replaced the diagenetic quartz cement and detritus. Three types of carbonate textures were sequentially formed: 1) Oscillatory zoned ankerite rhombs, 2) aggregates of ankerite-pyrite-sericite and 3) ankerite-calcite-albite-kaolinite. EPMA of carbonates revealed Na/Cl molar ratios of ~1 similar to seawater. The bulk δ¹³C_PDB of carbonates ranges from +1.9 to +2.3 ‰, typical of a marine origin. The δ¹⁸O_SMOW is homogeneous at +15 ‰, similar to deep-burial carbonates.

CAIs in Rumuruti chondrites

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Rumuruti chondrites (R-chondrites) are a group of chondritic meteorites that are highly oxidised, poor in metals, olivine rich (with high Fe content of ~39 mol%), and have high Δ⁴⁰Ca values. Barely any description of Al-rich objects has been reported till now (Bischoff and Srinivasan, 2003; Berlin, 2003). Here, we present the results of our search and analysis of CAIs and Al-rich objects in the R-chondrites.

We studied 14 R-chondrites (NWA 753, 755, 1472, 1476, 1477, 1478, 3364, Rumuruti, Dhofar 1223, Acfer 217, Dar al Gani 013, Hughes 030, Hammadah al Hamra 119, and Sahara 99537) and found 102 Ca,Al-rich objects (87 CAIs, 13 Al-rich chondrules and 2 spinel-rich fragments). Based on the mineralogical characterisation by SEM and electron microprobe the inclusions can be grouped into seven classes: (1) Concentric spinel-rich inclusions (30). These CAIs have abundant spinel and based on the presence or absence of major Al phases can be subdivided into three groups: (a) 18 CAIs dominantly consist of a spinel core rimmed by Al-rich diopside. (b) Five of the spinel-rich CAIs also contain abundant fassaite. These CAIs have a rim of diopside occasionally including olivine. (c) Within seven inclusions besides spinel abundant Na- and/or Cl-rich alteration products (probably napheline and/or sodalite) were observed within the cores rimmed by diopside and, rarely, by olivine. (2) One concentric hibonite-rich CAI has been found. (3) Concentric fassaite-rich CAIs have no rims and contain either hibonite or spinel and/or olivine and ilmenite as additional phases. (4) Complex spinel-rich CAIs are the most abundant variety of CAIs (30). Based on their mineral abundances these CAIs can be subdivided into four other groups: (a) Two inclusions have also abundant hibonite. (b) 29 inclusions are rich in plagioclase (anorthite and/or oligoclase), and contain either hibonite or spinel and/or olivine. Other CAIs have diopside rims. (d) Complex spinel-rich CAIs with abundant Na-Cl-rich alteration products (probably napheline and/or sodalite) were observed within the cores rimmed by diopside rimmed by olivine.

References

Constraints on lithospheric enrichment and crustal contamination in the central Rio Grande Rift (New Mexico, U.S.A.): Volatile and trace-element variability in basaltic melt inclusions

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Many basalts erupted during the early stages of rifting throughout the southwestern United States have a preferential enrichment in water-soluble elements relative to insoluble elements, e.g. Ba/Nb, K/Nb, and Sr/Nd. These high ratios are characteristic of “arc-like” or “subduction-related” basalts often found in volcanic arcs. Numerous studies have suggested that these basalts originate from melting of a mantle source that has undergone hydrous metasomatism as a result of shallow subduction of the Farallon Plate beneath western North America during the Laramide orogeny (80-40 Ma).

We have analyzed olivine- and orthopyroxene-hosed melt inclusions from Rio Grande Rift (New Mexico, U.S.A.) tholeiites and alkaline basalts for major-, trace-, and volatile-element concentrations in conjunction with whole rock geochemistry. If prior petrogenetic models requiring melting of hydrous metasomatized mantle are correct, then melt inclusions from lavas with an “arc-like” signature (e.g. elevated Ba/Nb or Sr/Nd) should be enriched in volatile species such as water and Cl.

In melt inclusions from Rio Grande Rift tholeiites and alkaline basalts Cl/K and Cl/Nb ratios broadly correlate with Ba/Nb and Sr/Nd. In melt inclusions with high Ba/Nb and Sr/Nd ratios (up to 32 and 31, respectively), Cl/Nb (~20-35) and Cl/K (0.04-0.08) ratios are also elevated. Similarly, tholeiitic basalts with lower Ba/Nb and Sr/Nd possess low Cl/Nb and Cl/K ratios (Cl/Nb 8-17; Cl/K 0.02-0.04), more consistent with ratios observed in fresh MORB (Cl/Nb 3-8; Cl/K 0.02-0.04). However, at a given Ba/Nb ratio, Cl/Nb ratios are generally low compared to melt inclusions from present day arc and backarc basalts from the Cascade range in western North America.

The observed correlation between Cl enrichment and “arc-like” trace element ratios is consistent with a model for generation of Rio Grande Rift basalts through melting of variably metasomatized mantle. However, partial melting and assimilation of continental crust could potentially produce qualitatively similar trends. No overall systematic variation in Ba/Nb, Sr/Nd or Cl/K is evident relative to the host Mg#, although within an individual sample host phenocryst compositions are restricted. Future in situ water and Pb-isotope analyses of melt inclusions will further constrain the role of crustal contamination and mantle source enrichment in the generation of the Rio Grande Rift basalts.

Sulfate reduction across a salinity gradient in hypersaline coastal pans

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The impact of salinity on the metabolic activity of sulfate-reducing bacteria in five highly saline to hypersaline coastal pans was studied using a radioactive tracer (35SO42-) technique. We recorded sulfate reduction at the higher in situ porewater salinity (422) than previously reported. The depth-integrated sulphate reduction rates (integrated to 12 cm) varied from 6 to 241 mmol m-2 d-1 and were also among the highest ever reported rates. The reduction rates decreased down-core and, surprisingly, were highest in the winter season when the lowest sediment temperatures were encountered.

High salt concentrations did not inhibit sulfate reduction rates. Rather, higher rates were measured at pans with higher in situ salinities. In laboratory slurry incubation experiments, sediments from the salt pans were treated with increasing salt concentrations. Regression analysis suggested that the short term response of microbial consortia to up-shock was an increase in sulfate reduction activity up to salinities of 350 – 400 and 200 – 300, in hypersaline and highly saline pans, respectively. Beyond these salinities, the cells showed evidence of reduced activities.

Surprisingly, sulfate reduction rates also show an increase with increasing sulfate concentration of up to 600 mM. This is unusual, as for sulfate reduction, the highest reported half-saturation constant values in the literature lie below 10 mM. Does this suggest that there is a third sulfate transport mechanism that becomes active among sulfate reducers thriving in hypersaline environments?
Migmatisation in the Central Alps lasting 10 m.y.

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The southern part of the Central Alps underwent Barrovian style metamorphism that reached partial melting at upper amphibolite facies conditions. Previous geochronological constraints indicated that melting occurred in the Oligocene, around 29-32 Ma, with cooling extending into the Miocene.

SHRIMP U-Pb dating of zircons from migmatite suite from the southern Central Alps yielded variable and distinct ages between circa 31 and 22 Ma. A similar age range is recorded by the U-Th-Pb system of allanite. This range in ages is found not only across different samples, but also within single samples. For example, a leucosome from the locality of Bellinzona contains zircon grains with inherited Permian cores remnants of the magmatic protolith. The cores are overgrown by three zircon rims with different internal zoning and chemical composition, which yield distinguishable ages at circa 31, 26 and 23 Ma. In the locality of Valle Arbedo (25 km to the E) similar migmatites show distinct zircon overgrowths at circa 31, 28, 23, and 22 Ma. For all of the zircon overgrowths the inclusions, trace element composition and Ti-in-zircon thermometry indicate growth in the presence of melt at similar temperatures between 600 and 700 °C. Therefore, we conclude that this region of the Central Alps repeatedly underwent melting at similar conditions over an extended period of at least 10 Ma.

These geochronological constraints support a model where episodic melting is controlled by the availability of aqueous fluids (Berger et al., 2007). Local infiltration of aqueous fluid in rocks of different composition thus produced diachronous melting episodes. The southernmost part of the Central Alps evidently remained at temperatures above the wet granite solidus for at least 10 million years.

Reference

New constraints on conditions of core formation and the light element content of the Earth’s core

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The concentrations of light elements in the Earth’s core must have been set by metal-silicate equilibration during core formation, as was likely the case for the moderately siderophile elements. It has been shown recently that equilibration conditions of core formation can be constrained by the partitioning of FeO between liquid Fe-alloy and silicate melt in a magma ocean, based on the mantle composition and the light element content of the core (Rubie et al., 2004; Asahara et al., 2007). This is because the partitioning of FeO into liquid iron increases strongly with increasing temperature (and therefore magma ocean depth), thus decreasing the FeO content of the mantle and increasing the O content of the core. Based on a simple core formation model, Asahara et al. (2007) estimated that the maximum depth of metal-silicate equilibration was ~1700 km, which would have resulted in a maximum of ~8 wt% oxygen in the core. However, lower limits could not be constrained because the oxygen content of the starting (chondritic) composition is poorly constrained.

Traditionally, experimental data on the metal-silicate partitioning of siderophile elements have been used to constrain the conditions of core formation, for which an estimate of the prevailing oxygen fugacity is required. However, for a given metal-silicate bulk composition, the oxygen fugacity is fixed by the partitioning of FeO, which is a function of pressure and temperature only. Therefore we are developing core formation models based on the combination of FeO and moderately siderophile element partitioning. The model bulk composition is chondritic with an initial oxygen content that can be varied. Liquid metal and liquid silicate are assumed to equilibrate near the base of a magma ocean (defined by the peridotite solidus) and the compositions and relative proportions of the two phases are calculated using mass balance combined with formulations describing the partitioning of FeO and siderophile elements as a function of P and T. The results enable new constraints to be placed on (i) conditions of metal-silicate equilibration and therefore magma ocean depth, (ii) the bulk oxygen content of the Earth and (iii) the oxygen content of the Earth’s core.

References
Fluid-rock interactions recorded by kinetic fractionation of Li isotopes

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Li diffuses relatively rapidly through minerals and fluids and this, coupled with the large differences in diffusivities between its two isotopes (Richter et al., 2003), can lead to large kinetic isotopic fractionations parallel to the diffusion pathways. Thus, Li isotopes can be used to trace fluid-rock interaction. Here we summarize three different pluton-country rock settings that illustrate the controls and limits on kinetic Li isotopic fractionation. Lithium diffused over distances of >30 m from the Li-rich Tin Mt. pegmatite into metamorphic country rocks along fluid-filled grain boundaries accompanied by large, kinetically induced isotopic fractionations (>30‰, Teng et al., 2006). Li diffused over an order of magnitude further into the country rocks than other fluid-mobile trace elements (e.g., Na, Rb, Cs and Sb), making Li perhaps the most sensitive tracer of fluid-rock interaction among the lithophile elements. In contrast, metapelitic country rocks surrounding the Onawa granodiorite are not enriched in Li, reflecting the low Li content of the intrusion (45 ppm) relative to the country rocks (130 ppm) and hence the lack of a chemical potential gradient to drive diffusion. Indeed, Li content of the metapelites decreases by a factor of two adjacent to the pluton, reflecting the loss of Li during metamorphic devolatilization (Teng et al., 2007). The constant δ6Li in the country rocks is consistent with equilibrium fractionation during Li loss via Rayleigh distillation at the temperatures of metamorphism (>500°C). Finally, large, kinetic Li isotopic fractionations are observed perpendicular to the contact between an alkali syenite and granitic country rocks of the Ilímaussaq Complex, Greenland (Marks et al., 2007). Here, however, the syenite is barely enriched in Li relative to the country rocks (25 vs. 14 ppm, respectively), and this concentration difference is not large enough to account for the large isotopic fractionations observed over distances of up to 150 m (δ6Li ≥ −9 in the granite country rocks and ≤ +16 in the syenite). These large fractionations reflect the circulation of isotopically heavy, Li-bearing fluids adjacent to the syenite-granite contact.

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Studies of continent stability using joint petrological and geodynamical models

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Continents are remarkably stable features of our dynamic Earth. Extreme examples of this are Archean cratons, which have resisted erosion by lithosphere delamination and mantle convection for billions of years. However, continents are not stable under all conditions. In fact, delamination of continental lithosphere has been related to intra-plate volcanism and uplift in the absence of shortening. The main goal of this study is to identify and quantifying the key factors that control the stability of continental lithosphere.

To simplify this task we regard lithosphere delamination as a Rayleigh-Taylor instability. Rayleigh-Taylor instabilities have been extensively studied analytically, numerically and experimentally - also with regard to continent stability. It is clear from these studies, that the growth rate of the instability is primarily controlled by the density and viscosity contrast. The density (and viscosity) contrast between the lithosphere and asthenosphere is a complex function of temperature, pressure and, often neglected, chemical and mineralogical composition. Chemical composition can vary significantly among different continents and it may well be that chemical and mineralogical variations determine if the lithosphere is gravitationally stable or not. To test this hypothesis, we use a joint petrological and geodynamical approach. The petrological model is based on a companion study (Simon et al. 2007 – this volume), which explores the dependence of mantle density on chemical composition using thermodynamics. The key metamorphic reaction for continental stability is the garnet-in reaction. The location of this reaction in p-T space is strongly dependent on the Cr2O3/Al2O3 ratio, while the amount of formed garnet mainly depends on the Al2O3 content. This suggests that relatively fertile mantle compositions rich in aluminum will tend to destabilize continental roots. To quantify the effect of mantle composition on continent stability, we will integrate thermodynamically computed densities for various mantle compositions into a geodynamic flow model. Using this joint petrological and geodynamical model, we will explore for which mantle composition continents are stable over geological time and define a critical enrichment for which continental lithosphere becomes gravitationally unstable.
Prebiotic chemistry in iron-rich water medium: Fixation of cyanide as Prussian Blue

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Water based aerosols are ubiquitous in the actual troposphere and it has been suggested that they could play an important role as prebiotic micro-reactors in the origin of life. The salinity and pH of the aqueous phase may have an important influence in the gas-liquid interfaces, which are expected to be special sites for relevant prebiotic reactions (1). The presence of the Archean banded iron formations strongly suggests that dissolved iron (ferrous ion) was present in high quantities in the ancient sea and it has been postulated that the ancient sea had a salinity of the 1.5 to 2 times the modern value and its pH ranged between 4 to 10 (depending of the author).

In this work, we explore the effects of pH (between 5.8 to 9.8) in the generation of biomolecules in prebiotic simulation experiments using aqueous aerosols of saline iron rich solutions and spark discharges in a suitable prebiotic atmosphere.

In all experiments, we observed that the presence of ferrous iron leads the formation of Prussian Blue, a strongly reduction the final pH of the aqueous pool and the lack of small molecules in the raw of reaction. Under the assayed conditions the Strecker reaction is inhibited and the formation of heterocycles is stopped but a rich mixture of carboxylic acids is obtained (Fig. 1). Therefore, independently of the pH, in the studied range, the ferrous ion seems to have an important influence in the formation of the organics and their precursors.

Reference
Formation of high alumina phases in sediments and soils of different ages without inherited weathering products

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We investigated the mineralogy and geochemistry of moraine forest soils in the former ice-covered granitic areas in Kings Canyon and Yosemite National Parks (Sierra Nevada, California), soils on sand dunes at the Pacific coast in Oregon (USA), as well as moraine profiles in the Dry Valley (Antarctica). The profiles did not contain any inherited weathered phases. So the neoformed phases represent the weathering products and help us decipher the weathering processes. Grain sizes of <0.2µm and 0.2-2µm were separated by plant debris. This trend is more pronounced in the 0-90cm section by plant roots and accumulation in the humic rich upper soil horizon. Inverse to that is the trend of the Al/Si ratios close to 1, which are approximately factor 5 higher than the ratios of the source material. Vermiculite is the main clay minerals formed during the last 10-20ky. The 60-80ky old soils in Kings Canyon additionally may contain gibbsite. Mobile nutrient elements such as K, Mn, Mg, and Ca are enriched in the uppermost horizons, because of mobilization by plant roots and accumulation in the humic rich upper soil section by plant debris. This trend is more pronounced in the older profile.

2. In the 120ka old soil profile of the sand dune in Oregon (pH around 5), the 0.2-2µm fractions in the 0-90cm section show Al2O3/SiO2 ratios close to 1, which are approximately factor 5 higher than the ratios of the source material. Vermiculite is the main clay minerals formed during the last 10-20ky. The 60-80ky old soils in Kings Canyon additionally may contain gibbsite. Mobile nutrient elements such as K, Mn, Mg, and Ca are enriched in the uppermost horizons, because of mobilization by plant roots and accumulation in the humic rich upper soil section by plant debris. This trend is more pronounced in the older profile.

Results:

1. In the soils of the Sierra Nevada with soil solution pHs around 6, the fraction 0.2-2µm has fairly high Al2O3/SiO2 ratios close to 1, which are approximately factor 5 higher than the ratios of the source material. Vermiculite is the main clay minerals formed during the last 10-20ky. The 60-80ky old soils in Kings Canyon additionally may contain gibbsite. Mobile nutrient elements such as K, Mn, Mg, and Ca are enriched in the uppermost horizons, because of mobilization by plant roots and accumulation in the humic rich upper soil section by plant debris. This trend is more pronounced in the older profile.

2. In the 120ka old soil profile of the sand dune in Oregon (pH around 5), the 0.2-2µm fractions in the 0-90cm section show Al2O3/SiO2 ratios close to 1, 20 times higher than that of the bulk material. In the section below 90cm, the Al2O3/SiO2 ratios increases to 4. Inverse to that is the trend of the Al/Si ratio in the separation solutions (0-90cm: Al2O3/SiO2 ratio of ~11, below 90cm: ~3). We suppose, that this dissolved or colloidal organic complexes extremely enriched in alumina are translocated from the upper soil horizon into the deeper profile facilitated by the enormous pore space. On the way down the organic ligands are oxidized leading to precipitation of Al-rich phases such as allophane and gibbsite.

3. The composition of the clay fraction of the profile from Dry Valley has low Al2O3/SiO2 ratios close to 0.3, which are close to that of the parent rock. The separation solution is higher in Si (0.7-5.1ppm SiO2) and lower in Al (0.0-0.7ppm Al2O3). No trends of the element contents with age (20ka, 200ka, 2000ka) are discernible. Although the soil solution has pH-values between 8.8 and 10.2, the chemical weathering is insignificant, presumably because of lacking plant material which promotes chemical weathering.

238U-230Th and 226Ra-230Th crystal ages at Volcán Quizapu: A prime location for studying magma mixing processes on short time scales

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Despite significant innovation in textural, crystal-chemical analysis as well as U-series and diffusion age dating of igneous materials, the physical processes associated with measured time scales are unclear. For example, there is often discordance between diffusion ages and absolute ages of mineral separates derived from U-series (238U-230Th and 226Ra-230Th) disequilibria, and the two techniques may be measuring different processes. A simple system with well defined boundary conditions is necessary to understanding the information contained in ages measured by different techniques. We present U-series data for the historic eruptions of Volcán Quizapu, Chile, (5 km3 of lava in 1846/47 and 4 km3 of pumice in 1932). Both dacitic eruptions of Volcán Quizapu were accompanied by andesitic recharge magma. The lavas of the earlier eruption show extensive but incomplete mixing and mingling, while the plinian eruption of 1932 displays less interaction between the recharge and host magmas. 238U-230Th ages indistinguishable from the eruption age and Ra-Th ages of 2-3.5 ka for plagioclase and hornblende separates indicate a relatively short and simple magmatic evolution of Volcán Quizapu that stresses the dominance of short time scales processes associated with the magma mixing. This simplicity, along with the well-constrained repose time between the two major eruptions, makes Volcán Quizapu a perfect location to further investigate the information provided by diffusion and short-lived radioactive isotopic clocks. 226Ra-230Th dating of selected populations from the recharge and host magmas will allow us to integrate textural and crystal-chemical information with crystal ages. In addition, tracking changes in phenocrysts from recharge magma that were not evacuated during the first eruption, but remained in the reservoir and subsequently erupted in the second pulse has the potential to unravel the interplay between diffusion, crystal growth and resorption during a simple magma overturn.
Photoluminescence recovery upon annealing of fergusonite

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Fergusonite [general formula YNbO 4], due to its actinide content, is commonly found in the metamict state. In dry annealing experiments, the majority of structural recovery occurs at temperatures of >800 °C (Tomašić et al., 2006). This process involves intermediate formation of tetragonal α-fergusonite below ∼1000 °C and monoclinic β-fergusonite above this temperature.

We have studied changes in laser-induced photoluminescence (PL) spectra, which are dominated by emissions of centres related to rare-earth elements (REE), upon gradual reconstitution of the crystallinity. For this, a metamict fergusonite sample from Madagascar (Th 1.9 wt%, U 4.3 wt%) was subjected to dry annealing for 100 h at different temperatures. Analogous to observations on annealed zircon (Nasdala et al., 2002), annealed fergusonite yields considerably intensified PL (Fig. 1). General sharpening of bands at higher annealing temperatures is due to increasing crystal field effects and indicates recovery of the fine structure.

Figure 1: Photoluminescence spectra of natural and annealed fergusonite, dominated by trivalent REE (Nd, Er, Pr, Ho, Tm) emissions.

References

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Worlds frozen in time:
Dawn explores 1 Ceres and 4 Vesta

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Dawn is a low-cost planetary mission that uses ion propulsion to rendezvous with and orbit the two most massive members of the asteroid belt, 1 Ceres and 4 Vesta. Our current understanding of Ceres is based almost entirely on remote sensing while our understanding of Vesta is based predominantly on cosmochemical evidence obtained from the Howardite-Eucrite and Diogenite meteorites. These data suggest that these two bodies are quite dissimilar: Ceres being wet with perhaps a 100 km thick ice mantle covered with dust and Vesta being dry with a basaltic surface similar to the moon. Both bodies have clearly undergone thermal evolution to reach their current state but, we believe, did so rapidly in the first 1 – 3 million years of the early solar system well before the larger terrestrial planets were formed. The surfaces of these two survivors of the collisional environment established with the formation of the gas giants have remained frozen in time allowing the Dawn mission to effectively travel not only in space but also take us backward in time to learn the conditions at the earliest epoch of our solar system. Dawn carries redundant framing cameras, a visible infrared mapping spectrometer and a gamma ray and neutron detector. These instruments together with radiometric data provide geologic context, mineralogical data, elemental composition and internal structure. Vesta will be orbited in 2011 and Ceres in 2015.
Site-specific, size-dependent reactivity of Al-oxide nanoparticle surfaces

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We use molecular dynamics calculations to estimate water-exchange rates for a series of aluminum (oxy)hydroxide compounds. These include the Al(OH)64+ monomer; the ε-Keggin ion [AlO4Al12(OH)24(H2O)12]3+/8+ (Al13); the [Al2O2Al26(OH)26(H2O)26]18+ (Al30) aqueous polynoxocation; the surfaces of Al-oxyhydroxide minerals boehmite (AlOOH) and gibbsite (Al(OH)3); and the aluminosilicate mineral kaolinite (Al2Si2O5(OH)4). X-ray structural data can be used in conjunction with rate data from 17O NMR studies2 to test predictions of reactivity trends at a site-specific level. The molecular dynamics calculations here tie these structurally diverse systems together into a simple structure-reactivity trend based on Al-water bond lengths, and highlight the role of the Al13 and Al30 ions in systematically bridging the structural gap between the hexaaquo ion and the oxide surfaces.

Water-exchange rates were calculated for each species using the reactive-flux method. The rate constant is taken as k = kTST where kTST is the transition state rate constant and κ is the transmission coefficient. κ is highly variable across the spectrum of reactive sites, ranging from 0.1 to 0.001.

Overall, the estimates of τ298 for the aluminous minerals are surprisingly short, falling within the range of ~10−5–10−10 s, close to those for alkali and alkaline-earth metal ions. Waters bound at the edges of the minerals will exchange rapidly with bulk waters and with other ligands. The fast rates for these surface sites are consistent with the long Al-water bond lengths and also follow the general trend that rates increase, and ΔH‡ values decrease, with increasing size and decreasing charge/Al ion of the complex.

This framework provides, for the first time, a means for estimating kinetic parameters for individual sites at aqueous polynuclear ions and oxyhydroxide surfaces. This result is enormously important for environmental chemistry where treatment of reactions at the aqueous-mineral interface is a long-standing problem. The structure-reactivity relation presented here places the ligand-exchange properties of extended interfacial systems on a new site-specific, quantitative footing.

References

Potential temperature and volatile contents in mantle plume of Siberian trap province

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Magmatism in the Siberian CFB province is mainly represented by the voluminous lava flows of tholeiitic plateau basalts and subordinate amounts of highly magnesian volcanics and dyke rocks. These highly magnesian rocks are strongly enriched in incompatible trace elements and are characterized by high LREE/HREE ratios. It suggests that their primary magmas were near solidus melts formed at high pressures. P-T conditions of the generation of these hi-Mg melts must be nearly identical with the P-T parameters characterizing magma-generating mantle plume.

To assess the formation conditions of hi-Mg Siberian magmas we investigated melt and fluid inclusions in the phenocrysts of these rocks, which were analyzed for major and trace elements (EMPA and SIMS methods). High Ti/Na ratios and high normative olivine contents in the melt compositions recalculated to the condition of equilibrium with mantle peridotites imply, that initial pressure of magma-generation is in the range of 7–9 GPa.

Ion microprobe data for reheated melt inclusions in phenocrysts from Siberian rocks show low concentrations of volatile and fluid-mobile components. H2O/Ce ratios in melt inclusions from picrobasalts and meimechites are significantly lower than from MORBs and many OIBs. This implies that the source of Siberian magmas was even poorer in water by comparison with convecting mantle peridotites. The same relations are observed for the ratios of a number of other volatile and fluid-mobile components to their non-volatile geochemical analogues, like B/Ce, Pb/Nd etc.

Low levels of volatiles contents imply that the estimates of near-solidus transition temperatures based on comparison with volatile-free systems would not be changed significantly. Comparison of the estimated from melt inclusion data pressures with experimental data shows that the temperature of rising plume material was ca 400°C higher by comparison with convecting upper mantle at the same depth. This proves that plume material arrived from deep levels in the mantle.
Tracking subduction zone fluxes off slabs, across arcs, and into the mantle: B-Li isotopic evidence

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New light element abundance and B and Li isotopic results from forearc settings and samples reflecting deep recycled mantle sources have begun to complete the picture of subduction zone chemical cycling for the fluid-mobile elements (FME). Progressive boron and FME declines with increasing metamorphic grade in forearc “subduction complex” massifs (i.e., Bebout et al 1999), are complemented by signatures observed in diapiric serpentinites and associated fluids erupting in the Mariana forearc, which preserve dramatic enrichments in B and select FME, but are not elevated in most large-ion lithophiles (Savov et al 2005). Declines in B and $\delta^{11}$B across volcanic arcs point to continued removal from slabs by metamorphism, and depleted B and $\delta^{11}$B in ocean island lavas suggest deeply recycled slabs are stripped of boron. B isotopic variations in forearcos point to extensive boron removal at low temperatures, as the $\delta^{11}$B of slab materials (~0 to -3‰ on average) are substantially lower than that of Mariana forearc serpentinites (+13 - +18‰; Benton et al 2004) or of B-enriched arc lavas. High $\delta^{11}$B releases at shallow depths indicate isotopic “lightening” of the slab, such that the $\delta^{11}$B systematics in arc lavas require inputs both of downdrugged forearc mantle materials with high B and $\delta^{11}$B, and of a B depleted, low $\delta^{11}$B slab component.

Li isotopic variations in the forearc mantle are divergent, with serpentinite muds showing uniform $\delta^7$Li indicating equilibrium with high $\delta^7$Li porefluids, while entrained ultramafic clasts record highly variable $\delta^7$Li. Relatively high $D_{Li}$ for mafic minerals (especially Mg-rich sheet silicates) combined with high Li diffusion rates result in exceptionally diverse $\delta^7$Li in mantle-derived ultramafic samples. However, $\delta^7$Li in young volcanic rocks from all tectonic settings are remarkably uniform, ranging from +3‰ to +6‰, indicating buffering by a uniform, Li-rich upper mantle reservoir, and/or limited Li isotopic change due to subduction zone chemical processing, despite evidence for Li and $\delta^7$Li depletion in eclogitic rocks (Zack et al 2003). Interestingly, substantial $\delta^7$Li changes can occur over time in lavas from “dying” subduction systems, suggesting that such changes may only be observed when processes that homogenize the mantle (i.e., wedge convection) shut down.

References

Chemical weathering in the Han River Basin, South Korea: Carbonate and silicate weathering

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This study focuses on the fluvial geochemistry of the Han River, South Korea to determine its chemical weathering rate and associated CO2 consumption rate. The Han River draining approximately 26,000 km$^2$ is the largest river in South Korea in terms of water discharge and the total river length, and consists of two major tributaries: the North Han River (NHR) and the South Han River (SHR). A remarkable difference in basin geology (silicate vs. carbonate) between the NHR and the SHR provides a good natural example to understand the processes of weathering and the influence of basin geology on water quality.

In this paper we report dissolved major elements and Sr isotopic compositions of a total of 58 samples collected seasonally from the Han River system for two years (2000 and 2006). A big difference in the concentration of dissolved loads is observed between the NHR and the SHR: the NHR is much lower in total dissolved solids (TDS), Sr, and major ion concentrations relative to the SHR, while higher in Si concentration and $\delta^{87}$Sr/$\delta^{86}$Sr ratios.

Using the forward model, it is calculated that the dissolved loads of the NHR are primarily from silicate weathering (55±11%) with relatively smaller portion of carbonate weathering (30±14%), whereas those of the SHR mainly from carbonate weathering (82±3%) with minor portion of silicate weathering (11±4%). These results are consistent with geological characteristics of their drainage basin: silicate rocks in the NHR vs. carbonate rocks in the SHR. Unlike the NHR basin, sulfuric acids derived from sulfide dissolution play an important role in carbonate weathering in the SHR basin because of widely distributed coal-containing sedimentary strata. Silicate weathering rate (SWR) of the NHR basin is much higher than that of the SHR basin, indicating higher CO2 consumption rate in the NHR basin.
U$^{4+}$ and Pu$^{4+}$ incorporation in zircon and their effect upon helium diffusion in the host lattice

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Zircon mineral (ZrSiO$_4$) is a potential host matrix for the encapsulation of highly radioactive materials, such as dismantled weapons and nuclear waste from power stations (Ewing, 2001).

We report a detailed computer modelling study, based on interatomic potentials, to address two fundamental issues concerning radiation processes in the zircon mineral: first, the physics and chemistry of U$^{4+}$ and Pu$^{4+}$ inclusion in the crystalline matrix of zircon and, second, the effect of U$^{4+}$/Pu$^{4+}$ dopants on the incorporation and diffusion behaviour of helium in zircon.

Our results show that U$^{4+}$ and Pu$^{4+}$ can incorporate isomorphously in zirconium sites (Zr$^{4+}$). The solution energies of U$^{4+}$ and Pu$^{4+}$ are 0.18 eV and 0.03 eV respectively, which indicates that Pu$^{4+}$ is more readily incorporated as a dopant than U$^{4+}$. However, the positive solution energies show that the inclusion of the two species in the crystalline matrix would occur only under high temperature conditions.

Interstitial incorporation of helium in zircon is an energetically unfavourable process, which causes strong deformation in the host lattice due to movement of atoms in the channel walls to accommodate He. Moreover, the presence of Pu$^{4+}$ and U$^{4+}$ dopants in the zircon lattice has a direct effect upon the energetics of helium diffusion between interstitial sites. For instance, activation energies calculated for He diffusion are dependent upon the distribution of U$^{4+}$ and Pu$^{4+}$ in the lattice, and can differ by as much as 0.2 eV from those calculated for the perfect zircon.

Short-lived naturally occurring radioisotopes ($^{234}$Th, $^{7}$Be, $^{210}$Pb) as a tracer for particle transport in the Gironde fluvial-estuarine system (France)

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Human activities release various chemical species to the environment. Many of these substances bind strongly to sediments, which are then delivered to rivers. Thereafter the fate of pollutants in fluvial environments is linked to particle transport. The short-lived, naturally occurring radioisotopes, $^{234}$Th ($T_{1/2} = 24.1$ days), $^{7}$Be ($T_{1/2} = 53.3$ days) and $^{210}$Pb ($T_{1/2} = 22.3$ years), can be used as potential tracers to investigate particle transport from land to sea. However, up to now, their use is still rare and for $^{234}$Th mainly devoted to marine environments. Uranium ($^{238}$U) forms $^{234}$Th through radioactive decay in the dissolved phase. However, due to the typically low and invariable concentrations of $^{238}$U in riverine environments, the formation of $^{234}$Th is often insufficient to be used as a tracer.

The programme ARTTE “Application Radioisotopes as Tracers of particle transport in environment”, has been carried out to develop the application of $^{234}$Th, $^{7}$Be and $^{210}$Pb in the polluted (e.g. Cd, Hg (e.g. Schäfer et al., 2006)) Gironde fluvial-estuarine system (South-West France). A preliminary investigation in 2005 has revealed adequately elevated and spatiotemporally stable dissolved $^{238}$U activities within this system (Saari et al., submitted), allowing the $^{234}$Th application.

$^{234}$Th, $^{7}$Be and $^{210}$Pb activities in suspended materials were measured monthly (2006-2007) by $\gamma$-spectrometry within the Garonne and Lot Rivers, and the Gironde estuary. The first results reveal: (1) $^{7}$Be/$^{210}$Pb activity ratios decrease from river to estuary, due to aging of sediments and/or to resuspension of old bottom sediments (2) $^{234}$Th$_{ds}$ activities show large variabilities with time, from negligible values up to about 300 mBq g$^{-1}$, probably due to differences of particle residence time in the river channels.

References


Figure 1: Diffusion pathways for helium movement along the x-direction of U-doped zircon.

References:

The Formation of the Fe skarn deposit between Camibogazi and Arnastal (Gumushane, NE Turkey): Evidence from mineral chemistry

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The Fe skarn deposit in the Camibogazi and Arnastal area is located about 50 km north of Gumushane in NE Turkey. The deposit is hosted by Late Cretaceous Carbonate rocks which comprise dolomitic and sandy limestone, and limestone, adjacent to the Eocene Zigana Granitoid [1]. Petrographically, granitoid consists of syenogranite, monzogranite, quartz-monzonite and granite. Fe skarn deposit has mineral paragenesis of vesuvianite (idocrase), phlogopite, diopside, andradite, actinolite, tremolite, epidote, quartz, magnetite, hematite and less pyrrhotite and pyrite. Vesuvianite, diopside and phlogopite mineralization are only seen in a very narrow field of the Camibogazi Plateau (altitude of c. a. 2450 m). Magnetite, hematite, andradite, actinolite, tremolite, epidote, quartz and less parroting and pyrite are seen in Aransas Plateau.

Microprobe analyses indicate that majority of the skarn minerals are calcic and have high Mg/(Mg+Fe). Clinopyroxene consists of diopside (Di0.66,99.04 Hd0.67-2.80 Jo0.29-0.55). Vesuvianite is mostly Mg-rich, and has very low MnO content (< 0.1 %). Phlogopite has high and nearly constant Mg/ (Mg+Fe) ratios, 0.93 to 0.94. The Ba content of phlogopite is low. Magnetite is generally massive, and some of them are martitization. According to vesuvianite-diopside geothermometry, the formation temperatures of skarn minerals in Camibogazi range from 329 to 558 °C.

The Fe exoskarn skarn deposit was characterized by early, high-temperature mineral assemblages dominated by anhydrous minerals diopside and garnet, and late low-temperature assemblages with hydrous minerals vesuvianite, phlogopite and epidote. Types of clinopyroxene and garnet, the abundance of magnetite with minor pyrite, and widespread occurrence of epidote suggest that the Fe skarn deposit between Camibogazi and Arnastal Plateau was formed under relativized oxidized conditions.

Reference


Modelling pore water B and $\delta^{11}B$ signatures in the shallow subduction zone forearc: Examples from Barbados, Costa Rica and N. Japan

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At many subduction zones, pore water geochemistry from boreholes and mud volcanoes indicate a contribution from deep sources. These observations include pore water freshening, but enrichment in volatiles such as B and Li, and decreased $\delta^{11}B$, $\delta^6Li$, and $\delta^{37}Cl$. Identifying the location and distribution of source regions for these tracers is one critical step toward characterizing subduction zone fluid transport. Here, we present a simple model to combine (1) heating and compaction that accompany progressive burial of sediment in subduction zones with (2) previously published laboratory experimental data that constrain the distribution coefficient ($K_d$) for B in marine sediments as a function of temperature, to quantify the expected distribution of [B] $\delta^{11}B$ within bulk mudstones in subduction zones. In a generic subduction zone with a taper angle of 8º, we evaluate two end-member cases: a “cold” (60 mW m⁻²) and a “warm” (120 mW m⁻²) scenario. For the first, simulated values of [B] within the subducted sediment at 30 km from the trench range from 650–1200 µM and values of $\delta^{11}B$ range from 23.4-30.6‰. At 60 km from the trench, [B] ranges from 1010-3340 µM and $\delta^{11}B$ from 18.0-25‰. For the warm scenario, simulated [B] is 970-2400 µM at 30 km and 2250-11480 µM at 60 km; $\delta^{11}B$ ranges from 19.2-25.2‰ at 30 km and 15.92-19.5‰ at 60 km. These signatures are generally stronger than those observed in pore fluids at shallow depths, as would be expected due to probable re-adsorption of some B during updip or vertical advection. Ultimately, our results can be used for hydrologic models to quantitatively assess the fluid flow rates and permeabilities required to transport B at rates high enough to produce the observed signature.
The formation of calcium perovskite from majoritic garnet – Implications for splitting of the 520 km seismic discontinuity

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Global seismic observations show complexity in the region of the 520 km seismic discontinuity (Deuss and Woodhouse 2001). In some regions of the mantle this discontinuity seems to be split into two discontinuities at approximately 500 km and 560 km. In addition to the wadsleyite to ringwoodite transition, the exsolution of calcium perovskite (Ca-Pv) from majoritic garnet (gt) may be capable of producing a seismic discontinuity. This, however, would require the reaction to occur over a sufficiently narrow depth interval and to cause a significant change in elastic properties.

We have experimentally studied the calcium perovskite forming reaction in high pressure and temperature multi anvil experiments to determine if it is likely to cause an observable discontinuity. Experiments were performed by equilibrating Ca-free majorite gt with Ca-Pv to determine the saturation level as a function of pressure, temperature and garnet majorite content i.e. (Al/Mg+Si).

Experimental results show that because the reaction results in a strongly non-linear yield of Ca-Pv with pressure, a significant portion of the reaction is completed over a quite narrow initial depth interval. The sound velocity changes over this interval for a fertile peridotite composition are smaller but of a similar magnitude to those of the wadsleyite-ringwoodite transition and would likely cause a weak discontinuity at approximately 560 km in line with seismic observations. If, however, the mantle contained a significant component of recycled basaltic crust the higher mantle Ca contents would result in a much stronger discontinuity. For this reason the feature observed at 560 km will be sensitive to the proportion of basaltic components in the mantle at transition zone conditions and is therefore an indicator of chemical heterogeneity.

References

Fulgurites from Garuamukh, Assam, India – FTIR spectroscopic study

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There are two phenomena that are responsible for making natural glass on Earth: meteorites and lightning. Glass that is made as a result of the collision of a meteorite with the Earth's surface is called meteoritic glass or tektite. Glass (a glassy object, to be exact) that is made as a result of a cloud-to-ground lightning discharge is called a fulgurite (from the Latin "fulgur" which means lightning). Fulgurites come in a great variety of forms and can be viewed as nature's own works of art. It is worth noting that lechatelierite (natural silica glass) is not present in obsidian, a glass-like material associated with volcanic activity. On the other hand, volcanic activity is known to generate lightning which, if it strikes sandy soil, may produce a fulgurite. The black-brown natural glass found at Garuamukh near Nagaon town (Lat.26°19´N, Long. 94°30´E, Assam, India) is due to the fourth category of formation. The colloidal material comes out from the earth's surface making a number of branching with fire and foul odour smoke and the upper part of it is gradually solidified to natural glass within a few hours. The solid material have been found to have a temperature of about 80 ºC even after a lapse of two days after occurrence of the event whereas the room temperature during that period was 28 ºC. The increasing of temperature is observed on the spot with the increasing of depth. In order to understand the possible meteoritic or fulgurite origin of the glassy materials, we made an attempt to characterize the sample by using FTIR spectroscopy, and powder x-ray diffraction. The present investigation of the naturally occurring glass sample reveals the characteristic features of amorphous silica with some other minerals as trace. As the structural change taking place in the octahedral symmetry in the formation of the sample so, the possibility of producing this silicate glass is by ultra high-temperature that is higher than the corresponding fusion point of the crystalline state, indicating the nature of a fulgurite.
Organic compounds in H5 meteorite: Spectroscopic investigation of Dergaon H5 Chondrite

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On March 2, 2001, at 16:40 local time (GMT+5:30hrs), four fragments of a meteorite fell near Dergaon town (Lat. 16° 41’ N, long. 93° 52’E, Assam, India. Based on the petrography and chemical composition of the stony iron Dergaon meteorite has been classified as H5 chondrite. But from the chemical composition, the previous workers reported that the meteorite is an unusual H chondrite. In this present work we analysed the sample with the help of FTIR and Diffused Reflection Spectroscopy and found the SiO4 tetrahedron at 800-1100 cm⁻¹ and aliphatic functional CH₂ and CH₃ groups in the spectral region around 2800-3000 cm⁻¹. In 2800 – 3000 cm⁻¹ region (3.4 µm region), the hydrated and anhydrous interstellar dust particles attribute CH₃ and CH₂ stretching vibrations of aliphatic hydro carbons which is similar to the spectra found from the meteorite in this frequency region. The silicate grain in the interstellar medium and meteorites consist predominantly of olivine [(Mg,Fe)SiO₄] or of non-crystalline silicates of intermediate compositions associated with organic matter. The organic matter can extract the poly atomic carbon based molecules by crushing the MgO and (Mg,Fe)SiO₄ crystals. Generally four peaks are observed in this region. The symmetric CH₂ stretching vibration at 2850 cm⁻¹, symmetric CH₃ stretching vibration at 2865 cm⁻¹, asymmetric CH₂ stretching vibration at 2922 cm⁻¹ and asymmetric CH₃ stretching vibration found at 2958 cm⁻¹. The spectral features in the mid infrared region were found to be identical to that of the interstellar dust gain particles. Most of the strong IR absorption bands are due to olivine. Few weak absorption bands observed in the Dergaon meteorite are due to organic compounds present in the meteorite, the features observed in other H-chondrites by Lawless et al. (1972).

Reference:

Experimental study on gas emission using fault rock core penetrating Atotsugawa fault, central Japan

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Crustal gas-anomalies with earthquakes have been observed around active faults. However few experimentel studis have been done for this problem. Therefore fundamental processes are largely unknown. In order to examine the processes, grinding experiments were carried out under wet condition using two types of rocks taken from drilled core penetrating Atotsugawa fault: (1) Weakly Pulverized and Altered Rock (WPAR) and (2) Fault Gouge.

Result of the experiments show that positive relationships between surface area (ΔS) and amount of gas (n) (Fig.1). For hydrogen, the relationships can be expressed as: n = kΔS, which is in good agreement with those reported by Kameda et al., (2003). For methane, the relationships can be expressed as: n = A(1 - EXP[-kΔS]). The equation corresponds to solution: dn/dΔS = k(A - n). A will be max amount of methane contained in a sample and k shows degree of evolution of gas when samples are crushed. This diferencial equation indites that methane gas contained in the rock sample were released by fracturing and release ratio( dn/dΔS ) is proportional to (A - n), which means the amount of methane gas remains in the rocks.

Figure 1. Amount of released gases (methane and hydrogen) during wet grinding experiment.

Microstructural observation of thin sections clarified that fluid inclusions are abundant in quartz or calcite in granitic rocks, metasediments, and less in calcareous rock, which released methane gas by grinding. On the contrary, no fluid inclusion is observed in the minerals of andesite that did not released methane gas by grinding.

Combining experiment results and microstructural observations, we conclced that methane gases were included in fluid inclusion and released by fracturung minerals.

References
Adsorption behavior of gold (I and III) complexes on manganese dioxide

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It is essential in geochemistry to elucidate the uptake mechanism of trace elements into manganese nodules. It is well known that transition metals such as Co, Cu and Zn are concentrated in manganese nodules. However, only a few investigations have conducted on the uptake of noble metals such as Au, Pd and Pt. It is recognized that adsorption of metal ions on manganese dioxide was investigated to explore their uptake mechanism into marine manganese nodules.

In this study, a model compound of manganese nodule was manganese dioxide. As model compounds of gold, [Au(S2O3)2]3- and [AuCl4-n(OH)n]- complexes were selected for convenience because gold(I) and gold(III) ions present in hydrosphere.

The adsorption behavior of [Au(S2O3)2]3- and [AuCl4-n(OH)n]- complexes on the surface of manganese dioxide was investigated with pH. The adsorption behaviors were quite different. The percentage of [Au(S2O3)2]3- adsorbed increased with decreasing pH (from 8 to 4). Above pH 8, which is the same pH of ocean water, no [Au(S2O3)2]3- was adsorbed on manganese dioxide. Since the isoelectric point of the manganese dioxide was around pH 4-5, the surface negative charges increase with increasing pH above pH 4-5. This opposite correlation between the surface charge and percentage of [Au(S2O3)2]3- adsorbed suggests that the adsorption of [Au(S2O3)2]3- may be controlled by electrostatic force. On the other hand, the percentage of [AuCl4-n(OH)n]- adsorbed increased from pH 4 to 6 and showed a maximum at pH 6-8. This result indicates that the adsorption of [AuCl4-n(OH)n]- occurred by overcoming the electrostatic repulsion.

In addition, the chemical state of gold adsorbed on manganese dioxide was examined by XPS. The results showed that [Au(S2O3)2]3- and [AuCl4-n(OH)n]- complexes adsorbed on manganese dioxide were spontaneously reduced to elemental gold. [AuCl4-n(OH)n]- may be specifically adsorbed by condensation reaction (the formation of Au-O-Mn bond) between two OH groups in the [AuCl4-n(OH)n]- and two OH groups on manganese dioxide. The adsorbed [AuCl4-n(OH)n]- may be distorted due to the regulation by the two OH groups on the manganese dioxide, and then its redox potential may be changed and reduced by water molecules. In contrast, the adsorbed [Au(S2O3)2]3- may disproportionate to form Au(0) and Au(III) species. The resulting Au(III) may be reduced to Au(0) by the above same mechanism.

Based on the results of this study, the chemical state of gold in marine manganese nodules should be investigated spectroscopically.

Dissolution and precipitation kinetics of magnesite at conditions relevant for CO2 geologic sequestration

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Understanding carbonate mineral reactivity is of critical importance to assessing and optimizing potential CO2 storage sites (c.f. Oelkers and Schott, 2005). In particular, carbonate dissolution and precipitation rates play a fundamental role in CO2 mineral fixation. To address this need, the dissolution and precipitation rates of magnesite (MgCO3) have been studied as a function of pH (2<pH<10), solution composition and P CO2. Experiments have been performed using both open and closed-system reactors at temperatures from 100°C to 200°C and reactive fluid concentrations having ionic strengths varying from 0.01 to 1 M.

Measured dissolution rates decrease strongly with decreasing chemical affinity and increasing HCO3- concentration. The last observation is in agreement with the magnesite surface speciation model of Pokrovsky et al. (1999). Within this model all aqueous species able to form complexes with Mg surface hydrated sites, and thus decreasing >MgOH2+ concentration, inhibits magnesite dissolution. In addition, a significant increase in dissolution rates is observed with increasing reactive solution ionic strength: rates measured in 1 mol/kg NaCl solutions are on average 5 times faster than those observed in < 0.1 mol/kg NaCl solutions at a pH of ~ 7.

Magnesite is observed to precipitate at 150°C only at relatively high degrees of supersaturation. For example measured magnesite precipitation rates are found to be 2x10^-12 only at a saturation index > of ~ 30, when the CO2 pressure is at atmospheric or lower values. Moreover, the degree of supersaturation required for magnesite precipitation is observed to decrease with increasing temperature.

References
Natural and experimental multiscale F diffusion profiles in biotites from the Seridó micaschists, Northeastern Brazil

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We examined the F distribution in Seridó Fold Belt biotite at the regional, contact, and grain scale through electron probe microanalysis. At the regional scale biotites show largely homogeneous F contents varying from 0.30 to 0.40wt%. The uniform concentration suggests the biotites equilibrated with F-poor fluids (log[H2O]/[HF] = 4.5 to 5.0) at upper amphibolite metamorphic conditions. At the contact with pegmatoid intrusions, schist biotites are enriched at different levels F = 0.5 to 2.5wt%, similar to those observed for biotites in the pegmatoid biotites. This suggest that schist biotites were locally reequilibrated at 600-700°C by pegmatoid related F-rich fluids (log[H2O]/[HF] = 3.8 to 4.3).

At pegmatoid contacts the F contents of schist biotites decrease to background contents in metric and centimetric diffusion profiles. At the Areias pegmatoid sill the F content of biotites decrease from 0.95wt% to the regional background F = 0.03wt% in 5.2m. In the same distance the F contents of amphiboles decrease from 0.47 to 0.32wt% and apatites show a near constant content F = 0.2-0.3wt%. At the Pedra Lavrada pegmatoid stock the F content from biotites in a schist enclave decrease from F = 0.43 to 0.37wt% in the narrow range 20 cm. The obtained diffusion profiles can be related to the interplay of three major factors: (i) fluid [H2O]/[HF] chemical gradient, (ii) thermal gradient and (iii) fluid advection into micaschists.

AFSQ-buffered experiments on a mixture of two Seridó biotites (F = 0.3 and 2.5wt%) at 750°C, 0.4 GPa produced strong F zonation. X-ray maps show zontations from F-rich borders to F-poor cores, with F-rich incursions along the c-perpendicular direction. A 4 micron profile perpendicular to the c-axis from F = 3.0wt% on the border to F = 0.5wt% in the core was fitted using $C(x) = 1 - C_0 \exp[-(4Dx)^{1/2}]$ to produce an F diffusivity in biotite $D = 2.75 \times 10^{-15}$ m$^2$/s. The value is larger order of magnitude higher than F diffusion in apatite and four orders higher than F diffusion on tremolite. The constant F contents of apatites at the Areias sill should be related to its poor cleaved non-permeable structure.

The Geochemical Atlas of Europe – Continent-wide distribution patterns of elements

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The European geochemical baseline survey covers 26 countries, and provides invaluable information about the natural and human-induced concentrations of chemical elements in different sample media of the near-surface environment (topsoil, subsoil, humus, stream sediment, stream water and floodplain sediment). This is the first multi-national project of its kind – performed using harmonised sampling, sample preparation and analytical methodologies, and producing high quality compatible data sets across national borders. Over 60 determinands were studied, most for both total and aqua regia extractable concentrations. The results of the project are published in a two-volume set, which is freely available for viewing and downloading from www.gtk.fi/publ/foregsatlas together with the analytical data and photograph archive.

Over 400 maps were plotted and interpreted. The geochemical distribution maps show distinct geographical differences in the levels of potentially harmful elements, for example, arising from natural geogenic sources, including lithology and mineralisation, and from natural processes, such as climate, which influence the original concentrations.

The data from minerogenic samples reflect mostly geological variation in element distribution throughout Europe. In contrast, stream water data tends to reflect both the results of exogenic processes and the anthropogenic input of elements to the surficial deposits, although some elements give a direct signal related to the chemical composition of the bedrock. In central Europe, nitrate concentrations in stream water form a large anomalous area due to intensive agricultural practices. In northern Europe, stream water is more acidic than in central and southern Europe due to the low base cation capacity of the metamorphosed bedrock and the high concentration of humic and fulvic acids typical of the boreal climate. These low pH waters result in higher solubility of aluminium and some transition metals. Another striking feature is a relatively large anomaly of REEs detected in stream water in the area of southern Fennoscandia extending to northern Germany and Scotland. Reasons for this regional anomaly are unknown.

The geochemical maps may be used to delineate areas of ore potential interest across Europe. They may also be used to identify potential geohazard and health risks in particular regions that may warrant more detailed investigation. The observed geochemical variations do, however, illustrate the difficulty in defining a single guideline value for ‘water’, ‘soil’ and ‘sediment’ to be applied throughout Europe.
Coupled biological, geochemical and physical processes in acidic mine lakes: Model development and application.

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Existing water quality models for aquatic ecology and hydrodynamics have been extended to include representation of (bio)geochemical processes of relevance for acidic lakes and their sediments. The developed model allows quantitative investigation of biological, geochemical, and physical processes and their interactions, to assess controls on key water quality parameters, such as acidity.

The initial case study for model development was acidic Lake Kepwari, a decommissioned and flooded coal mine pit in Collie, southern Western Australia. Largely without calibration, the numerical model prediction of Lake Kepwari water quality over an annual cycle closely reproduced the patterns of stratification and overturn observed in the lake, as well as evapoconcentration. The model also reproduced major temporal and spatial patterns for non-conservative species, such as NH4, DOC, pH and Al. A sensitivity analysis indicated that even though the lake is now at full capacity, surface and groundwater inflows may still be important factors in the long-term evolution of the lake water quality. The model also allowed us to test the importance of geochemical processes for lake water quality, for example solubility equilibrium control of pH by Al hydroxide phases.

The modelling study of Lake Kepwari demonstrated the capability of the model to reproduce the main features of the current water quality in the lake, and highlighted the need for testing against data sets which include e.g. well-constrained water and mass balances over the lake.

It should be noted that the generic process descriptions in the developed model can be applied to almost any aquatic system. While the initial field site was a coal mine pit lake, the model is based on sophisticated process description and parameterisation; this allows immediate application to mine lakes of widely varying water quality.

We now require a comprehensive validation exercise of model predictions against high quality datasets from acidic water bodies; it is essential to increase our confidence in the simulation results. In particular, there is a need for testing model performance against long-term data sets from acidic systems with well constrained groundwater inflow, sediment fluxes and aquatic food web data, as well as hydrodynamic and geochemical state variables. The result will be an improved tool for management and remediation of acidic water bodies, including design optimisation for future field and laboratory sampling campaigns.

U-Pb age and REE data (SHRIMP II) on zircons in mantle xenoliths from alkaline basalts (Vitim area, Transbaikalia): Implication for the upper mantle partial melting

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Isotope dating of the upper mantle ultramafic rocks is difficult because their isotope systems are disturbed and mineral isochrones yield volcanic episode age. We report the U-Pb age and REE pattern of zircons from peridotite nodules in Cenozoic alkaline basalts of the Vitim volcanic area to display complicated evolution of the upper mantle.

The zircons 0.06 – 012 mm size were separated from nonmagnetic heavy concentrate. U-Pb and REE analyses have been carried out using SHRIMP-II in the CIR VSEGEI.

The protogranular spinel-garnet peridotite formed at P-T conditions of 45-50 kbar and 1400-1500 °C (data on Gar – Opx equilibria, Nikitina, 2000) bears prismatic or rounded zircons, colorless, with abundant fluid-melt and mineral inclusions. CL – images show their oscillatory and sectorial growth zoning and convoluted recrystallization domains.

The dating results are grouped in four age-spans with concordant 206Pb/238U ages of 1462±19 – 1506±4.0 (PR 1), 264.0±7.3- 295.7±0.76 Ma (P 1), 164.6±1.6 – 183.4±2.0 (J 1) and 135.5±2.7 to 141±3 Ma (K 1). Regression through two discordant data points has lower intercept of 138,0±5,7 Ma falling within K 1 age group. Its upper intercept of 1891±26 overlaps with other Proterozoic 207Pb/206Pb ages, ranging 1835 -1955 Ma. No volcanic episode age (48 – 28 Ma, Ionov et al. 1992) was noticed.

Chondrite-normalized REE distribution patterns in zircons show a LREE and HREE enrichment up to 100 and 1000 normalized units respectively. They are complicated by Ce and Eu minimum. Total REE content and Eu anomaly increase with the age.

The ages obtained are in agreement with main Phanerozoic intraplate magmatic events in the Central Asia region (Yarmoljuk et al., 2000). The studied zircons crystallized during partial melting of the peridotites initiated by gas-saturated fluid. Variation of the REE pattern with the zircon age indicates the multiple partial melting.

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The Dynamics of Core Formation in Terrestrial Planets by Negative Diapirism: Timescales, Heat Distribution and Metal-Silicate Equilibration

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Geochemical constraints on core formation provided by Hf/W systematics suggest it is a relatively fast process which may have been completed within less than 100 Myrs for the Earth or Mars. In addition, the overabundance of siderophile elements in the Earth’s mantle suggests that metal silicate equilibration occurred during core formation processes.

We investigate dynamically the timing and metal-silicate equilibration processes during core formation by negative diapirism. Using numerical modeling, we follow the sinking of iron-rich diapirs through a viscous silicate mantle, in 3D axisymmetric geometry. We carried a parameter study in which shear heating as well as several viscous rheologies were considered and systematically varied. General scaling laws are derived for the diapir sinking velocity as well as for the heat distribution. These scaling laws are subsequently used to investigate the ability of negative diapirism to explain core formation in Terrestrial planets within the timing and metal-silicate equilibration constraints provided by geochemistry and mineral physics.

Different types of hydrochemical stratification in the acidic mine pit lakes of the Iberian Pyrite Belt

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Meromixis in pit lakes of the Iberian Pyrite Belt

Many acidic pit lakes formed in the abandoned mines of the IPB during the last decades are meromictic, showing a bottom, anoxic water body (called monimolimnion) which is permanently isolated from the rest of the water column, and an upper, oxygenic mixolimnion that periodically circulates.

Results and Discussion

On-going research in pit lakes of the IPB has revealed different types of perennial hydrochemical stratification, which ranges from a simple model with two internally homogeneous layers separated by a well defined chemocline, to a more complex, multi-layer model that display numerous steep salinity gradients and different strata with continuously increasing dissolved solids content with depth (Figure 1).

Figure 1: Vertical profiles of electric conductivity (EC) and dissolved oxygen (DO) in the pit lakes of San Telmo (left) and Cueva de la Mora (right).

These different models of chemical stratification do not correlate with the age of the pit lakes (15-100 years), their relative depths (13-45%) or the geometry of their pit basins. It is hypothesized that the different vertical trends are the result of the interplay between different types of processes, including (i) physical mixing (e.g., wind-induced advection, heat-driven convection) in the mixolimnion, (ii) geochemical and microbiological reactions (bacterial oxidation of Fe(II), photoreduction of Fe(III), precipitation of Fe(III) phases, metal sorption) in the mixolimnion, (iii) bacterial reduction of Fe(III) and SO$_4^{2-}$ coupled with fermentation in “reactive” lake bottoms (water/sediment interfaces), (iv) groundwater input at depth, and (v) warm salt-laden water descending into the basin along the pit contours.
**Interaction between barite and celestite cleavage surfaces and carbonate bearing aqueous solutions**

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In nature, crystals of the witherite-strontianite solid solution series often show a significant chemical bimodality, i.e. intermediate compositions in this solid solution are very rare. Such a chemical bimodality can not be easily justified by invoking thermodynamic arguments. However, it has been suggested that witherite-strontianite crystals can result from the replacement of crystals of the barite-celestite solid solution which act as precursors. Consequently, the chemical bimodality in the carbonates might be a compositional feature inherited from the original sulphates. In this case, the replacement implies the coupling of dissolution and crystallisation reactions occurring on the interface between the $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$ crystal surfaces and carbonate bearing aqueous solutions.

In this work, we present in situ Atomic Force Microscopy (AFM) observations of the interaction between barite and celestite (001) and (210) faces with static $\text{Na}_2\text{CO}_3$ aqueous solutions at room temperature. The concentrations of the solutions used were in the range between 0.001 mol/l and 0.1 mol/l. Typically, such interaction is characterised by the dissolution of the original faces and the rapid nucleation and spreading of islands (~3 nm in height). The coalescence of the islands leads to the formation of a homogeneous epitaxial layer. Measurements on series of AFM images provide quantitative information about coupled dissolution-growth rates. On the basis of our results, we discuss the viability of the transfer of chemical information at a nanoscale during the replacement of the barite-celestite crystals by witherite-strontianite.

**Experimentally determined biomediated $\text{Sr}^{2+}$ partition coefficient for dolomite**

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Aerobic culture experiments with two strains of moderately halophytic bacteria grown in solid medium have been used to determine the $\text{Sr}^{2+}$ partition coefficient for dolomite at different temperatures and chemistries. The $\text{Sr}^{2+}$, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ data and results from XRD studies indicate that $\text{Sr}^{2+}$ incorporation into dolomite crystals is not by substitution of $\text{Ca}^{2+}$, but instead, in our experiments, $\text{Ca}^{2+}$ is replaced by $\text{Mg}^{2+}$. $\text{Sr}^{2+}$ enrichment is probably via surface adsorption or occlusion. Thus, the experimental $\text{Sr}^{2+}$ partition coefficient between dolomite and fluid is represented here by the ratio of the $\text{Sr}^{2+}$ concentration in the solid phase (dolomite, “dol”) over that in the fluid (site of dolomite precipitation = bacteria-medium interface, “bmi”), $D_{\text{Sr}}^{\text{dol}} = \frac{\text{Sr}_{\text{dol}}}{\text{Sr}_{\text{bmi}}}$. Together, our observations suggest that $D_{\text{Sr}}^{\text{dol}}$ is apparently related to microbial activity, temperature and sulfate concentration. Therefore, the highest values calculated in the experiments, in comparison with the theoretical values, have implications for interpretation of depositional environment of ancient dolomite. The results of our cultures experiments show that high very high $\text{Sr}^{2+}$ concentrations in ancient dolomite could reflect microbial mediation.
Equation of state of fluids from sound velocity measurements in the diamond anvil cell using Brillouin scattering spectroscopy

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Saline-rich aqueous fluids play an important role in metamorphic reactions and chemical transport in a wide range of geological environments. In subduction zones, aqueous fluids expelled from subducting slabs lead to the important geochemical phenomena of mantle wedge metasomatism and arc magmatism and mediate the recycling of elements in the Earth. Reconizing the role of deep fluid in these processes a number of significant but unanswered questions arise as to their chemical composition, the extent of mass transfer, or the mechanism of elemental transport from the slab to the mantle wedge. Answers to these questions depend on quantitative thermodynamic modelling of fluid-mineral interactions, that is greatly limited by the lack of thermodynamic data of complex aqueous fluids at high pressure and temperature conditions [1].

To address this problem, we conducted sound velocity measurements in the diamond anvil cell using Brillouin scattering spectroscopy to determine the equation of state (EoS) of H2O and chlorine-bearing solutions (1m and 3m NaCl) up to 400 ºC and 7 GPa. Sound velocities measured in H2O are in excellent agreement with previous measurements using the Impulsive Stimulated Brillouin Scattering technique [2]. The newly determined equation of state is used to evaluate the pressure and temperature dependences of thermodynamic properties of water and NaCl solutions, including thermal expansion coefficients, isothermal and adiabatic compressibilities and heat capacities. The results are combined with previous experimental and theoretical EoS of H2O-NaCl mixtures to provide an internally consistent dataset for the thermodynamical properties of the most relevant aqueous systems involved in subduction process.

References

Effect of Al3+ on the elastic properties of ferropericlase at high pressure

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Main features of the Earth’s mantle structure revealed by seismic observations, including the radial profile, lateral heterogeneity, and anisotropy are largely determined by the elasticity of the materials present in this region [1]. Mineralogical models indicate that the lower mantle consists of approximately 20% ferropericlase (Mg,Fe)O and more than 70% of silicate perovskite [(Mg,Fe)SiO3], containing minor amounts of aluminium. Although the effect of Al3+ incorporation on the elastic properties of MgSiO3 perovskite has been constrained from several studies [2,3], nothing is known about how this element can affect the sound velocities and elasticity of (Mg,Fe)O.

In this contribution we present high-pressure measurements on the sound velocities and single-crystal elastic properties of aluminium-bearing ferropericlase (containing 2.4 atom% Al3+ and 8.7 atom% Fe2+) to 25 GPa at room temperature. Measurements were performed by Brillouin scattering in samples compressed in the diamond-anvil cell using alcohol-water mixtures as pressure transmitting media. The pressure-dependence of the aggregate compressional (Vp) and shear (Vs) wave velocities, as well as, the adiabatic bulk (Ks), shear (µ) moduli and elastic anisotropy were obtained. In view of these results and previous elastic data for (Mg,Fe)O [4], the effect of Al3+ incorporation on the elastic properties ferropericlase and the implications for the chemical composition of the Earth’s lower mantle will be discussed.

References:
Comparative study of organic Cd and Zn complexation in lake waters

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The complexing capacity and associated stability constants of Zn and Cd in three alpine lakes in New Zealand has been determined using Competitive Ligand Equilibration-Cathodic Stripping Voltammetry (CLE-CSV) with ammonium pyrrolidine dithiocarbamate (APDC) [1] as competing ligand for Zn and Anodic Stripping Voltammetry (ASV) was used to measure the complexing parameters for Cd [2].

We compared depth profiles, seasonal variability, pH dependence and selectivity of the natural organic ligands for both elements and took a view to similarities and differences with Cu speciation in the same lakes.

Probably the most noticeable and interesting result of our study on the speciation of Cd an Zn in three freshwater lakes in southern New Zealand is the apparent difference of the Cd-binding ligand composition with depth, but also differences in summer and winter. While our data gives evidence for a rather unspecified binding affinity towards Cd in winter and in deep water, the specificity seems to be increased at the surface in summer. Both the higher stability constant and selectivity against competing elements could indicate towards a compound of recent biological origin. Ligands with a lower stability found in winter at the surface and all year around in the deep water samples are probably non-specific degradation products.

The chemistry of Zn is much more uniform throughout the depth profiles and seasons, with Zn speciation being dominated by strong organic complexes. On average 95%±5% of Zn is present as organic complex, compared to only 70% ± 22% of Cd being organically complexes. Zn binding ligands also seem to be very selective towards Zn, and thus, probably produced in response to the presence of this element on the water. The pH dependence of the complexation of both metal ions is indicating that the composition of ligands is not uniform and functional groups may consist potentially of carboxylic groups (pKₐ 3-5) and groups being incompletely deprotonated at pHs as high as 8.2 (e.g. phenolic and amino groups).

Comparing the speciation of Cd and Zn with that of Cu in the same lakes, it strikes that the concentrations of all ligands for all three elements is very similar with an over all average of 6.8 nM ± 3.1 nM (SD) although the total metal concentration vary in the range of two orders of magnitude, with Cd being the least prevalent element. However, the different complex stability constants, inorganic speciation and ligand selectivities for Cd, Zn and Cu in combination with their concentration is leading to the fact, that probably the highest risk of toxicity for organisms is coming from cadmium.

References

Interactions of uranium with Fe(III)-(hydr)oxides under sulfate reducing conditions

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Uranium (U) contamination is a global problem in water supply and related ecosystem health, and it is the primary radioactive metal contaminating subsurface environments at many sites and is of particular concern because of its carcinogenicity. The high solubility of its hexavalent form can result in U transport to sensitive receptors such as drinking water sources. One potential method of treating U contamination is by using natural dissimilatory metal reducing bacteria including sulfate reducing bacteria (SRB) to reduce soluble U(VI) to insoluble U(IV) (as uraninite, UO₂). This reduction can lead to in situ U immobilization; however, it is vital to understand the reactivity and stability of microbially-mediated uraninite. Our recent published HR-TEM, SAED, and EDS analysis data showed that SRB transformed U(VI) into colloidal uraninite with particle diameters of 3–5 nm. Further, we recently showed that under lactate-limited sulfate-reducing conditions, this biogenic uraninite can be oxidized by common Fe(III)-(hydr)oxides such as hematite, goethite, and ferrihydrite. In addition to the oxidation of biogenic uranium under biotic conditions, in this paper we review the oxidation of aqueous phase biogenic uraninite by Fe(III)-(hydr)oxides under abiotic conditions. These aqueous uraninite particles were separated from SRB using 0.2 µm membrane filter, and treated with hematite and ferrihydrite under strict anaerobic conditions. Our results suggest that Fe(III)-(hydr)oxides oxidized uraninite; however, the reactivity of biogenic uraninite was greater with ferrihydrite as compared to the more crystalline structure of hematite. Thermodynamic calculations also indicate congruent favorability of these reoxidation reactions. The results have strong implications for field application of in situ biological reduction of U(VI) since oxidation of bioreduced uraninite by Fe(III)-(hydr)oxides in situ may limit U immobilization even under reducing conditions.
Reactivity of heavy rare gases with silicates at deep Earth conditions

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The incompatible [1-3] and inert [4-5] character of atmospheric rare gases varies with pressure and temperature. This variation is poorly understood, yet it challenges our current appreciation of the formation of Earth’s atmosphere and mantle dynamics. The levels of the noble gas Xe in the atmospheres of Earth, and Mars are much lower than those of other noble gases, a puzzle known as the “missing Xe problem” [6]. One solution would be that Xe is hidden in other phases in a deep Earth reservoir. From a geochemical point of view, not only Xe, but all rare gases could be partly hiding in the deep Earth [7].

X-ray diffraction were conducted in situ on the SiO2-Xe and San Carlos Olivine-Xe systems, and completed by chemical analysis and Raman spectroscopy on quenched samples. We have shown that at high T and P, the normally unreactive Xe can bond covalently with oxygen in quartz 5, displacing Si atoms in the crystal lattice. A similar behavior of Xe is observed in the olivine lattice. Xe could therefore be trapped in deep Earth silicates. The results provide an answer to the paradox of "missing Xe" in the atmospheres of the Earth and Mars. Preliminary results will be shown on silicate-Ar systems, and discussed in relationship with the observed solubility drop of Ar observed at high pressure in silicate melts 1,3.

Geographical distribution of helium isotope ratios and seismic tomography in Japan

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The 3He/4He ratios (Ra) of natural gas, volcanic fluid, and groundwater are compiled in the Japanese Islands and their geographical distributions are discussed in the tectonic frame work of subduction zone together with precisely-determined seismic velocity structures. In Northeastern (NE) Japan where typical island arc signatures are developed, there is a clear contrast of 3He/4He ratios perpendicular to the trench axis, low-Ra in the frontal arc and high-Ra in the volcanic arc. This may reflect the presence or absence of magma with high-Ra in the shallow crust [1]. As a carrier of primordial helium, source melt may be generated in low-V zone of the wedge mantle by dehydration of Pacific slab at about 150 km deep and may flow upward sub-parallel to the slab, which is well constrained by S-wave velocity perturbation [2]. In the Chugoku and Shikoku districts of Southwestern (SW) Japan, there is a geographical contrast of Ra similar to NE Japan except for the region at about 100 km from the volcanic front where medium-Ra was found. High-Ra observed in volcanic arc of the Chugoku district may be attributable to the mantle helium derived from the magma source generated below the Philippine Sea slab [3]. Medium-Ra in the Shikoku district is explained by dehydration of the young slab with a moderate aging effect [4]. These features are again consistent with the results of seismic tomography [5]. In the Kinki district of SW Japan, anomalously high-Ra was observed in the frontal arc region that was called by “Kinki Spot”[6]. Since the high-Ra is located at much wider region from the volcanic front when compared with NE Japan, the melt generated below the Philippine Sea slab may penetrate into the fissure of the slab tear and may arrive at the shallow crust by upwellling flow.

References

References
D/H ratios in n-alkanes as a proxy for paleoclimatic changes in a Brazilian lacustrine rift sequence

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Meteoric water is considered the main hydrogen source for primary producers (Schimmelmann and Vogel; 1970), and fossil hydrocarbons can preserve most of their source D/H signature throughout geologic time (Santos Neto and Hayes, 1999; Li et al., 2001, Dawson et al., 2004), and even during catagenesis (Schimmelmann et al., 2006).

Examination of n-alkanes from organic extracts of representative core samples of an early Brazilian Cretaceous paleolake sediments showed that $\delta D_{DSMOW}$ of n-C20 to n-C32 varied mostly between $\approx -60\%$ to $-100\%$ (Fig. 1). Spikes up to $-125\%$ probably are related to coelution of compounds. The cyclic fluctuations of $\delta D$ in n-alkanes are significant, correlative to inorganic indicators of environment changes, and largely independent of secondary exchanges. This suggests that D/H ratios are reflecting periods of more and less water evaporation, during the lake evolution, and can be an useful proxy for paleoclimatic studies.

Figure 1: Graph showing the $\delta D$ (%) variation for the n-paraffins ranging from 20 to 32 carbon atoms

Emplacement of the Monchique alkaline massif (SW Portugal): Microstructures and magnetic fabric constraints

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The Monchique massif aged of Upper Cretaceous ($^{40}$Ar/$^{39}$Ar 72.7±2.7 Ma, Valadares et al., 2005) covers an area of 80 km² and has an east-west elongate shape. This massif is composed by two principal units: the central one corresponding to a coarse grained nepheline syenite and a marginal unit represented by a heterogeneous syenite. The central unit contains large crystals of alkali feldspars, nepheline (25% to 40%), pyroxene, biotite and plagioclase. The marginal unit has a variable granulometry and is poorer on nepheline (10 to 20%) (Gonzalez-Clavijo & Valadares 2003). Gomes & Pereira (2004) considered this massif as an intrusion in an antiform structure and controlled by a NE-SW shear zone.

All the thin sections display microstructures typical of magmatic or submagmatic state and no microstructures indicate of strain developed under near-solidus conditions were observed. Preliminary studies of Anisotropy of Magnetic Susceptibility (AMS) were carried out measuring 102 oriented core samples from 12 sites, using an Agico Kappabridge (KLY-4S), at the Geology Dep., Porto University. The high average bulk susceptibility (23.83E $^{-3}$ SI) together with previous paleomagnetic works (Gomes & Pereira, 2004) indicates that magnetite controls the magnetic behaviour. Magnetic anisotropy magnitude (Kmax/Kmin) is quite low, 1.065 on average. AMS fabric patterns show subvertical magnetic foliations associated with subhorizontal magnetic lineations. They have both a tendency to display NE-SW trends on the east and west sectors of the massif, passing to an E-W trend on the centre of the massif, drawing a sigmoid shape. Considering the AMS fabric as magma flow indicators, we propose that Monchique massif is a subvertical intrusion and that the steeply dipping magnetic foliations related to gentle dipping lineations represent an E-W trending of the magmatic flow controlled by a NE-SW left strike slip fault.

References


References

Sr isotopic composition in Variscan granitoids, Silurian metasediments and waters from the Boticas area (Northern Portugal)

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The processes of water-rock interaction controlling the Sr isotopic composition of superficial and groundwaters from the Boticas sanitary landfill and the Carvalhelhos mineral waters are investigated in this work. The Boticas region is composed of several intrusions of Variscan granitoids emplaced into Silurian metasediments. The granitoids, consisting of quartz, K-feldspar, plagioclase (albite - oligoclase) and micas show Sr content, and present-day 87Sr/86Sr isotopic ratios varying between 37-105 ppm and 0.749238-0.886953, respectively. In the Silurian metasediments, quartz and mica are modally important mineral phases and plagioclase is absent. Their Sr contents range from 41-60 ppm and their 87Sr/86Sr ratios from 0.760103-0.782684. The surface and groundwaters from the Boticas sanitary landfill have bicarbonate compositions with relatively high calcium and magnesium contents (mixed-type), whilst the Carvalhelhos mineral waters show sodium bicarbonate compositions. The range of Sr and 87Sr/86Sr values in the Boticas waters (Sr = 0.0042-0.056 ppm; 87Sr/86Sr = 0.718106-0.726322) is much wider than those of the Carvalhelhos mineral waters (Sr = 0.072-0.076 ppm; 87Sr/86Sr = 0.718106-0.732276) and micas show Sr content, and present-day 87Sr/86Sr isotopic ratios varying between 37-105 ppm and 0.749238-0.886953, respectively. In the Silurian metasediments, quartz and mica are modally important mineral phases and plagioclase is absent. Their Sr contents range from 41-60 ppm and their 87Sr/86Sr ratios from 0.760103-0.782684. The surface and groundwaters from the Boticas sanitary landfill have bicarbonate compositions with relatively high calcium and magnesium contents (mixed-type), whilst the Carvalhelhos mineral waters show sodium bicarbonate compositions. The range of Sr and 87Sr/86Sr values in the Boticas waters (Sr = 0.0042-0.056 ppm; 87Sr/86Sr = 0.718106-0.726322) is much wider than those of the Carvalhelhos mineral waters (Sr = 0.072-0.076 ppm; 87Sr/86Sr = 0.718106-0.732276).

Adsorbed soil gas and microbial studies for Hydrocarbon prospecting: Jamnagar sub-basin, Gujarat, India

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This study was designed to combine and compare adsorbed gas (acid released gas) and Microbial methods with sub-surface geology. These techniques provides to understand the hydrocarbon generation, migration and accumulation processes within a basin prior to drilling. Sub-surface soil samples were collected on a detailed grid over the Jamnagar sub-basin, India. The area is largely covered and prominently exposed by the Deccan Trap (basaltic rocks), whose thickness varies from few hundreds to thousands of meters. Traps are underlain by thick Mesozoic sediments (100-4000 m), which can form potential source rock for hydrocarbon. Deccan Trap volcanoclasty during Late Cretaceous may have generated the requisite thermal conditions and acted as a catalysis in Mesozoic hydrocarbon-generation process. Sedimentation in marine intertonguing environments is considered to have been favorable phenomena for hydrocarbon generation and entrapment (Kumar et al., 2004).

Adsorbed soil gas of light hydrocarbons (C1 to C3) shows variations in concentrations of Jamnagar sub-basin. The C1, C2, and C3 concentration range from 3-518 ppb, 0-977 ppb and 0 – 331 ppb, respectively. Correlation factor is more than 0.9 between C1 - C2, C1 - C3, C2 - C3 and C1 - C2, which indicates that light hydrocarbon components are generated from a thermogenic source. The compositional ratio of C2/C1 varies from 60 – 68600 CFU/gm. Adsorbed soil gas and microbes intensities indicate that this is warm area for hydrocarbon. The adsorbed soil gas data and microbial population are concordant and coincide with major structural features in basin. This study clearly demonstrates that adsorbed soil gas and microbial methods with geology can be applied sucessfully to demarcate the hydrocarbon reservoir zone for future exploration.

References


A K-Ar age reset of frictionally melted gabbro and detect for degassed noble gas

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Radiometric age is defined as a cooling age or a closure age of a particular mineral or of minerals. With determination, quantitative analysis of thermal history of a rock or a geologic event (fault movement) could be performed with comparison of various minerals of radiometric age. Contrastingly, other method, e.g. ESR, FT and U-He age, the closure temperature of K-Ar system is rather high, a kind of melted-rocks under high temperature, such as pseudotachylytes, are widely applied to evaluation of fault activity with K-Ar dating method. To obtain reliable ages of fault activities, it is a key issue whether the ages were initialized by re-equilibrating their Ar isotopes with atmospheric Ar besides to be rejuvenesced, and other noble gas isotopes are re-equilibrating from original rock ratio to atmospheric ratio. In the case that such a rejuvenescence can explicate one of a geochemical phenomena of field observation, analyses of apparent K-Ar ages could be applied for fault rocks for thermal history.

Here we report a preliminary experiment that effectuates high temperature frictional melting experiments with using a high-velocity friction apparatus in Kyoto Univ. in order to test whether age is reset by frictional heating of fault or not. A pair of gabbro chunks cut into hollowed cylinder was slid at a slip velocity of 1.3 m/s and a normal stress of 1.4 MPa. Under this condition, local frictional melting started into 5 sec. and temperature around an artificial fault reached around 1100 C in ca. 20 sec., then fault plane is well above the closure temperature of K-Ar system. Due to rapid equilibrium of volatiles during frictional melting of rocks, we expect that the K-Ar age should be reseted. This age-reset is only observed in glass completely melted. In natural field observation, such completely melted glassy materials, are faced on fault planes. Such glassy materials age are regarded to be reset during fast fault movement by re-equilibirating of Ar isotopes to atmospheric one at the event. An apparent incomplete initialize was observed in the part including some un-melted gabbro fragments. In the part, mechanically fractured pieces are mixed in the glass matrices in frictional zones. That’s why the Ar isotope ratios might not be re-equilibirated in the experiments. However, U-He age is also initialized as for re-equilibrating of He isotopes, which is more sensitive and degassed earlier than Ar isotopes such as low speed frictional and low temperature (un-melted), just crushed rock.

Sulfur/Selenium ratios in Bushveld Complex, South Africa

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Introduction

Over the past decade S/Se ratios have been used in modeling the processes leading to magmatic ore deposits. Sulfur and selenium have many chemical similarities but the use of S/Se ratio is based on the idea that Se is less mobile. Thus, magmatic sulfides ore deposits have S/Se ratio close to mantle values (~2500-4000). If sulfides are altered S may be preferentially removed resulting in rocks with low S/Se.

It has been suggested that the Pt-rich Merensky Reef in the Bushveld Complex formed when Pt-bearing disseminated sulfides in the underlying cumulate rocks were dissolved by Cl-rich fluids. The S and Pt were deposited at the level of the reef when this fluid dissolved into the intercumulate silicate liquid. An alternative model for the formation of the reef is that sulfides segregated from the mafic magma a little above the reef then collected on the cumulate pile. We have investigated these models with the idea that if the Pt and S were collected from bellow the reef then the S/Se ratios of the cumulate pile should be less than normal magmatic values and S/Se ratios in the reef should be higher than magmatic values. Alternatively if the sulfides in the reef segregated from a mafic magmaw have S/Se ratios close to mantle.

Results and conclusion

The S/Se ratios of the reef rocks is approximately 2000 and the S/Se ratios of the rocks below the reef are in most case >2000, within or close to S/Se mantle range (Fig. 1). Therefore S/Se ratios are consistent with the magmatic model for the formation of the reef.

Figure 1: Statigraphic distribution of S/Se ratios in Bushveld (Union section)
Sorption removal influence on the transformation of dissolved uranium (VI) runoff in the river water – seawater mixing zone

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Special attention is paid to radio ecologic research, when studying chemical transformation of continental runoff in river mouth areas. Sorption-desorption processes are especially important for trace elements characterized with low coefficients of biologic accumulation. Experimental simulation of interaction between waters of various salinity which contain uranium (VI) and terrigenic clay minerals was provided aimed at revealing the role of sorption-desorption processes in transformation of runoff of dissolved uranium in the river water – seawater mixing zone.

The resultant action of sorption-desorption processes was estimated based on experimental parameters of isotherms of uranium sorption at natural clays of different composition. Calculations showed that sorption removal of essential amounts of dissolved uranium occurs when river suspended solids interact with salinous waters. These amounts approach amounts of dissolved uranium occurs when river suspended solids for rivers of the world, with only exception for montmorillonite. When accounting of correction coefficient for difference in total amounts of clay minerals in the Gzhel clay (53%) and in the global solid runoff (67%), the value of specific sorption of uranium at the Gzhel clay rises from 0.13–0.16 nmole/g up to 0.16–0.20 nmole/g or 39–48 ng/g at transition from river water to seawater. The total amount of suspended solids removed to the Ocean was estimated varying from 15.7 to 18.5 billion ton per year [Walling, Webb, 1987; Lisitsiyn, 1978]. Consequently, the amount of sorption removal of uranium values 610–890 ton per year at the river–sea barrier, when applying the Gzhel clay as the analog of suspended solids in continental runoff.

Values of uranium sorption at montmorillonite clay are an order of magnitude higher than values for the Gzhel clay (1.5–2.9 nmole/g). As the result the presence of montmorillonite in suspended solids causes essential increase of uranium removal from solutions. River suspended solids contain ~3% of montmorillonite, thus additional removal of uranium was estimated at 170–380 ton per year. Hence the total amount of uranium removed by sorption at terrigenic solids is equal to 780–1270 ton per year. The amount of dissolved uranium entering seawater with river runoff was estimated at 20 000 ton per year. Considering this estimation the sorption removal of uranium is insignificant (4–6%).

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Li-Sr-Lu-Hf isotope and trace element systematics of eclogites from Bulgaria

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Ecl ogites from the Sredna Gora Terrane and the Rhodope (UHP) Massif lie in southern Bulgaria and northern Greece and are part of the Alp-Himalayan orogenic belt. Two groups of eclogites were studied. Group 1 eclogites (Verila Mts., Ograzden Mts., E. Rhodope Mts.) have 1-10 x chondrite (CI) HREE concentrations and [La/Sm]N = 0.2-1 and variable 87Sr/86Sr (0.7035-0.7098). This group also shows MORB-like trace element systematics and Nb/Zr (0.07-0.26), Nd/Pb (~1), Hf/Yb (~0.22-0.48) and Nb/U (~29) ratios. Group 2 eclogites (Central Rhodope Mts.) have 30 x (CI) chondrite HREE abundances, 87Sr/86Sr ratios between 0.7057 and 0.7077; enriched LREE ([La/Sm]N = 1.1-2.5), elevated LILE contents and Nb/Zr (0.25-0.94), Nd/Pb (~9.5) and Nb/U (~32) ratios, but relatively low Hf/Yb (0.17-0.20). One interpretation of the data is that group 1 eclogites represent metamorphosed altered oceanic crust and group 2 eclogites record interaction with crustal melts/fluids possibly in an arc crust environment. In situ analyses by SIMS (Cameca 6f) of garnets and omphacites show depleted LREE and little core to rim trace element variations. The Li abundances of all garnets (1-2.5 ppm) and omphacites (45-56 ppm) are in the typical range for eclogites [1]. Mineral separates and bulk rocks from group 1 have extremely light Li-Sr-Lu-Hf isotope and trace elements ratios (δ7Li = +1.2 and –12.9 ‰) compared to group 2 (δ7Li = –0.26 to + 5.7 ‰). Our data confirm earlier studies reporting very light δ7Li in eclogites from the Alps[1].

The Lu/Hf isotope systematics of omphacite-garnet pairs suggest that eclogites from Central Rhodope Massif are of Late Proterozoic (Pan African) age [Beden eclogite = 567 Ma], almost identical to ophiolite successions throughout the basement of the Balkan Terrane to the north. Eclogites from Ograzden Mts. and Verila Mts. record Carboniferous metamorphic overprint [Gega eclogite = 293 Ma; Krainitsi eclogite = 320 Ma]. The Variscan orogeny in Bulgaria was established based on stratigraphy and abundant 300-315 Ma granitic intrusions [2]. The reported Lu/Hf age of eclogites from the Ograzden and Verila Mts. (in addition to zircon metamorphic rim geochronology [2]), implies the existence of previously not known high-grade metamorphic event similar to the one recorded in western and central Europe. These results on well-preserved Bulgarian eclogites provide a sensitive record of the pre-Mesozoic subduction events in the southern margin of the European continent.

References

Effects of cations and pressure on the structure of aqueous solutions as evidenced by IR OH bands

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In order to study effects of cations and pressure/temperatures on the st ructure of aqueous solutions, infrared (IR) spectra were measured for salt solutions under different pressures/temperatures.

IR spectra of synthetic salt solutions (LiCl, NaCl, KCl, RbCl, CsCl, MgCl₂, CaCl₂, SrCl₂, BaCl₂ ) were measured by attenuated total reflection (ATR)-IR spectroscopy at room temperature under atmospheric pressure. The peak positions of OH stretching bands shifted to higher wavenumbers with increasing salt concentrations.

**Figure 1:** The peak positions of OH stretching bands.

By taking difference spectra from the pure water, the higher wavenumber component (3430 cm⁻¹) increases, while the lower wavenumber component (3170 cm⁻¹) decreases for most of the salt solutions. The addition of these salts to pure water resulted in the increase of water molecular clusters with longer H-bond distances.

In order to measure IR transmission spectra of fluids at different pressure/temperature conditions, a high pressure/temperature IR transmission cell has been developed to be used under an IR microscope.

First, IR spectra of pure water was measured at different pressures from 0.1 to 15.6 MPa. The OH stretching peak position did not change significantly upto 15.6 MPa. The above salt solutions are now being examined at different pressure/temperature conditions.

Geochemistry of Kairouan plain, Tunisia

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The aquifer of Kairouan, located in the central part of Tunisia, is the main water resource for drinking supply, agriculture and industrial use in the region. It is composed of a shallow and a deep units and its main feeding comes from natural recharge in wadis. Because of the demographic, agricultural and industrial development in the region, the aquifer knows an increasing exploitation with more than 5000 wells and 400 drillings. The actual exploitation volume exceeds the aquifer capacity and thus can threaten the water quality there. The main risks are dealing with deep saline water upcoming and Sebkha water intrusion. Another risk can come from irrigation water recycling which can only be very saline because of the climate aridity in the region.

In this work, we present the main results of a geochemical study of Kairouan aquifer. Major elements were used to identify the water types and a statistical study was performed to determine the salinity origin as well as the inter connection between the surface water and the two aquifer layers.

The richness of the mineralization by different major elements has been explained by the probability of rocks alteration, meteoric contribution and salt migration in the atmosphere from Sebkhas that constitute the Kairouan groundwater outlet.

**Reference**

Palaeoweathering chemistry of some flood basalt hosted fossil soils and their palaeoclimatic significance

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Ancient soils have been largely used to understand the palaeoclimates because the chemical weathering was in response to the contemporaneous reactions between the meteoric water equilibrated with the atmospheric gases and the protoliths. The present paper attempts to compare chemical weathering patterns of the fossil interbasaltic soils (from the published geochemical data) from some flood basalt provinces. These include from Late Triassic Ischigualasto basin (NW Argentina), end-Cretaceous Deccan Traps (India), British Tertiary Basaltic Province and Tertiary lavas of Northern Ireland. The published geochemical data of the basalts and modern soils (Mumbai) developed upon them from Deccan Traps have been used for comparison. In general the CIA values do not show many variations from the Deccan boles but if studied from two spatially separated areas they have appreciable differences; the Ischigualasto palaeosols, however, show a wide range of CIA values. The higher CIA values in the Skye and Mull boles from British Tertiary basaltic province, than the Deccan boles, indicate their quite intensive weathering conditions while Tertiary interbasaltic formation of Northern Ireland conspicuously shows very high CIA values, indicating highly intense and/or prolong chemical weathering. Hydrolysis show good correlation with MAP and CIA but the Tertiary interbasaltic formation shows exceptionally higher hydrolysis. When plotted on the triangular diagrams the Deccan boles and the Tertiary interbasaltic formation show distinctive fields. The Skye and Mull boles, Ischigualasto palaeosols and Mumbai modern soils plot close together. Thus from the fossil interbasaltic soil geochemistry it is evident that the palaeoweathering characteristics are different in different flood basalt provinces and the different chemical weathering characteristics should be correlated with the time gap (quiescence periods) between the successive lava flow eruptions and the palaeolatitudinal positions influencing the palaeoclimates.

Age evolution of Gold concentrations in metamorphic rocks

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The results of examination of gold-bearing rocks in Achaean, Proterozoic and Oligocene metamorphic complexes are presented below. The territories under study are located within the blocks of the basement and the folded frame of old platforms (the Siberian platform, the East–European platform) and the Oligocene folded structure of the Eastern Pamir (Central Asia). The distribution of gold in metamorphic rocks depends on the next regularities.

The oldest super-crustal metamorphic rocks of the granulite facies are characterized with higher concentrations of gold in comparison with clark (12.18 – 55.3 ppb). Charnokites formation, granitization, migmatization and diaphthorezis in the granulite series lead to gold carrying out – 20-55 ton / km³. These series could be one of the sources of metal for Proterozoic and Phanerozoic mineral deposits.

Gold concentration in the Proterozoic and Phanerozoic metamorphic complexes is 2-5 times more than concentration in the surrounding aleuropelite sedimentary rocks. Gold is introduced with deep fluids into the metamorphism area.

Rocks of the amphibolite facies of zoning metamorphic belts are characterized with the lowest concentration of gold (2.92-4.5 ppb). Double exceeding of gold grades is typical for the greenschist facies (4.25-6.19 ppb) and epidote-amphibolite facies (4.4-6.7 ppb) in comparison with the amphibolite facies. Accumulation of gold takes place under marginal P-T conditions of metamorphism, in the rocks near the boundaries between facies or subfacies (8.21-24.00 ppb).

The distribution of gold in the zoning metamorphic Oligocene rocks of the S-E Pamir is similar to Proterozoic rocks, but gold grades in these units are more than 20% higher in comparison with Proterozoic series.
Patterns and processes of long-term drainage exports from a pine chronosequence on restored lignite-mining dumps in Lusatia, Germany

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Open cast lignite mining results in severe multiple disturbances of ecosystem functions. In the Lusatian lignite mining district (E-Germany), an area of 80.000 ha is characterized by overburden dumps, tailings and mining lakes due to intensive lignite mining. Pyrite oxidation and AMD result in initially phytotoxic site conditions. On 60% of this area pine forests have been restored after intensive amelioration measures.

Characteristic features of the soils developing at these sites are sandy texture, poor water and nutrient storage capacity, high acidity and salinity, secondary mineral formation, and a high content of geogenic organic matter in various forms and spatial distribution (Schaaf and Hützl 2006). We studied the relevant soil structures and processes along a chronosequence of mine sites as well as the effects of its specific properties on element budgets and drainage exports at various scales using intensive field measurements, small-scale monolith sampling, and soil column experiments.

Pyrite oxidation itself and labile secondary minerals as well as the content and distribution of geogenic organic matter and its related physico-chemical properties affects water and element transport, element transformation and release processes, nutrient cycling, and soil development. The disturbance effect on element exports is declining over time, but can be clearly identified over a period of at least 60 years with considerably increased leaching rates from the restored ecosystems (Schaaf 2001).

References

Numerical study on shock effects in impact-rocks due to porosity

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Motivation and method
The heterogeneous distribution of crystalline shock polymorphs is commonly observed in impact rocks, and results from impedance contrasts between different minerals (e.g. Heider and Kenkmann, 2003) and pore spaces (e.g. Kieffer, 1976, Steward, 2007). We present numerical simulations of pore collapse due to shock wave loading to analyse the dependency of pre-shock internal rock structure on the resulting variety of shock features. We use the 2D hydrocode iSALE (e.g. Wünemann et al., 2006) and the analytic EOS (ANEOS) for dunite and quartzite. Pore spaces are represented by simple geometries, aligned by varying their sizes, distances and numbers.

Results
Significantly enhanced high temperatures and pressures occur when the collapse of a pore is completed. The maximum and distribution of peak pressures dependents on the geometry (Fig. 1), number and alignment of pores.

Results will be furthermore compared analytically with impacted terrestrial and meteoritic rocks.

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Novel cosmogenic isotope tools and progress towards historic time-scales

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Terrestrial cosmogenic isotope techniques have been revolutionizing earth sciences over the last decade and the methodological progress is accelerating. Related to the US/EU framework of the CRONUS initiative, substantial advances have been made over the last two years in developing new cosmogenic isotope systems and in sharpening existing cosmogenic tools.

We present analysis and production rate calibrations of several cosmogenic isotope systems focusing on terrestrial $^{53}\text{Mn}$, a long-lived radio isotope previously limited to extraterrestrial applications. This novel tool will allow new insights into landscape dynamics in arid regions on the million year time scale. On the other end, we present recent progress in the $^{10}\text{Be}$ technique allowing precise and accurate dating of Holocene climate changes including processes less than two hundred years in age.

Weathering rates determined on eroding moraine crests using cosmogenic $^{10}\text{Be}$ and base cation depletion

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Quantification of weathering rates is important for the understanding of landscape evolution and soil formation. Chemical weathering rates are influenced by many factors such as climate, vegetation, physical erosion, parent material composition, and soil age. Weathering rates of soils are typically calculated from non-eroding surfaces of known deposition age (e.g. Bain et al., 1993; Taylor and Blum, 1995) or surfaces assumed to erode at steady-state (e.g. Green et al., 2006; Riebe et al., 2001). Unfortunately, the assumption of non-eroding or steady-state landscapes is not always justified (e.g. moraine crests). In this study we integrate cosmogenic radionuclides ($^{10}\text{Be}$) and base cation depletion in two ~2 m depth profiles from moraines of different age to quantify soil mixing, denudation, and chemical weathering.

Depth profiles were sampled from terminal moraines in the Wind River Mountains, Wyoming. The two profiles were collected on the crests of the Pinedale (~21 ka) and Bull Lake (~140 ka) moraines. Calculations of weathering rates are based on base cations (Ca, K, Mg, Na) and reported as g(oxide) cm$^{-2}$ yr$^{-1}$. Weathering rates assuming no physical erosion of the moraine surfaces are 1.0 x 10$^{-5}$ and 3.1 x 10$^{-5}$ g(oxide) cm$^{-2}$ yr$^{-1}$ for the Pinedale and Bull Lake moraines, respectively. Measurement of in situ-produced cosmogenic $^{10}\text{Be}$ in each depth profile suggest denudation rates of 0.01 mm yr$^{-1}$, and soil mixing depths of 40 to 60 cm. Results to date suggest the assumption of steady-state denudation is not applicable to the investigated moraines due to their young age. Calculation of weathering rates based on transient denudation of the moraines needs to be investigated further.

Preliminary Results suggest that weathering rates accounting for physical erosion are higher than rates based on the assumption of no erosion. The increase in weathering rates might be larger for older surfaces as more weathered material has been eroded. Taking into account physical erosion, the decrease of weathering rates over time might be less than previously determined by assuming no erosion (e.g. Taylor and Blum, 1995).

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Precise ages for the Triassic/Jurassic boundary and Hettangian recovery from northern Peru

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The end-Triassic extinction is considered to be one of the most important biotic crises our planet has experienced, involving the disappearance of about 80% of the known species. Flood basalt volcanism of the Central Atlantic Magmatic Province (CAMP) has repeatedly been invoked to have caused this catastrophic event. New precise zircon U-Pb ages are proposed for the Triassic-Jurassic and the Hettangian-Sinemurian boundaries. The ages were obtained with ID-TIMS techniques from single chemical-abraded zircons from volcanic ash layers within the Pucara Group, Aramachay Formation, in the Utcubamba valley, northern Peru. Ammonite biostratigraphy is combined with U-Pb dating to indicate 206Pb/238U ages of c. 201.5 Ma for the Triassic-Jurassic and of c. 199.5 Ma for the Hettangian-Sinemurian boundaries. The former is established on a tuff located 1 m above the last local occurrence of the topmost Triassic genus Choristoceras and the latter was obtained from a tuff collected within the Badouxia canadensis beds. Our new ages document total duration of the Hettangian of c. 2 Ma, which has fundamental implications for the interpretation and significance of the ammonite recovery after the end-Triassic extinction.

The new zircon 206Pb/238U age for the T/J boundary is 2 Myr older than the currently accepted 206Pb/238U date for this boundary, and is in agreement with the published database of 40Ar/39Ar ages, taking into account the systematic 0.6-1.0% age difference between the two isotopic systems. The most precisely dated CAMP rock – the North Mountain Basalt in Eastern United States – is slightly younger than our date for the T/J boundary, with a 206Pb/238U date of 201.27 ± 0.06 Ma (Schoene et al., 2006). Resolving the question of synchronicity between CAMP volcanism and the T/J extinction, and thereby supporting a causal relationship between these two events, requires further high-precision U-Pb dating of potentially older basaltic units within the CAMP.

References

Estimating magnesium and silicon isotope fractionation with first-principles lattice dynamics

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Silicon and magnesium are major elements that undergo differentiation in a variety of igneous, metamorphic, and low-temperature environments. In this study first-principles methods are used to calculate equilibrium isotopic fractionations involving these elements, in order to assess potential applications of isotope measurements to understanding geochemical processes. Calculations focus on silicate and oxide minerals, and aqueous Mg2+ (by analogy to crystalline Mg(H2O)6•SO4).

Isotopic fractionations are calculated using density functional perturbation theory (DFPT), with norm-conserving pseudopotentials and a gradient-corrected functional (PBE). The energies driving fractionation are determined from changes in the density of states of vibrational (phonon) frequencies when isotopes are substituted into each crystal structure. Comparison with measured infrared and Raman spectra suggests that the DFPT-PBE method underestimates frequency changes in the density of states of vibrational (phonon) spectra. Comparison with measured infrared and Raman frequencies when isotopes are substituted into each crystal structure suggests that the DFPT-PBE method underestimates frequency changes in the density of states of vibrational (phonon) spectra. Comparison with measured infrared and Raman frequencies when isotopes are substituted into each crystal structure suggests that the DFPT-PBE method underestimates frequency changes in the density of states of vibrational (phonon) spectra. Comparison with measured infrared and Raman frequencies when isotopes are substituted into each crystal structure suggests that the DFPT-PBE method underestimates frequency changes in the density of states of vibrational (phonon) spectra. Comparison with measured infrared and Raman frequencies when isotopes are substituted into each crystal structure suggests that the DFPT-PBE method underestimates frequency changes in the density of states of vibrational (phonon) spectra. Comparison with measured infrared and Raman frequencies when isotopes are substituted into each crystal structure suggests that the DFPT-PBE method underestimates frequency changes in the density of states of vibrational (phonon) frequencies by 3-5%, and a fitted scale factor is used to adjust model frequencies. 1-5 phonon wave vectors appear to give a sufficiently large sample of the phonon density of states for each crystal.

The models predict measurable equilibrium isotopic fractionation of both magnesium and silicon in common minerals at metamorphic and igneous temperatures. At 1000°C, 26Mg/24Mg will be higher in spinel than silicates (0.6% for spinel-forsterite). This agrees with preliminary measurements of peridotite mineral separates (Tonui et al., this meeting). Silicates will have higher 26Mg/24Mg than carbonates (0.5% for diopside-dolomite at 600°C). Aquous Mg2+ will also have higher 26Mg/24Mg than coexisting carbonates (by ~2-3% at 25°C), in qualitative agreement with speleothem data [1]. There may be a small (0.1% at 1000°C) fractionation between forsterite and diopside, with diopside tending to be heavy.

30Si/28Si will also vary, tending to be highest in quartz. This agrees with previous Si-isotope fractionation models [2]. Quartz-zircon fractionation is expected to be ~0.5% at 800°C, compared with 0.3% observed in a granodiorite. Forsterite-diopside fractionation is small (~0.1% at 1000°C, diopside being light), consistent with xenolith data. Our results indicate that processes of igneous and metamorphic differentiation and metasomatism are likely to cause detectable Si- and Mg-isotope signatures.

References
Molecular and geochemical investigation of sediments covered with white mats at the Logatchev hydrothermal vent field

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Microbial mats have been described for different hydrothermal vent sites, e.g. along the East Pacific Rise (Taylor et al., 1999), in the Western Pacific (Takai et al., 2003), and at the Loihi Seamount (Moyer et al., 1995). In our study, we investigated the microbial community of two different sediments covered with white mats at the Logatchev hydrothermal vent area on the Mid-Atlantic Ridge (14°45’N). The white areas were occasionally interspersed with mussels at diffuse venting sites.

Temperature measurements showed 2-3 °C in the surface layer of both sediments increasing to up to 99°C in 28 cm depth. The corresponding temperature profiles revealed a linear temperature gradient indicating a high convective heat flux and no fluid flow. In contrast, the temperature of the sediments outside of the white-covered areas increased from 2-3°C to a maximum of only 8°C in 28 cm depth. To investigate the microbial diversity within the sediment surface layer (0-1 cm) of the white-covered areas 16S rRNA clone libraries were constructed. The analysis of about 100 clones per site resulted in 10-13 detected phyla. Using operational taxonomic units (OTUs), members of the Gamma-, Delta-, and Epsilonproteobacteria as well as of the phylum Bacteroidetes were identified as mat specific. CARD-FISH experiments confirmed that members of these four phylogenetic groups constitute the majority of microorganisms in the surface sediment layer of the “white mat” community. Typical filamentous sulphur-oxidizing bacteria of the genera Beggiatoa and Thiothrix were not detected.

In conclusion, the microbial community of the white mats was found to be highly diverse. However, mat specific groups were identified, which phylogenetically affiliated mainly with cultured sulphur-oxidizing bacteria. The high temperature in the deeper sediment layers correlates with the appearance of the white mats on the sediments. This suggests that a high subsurface temperature could cause processes supporting the formation of white mats on hydrothermal sediments.

References

U-Th magma residence times of the Plinian Mercato eruption at Mt. Somma-Vesuvius (Southern Italy)

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Plinian phonolite eruptions are a permanent dangerous threat for the population close-by to explosive volcanoes and have an effect on global climate changes. Hence, phonolite residence times in the crust are critical for assessing the potential hazard and frequencies of such explosive phonolite volcanic systems. So far, previous U-Th-studies on phonolites suggest time scales for the whole differentiation process forming a basanite to a phonolite of hundred of years up to hundred of thousand years. However, it is still unclear how long an differentiated phonolite and potentially explosive magma can reside in the crust without eruption or solidifying. Our combined petrological, geochemical and isotope study on late-stage phenocrystic unzoned phonolite Ca-garnets from a phonolite sample of the Pomici di Mercato eruption from Mt. Somma-Vesuvius (Southern Italy) permit for the first time the precise determination of the residence time of a differentiated phonolite magma in the shallow crust: These Ca-garnets, glass and whole-rock from the 8.1 ka-old phonolite Pomici di Mercato eruption define an U-Th-isochrone age of 14.4 ± 1.1 ka (2σ). It follows that explosive phonolite magma resided for more than 5 ka before eruption beneath Mt. Somma-Vesuvius in the shallow crust. In addition, given the recorded frequencies of eruptions from this volcano over the time, the Pomici di Mercato eruption was preceded by an exceptionnel long repose time. This could be explained by the closed-system behaviour of the Mercato reservoir, that was not refilled since Ca-garnet crystallisation and was not triggered by an input of new volatile-rich, less-differentiated magma.
Noble gases in fluid inclusions in speleothems

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Speleothems contain various paleoenvironmental proxy records on long time scales with high temporal resolution. Air and water inclusions formed during speleothem growth both represent potentially valuable archives of past climate conditions. First semi-quantitative analyses of air inclusions indicate that the major components (N2, O2, Ar) are present in near-atmospheric abundances. In contrast, trace gases (CO2, N2O, CH4) are enriched in the inclusions and hence the cave air. Therefore, similar to air trapped in ice cores, air inclusions in speleothems have the potential to reconstruct past climate conditions from regions where no ice is available. The concentrations of dissolved noble gases in water inclusions directly reflect the atmospheric pressure as well as the trace gas abundances from air inclusions. Moreover, the noble gas signature after heating is dominated by noble gases from water inclusions. However, the noble gas signature after heating is dominated by noble gases from water inclusions. Therefore, similar to air trapped in ice cores, air inclusions in speleothems have the potential to reconstruct past climate conditions from regions where no ice is available. The concentrations of dissolved noble gases in water inclusions directly reflect the atmospheric pressure as well as the temperature and salinity of the water at the time of formation of the inclusions. To infer past climate conditions, the parameters T, p, S and “excess air” have to be determined from four measured noble gas concentrations (Ne, Ar, Kr, Xe), analogous to the noble-gas thermometer employed in lakes and groundwater. The separation of noble gases from air and water inclusions is crucial to determine paleotemperatures from noble gases is water inclusions. Microscopical investigations show that air and water inclusions differ in size and position within the speleothem. Hence, a sufficient separation should be achievable by extracting noble gases in two subsequent steps (crushing and heating). First results show that crushing mainly opens inter-granular air inclusions whereas heating cracks intra-granular water and air inclusions. However, the noble gas signature after heating is dominated by noble gases from water inclusions.

The salinity of the drip water before incorporation into the speleothem - determined by microthermometry - ranges from 7 – 15 ‰ and therefore can be assumed to be equal to that of freshwater. Since tritogenic and radiogenic 3He in the water inclusions are probably negligible, 3He is purely atmospheric, in contrast to 4He. This would allow 3He to be used as an additional constraint to reconstruct the paleoenvironmental conditions.

With the potential of a quantitative separation of noble gases from air and water inclusions before analysis and additional measurements of 3He, the determination of paleotemperatures from noble gases in fluid inclusions seems to be possible.

In summary, dissolved noble gases from water inclusions, as well as the trace gas abundance from air inclusions are emerging proxies that will complete the available methods to reconstruct past climate conditions from speleothems.

Selenite reduction by nano-crystalline green rust, magnetite, siderite and mackinawite: EXAFS identification of Se species

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Selenium oxoanions are abiotically reduced on Fe(II/III) hydroxide (green rust) and Fe(0) metal surfaces to Se oxidation states of 0, -I or –II with relatively slow reaction kinetics [1, 2]. The unequivocal phase characterization by EXAFS spectroscopy, which is a key for the determination/prediction of Se solubility, was hindered by incomplete reduction, insufficient spectral data ranges and the similarity in short-range structures of the potential mineral phases. In a recent study [3], however, we were able to clearly identify the reduction product of selenite co-sorbed with FeII to montmorillonite as nano-particulate, trigonal Se(0) by collecting low-noise EXAFS spectra at 15 K (Rossendorf Beamline at ESRF, Grenoble, France) and by employing advanced data analysis methods [4, 5].

Here, we present data on the reduction of selenite by green rust, magnetite, siderite and mackinawite. In the presence of green rust, selenite was completely reduced to trigonal Se(0) within one day, which was further converted to ferroselite (orthorombic FeSe2) within one month. The associated Fe(II) oxidation and magnetite formation quantified by Moessbauer spectroscopy allowed us to establish the following reaction scheme: 32 [FeII3FeIII4(OH)12 Cl] + nH2O(s) + 38 SeIVO3(s) ⇌ 19 [FeIVSeI2](s) + 175 [FeIIIFeII3O4](s) + 160 Cl - + 502 H2O + 84 H±

Similar to green rust, mackinawite and magnetite reduced all selenite within one day, whereas reduction by siderite was incomplete. Depending on type of mineral and Se-to-mineral ratio, trigonal Se(0), ferroselite or achavalite (hexagonal FeSe) formed. The observed differences in reaction end products and reduction kinetics may significantly affect Se bioavailability and Se migration.

References
Formation of Liesegang rings in borosilicate glass during experimental alteration

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Borosilicate glasses are currently the standard material for the immobilization of high-level nuclear waste. Numerous studies have been carried out to study the aqueous durability of such glasses, which have indicated that under ambient conditions the corosion of the glass is initially controlled by ion exchange and later by hydrolysis of the glass network, forming a so-called “leached layer”, before the glass dissolves. For the present study we have synthesized a borosilicate glass with a complex composition, including network modifiers such as Na, Ce, Al, Mn, Li, Ca, Mg, and Ti (WAK glass), from which we cut cuboids with edge lengths of about 2.6 mm. These cuboids were treated in a 1 M HCl solution at temperatures between 100 and 220 °C for 4 days. For one experiment (at 150°C) the solution was enriched with 47.5 at.% 18O. After the experiments, the formerly translucent, yellowish glass cuboids showed a milky-white color, but their external shape has not changed, as in pseudomorphism. Interestingly, the measured weight and elemental loss values increase regularly from 100 to 150°C, and then decrease towards a local minimum between 170 to 190°C before they increase again. Backscattered electron images on cut glass samples revealed reaction rims (“leached layers”) with complex oscillatory banding structures and bifurcations (Liesegang rings), which form a layer between the unaltered glass and an unpatterned outer rim. Whereas the outer rim consists of almost pure SiO₂, the patterned layer retained some Ce, Ti, and Al, located now within distinct bands. The occurrence of Liesegang-like banding structures suggests, at first glance, a diffusion-controlled alteration process. However, infrared spectroscopic measurements on the alteration rim formed in the 18O-enriched solution show a large mass shift of the Si-O vibrational modes (even close to the interface between the unaltered glass and the alteration layer) when compared with measurements on the alteration layer formed in “normal” 16O-enriched solution. This indicates a high concentration of 18O throughout the alteration rim. Furthermore, the chemical interface between the unaltered glass and the alteration rim is sharp on a micrometre scale with no apparent chemical diffusion profiles. Such features are not compatible with a process that is solely controlled by diffusion of cations and hydrogen species. Here we suggest that during the first step the borosilicate glass dissolved congruently followed immediately by the precipitation of amorphous SiO₂ at an inward moving interface. Once the SiO₂ layer became too thick, the communication between fluid and the reaction interface ceased and the SiO₂ layer increasingly incorporated Ce, Ti, and Al. In a second step the Liesegang bands were formed by a diffusion-controlled process.

Metamorphic reworking of the Congo Craton in Uganda

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The Basement Complex of Uganda (BC) forms the NE corner of the Archean Congo craton bordering the Pan-African Central African Fold Belt (CAFB) in the N and the East African Orogen (EAO) in the E. We studied the tectonic history of the Archean basement and of its Neoproterozoic cover series by means of metamorphic P-T paths and metamorphic ages (SHRIMP dating of zircon and U-Th-total Pb chemical dating of monazite).

A clockwise P-T evolution during a first metamorphism (M1) along the northern craton border is constrained by prograde sillimanite and later formed kyanite included in garnet, peak-metamorphic Grt-Sil-Bt assemblages and the late-stage formation of cordierite rims around garnet. Peak conditions (9-10 kbar; ca. 940 °C) were followed by decompression to about 8 kbar and subsequent near-isobaric cooling. A second metamorphism (ca. 750°C at 7 kbar) is evident from new garnet overgrowing Bt-Sil/Ky-Crd symplectites formed during retrogression after M1. Dating revealed ca. 2.6 Ga for M1 and ca. 650 Ma for the reworking, indicating that the granulites formed the deep cratonic crust for about 2 Ga prior to their Pan-African uplift.

At the eastern craton border, aluminous Opx (up to 11.5 wt% Al₂O₃ when coexisting with Grt) and assemblages with Spl-Spr-Qtz-Grt-Osumilite (pseudomorph), Opx-Sil-Grt or inverted pigeonite point to extreme metamorphic temperatures (>1000°C) at 8-10 kbar in a very large area (including the Labwor Hills). In contrast, late-stage Grt-Cpx-Qtz coronas in charnockitic and metabasitic rocks were formed at 6-7.6 kbar only after near-isobaric cooling to temperatures of 650-680°C. The reaction history in metapelites points to an anti-clockwise P-T evolution. UHT metamorphism and magmatism of high-temperature A type granitoids are spatially and timely associated and lasted for about 70 Ma between 700 and 630 Ma. The intrusion of the magmas is interpreted as the cause of the UHT metamorphism.

Neoproterozoic cover series (NW Uganda) have not experienced granulite facies metamorphism unlike the basement rocks on which they are resting. They are Grt-Ky-Ms-Bt-Pl-Qtz bearing micaschists metamorphosed at 8 kbar and 650-680°C during a clockwise P-T path. Monazites show a one-stage growth history and give ages of 621±26 and 633±27 Ma for the metamorphic event that was caused by thickening of the cratonic crust.
The Lu-Hf systematics of meteorites: Consistent or not?

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The discrepancy between the $\lambda_{176}^{176}\text{Lu}$ value determined from terrestrial minerals ($1.867 \pm 0.011 \times 10^{-11}\text{yr}^{-1}$; [1-3]) and those derived from meteorite WR isochrons (1.93-1.98 $\times 10^{-11}\text{yr}^{-1}$; [2,4-8]) remains unsolved. Meteorites that violate isochron assumptions are not ideally suited for $\lambda_{176}^{176}\text{Lu}$ measurements [9]. Nevertheless, some internal (mineral) isochrons may yield valuable insights about the early solar system. Amelin [9] compared the Lu-Hf and U-Pb systematics isochrons may yield valuable insights about the early solar system. Amelin [9] compared the Lu-Hf and U-Pb systematics isochrons may yield valuable insights about the early solar system. Amelin [9] compared the Lu-Hf and U-Pb systematics isochrons may yield valuable insights about the early solar system. Amelin [9] compared the Lu-Hf and U-Pb systematics isochrons may yield valuable insights about the early solar system. Amelin [9] compared the Lu-Hf and U-Pb systematics isochrons may yield valuable insights about the early solar system. Amelin [9] compared the Lu-Hf and U-Pb systematics.

Lipid biomarkers as indicators for environmental stress in cyanobacterial mats of Abu Dhabi, United Arab Emirates

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Intertidal cyanobacterial mats in the coastal flats of the Arabian Gulf in Abu Dhabi (United Arab Emirates) grow under locally different conditions. Salinity ranges from 60 to 200 due to the high evaporation rates of the tidal waters caused by shadowless sunshine exposure for nearly 12 hours a day.

We compared the phospholipid fatty acid profiles of six mats from lower, middle and upper tidal zones. The analysed mats show differences in their texture and horizontal layering. As the species of the layers are attributed to the activity of physiologically different bacterial populations we sliced the mats accordingly and compared the results of single-layer analyses with the data for the whole mats. Phospholipids are main constituents of cell membranes and are easy to extract and identify. Differences in concentrations and distributions will reflect changes in microbial populations and reactions on environmental stress, e.g. desiccation.

Former studies had shown that lipids may be involved in the protection against environmental stress as they maintain the membrane fluidity. In our mats, increased ratios of saturated to unsaturated fatty acids, cyclopropyl to monounsaturated fatty acids and trans- to cis-monounsaturated fatty acids are interpreted as response to environmental stress in the region. The trans- to cis-monounsaturated fatty acid ratios reached up to 1.6, e.g. for elaidic acid in our mats.

References

What governs the transition from miaskitic to agpaitic assemblages in peralkaline rocks?

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Peralkaline igneous rocks (molar (Na+K)/Al>1) are characterized by exceptionally high contents of generally incompatible elements like Na, Li, Be, Rb, REE and HFSE (Ti, Zr, Hf, Nb, Ta). However, based on their mineral assemblages, they can be subdivided into two groups: In the case of peralkaline miaskitic rocks, HFSE are incorporated in minerals like zircon, titanite and ilmenite, whereas in agpaitic varieties, these elements occur in complex Na-(Zr,Ti)-silicates such as eudialyte, rinkite and lävenite (Sørensen, 1997). Commonly, peralkaline igneous complexes worldwide show either a miaskitic or an agpaitic character, or at least distinct melt batches within the same complex tend to develop to either miaskitic or agpaitic assemblages. Still, it is not clear, which processes cause either miaskitic or agpaitic assemblages to crystallize.

In the special case of the Eocene Tamazeght complex (Moroccan High Atlas mountains), a continuous transition from miaskitic nepheline syenites to agpaitic ones, including late-stage agpaitic pegmatites and veins, is observed. The earlier miaskitic rocks are characterized by nepheline, K-feldspar, aegirine-rich clinopyroxene, sodalite, titanite and rarely developed zircon. In contrast, the agpaitic varieties bear eudialyte instead of titanite and zircon, without showing any replacement textures between these minerals. However, the major mineral assemblages in the agpaites show no obvious difference compared to their miaskitic counterparts.

In this study, we compare electron microprobe data for nepheline, sodalite and clinopyroxene as well as mineral stable isotope data (O, H) of both miaskitic and agpaitic samples. Additionally, eudialyte from agpaitic samples was analyzed by electron microprobe. Preliminary fluid inclusion investigations indicate two types of inclusions in both nepheline and eudialyte, including a methane- and hydrogen-bearing population, which is known to be typical of peralkaline rocks (Potter & Konnerup-Madsen, 2003).

Based on this, we will try to shed light on the relevant changes of parameters being responsible for the transition from miaskites to agpaites.

References

Werner Schreyer and the MASH-system: Results from investigations on natural rocks and experiments

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Nearly iron-free metamorphic rocks of sedimentary and metasomatic origin are found in several parts of the world (e.g. Sar-e-Sang/Afghanistan, Dora-Maira-Massif/Western Alps, Eastern Alps/Austria). All these rocks have experienced metamorphic conditions at moderate temperatures and relatively high to ultrahigh pressures. Chemically, these rocks can be well described with the MgO-Al2O3-SiO2-H2O (MASH) experimental model system, and thus provide an excellent independent check on it. In so-called leucophyllites from the Eastern Alps the assemblage chlorite + quartz is found which is stable to only 600°C (Chopin and Schreyer, 1983). Towards higher pressures these phases react to the "whiteschist" assemblage talc + kyanite (Sar-e-Sang) with a temperature of 750 - 800°C this is replaced by the ultra-high-pressure assemblage pyrope + coesite (Schreyer and Yoder, 1988). At all times, Werner Schreyer recognized the significance and interaction of nature and experiment. From experimental studies in the MASH-system he and his working group mapped out petrogenetic grids which allow HP-metamorphic sequences in natural rocks to be seen in a geodynamic context, while at the same time these natural occurrences also served as a template for delineating stability/compatibility fields of the observed nearly iron-free phases and assemblages in the laboratory (e.g. Fockenberg, 1995).

References
Europa’s subsurface ocean

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Recent geological and geophysical observations from the Galileo spacecraft indicate that Europa, one of the icy moons of Jupiter, harbors a salty ocean of liquid water beneath its icy surface. Magnetic field perturbations observed by the Galileo spacecraft at Europa, are consistent with induced magnetic fields from the interior of the moon. These magnetic fields are very likely caused by electromagnetic induction in a subsurface water ocean with high electrolytical conductivity. An additional process, which also generates magnetic field perturbations at Europa and therefore competes with induction, is the interaction of Europa’s oxygen atmosphere with the magnetospheric plasma in which the moon is embedded. We have developed a time dependent 3D model to study simultaneously the electrical conductivity distribution inside Europa and the time-varying interaction of Jupiter’s magnetosphere with Europa’s atmosphere. By comparing our simulation results to the Galileo spacecraft measurements by Europa, we place the so far strongest constraints on the conductivity and the thickness of Europa’s subsurface ocean. We find an internal ocean close to the surface with a conductance of 50,000 S or larger to be most suitable to explain the magnetic flyby data. These results suggest that a global subsurface ocean at Europa with terrestrial “sea water” would have to be thicker than 10 km.

In situ cosmogenic $^{36}$Cl production rate calibration on basaltic flows of Mount Etna (Sicily, 38°N)

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One of the CRONUS-EU goals is to provide high quality calibration sites from independently dated surfaces. Several previous studies have been conducted on $^{36}$Cl production rate calibration (e.g. Stone et al. 1996, Phillips et al. 2001), which, however, used different protocols and yielded $^{36}$Cl production rates with up to 40% discrepancies. The objectives of this study are 1- to understand the source of these discrepancies and 2- to calibrate $^{36}$Cl production rates from its most abundant target elements $^{40}$Ca, $^{39}$K and $^{35}$Cl.

As a first step we focused on testing the chemical protocol by performing a sequential $^{36}$Cl extraction experiment on whole rock grains and Ca rich plagioclase from the same sample. The sample was collected at Mt. Etna on a pahoehoe flow which has a K-Ar fossil exposure time of 10±3 kyr. Cosmogenic $^4$He of this sample was also precisely measured within cogenetic olivine phenocrysts (Blard et al. 2005) and yields an exposure time of 10.4±1.5 kyr.

Both, total Cl and $^{36}$Cl concentrations from the first dissolution steps are high, 5800 ppm (whole rock) and 450 ppm (plagioclase) Cl, and $10^7$ - $10^8$ atoms $^{36}$Cl/g of rock dissolved. After about 20% dissolution of the plagioclase sample, Cl is almost completely removed (1-3ppm) and $^{36}$Cl concentrations reach a plateau value of $2*10^5$ atoms/g of rock. Using the Stone et al. (1996) and Evans et al. (1997) $^{36}$Cl production rates for the target elements Ca and K, respectively, this plateau concentration yields an exposure age which is in agreement, within uncertainty, both with K-Ar dating and cosmogenic $^4$He ages. On the contrary, in the whole rock sample total Cl concentrations remain high ($>330$ppm) resulting in a considerable $^{36}$Cl production from capture of low-energy neutrons by $^{35}$Cl, an additional and still not well-constrained $^{36}$Cl production mechanism. The resulting exposure ages from the whole rock are 20-30% higher than the independent $^4$He ages.

To better constrain the different sources of $^{36}$Cl in basaltic rocks and their production rates we will perform a similar experiment on separated sanidine (K-rich feldspar) from an independently dated basaltic flow of another volcano.

References
Blard P.H., et al. (2005), EPSL 236 613-631;
Simultaneous determination of Se and Te in different geological matrices with DRC-ICP-MS

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An investigation of ferro-manganese crusts conducted by Hein, Koschinsky et al. (2003) had shown an extreme enrichment of tellurium, but no comparable concentrations of the geochemically very similar element selenium. This Te enrichment was related to a surface oxidation process of Te(IV) to Te(VI) on the Fe-Mn oxide surfaces, which apparently does not take place for Se(IV). Therefore the element pair Se and Te seems to have an interesting potential as paleo-proxy to investigate in situ redox conditions. In a next step Se and Te are investigated in more detail in different geological matrices to gain knowledge of the usability of this element pair to describe geopaleontogical redox processes.

Very little Te data of different geological materials have been available so far. A first challenge to be addressed is the precise determination of these two elements with quadrupole DRC-ICP-MS. In this context an analytical approach was developed, using different methods for sample digestion, enrichment and analysis.

Two well known problems connected with the determination of Se and Te with standard quadrupole ICP mass spectrometry are low sensitivities (max. ~3 kcps and ~15 kcps for 10 ppb Se and Te respectively) and severe interferences, especially on Se (e.g. $^{40}$Ar$^{+}$ on $^{80}$Se). This fact is accompanied by the overall low concentrations in the different matrices, especially in water. Another problem with respect to the acid pressure digestion is the instability of Se in chloride matrix and at temperatures above 80 °C.

All these analytical problems where addressed by optimizing the ICP-MS conditions, the digestion procedure and by the use of thiol cotton separation for samples with very low Te and Se concentrations, first described by Mu-Qing and Gui-Qin (1983). Data for Te and Se in various sample types including marine ferromanganese crusts, weathered basalt and dolomites will be presented.

References

Influence of Hydrogen on electrical conductivity in enstatite

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Hydrogen has a significant influence on several physical properties of upper mantle rocks. Models for electrical conductivity, for instance, are mainly based on conductivity data for olivine. Therefore, systematic laboratory data on electrical conductivity of other H-bearing nominally anhydrous minerals (e.g. enstatite, MgSiO$_3$) are needed. An important mechanism for electrical conduction in enstatite requires the presence of protons, because they are the major mobile charge carriers. Key factors for this conduction mechanism are concentration and mobility of protons. In this study, we measured electrical conductivity and H-diffusivity in pure, Al-, and Fe-doped synthetic enstatite. As incorporation of additional cations, such as Al and Fe, create new point-defects in the crystal lattice, transport mechanisms might depend on the defect chemistry.

Diffusion experiments were conducted at 1 bar and 1000°C to 1000°C in air. Electrical conductivity was measured at same conditions with an impedance analyzer (0.1 - 10000 Hz), and H-concentration was monitored by FTIR-spectroscopy.

Initial results show that H-diffusivity from dehydration experiments in Fe-bearing enstatite is about one order of magnitude faster than in pure enstatite, whereas it is slower in Al-bearing enstatite. A similar behaviour was observed for electrical conductivity.

Application of the Nernst-Einstein equation to the diffusivity results for pure enstatite are in good agreement with our preliminary conductivity data; this supports the hypothesis that H is the major mobile charge carrier.
Cation sorption at the smectite edges: From transition metals to Y and Lu

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Introduction

Clay minerals can adsorb trace elements in soils and weathering formations, a sorption property which is also a key-point for the use of clay materials in nuclear waste repositories. Retention can occur either by adsorption on the clay basal plane or at the layer edges, depending on physico-chemical conditions. Building on previous identification of sorption sites of transition metals [1-3], this study shows how the geometry of Y and Lu surface complexes on layer edges of clay minerals can be identified.

Materials and methods

Suspensions of purified clay minerals (hectorite or Al-montmorillonite, 2 and 1 g/L, respectively) were reacted in 0.5 M NaCl at pH 6 (Al-montmorillonite) and 7 (hectorite) with sorbates at concentrations of 50 μM (Y) and 100 μM (Lu). Self-supporting films of reacted clay minerals were obtained by slowly filtering suspension aliquots on cellulose nitrate filters. Yttrium K-edge and Lu L3-edge polarized EXAFS (P-EXAFS) spectra of the self-supporting films were collected in fluorescence mode on the FAME beamline (ESRF, France). P-EXAFS data were reduced, and analyzed using standard procedures.

Results and interpretation

Small but significant angular dependences were observed for all P-EXAFS data, meaning that the Y and Lu binding environments are anisotropic. Coordination spheres of 7 O at 2.36 Å and 8 O at 2.27 Å, were observed for Y and Lu, respectively, comparable with d(Ln-O) distances measured by EXAFS spectroscopy [4]. Lutetium sorbed on Al-montmorillonite was surrounded by an Al-shell at 3.35 Å, consistent with Lu sharing edges with Al octahedra and partially incorporated in a gibbsite-like interlayer. Both Y and Lu sorbed on hectorite were surrounded by cationic silicates. Modelling of these cationic contributions yielded one out-of-plane Si/Mg shell at 3.16 Å (Y) or 3.04 Å (Lu), and two in-plane (Mg/Si) shells at 3.50, and 3.97 Å for Y, or 3.33 and 3.91 Å for Lu. These distances and angular orientations collectively suggest that Y and Lu form inner-sphere surface complexes at the edges of hectorite platelets, but slightly above/below the hectorite octahedral plane, and tend to share edges with silicate groups of the clay tetrahedral sheet.

References


Interaction between colloidal and organically complexed Iron (III) species in seawater by ultrafiltration

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Method and Theory

Ultrafiltration experiments (Viavflow 50 - 10kDa filter) were performed using 55Fe in combination with artificial and natural organic ligands (in excess) in seawater. The activity of the 55Fe in the permeate and retentate was measured using standard liquid scintillation methods. The permeation (Pc) and retention coefficient (Rc) were calculated as follows:

\[ P_c = 1 - \frac{\log c_p}{\log CF} \]
\[ R_c = 1 - \frac{\log c_R}{\log CF} \]

Where CF = concentration factor (CF). Some results are shown in the Table below:

Table 1: P_c and R_c values of the Fe (III) species

<table>
<thead>
<tr>
<th>Ligand</th>
<th>P_c</th>
<th>R_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>None - UV irradiated Seawater</td>
<td>0.49</td>
<td>0.44</td>
</tr>
<tr>
<td>Natural - Antarctic Seawater</td>
<td>0.96</td>
<td>0.58</td>
</tr>
<tr>
<td>Natural - Coastal Seawater</td>
<td>0.93</td>
<td>0.63</td>
</tr>
<tr>
<td>2-(2-Thiazolylazo)-p-cresol (TAC)</td>
<td>0.99</td>
<td>0.75</td>
</tr>
<tr>
<td>Ethylenediaminetetraacetic acid (EDTA)</td>
<td>1.00</td>
<td>0.85</td>
</tr>
<tr>
<td>Desferrioxamine B (DFO_B)</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>2-Keto-D-Gluconic Acide</td>
<td>0.88</td>
<td>0.59</td>
</tr>
<tr>
<td>Protophorphyrine IX</td>
<td>0.89</td>
<td>0.49</td>
</tr>
<tr>
<td>Phytic Acide</td>
<td>0.97</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Discussion

These 2 parameters allow us to differentiate between very strong, strong and weak ligands based on their ultrafiltration properties. Pc=Re=1 are significant for very strong ligands (e.g. DFO_B), where all added Fe is organically complexed. Strong ligands (e.g. TAC, EDTA) have additionally a colloidal fraction, but no interaction between both species (Pc=1, Rc<1). Pc=Re<1 are observable for weaker ligands (e.g. Protophorphyrin IX) with an identifiable interaction between both species.

Conclusion

Using this approach helps us better understand the relationship between colloidal and dissolved Fe concentrations in natural seawater and how to quantify the interconnections between natural organic complexes and colloidal iron. The results strongly suggest that information on colloidal Fe concentrations is dependent on CF and this needs to be taken into account when reporting ultrafiltration data. This approach is particularly useful for assessing the bioavailability of iron in natural seawater as most colloidal iron is believed to be weakly bioavailable.
Hydrothermal AFM and mixed-flow reactor studies of ZnS dissolution

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Sulfide minerals are the major contributors to acid mine drainage (AMD) and heavy metal release. While the weathering of iron sulfides has been studied intensively only little attention has been paid to the zinc sulfides. To understand the mechanisms and kinetics of sphalerite reactions in aqueous solutions, a combination of high resolution microscopy methods and chemical analytical methods proved to be perfect as it correlates nano-scale observations with macro-scale data.

Here, in situ hydrothermal AFM (HAFM) measurements and mixed-flow reactor experiments were conducted at pH 1-2 and a temperature of 125 °C. While HAFM measurements were performed on the (110) surfaces, sphalerite powder was used for mixed-flow reactor experiments.

Mixed-flow reactor experiments showed an initial maximum of zinc and sulfur release. This initial maximum in dissolution was followed by an exponentially decreasing part, which converted into a steady state after ca. 10,000-15,000 min. Within the accuracy of the data, the mixed-flow experiments revealed no incongruent or not stoichiometric dissolution. in situ HAFM measurements showed the formation of a thin altered layer on the surface during the initial state of dissolution followed by a development of facets.

From the mixed-flow reactor experiments it can be concluded that the leached layer observed in HAFM experiments can only be caused by a minimal shift in the chemical composition of the surface.

The HAFM experiments further showed the decomposition of the cleavage morphology into facets with three prominent orientations. These observations indicate that the observed initial maximum in zinc and sulfur concentration was caused by a change of the surface morphology from one morphology with high dissolution rates to another morphology with lower dissolution rates. As proved by SEM investigations, small particles on the crystals can be excluded as a reason for the observed rate maximum. Until now tip-surface convolution disabled crystallographic indexing of the facets by AFM. Indexing the facets via LEED remained difficult because the facets were not persistent while LEED sample conditioning. Further experiments are in progress.

In summary, the two different experimental approaches yielded complementary information which in combination allowed one to obtain a significantly more comprehensive understanding of the mechanisms and kinetics of sphalerite dissolution.

Architecture of phosphatic and calcitic brachiopod shell materials – A comparison.

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Brachiopods have developed shell materials employing the two principal mineral groups of hard biologic tissue: calcium carbonate and calcium phosphate, each with distinct hierarchical architecture. The “phosphatic” shells consist of a predominantly chitin fibrous matrix, which is reinforced by isometric hydroxyapatite or similarly sized amorphous Ca-phosphate particles attached to the fibres [1]. The fibre composit is not unlike vertebrate bone. A laminated structure is created by changing volume ratios of chitin and reinforcing particles. In contrast, the composit structure of calcitic brachiopod shells employs inorganic single-crystal fibres reinforced by thin intercrystalline and extremely thin intracrystalline organic membranes [2, 3]. The pronounced crystallographic texture of the fibres [2, 4] appears to originate from growth selection. Over lengths well exceeding hundred micrometers the fibres change crystallographic orientation continuously in the order of one degree. While the laminated organic fibre/inorganic nanoparticle strategy provides a degree of shell flexibility the inorganic fibre/polymer membrane composit provides a high stiffness and micro- and nanohardness.

References
Lu-Hf geochronology of eclogites from the Dabie-Sulu terrain: Constraints on the timing of eclogite-facies metamorphism

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The Qinling-Tongbai-Dabie-Sulu belt was formed by the collision of the Yangtze and the Sino-Korean cratons, and is one of the largest ultrahigh-pressure metamorphic belts worldwide. Micro-diamond and coesite was found in eclogites and country rocks of this area, indicating a deep subduction of continental material at mantle depth. The eastern UHP part of the belt is subdivided in the Dabie and the Sulu terrain. The latter was offset 500km to the North by the Tan-Lu fault. Various geochronometers (U-Pb, Sm-Nd, Rb-Sr, Ar-Ar) have been applied to date the metamorphic events in this collision zone. However, UHP and eclogite facies metamorphism are controversially constrained to a Triassic age between 210 Ma and 245 Ma.

Here we present a new approach using the Lu-Hf isotope system to date garnet-clinopyroxene mineral assemblages in three eclogites from the Dabie terrain (sample localities are Bixiling, Shima and Lidu) and three eclogites from the Chinese Continental Scientific Drilling Program (CCSD) in the Sulu terrain. Garnets of our samples are very homogeneous and virtually non-zoned.

The Lu-Hf isochrons yield tightly grouped ages between 219.6 Ma and 223.4 Ma for both terranes (Dabie Shan and Sulu), yielding a mean age of 222.0 Ma for all six samples. This age is in good agreement with earlier estimates on the timing of UHP metamorphism. However, in contrast to previous studies our results indicate a tight age range for eclogites of the entire Dabie complex. Based on U-Pb zircon ages, Liu et al. (2006) and Hacker et al. (2006) recently proposed three metamorphic events within age ranges of 244-236 Ma, 230-220 Ma and 220-205 Ma, respectively. Liu et al. (2006) interpreted their ages as distinct eclogite facies events. In contrast, our Lu-Hf results show no evidence of multiple or long lasting eclogite facies conditions. Alternatively, Hacker et al. (2006) proposed a "precursor" UHP, a "main" UHP and an amphibolites facies metamorphic event for the Dabie-Sulu area. Our Lu-Hf ages fall into their proposed UHP event (220-230 Ma), however, define a much smaller range. This implies a very rapid UHP event on a large regional scale. Alternatively, not UHP, but the transformation of pre-cursor rocks into ecлогite or closure of the Lu-Hf system in garnet in the Dabie and Sulu terrain occurred within a very limited timescale.

References
Liu, D. et al.; EPSL 250 (2006); pp650-666

Using 222Rn as environmental tracer for assessing groundwater/surface water interaction

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The exchange of water between lakes or rivers and hydraulically connected aquifers provides a major pathway for chemical transfer between the respective water bodies. For instance, the migration of dissolved carbon, oxygen, and/or nutrients coupled to such exchange processes has to be considered a main driver for biogeochemical processes on both sides of the surface water/groundwater interface. Furthermore, dissolved contaminants, such as dissolved NAPL, pharmaceuticals, or heavy metals, are not only influential on the aquatic life or the biological properties of the affected water body, but also on its overall water quality. Generally speaking, if the status of a surface water or groundwater resource is to be assessed or its fate to be predicted it must not be looked at as a separate aquatic system but interactions at the surface water/groundwater interface have to be taken into account.

The groundwater flux into a meromictic lignite mining lake (Lusatia Mining District, Germany) was quantitatively assessed by means of a geochemical tracer technique using the naturally occurring radio isotope 222Rn. The noble gas radon makes an ideal environmental tracer because of its chemically inert behaviour and its ubiquitous presence in groundwater, where it appears in concentrations well above the commonly used ones in surface waters (Nazaroff and Nero, 1988). In a long-term project radon concentrations in the water of the studied mining lake and in the groundwater sampled from surrounding monitoring wells were determined monthly over a two-year period. Evaluation and interpretation of the data sets allowed for assessing the dynamics of the local groundwater/surface water exchange processes. It can be shown that there is a high variability in the groundwater/surface water interaction rate, depending on changes of the (seasonal) precipitation rate, even within very short time scales.

The radon technique used has a high potential to improve the quality of the investigation of limnic environments. As a additional advantage the possibility of on-site determination of radon concentration in water samples (Schubert et al., 2006) allows for straightforward decisions concerning the further strategy of ongoing sampling campaigns.

References
**In situ** studies of aqueous fluid properties at high pressures and temperatures using hydrothermal diamond-anvil cells

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Aqueous fluids and their interaction with mineral assemblages play a key role for the mobility of elements and, thus, material flux in the lithosphere. The invention of the hydrothermal diamond-anvil cell (HDAC) [1] has extended the **PT** range, in which aqueous fluid properties can be studied **in situ**, up to the conditions of the lower crust and dehydrating slabs.

Modifications of the HDAC design [2,3] permit application of synchrotron-radiation X-ray techniques to investigate the behavior of dissolved heavy elements with X-ray emission energies as low as ~4 keV and absorption edge energies as low as ~5 keV. Time-resolved SR-XRF analyses have been used to study the solubility of minerals containing elements with Z≥22 in aqueous fluids, the kinetics of fluid-mineral interaction, and trace element partitioning between aqueous fluids and silicate melts [e.g., 4, 5]. A minimum detection limit of about 2 ppm for Ti (Ko energy=4.5 keV) was achieved in recent in situ SR-XRF experiments on the solubility and dissolution kinetics of rutile in H₂O+NaAlSi₃O₈ and H₂O+Na₂Si₃O₇ fluids to 800 °C and 1.3 GPa. Complexation and speciation of heavy elements in aqueous melts and fluids have been investigated in situ by X-ray absorption techniques, e.g., SR-XAFS analyses of the La L₂,3-edge in a study of the hydration structure of aqueous La₃⁺ (0.007 m) to 300 °C and 160 MPa [6] or SR-XANES measurements on Fe²⁺ in water-saturated haplogranitic melt up to 700 °C and 500 MPa [7].

Raman spectroscopy and Bassett-type HDACs have been used in a number of studies to obtain information on the behavior of light elements at high **PT**, e.g., on the speciation of silica to 900 °C and 1.4 GPa [8] or the complexation of boron to 600 °C and 2 GPa [9]. However, utilization of Raman spectroscopy as a quantitative tool is still in an early stage. Much remains to be learned about fluids in deeper portions of the lithosphere, and further method developments (e.g., to determine electrical conductance and density of such fluids) are needed.

References


**Trace elements in foraminiferal calcite: New understanding based on** **in situ** **analysis**

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Trace element concentrations in foraminiferal carbonates are a widely used as proxy to assess past climates and ocean circulation. Planktic foraminifers strongly discriminate against trace element incorporation, resulting in Me/Ca ratios which are significantly lower than ambient sea water concentrations. Physiological (e.g., photosynthesis, respiration, and calcification) and ecological processes (e.g., depth migration) can modify the trace element uptake into the foraminiferal calcite and thus exert an important influence on Me/Ca ratios.

**in situ** analysis of spatially resolved elemental ratios increase our understanding of biological processes influences in incorporation of these proxies in foraminifers. The applicability of the proxy and the precision of palaeoclimatic assessment will depend on our understanding of the incorporation of these trace elements into foraminiferal carbonate.

To this end, we have performed trace element analysis using Secondary Ionization Mass Spectrometry and Electron Microprobe on planktic foraminifers from sediment samples and sediment traps. The sediment trap samples from the Canary Islands and the western equatorial Atlantic allow for direct comparison between ambient conditions and Me/Ca ratios. We analysed symbiont bearing (*G. ruber, G. sacculifer*) and asymbiotic (*G. truncatulinoides, G. tumida*) species which are living in different depth habitats. Mg/Ca, Ba/Ca, Li/Ca and Sr/Ca ratios were analysed in profiles and spot measurements in and across several chambers and specimens. The profiles at a resolution 2.0 µm clearly display the chemical variability within the multi-layered foraminiferal test. Additionally, we document Me/Ca variability during the development of the organism and, using specimens from different seasons with optimal and suboptimal growth rates, assessed the influences of foraminiferal growth rates on element incorporation.

Foraminiferal test displays strong heterogeneity in Mg/Ca, B/Ca, Ba/Ca, and Li/Ca but not in Sr/Ca ratios. B/Ca within one specimen range from 20 to 120 mmol/mol, Ba/Ca from 1.2 to 4.5 mmol/mol, Mg/Ca ratios from 0.6 to 1.2 mmol/mol. The proloculus, the first chamber, displays significantly higher Mg/Ca and B/Ca ratios but not Sr/Ca and Ba/Ca which can not be explained by environmental conditions alone.
Influence of impactors on the chemical composition of the Earth

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The relative abundances of highly siderophile elements (HSE: Os, Ir, Ru, Pt, Rh, Pd) in the Earth’s primitive upper mantle (PUM) and the continental upper crust (UCC) is a key issue for understanding their origin and the influence of impactors on the chemical composition. The past twelve years we have measured the HSE in many mantle suites of the Earth by neutron activation. Estimates of Rh/Ir, Ru/Ir, Pd/Ir, and Pt/Os derived from most mantle suites indicate modestly suprachondritic compositions for average PUM. The enigmatical mantle Ru/Ir ratio of 2.01 ± 0.12 (Schmidt 2004) in comparison of 1.51 ± 0.04 of the known different chondrite groups has been observed by other groups as well (Pattou et al. 1996; Becker et al. 2006). From highly melt depleted peridotites (Schmidt et al. 1998) and metasomatized mantle xenoliths (Schmidt et al. 2003) we conclude that the effects of melt depletion, refertilization and metasomatism can be discounted. However, the Os, Ir, Ru, Pt, and Pd pattern on melt depletion, refertilization and metasomatism can be unparalleled in terrestrial magmatic systems. In fact, the HSE (UCC) is strongly fractionated. Highly fractionated Ru/Ir is formation (Snow and Schmidt 1998)?

The HSE and Ni pattern of the upper continental crust (UCC) is strongly fractionated. Highly fractionated Ru/Ir is unparalleled in terrestrial magmatic systems. In fact, the HSE and Ni systematics closely resembles IIIAB iron meteorites (many impact craters on Earth are produced by this type of projectile with a radius of 54 ± 4 km as an upper limit that a projectile with a radius of 54 ± 4 km as an upper limit would yield the abundances of HSE and Ni in the UCC.

References

First direct sampling of superhot supercritical vapor phase fluids at the Mid-Atlantic Ridge

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Within the German Special Priority Program 1144 "From mantle to ocean: energy-, material-, and life-cycles at spreading axes", unique hydrothermal fluids were sampled at two newly discovered hydrothermal vent fields located at the spreading axis of the Mid-Atlantic Ridge at 4°49’S. Turtle Pits and Sisters Peak, both located at 3000 m water depth, emanate vapor phase fluids with stable sampling temperatures of about 390°C–407°C. In addition, temperature measurements recorded short-term spikes of up to 464°C, by far the highest temperature ever measured in submarine hydrothermal fluids. The fluids, representing a supercritical vapor phase sampled near the critical point of seawater, are characterized by a Cl depletion of 50% compared to seawater. The estimated temperature and depth of the initial phase separation with ~430°C, and 360 bar agree with the depth of the reaction zone about 500 m below the seafloor (constrained by Si concentrations). The overall fluid geochemistry is similar to those observed in other phase-separating systems at mid-ocean ridges, with an extremely high mobility of Fe and enhanced H2 concentrations. Most chloride-normalized element concentrations are greater than seawater, indicating advanced water-rock interaction. Despite a similar chlorinity and major element composition, different fluid samples emanating from the same vent orifice show a very heterogeneous endmember composition with respect to metals such as Cu, Zn, Pb and rare earth elements, indicating the mixing of the superhot vapor phase with another liquid or solid phase. Small differences in the fluid geochemistry between Turtle Pits and Sisters Peak can be related to a somewhat deeper zone of phase separation beneath the Sisters Peak field.

Total and Cl-normalized major and trace element concentrations will be evaluated with respect to possible mixing processes of different types of fluids in the subsurface. The respective influences of vapor-brine fractionation, (low-Cl) water-rock equilibria, and a different elemental speciation in supercritical vapors on the fluid geochemistry of the Turtle Pits and Sisters Peak fluids will be discussed.
Fluids, melts, and supercriticality in the MSH system and element transport in subduction zones

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The dichotomy of aqueous fluids and hydrous melts which includes fluid saturated melting is known to be limited in pressure, as the critical temperature of the miscibility gap between the two liquid phases strongly decreases with pressure. The critical P-T curve of the immiscibility gap intersects with the fluid saturated solidus at a critical pressure between 1 (SiO$_2$-H$_2$O) and 12 GPa (MgO-SiO$_2$-H$_2$O), nevertheless, the critical pressures for natural rock systems are largely unknown and under discussion. This discussion stems from the imperfection of all available experimental methods, which will be critically reviewed.

Our new experimental results on the MSH peridotite model system suggest that the entire system goes supercritical around 12 GPa, where phase A and chondrodite are stable at the solidus in the Mg-rich portion of MSH. Supercriticality moves stepwise from the SiO$_2$-rich side to the MgO-rich side, and hitherto insufficiently defined equilibria involving enstatite are needed to define the MSH phase diagram completely. While supercriticality eliminates fluid saturated melting, it is irrelevant to fluid-absent melting, and thus to devolatilization of deeply subducted oceanic mantle. Even above 12 GPa, phase E has a realistic chance to undergo fluid absent melting in thermally relaxing subducted lithosphere.

Secondly, while the question of supercriticality of the fluid-melt pair is petrologically challenging, it is, also in the presence of a fluid, of moderate practical relevance to the real world. In subduction scenarios, we do expect to have one liquid (either fluid, or melt or supercritical liquid), compositionally buffered by and coexisting with the residual minerals. The main questions relate then to solubilities of key elements in and to the viscosity and wetting behavior of this liquid.

Is “ballen quartz” diagnostic for shock metamorphism?

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Ballen quartz has been observed in impactites from a number of terrestrial impact structures, predominantly in impact melt rocks, suevites, and target rock clasts affected by strong post-shock heating. In thin section, ballen are generally roundish to oval-shaped and typically range in size from several microns to ~200 µm. Ballen rims may vary in brightness and colour, and appear as curved open fractures, fractures filled by submicroscopic phases, or very faint lines. Accordingly, ballen quartz, with its typical crackled “fish-scale” pattern, has turned out to be a distinctive textural feature suggestive for shock metamorphism [1-5].

In addition to the reports available in literature, we detected ballen quartz in impact melt rocks from Manicouagan, Rochechouart, Kara, Terny, and strongly heated crystalline basement clasts from the Ries crater and Ilyinets. As ballen quartz is known from very small but also the largest terrestrial impact structures (e.g., Tenoumer or Chicxulub), one must assume that ballen quartz should have been primarily present at all terrestrial impact sites.

Three types of ballen quartz (homogenous ballen, optically individual ballen, and microcrystalline ballen) are distinguished by their optical properties corresponding to different shock stages [2]. Various models of ballen quartz formation have been proposed to date, such as by prograde silica transformations in the solid state [3;4] or by the melting of silica, lechatelierite formation, and retrograde recrystallisation [1;5]. However, it is widely accepted that quartz ballen represent pseudomorphs after cristobalite [3-5]. The formation mechanism of ballen quartz, nevertheless, still appears to be somewhat enigmatic.

Domains of typical “granular cristobalite” in siliceous volcanic rocks [6], fulgurites [7], and heated industrial quartz ceramics [8] - i.e., non-impact materials of emphasised thermal history - display essentially the same textural pattern, which further suggests that ballen quartz originates from granular cristobalite and that ballen texture develops during cristobalitization of silica (and the high-low inversion of cristobalite [5]) at high temperatures. Therefore, ballen quartz might not be restricted to impactites, and we put into question that the sole presence of ballen quartz can be considered as reliable evidence for shock metamorphism.

References
Natural mass-dependent Cd isotopic variations determined by TIMS
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We present a high-precision double spike (DS) technique for Cd isotopes in which the Cd is measured by thermal ionisation mass spectrometry (TIMS). Since we observe anomalous odd-even isotope mass bias during measurement, we utilize even isotopes of Cd only. The "natural" fractionation is expressed as deviations in \(^{112}\text{Cd}/^{110}\text{Cd}\) (in parts per 10\(^{-6}\)) from our JMC Cd shelf standard. The commonly-used "JMC Münster Cd" standard lies at -1.11 \(^{112}/^{110}\text{Cd}\) on this scale. The external reproducibility (2SD) for double-spiked JMC Cd shelf (100 ng) is ±0.14 \(^{112}/^{110}\text{Cd}\) (i.e. ±7 ppm/amu) which is a factor of 4 to 10 times better than that reported in previous MC-ICP-MS studies (e.g. Wombacher et al., 2003; Lacan et al., 2006; Ripperger and Rehkämper, 2007).

We have analyzed \(^{112}/^{110}\text{Cd}\) in over sixty samples from different terrestrial reservoirs and environments (MORB, OIB, loess, Fe-Mn nodules, continental and hydrothermal sulphides). Our study confirms the limited variations found by Wombacher et al. (2003) in terrestrial materials—the total range is ~5 \(^{112}/^{110}\text{Cd}\), but most samples lie between -1.0 and +1.0. Three mid-T hydrothermal sulphides differ by ~4 \(^{112}/^{110}\text{Cd}\), suggesting significant Cd isotopic fractionation occurs in this setting, though other sulphides are much more tightly clustered. Analyses of 31 hydrogenous Fe-Mn deposits (and phosphorites) worldwide range from -0.6 to +2.0, and display isotopically heavier Cd (by 1 to 2 \(^{112}/^{110}\text{Cd}\)) in the top 2000 m than in the deeper ocean. These differences might reflect shallow inorganic scavenging of Cd by Fe-Mn oxides and its remineralization at depth. However, allowing for interlab bias, three shallow seawater samples of Ripperger and Rehkämper (2007) have \(^{112}/^{110}\text{Cd}\) of +0.5 to +2.2. These data are quite consistent with our shallow Fe-Mn nodule data, implying that only minor Cd isotope fractionation occurs on Fe-Mn oxide precipitation from seawater. The principal cause of the heavy Cd in the surface ocean then appears to be partitioning of light Cd into phytoplankton, entirely consistent with the sense and magnitude of the fractionation factor (7 ± 3 \(^{112}/^{110}\text{Cd}\)) determined by Lacan et al. (2006). Overall, these considerations suggest that \(^{112}/^{110}\text{Cd}\) is potentially useful as a paleoproductivity proxy, in much the same way as Cd/Ca.

References

Zircon U-Th ages from Laacher See indicate coeval crystallization of coerupted carbonatite and silicate magmas
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In order to constrain the origins of spatially associated carbonatite and silicate magmas and to quantify the time scales during which they interacted in a shallow magma system, we are employing U-Th dating of individual zircon crystals by secondary ionization mass spectrometry (SIMS). Laacher See (Germany) erupted a suite of crystal-rich xenolithic clasts that range from carbonate-free intermediate (dominantly syenitic) compositions to carbonatites (sövites). Because of the youthful age of the Laacher See eruption (~12,900 a BP), SIMS U-series geochronology can be applied which provides unrivalled temporal resolution in the order of ~10\(^3\) – 10\(^4\) years for individual grains or grain domains that are analyzed in situ (thin-section) at ~30 μm lateral resolution and crater depths <5 μm. Our initial results from three syenitic sövite clasts yield overlapping U-Th zircon isochron ages that average 15.8±2.7 ka (1σ; MSWD = 0.45; 30 spot analyses). This age overlaps within uncertainty with the U-Th isochron age for zircons from early erupted Laacher See differentiated phonolite and late-crystallized zircons in vesicles of carbonate-free syenite ejecta clasts (17.1±1.3 ka; Schmitt, 2006).

These results indicate coeval crystallization of carbonatite and differentiated silicate magmas that were stored at the top of a shallow magma body. Thus far, the zircon record lacks unequivocal evidence for protracted (several 10\(^3\) to 100’s of ka) pre-eruptive crystallization within a long-lived shallow Laacher See magma chamber and rather suggests crystallization and differentiation at most within few ka prior to eruption. The geochronological results are also in line with trace element evidence that indicate a close chemical affinity between carbonatites and Laacher See phonolites (Liebsch, 1996). Coeval zircon crystals in both, Laacher See carbonatites and phonolites/syenites have indistinguishable initial (\(^{230}\text{Th})/(^{232}\text{Th})\) ratios (0.885±0.013 and 0.894±0.010, respectively). This further supports the hypothesis of consanguineous carbonatite and silicate melts in the Laacher See magma chamber that originated by liquid immiscibility.

References
High resolution S-XRF study of stardust impact tracks

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Introduction
Stardust was the first sample return mission which captured extraterrestrial solid particles on a flight-by through the coma of a comet (Wild 2) which enables the investigation of cometary dust in its direct contextual setting [1] with the best available analytical system available in any laboratory on Earth. The nature of cometary material is of great importance for the understanding of the history of the early solar nebula and the protoplanetary disk.

Data processing
Several keystones, each including an impact track with a terminal particle (TP) at its end, were studied [2]. Track No. C2044, 37 was investigated with high resolution synchrotron XRF and XRD (S-XRF/XRD) techniques at beamline ID13 at the ESRF (Grenoble, France) with 13 keV to determine the elemental abundances from Ca to Se. The focus spot size was 200 nm enabling an investigation with very high spatial resolution of grains having sub micron size.

Results
The evaluation of the diffraction pattern obtained from the TP yield a mixture of olivine and pentlandite and/or pyrrhotite [3].

S-XRF data reveal several chemical hot spots along the track with most of these fragments having sizes of only several 100 nm. Some have Fe concentrations of more than 20 wt. % indicating Fe–Sulphide as possible phases along the track. These fragments are also high in Mn and Cr in comparison to the other hotspots. Fe-Ni sulphide or - metal is also assumed for a fragment containing up to 2.5 wt. % Ni.

For the TP, S-XRF reveals a complex chemical structure showing band like Fe- and Cr-features inside the particle. Fe- and C1 normalized abundances for the TP show relative enrichments for Mn and Cr and CI abundance for Ca, Ti, Cu and Zn.

References
Multiple hydrothermal fluid flow in the NW Rhenohercynian

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The NW Rhenohercynian belt of the Central European Variscan orogen, studied in the northern Eifel area, was affected by several pre-, syn- and postorogenic hydrothermal events.

Investigation of core material from the RWTH-1 drill hole in Aachen revealed mineralogical, geochemical and structural evidence of intense Variscan hydrothermal activity. Recently published temperatures of up to 370 °C (Lögering et al. 2006) but low illite ‘crystallinites’ can only be explained by a short duration (< 10000 a) of this hydrothermal event, which was initiated by dewatering of sedimentary rocks during Variscan compressional tectonics. This synorogenic fluid flow did not result in significant large-scale element transfer, except for nitrogen which was incorporated into clay minerals as ammonium.

Important postorogenic, sandstone-hosted Pb-Zn deposits in the northern Eifel have been dated at 170 ± 4 Ma (Schneider et al. 1999). This Jurassic event caused large-scale element mobilisation in the Palaeozoic sedimentary rocks, as indicated by the homogeneous Pb isotope signatures of the sphalerites. However, new geochronological data give evidence for at least one Cretaceous hydrothermal event in the NW Rhenohercynian. Direct Rb-Sr-dating of non-economic vein sphalerites from the Sandgewand fault (Hastenrath near Stolberg) yields an age of 134 ± 2 Ma, while the Pb isotope signatures of these ores are identical to the Jurassic ones.

Thermal spring waters in Aachen represent the youngest stage of hydrothermal events in the NW Rhenohercynian. They are characterized by high concentrations of particle-associated Zn. Isotope ratios of Pb and Sr determined directly on water and sinter samples indicate several metal sources, such as postorogenic base metal ores but also evolved Devonian-Carboniferous sediments and a yet unidentified source characterized by unradiogenic Pb isotope signatures.

References


The Cr isotope label of the solid Earth and hydrothermal pathways

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The Cr isotope compositions of Earth’s major silicate rock reservoirs and Cr-bearing minerals of metamorphic and high-temperature hydrothermal origin were obtained by high-precision double-spike MC-ICP-MS Cr measurements.

The principle igneous reservoirs of the Earth share a common stable Cr isotope composition. Within the 95% confidence interval, Student’s t-tests do not allow to distinguish the Cr isotope compositions of several mantle lherzolites (δ53/52CrSRM979 = –0.104±0.110‰; 2 SD), ten ultramafic cumulate rocks (–0.119±0.113‰) and six continental and oceanic basalts that represent partial mantle melts (–0.151±0.050‰). Thus, unlike suggested for Fe isotopes [1], partial mantle melting does not appear to fractionate Cr isotopes. The average δ53/52CrSRM979 value of –0.082±0.058‰ for 12 different chromite seams from the Bushveld and Great Dyke layered igneous intrusions is identical to that of the silicate igneous Earth reservoirs. This again supports the notion that Cr isotopes do not fractionate during partial mantle melting, since chromites crystallize from Cr-rich partial mantle melts that enter an overlying magma chamber containing an evolved Cr-depleted liquid. The Cr isotopic compositions of Cr(III)-bearing uvarovite and fuchsite minerals from amphibolite-facies metamorphic terrains are also equal to those of igneous rock reservoirs. Since partial mantle melting and metamorphism do not involve redox-changes for Cr and differences in the Cr-ligands of solids and melts, high-temperature isotope fractionation appears to be too small to be detectable.

However, crocoite (PbCr(VI)O4), a mineral that forms in oxidizing zones of high-temperature hydrothermal systems, shows δ53/52CrSRM979 values from +0.640 to +1.037‰. Precipitation experiments of crocoite from Cr(VI) solutions reveal (equilibrium) isotope fractionation with Δ53/52Crcrocoite-Cr(VI)aq ≈ 0.1 to 0.2‰. This is too small to explain the heavy Cr isotope compositions of crocoite. One possible explanation is that oxidation of dissolved hydrothermal Cr(III) to Cr(VI) is accompanied by isotope fractionation. Alternatively, Cr behaves like its chemical twin Se that only fractionates during reduction [2]. Partial Cr(VI) reduction [3] may explain the heavy compositions of the crocoites, which in turn allowed quantification of redox-changes along the hydrothermal pathway.

References

Experimental study on crustal wehrlites of the Oman ophiolite

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In the Wadi Haymiliyah of the Oman ophiolite (Halyn block), discordant wehrlite bodies ranging in size from decameters to hundreds of meters intrude the layered gabbro series at different crustal levels. Common feature of all wehrlite bodies is the dominance of olivine and clinopyroxene with high Mg# (MgO/(MgO+FeO)*100, molar) varying between 85 and 95. SIMS analyses of clinopyroxenes from different wehrlite bodies reveal REE and trace element patterns suggesting that the clinopyroxenes were crystallized from tholeiitic, MORB-type melts which were highly depleted in incompatible trace elements. Some wehrlites from the upper section bear mm-sized poikilitic pargasite as magmatic phase, implying that the associated melts showed a high water activity, at least in a late stage. In order to evaluate the genesis of the Oman crustal wehrlites, we combined experimental work with investigations on natural rocks.

The experimental study under controlled $f_{O_2}$ and $aH_2O$ at pressure of 200 MPa is aimed to constrain the physical conditions of wehrlitic magmas within the lower oceanic crust. Especially, we want to clarify whether the crustal wehrlites from the Oman ophiolite are derived from wet primitive tholeiitic magmas, as suggested by a model of Feig et al. (2006). Starting material are mixtures of natural olivines and clinopyroxene separated from wehrlites from the lower Wadi Haymiliyah section, and a synthesized glass representing the "lost" equilibrium melt. Experiments were performed in AuPd capsules (pre-saturated with iron) at temperatures between 1020 and 1160°C with $f_{O_2}$ varying between QFM and QFM+2 (QFM=quartz fayalite magnetite buffer). First experiments at nominal dry conditions above 1140°C ($f_{O_2}$ ~ QFM) reveal the stability of plagioclase (newly formed crystals), while the doped clinopyroxene became unstable (decomposition by reaction with the melt). Thus, we were not able to reproduce the characteristic wehrlite paragenesis (olivine plus clinopyroxene without plagioclase) under dry conditions, implying that wehrlitic crystal mushes cannot be generated in dry, primitive tholeiitic systems at crustal pressure by simple accumulation of fractionating crystals. The corresponding experiments at wet conditions are in progress.

References

Recent developments in U-Pb thermochronology

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Investigations can now be designed to exploit and explore volume diffusion in accessory minerals with the goal of generating accurate temperature-time paths for rocks. Despite the abundance of high-U minerals with high to moderate nominal closure temperatures for the diffusion of Pb (e.g. titanite, apatite, and rutile; $T_c$ ~ 400-650 °C), U-Pb thermochronology has received little attention compared to lower temperature systems such as $^{40}$Ar/$^{39}$Ar and U/Th-Hc. However, understanding thermal histories of rocks in the 400-650 °C temperature range is crucial for deconvolving the thermal histories of middle and lower crustal rocks.

We have investigated the potential and limitations of U-Pb thermochronology through single- to sub-grain ID-TIMS analysis of apatite and titanite in conjunction with BSE and CL imaging and numerical modeling. The precision of U-Pb thermochronology is usually limited by relatively low ratios of radiogenic lead to initial (a.k.a. common) lead. In systems that have undergone complex rock-fluid interactions, the common Pb composition due to fluid interaction may be inaccurate. This is especially important in slowly-cooled rocks where the common Pb composition due to fluid interaction may change in time and/or space.

In minerals where volume diffusion controls the distribution of daughter product in a mineral, one expects intra-grain diffusion gradients such that the smallest grains and the rims of large grains record the youngest dates. We have explored relationships between grain size and date (here called a-t curves) in apatite and titanite in combination with CL imaging and numerical modeling. The precision of U-Pb thermochronology through single- to sub-grain ID-TIMS thermochronology has received little attention compared to lower temperature systems such as $^{40}$Ar/$^{39}$Ar and U/Th-Hc. Given some geologic constraints, utilizing a-t curves in two minerals from the same rock will allow, in some cases, the generation of unique and non-linear temperature-time paths regardless of the effects of post-cooling reheating from magmatic intrusions.

Numerical modeling can also be used to evaluate the effect of differences in U zonation, cooling rate, and grain shape on closure temperature and a-t curves. In many cases these minerals do not form a-t curves. This is likely because U-Pb thermochronometers are often involved in metamorphic reactions at a range of temperatures, and therefore characterizing the internal zonation, trace element patterns, and petrographic setting of these minerals may be crucial for generating accurate thermal histories of rocks. This work in conjunction with studies exploiting the U/Th-Hc method will become more useful in characterizing the behavior of U and its daughter products in high-U thermochronometers and determining thermal histories of rocks from lower-crustal to near surface conditions.
REE systematics of fluorites in (per-)alkaline systems

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The mid-Proterozoic Gardar Province (South Greenland) is a failed rift province hosting 12 major (per-)alkaline intrusions [1]. High fluorine contents occur in a great variety of magmatic rocks all over the Gardar Province. Rare earth element (REE) patterns of fluorite and associated minerals like cryolite (Na₃AlF₆), calcite and siderite provide information about the magma source, crystallisation history, fluid-melt interaction and late-magmatic processes.

We focused on fluorites from three intrusions representing the whole compositional range of the Gardar Province: the Ilímaussaq intrusion which is mainly composed of silica-undersaturated agpaitic nepheline syenites; the Motzfeldt intrusion with its mostly miaskitic nepheline syenites; and the Ivigtut intrusion famous for its now mined-out cryolite deposit hosted by an A-type granite [1].

All chondrite-normalized REE patterns of fluorite show a negative Eu anomaly which is attributed to feldspar fractionation. The REE patterns of the Motzfeldt and Ilímaussaq intrusions in the eastern part of the Gardar province show a positive Y anomaly if Y is plotted between Dy and Ho according to [2]. In contrast, the patterns of the Ivigtut intrusion famous for its now mined-out cryolite deposit hosted by an A-type granite [1].

All chondrite-normalized REE patterns of fluorite show a negative Eu anomaly which is attributed to feldspar fractionation. The primary magmatic fluorite of the Motzfeldt and Ilímaussaq intrusions show almost identical patterns with an enrichment in light REE suggesting an early crystallisation [3]. Later crystallised fluorites of veins are less concentrated in REE and exhibit flatter patterns or enrichment of the middle/heavy REE typical of the late-magmatic to hydrothermal crystallisation stage. The REE patterns of minerals from Ivigtut are slightly enriched in heavy REE and indicate a strong interaction with a fluid phase as evidenced by the very pronounced tetrad effect.

Our preliminary results show that REE in fluorite reflect the source but can also act as tracers for the transition from early magmatic to hydrothermal conditions during the crystallisation of (per-)alkaline intrusions. The tetrad effect reflects strong water-rock interaction and the fluid’s influence on the fluorite genesis.

References

Structural Chemistry of Cation-doped Bacteriogenic UO₂

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The chemical stability of bacteriogenic uraninite, “UO₂”, is one of the seminal issues governing its success as an in situ immobilization strategy in remediated subsurface locations. Little detail is known about the structure and reactivity of this material, but based on comparison to its closest abiotic analog, UO₂-x (0 < x < 0.25), we expect that it is complex and disordered, likely to exhibit non-stoichiometry, and capable of structurally incorporating common ground water cations and U(VI). These subtle changes in mineralogy are expected to substantially impact its stability in ground water.

In this study, the product of microbial U(VI) reduction under varying conditions of pH, carbonate and divalent cation concentration (Mg²⁺, Mn²⁺, and Ca²⁺) was investigated. To facilitate x-ray scattering measurements, a gentle aqueous cleaning method was developed to separate the bioxide and organic components without altering the biooxides. The material exhibits a range of particle sizes with a mean around 4 nm. The first oxygen shell is distorted, consistent with a nonstoichiometric composition. Mn²⁺ and Mg²⁺ were found to attenuate the particle size of bacteriogenic UO₂-x and to be structurally incorporated. These findings suggest that ground water composition can have a pronounced impact on the structure and properties of bacteriogenic uraninite.
Do particulate $^{231}$Pa/$^{230}$Th ratios depend on water depth?

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The natural radionuclides $^{230}$Th ($T_{1/2} = 75.6$ ky) and $^{231}$Pa ($T_{1/2} = 32.1$ ky) are widely used as tracers for paleoceanographic process studies. Both isotopes are produced in seawater by radioactive decay of uranium isotopes ($^{234}$U, $^{235}$U) and due to their particle reactivity they adsorb on sinking particles and are removed to the sediments. Since $^{231}$Pa is less particle reactive than $^{230}$Th i.e. $^{231}$Pa has a longer residence time ($\tau$) in the water column compared to $^{230}$Th ($\tau = 230$Th: 20-40y; $\tau = 231$Pa: 80-200y), $^{231}$Pa is preferentially removed in areas of higher particle flux like e.g. ocean margins (boundary scavenging); and the variable $^{231}$Pa/$^{230}$Th ratios stored in the sediment record are believed to reflect changes in the paleofluxes (or paleoproductivity) during the geological past. Further processes which may influence $^{231}$Pa/$^{230}$Th ratios are the composition of sinking particles, i.e. the higher affinity of $^{231}$Pa to adsorb on biogene opal compared to $^{230}$Th, and the dissolved $^{231}$Pa/$^{230}$Th in water masses.

In a study of $^{231}$Pa/$^{230}$Th ratios in surface sediments from the southeast Atlantic off Namibia we find $^{231}$Pa/$^{230}$Th ratios higher than the production ratio ($P$) of both isotopes ($P_{Pa/Th} = 0.093$) at the ocean margin and lower ones in the open ocean, a distribution typical of boundary scavenging. For this data set we observe a strong negative correlation ($r^2 = 0.82$) between $^{231}$Pa/$^{230}$Th in surface sediments and water depths. Also for previously published data from the Pacific and Arabian Sea we find negative correlations between $^{231}$Pa/$^{230}$Th ratios in surface sediments and water depths, however, these correlations are less strong. We will discuss to what extent changes in the fractionation between $^{231}$Pa and $^{230}$Th with depth, high opal content, and/or boundary scavenging may cause $^{231}$Pa/$^{230}$Th ratios to depend on water depth off Namibia.

Trace element behavior in sulfidic porewaters of the Oder estuary, SW Baltic Sea

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The diagenesis of trace elements in anoxic sediments of the Achterwasser lagoon, which is part of the Oder estuary in the Baltic Sea, is examined and evaluated in the context of pyrite formation.

Certain trace elements show the same distribution pattern within the pore water regime suggesting a similar diagenetic behavior. The release of Zn, Cu and Cd into the pore water occurs prior to the reduction of Fe and Mn, indicating that they are released from organic matter in the thin oxic surface layer of the sediments. While a considerable part of these elements is recycled into the water column another part diffuses downcore and is removed as soon as H$_2$S appears in pore water. Since degrees of trace element pyritization (DTMP) for Zn and Cd range well below 1%, it is inferred that they become trapped as monosulfide. Copper appears as both monosulfide and impurity in pyrite (DTMP: 12%).

The accumulation of V, Cr, Co and As in the pore water starts concomitantly to that of Mn and Fe suggesting that these elements are liberated through reductive dissolution of Mn- and Fe-oxyhydroxides. Increasing concentrations of dissolved V, Cr, Co and As with depth demonstrate that the fixation of these elements is not quantitatively controlled by the process of pyrite formation. While pyritization of Co and As is intense with median DTMP values of 35% and 17%, respectively, Cr (DTMP: 4%) is less and V (DTMP: <1%) almost not incorporated into pyrite.

The conconstant increase of DOP and DTMP with depth suggests that, in analogy to Fe pyritization, addition of trace metal sulfide complexes on preexisting pyrite grains may be responsible for increasing DTMP values for Co, Cu and Zn. Arsenic does not form sulfide complexes but rather As(III) oxyanions under reducing conditions, suggesting that again adsorption of complexes is responsible for increasing pyritization with depth.
Different sources of hydrocarbon pollution in surface sediments of the Campeche Sound, Gulf of Mexico, revealed by biomarker analysis

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The Campeche Sound in the Gulf of Mexico is the largest oil field in Mexico. Oil production, refinery activities, heavy ship traffic as well as natural petroleum seeps are potential sources of pollution of water and sediment in the area (García-Cuéllar et al., 2004). Embedded in a grid system of a long term environmental monitoring program (e.g., Vázquez and Virender, 2004) surface sediments from the shelf area of the Campeche Sound and also from the adjacent abyssal plain further west were studied. The nonaromatic hydrocarbon biomarkers in these surface sediments, several crude oils and drill cuttings samples were investigated by GC-MS.

The overlapping fossil hydrocarbon envelopes indicate multiple sources like discharged drilling fluids, the heavy ship traffic or land run-off. Samples taken close to known asphalt seeps exhibit biomarker patterns virtually identical to those of the reference crude oils, and thus have apparently escaped from petroleum reservoirs with fractured cap rocks. These sediments and the asphalts both lack of angiosperm biomarker oleanane (cf. Moldowan et al., 1994) as expected for crude oils from a Jurassic source rock. Other surface sediments, superimposed on the fossil hydrocarbons, contain biomarkers neither typical of mature fossil fuels nor of typical immature organic matter in marine surface sediments. Their origin from drill cuttings recovered from Tertiary to Cretaceous deposits and disposed of into the sea would be a reasonable explanation. The regional distribution of indicative biomarkers will be shown and discussed.

References

The timescale of the Earth’s accretion and volatile loss: New constraints from Pd-Ag systematics

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The extinct radionuclide $^{107}$Pd decays to $^{107}$Ag with a half-life of 6.5 Myr and is a useful chronometer to study early solar system processes [1]. It provides constraints for the accretion and subsequent chemical differentiation of planetary bodies in a similar way as the $^{182}$Hf-$^{182}$W system. In contrast to the refractory elements Hf and W, there is a distinct difference in volatility between the more refractory element Pd and moderately volatile Ag. Thus the Pd-Ag system can be used to study accretion and core formation but also volatile depletion.

In particular, the Pd-Ag decay system has been successfully applied to study the formation and differentiation of iron meteorites [1]. Internal isochrons determined for these meteorites generally yield initial $^{107}$Pd/$^{108}$Pd ratios in the range of $1.5 - 2.5 \times 10^{-5}$ [1]. Combined with recent results for carbonaceous chondrites, this suggests that the initial $^{107}$Pd/$^{108}$Pd ratio of the solar system may be in the range of $6 \times 10^{-5}$ [2].

Here we report new high precision Ag isotope data for a variety of terrestrial basalts from different geological settings. The data indicate an $\varepsilon^{107}$Ag of 2.1 ± 0.6 for the Ag isotopic composition of bulk silicate Earth relative to the NIST SRM 978a Ag standard. In contrast, the CV3 chondrite Allende has a well-constrained $\varepsilon^{107}$Ag of -0.4 ± 0.5. Assuming that the Earth accreted from material with similar volatile depletion as the CV3 chondrites and that Ag isotopes are not significantly affected by stable isotope fractionation, it is possible to model the Earth accretion and core formation. A simple two-stage model suggests that the last complete metal-silicate equilibration took place no longer than 15 Myr after the start of the solar system. This is at odds with the results of the well-investigated Hf-W system, where the same model yields a time of ~30 Myr. Different scenarios can be considered to reconcile the apparent discrepancy: (1) the Earth accreted from material having greater volatile depletion than CV3 chondrites (Pd/Ag > 20). Some ordinary chondrites feature such high Pd/Ag ratios. (2) Metal-silicate equilibration was incomplete and affected the Pd-Ag and Hf-W system differently. (3) Significant volatile depletion took place prior to the giant impact, for example during the accretion of the Earth.

References
Geomorphology and chemical weathering on basaltic islands
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We are investigating the relationship between geomorphology and chemical weathering on actively eroding basaltic oceanic islands in the tropics, using the Hawaiian islands as a natural experiment. Our field sites include the islands of Kaua‘i and Hawai‘i, which represent the extremes in ages and soil development on the islands. Hawai‘i is largely dominated by constructive volcanic shield topography. On Kaua‘i early shield topography has been heavily dissected by fluvial erosion, creating a landscape of high relief characterized by serrated ridges and deep fluvial valleys. Less than ~10% of Hawaii’s surface has undergone fluvial erosion while only ~20% of Kaua‘i’s original shield topography remains. This system, where relief increases substantially with age as the volcanic edifice is eroded by fluvial erosion, is very different from the conventional school of thought which postulates that after relief is created by an initial disturbance subsequent erosion will smooth the relief and lower it. We wish to investigate how the competing effects of increasing age and weathering are offset by increasing incision and development of relief.

Initial observations indicate a link between Si concentration in river water and hillslope, where watersheds with steeper slopes exhibit higher concentrations of Si than do streams draining more gently sloping topography under similar flow conditions. In the Waimea Canyon on Kaua‘i we have observed a nearly 4-fold increase in Si concentrations in the trunk of the river as it plunges over the edge of the Koke‘e Plateau (the only remnant of Kaua‘i’s original volcanic shield, ~1000 m a.s.l.) into the canyon (~300 m a.s.l.) and mixes with tributaries originating from the western wall of the canyon. The low Si concentrations in river water coming off the plateau reflect interaction with highly weathered and Si-depleted soils. The Si concentrations in the canyon tributaries tend to be 5-6 times higher than in the river water before it flows off the plateau, indicating that the tributaries tap sources of groundwater that has interacted with fresh rock at depth in the volcanic pile. Streams draining young bedrock on Hawai‘i, where the river profile still follows to a large degree the original shield topography, have nearly as low Si concentrations as rivers draining old, stable shield surfaces, indicating that rivers in an early stage of incision do not tap groundwater sources. Groundwater that discharges directly to the ocean is an important geochemical pathway on Hawai‘i and our data indicate its Si-concentrations are similar to the highest Si concentrations observed in the Waimea Canyon tributaries.

Development and application of novel organic proxies
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Sediments contain a myriad of organic compounds which potentially contain information on past microbial communities and the environments in which they lived. Research over the last few decades has improved our knowledge on the structure and origin of these compounds and their use as qualitative and quantitative proxies for past climatic conditions is rapidly increasing. Recently we developed several novel proxies based on the distribution and isotopic composition of terrestrial and aquatic biomarkers. Analysis of different soils from all over the globe showed a significant correlation between the distribution of branched tetraether lipids, derived from bacteria, and mean annual air temperature. We used this correlation to reconstruct continental temperature changes in several climatically important periods such as glacial-interglacial changes in the Quaternary and Cenozoic periods of global warming and cooling. Further validation of this proxy is currently underway by e.g. analysing soils surrounding hot springs. These soils are geothermally heated thereby providing a natural temperature gradient in soils of similar composition.

Another proxy which we are currently developing is the relative deuterium content of algal biomarkers as a proxy for sea water salinity. First results show a significant correlation between the δD of long chain alkenones with salinity and δD of growth water. This has been used to reconstruct past salinity changes in the Holocene Black Sea and the Aegean Sea during time of sapropel S5 deposition. Further culture studies are now underway to examine other factors influencing the δD of alkenones and to test other biomarkers as potential paleosalinity proxies.
Peering at the subsurface biosphere through a diamond window

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Investigations of the subsurface biosphere have pushed the depth limits of microbial ecosystems to greater than 800 meters below the seafloor in marine sediments and 3-4 km into the continental lithosphere. In subsurface environments, the mode-of-growth for microorganisms is attached to minerals in structures known as biofilms. In many rock-hosted, subsurface environments, organisms are confronted with multiple stressors including not only high pressures, but elevated temperatures and low energy fluxes. Subsurface microorganisms live at a precarious boundary between geologically-supported growth and cell death and remineralization. A significant limitation in the study of deep ecosystems has been an inability to distinguish and quantify microbial activities under conditions found in their native habitats. I will describe a research plan aimed at improving our ability to observe and characterize biogeochemical processes under conditions relevant to the deep subsurface environment. This plan relies upon the establishment of a one-of-a-kind research facility optimized for conducting high pressure experimental microbiology, borrowing from tools developed for materials science and hydrothermal geochemistry applications. Preliminary results show that the physiological status of microorganisms indigenous to the deep subsurface can be distinguished in vivo using molecular probes and geochemical measurements. A future goal is to make the system modular, allowing for its use in both laboratory and field-based studies. An analytical suite necessary to characterize biogeochemical transformations at microbe-mineral interfaces can be employed to follow the products of high pressure experiments, but will also be amenable to a range of studies in near-surface endolithic environments. The data obtained from these experiments will be important aid in deciphering both the extent and the biogeochemical consequences of a deep subsurface biosphere.

Using $^{222}$Rn for assessing nutrient transfer into the sea via SGD

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Submarine Groundwater Discharge (SGD) has to be considered an important pathway of contaminant/nutrient transfer from aquifers into the coastal sea. One of the main reasons for temporal changes in the SGD rate is the altering hydrological gradient between groundwater and sea determined by the tidal cycle.

While SGD is known to sum up to about 6% of the global river discharge into the oceans, the actual SGD rate in a particular coastal area is usually hard to be quantified due to the generally complex spatial SGD distribution. However, naturally occurring stable and radioactive isotopes have shown to be useful environmental tracers in SGD studies (e.g. Burnett and Dulaiova, 2003).

At Cabbé, Bay of Roquebrune (Mediterranean Sea, France), the temporal SGD pattern was investigated over a 24 h period using naturally occurring $^{222}$Rn as an environmental tracer. At a location at the shore, known to represent a SGD spring, $^{222}$Rn measurements of the sea water were carried out as time series using a portable radon monitor (Dulaiova et al., 2005). Tidal range, water temperature, and salinity were monitored using a CTD. Discreet samples for nitrate analyses were taken for assessing the nutrient transfer into the sea via SGD. In addition, off-shore surface water samples were taken along two near-shore transects.

Temporal variations in $^{222}$Rn show a clear dependence on the tidal cycle. The results are backed up by the temperature and salinity data. High tide periods are characterized by lower $^{222}$Rn concentrations, higher water temperatures, and higher salinities consistent with a decreased SGD rate.

Variations of nitrate concentrations basically follow those of $^{222}$Rn, suggesting a strong dependence of the nutrient input into the sea on the SGD rate. In conjunction with the transect data and based on the nitrate and radon endmembers representative for groundwater (29.7 µM and 28.3 kBq/m³, respectively) and off-shore water (both below detection limit) a nitrate flux was estimated. The results suggest that SGD may be an important nitrate source for the coastal area investigated.

References
Biogeochemical investigation of asphalt seepage at the Chapapote Knoll in the southern Gulf of Mexico

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Seepage of asphalt-laden heavy oils in 3000 meter water depth is fueling a unique cold seep habitat at the Campeche Knolls in the Southern Gulf of Mexico (MacDonald et al., 2004). We studied the Chapapote Knoll, one of the various salt domes in this area, which is covered with asphalt beds that extend over more than 1km².

During the expedition of RV Meteor M72/2 in 2006, we recovered a diverse set of asphalt samples and benthic organisms inhabiting this extreme environment to further explore mechanistic details of asphalt leakage and accumulation and its role for fueling benthic ecosystems.

The asphalt samples are highly diverse in terms of their content of gaseous hydrocarbons. Maximum concentrations of gaseous hydrocarbons were associated with methane hydrate. Samples with very low concentrations of methane and higher gaseous hydrocarbons were associated with methane hydrate. The relative distribution of individual hydrocarbons in the C1-C5 range is highly diverse in the asphalts. We interpret this diversity to be reflective of the postdepositional history, which could be due to outgassing, leaching or biodegradation.

Oily sediments recovered by gravity coring show evidence of a sulfate/methane transition zone at several meters subseafloor depth due to sulfate-dependent turnover of hydrocarbons. Stable carbon isotope analysis of methane in these cores indicate biological activity close to sulfate reduction. The resulting dactic magma evolves to rhyolitic composition through crystal fractionation. (ii) The basaltic magma itself differentiates by crystal fractionation forming a basaltic andesite magma. (iii) Andesites are produced by mixing of basaltic with dacitic melts. These processes were traced by iron isotopes: (i) During the differentiation from the dacites to the rhyolites the δ56/54Fe value increases successively. This increase (e.g., 0.15‰ for the 4000 B.P. eruption) can be described by a Rayleigh fractionation model using a constant bulk fractionation factor between the silicate liquid (L) and all mineral phases (M) of $\Delta^{56/54}Fe_{L} = -0.1‰$. (ii) No isotopic fractionation was found between the basalts and the basaltic andesites which have an average $\Delta^{56/54}Fe_{IRMM-014}$ value of 0.068 ± 0.057 (2SD), identical to mean basaltic values reported by other studies [2-5]. This observation is consistent with the limited change in iron concentration in the remaining silicate liquid during crystal fractionation and small mineral-melt Fe isotopic fractionation factors expected at high temperatures. (ii) The iron isotope composition of the andesites is matching the basaltic andesites and the less evolved dacites, compatible with a mixing process.

The observations suggest that the iron isotope composition of the crust can be slightly modified by magmatic processes and that magma differentiation processes are reflected in the iron isotope composition of some evolved silicic rocks.

References


Iron isotope fractionation during the volcanic evolution of Hekla, Iceland

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The aim of this study is to systematically investigate potential iron isotope fractionation in the Earth’s crust by magmatic processes. High precision iron isotope analysis by high resolution MC-ICP-MS were performed on a suite of rock samples representative for the volcanic evolution of the Hekla volcano (Iceland). The whole series of Hekla’s rocks results from several processes [1]. (i) Basaltic magmas rise and induce partial melting of meta-basalts in the lower part of the Icelandic crust. The resulting dacitic magma evolves to rhyolitic composition through crystal fractionation. (ii) The basaltic magma itself differentiates by crystal fractionation forming a basaltic andesite magma. (iii) Andesites are produced by mixing of basaltic with dacitic melts. These processes were traced by iron isotopes: (i) During the differentiation from the dacites to the rhyolites the δ56/54Fe value increases successively. This increase (e.g., 0.15‰ for the 4000 B.P. eruption) can be described by a Rayleigh fractionation model using a constant bulk fractionation factor between the silicate liquid (L) and all mineral phases (M) of $\Delta^{56/54}Fe_{L} = -0.1‰$. (ii) No isotopic fractionation was found between the basalts and the basaltic andesites which have an average $\Delta^{56/54}Fe_{IRMM-014}$ value of 0.068 ± 0.057 (2SD), identical to mean basaltic values reported by other studies [2-5]. This observation is consistent with the limited change in iron concentration in the remaining silicate liquid during crystal fractionation and small mineral-melt Fe isotopic fractionation factors expected at high temperatures. (iii) The iron isotope composition of the andesites is matching the basaltic andesites and the less evolved dacites, compatible with a mixing process.

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References

Neutron capture-induced $^{150}\text{Sm}$ anomalies in IAB Iron meteorites and Winonaites

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Isotope anomalies produced by neutron capture in nuclides with large neutron capture cross sections can be used to constrain the irradiation history of extra-terrestrial matter [e.g. 1]. This study investigates the exposure history of IAB irons and Winonaites, which are presumed to come from the same body [2], using the increase in $^{150}\text{Sm}$ as a result of neutron capture by $^{149}\text{Sm}$. For this purpose, Samarium was separated from 200-500 mg samples using standard dissolution and ion exchange techniques. The isotope ratios were measured on a Triton TIMS in static mode. Analytical uncertainties on the reported ratios are $<12$ ppm (2 sd; n=8) for the standard and $<35$ ppm for the samples (2 se).

Figure 1 shows the neutron capture-induced isotopic shifts in $^{150}\text{Sm}/^{152}\text{Sm}$ measured on three IAB silicates (1.1-1.8 $\varepsilon$-units) and two Winonaites (1.0-5.5 $\varepsilon$-units). The corresponding neutron fluences for the IABs (1.5-2.5 x 10$^{15}$ n/cm$^2$) and the Winonaites (1.4-7.4 x 10$^{15}$ n/cm$^2$) are similar to those of chondrites [1]. The similar fluences calculated for the IABs are difficult to reconcile with their different cosmic ray exposure ages [e.g. 3], unless one invokes a common regolith history on the parent body followed by high shielding depths within their meteoroids (so that they were only insignificantly affected by exposure to cosmic rays after ejection from the parent body).

Fig. 1: HaH = Hammadah al Hamra; CC = Caddo County; CD = Canyon Diablo; NWA = North West Africa; STD = terrestrial standard; Cosmic ray exposure age [Myr].

References
High-precision Pb isotope measurements discriminate different subduction components along the Solomon island arc

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Along the Solomon island arc, SW Pacific, the Indian plate is subducting beneath the Pacific plate. Geophysical evidence indicates the presence of a fossil slab of Pacific oceanic crust that was subducting until ca. 6 Ma [e.g., 1]. To assess the influence of subducted oceanic crust and Ontong Java Plateau material along the arc, we determined Pb isotope compositions of representative arc magmas covering the complete southern island arc chain (ca. 1000 km). Most of their Hf-Nd isotope compositions overlap with those of the Australian-Indian mantle domain, indicating that the active trench does not mark the boundary between the Australian-Indian and Pacific mantle domains [2]. In contrast to Hf-Nd, Pb isotope compositions of the lavas are dominated by subduction components. To achieve sufficient analytical resolution, Pb isotope compositions were obtained using MC-ICP-MS and normalization to Tl that was added prior to measurement.

High-precision Pb isotope data for silicate reference materials obtained by Tl normalization using MC-ICP-MS are in good agreement with previously published data, supporting the reliability of the analytical method. An external reproducibility of better than ±130 ppm (2σ) can be achieved. The measured 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb in the Solomon arc magmas range from 18.351 to 18.853, 15.479 to 15.564, and 38.105 to 38.462, respectively, indicating the absence of significant amounts of subducted pelagic sediments. The high-precision Pb data clearly reveal a bimodal distribution, reflecting the presence of two distinct types of subduction component, originating from either the currently subducting Australian plate or the fossil Pacific plate. Notably, domains with Australian-Indian type Pb isotope signatures are confined to the central New Georgia group, where the active Woodlark spreading center is being subducted. Due to a lower geothermal gradient, all other segments of the subarc mantle have apparently not yet been fluxed by subduction components from the Australian-Indian plate that has been subducting since ca. 6 Ma.

Lead isotope compositions of some samples show evidence that material from the Ontong Java Plateau was subducted together with the Pacific plate, consistent with geophysical evidence [e.g., 1].

References

Ultrastructure of bone: Hollow apatite crystals, solution chemistry and organic inhibitors

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The ultrastructural nature of bone is a matter of long debate. While all studies confirm that an apatitic mineral component makes up at least 60 wt % of bone, the morphology and even the composition of this phase is uncertain, due to the small size of the crystals (10’s of nm in maximum dimension).

TEM analysis of ion-milled and focused ion-beam milled sections of bone reveals that most of the apatite in bone is in the form of apparently hollow fibers 5 to 10 nm in diameter and several hundred nm long, which are oriented parallel to collagen fibers. Lesser amounts of apatite occur in the gap zones spaced at 67 nm along collagen fibrils. The core of the apatite fibers is assumed to be filled with a protein, probably collagen, making up ca. 5% of the total collagen in bone. The fibers are constructed of single crystals of apatite, with their c-axes oriented parallel to the fibers. Boyde (1974) found similar structures in dentine.

Although bathed in an extracellular fluid (ECF) which is supersaturated with respect to apatite, the crystals have remarkably uniform dimensions, implying that, after initial formation, further deposition of apatite is strongly inhibited. Osteopontin (OPN) and other molecules in the ECF (e.g., Pampena et al. 2004) are known to inhibit apatite growth.

Both Ca and PO₄ ions are essential to the vital activity of all metazoans. The ECF of invertebrates is also supersaturated in hydroxyapatite (HA), with saturation index values up to 10¹⁵. The relative scarcity of apatite as a biomineral suggests that strong inhibition of HA formation must occur in the ECF of invertebrates as well.

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References
Integrated air quality assessment – A synthesis of elemental and organic air pollution indicators

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In a multidisciplinary approach atmospheric quality in the Greater Cologne Area (GCA) was studied using pine needles as bioreceptors. This contribution describes accumulation behaviour, transport fractionation, source allocation, and the spatial distribution of major and trace elements including platinum group elements. Special emphasis is placed on synthesizing the inorganic and organic pollutant load on pine needles for improved differentiation of traffic, industrial and power plant emissions. The interpretation is corroborated by δ13C and δ15N isotopes and environmental magnetic data.

The GCA comprises various element emission sources, mainly lignite fueled power plants, urban regions of high traffic density and reduced air mixing, domestic heating and large industrial complexes along the Rhine Valley. We will first demonstrate that element accumulation on pine needles occurs in a systematic and predictable manner by analyses of 3 to 50 month old needles taken separately in summer and winter at six key locations. This allows for interpretation of spatial distribution maps constructed from 71 locations covering 3000 km² in the GCA. Absolute concentrations of elements and element enrichment factors were used for spatial analyses. Normalization to average dust composition was achieved using the sum of REE, as Ti was regionally enriched in the volcanic province of the “Siebengebirge”.

Source characterization based on element concentrations revealed that Mo was best suited to identify petrochemical emissions. Cu enrichment results from petrochemical emission and traffic sources. PGE showed a predominantly traffic origin for Pt and Pd, the latter also affected by fertilizer application in agricultural areas. Ru and Re were less traffic dependent, for Pt and Pd, the latter also affected by fertilizer application and traffic sources. PGE showed a predominantly traffic origin emissions. Normalization to average dust composition was achieved using the sum of REE, as Ti was regionally enriched in the volcanic province of the “Siebengebirge”.

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Traffic pollution was clearly depicted by enhanced Sb and Ba concentrations, whereby Ba showed a higher degree of dispersal. Fe and V were shown also to be related to traffic emissions in urban areas but as well originate from power plant emissions. Verificaton of emission sources was achieved by polycyclic aromatic hydrocarbon (PAH) pollution indicators. Lignite-fueled power plants emit preferentially phenanthrene, cyclopentenophenanthrene, and dibenzothiophene; urban traffic is characterized by higher load of alkylated phenanthrenes and different isomer patterns of e.g. methylphenanthrenes. Correlation of element and PAH pollution indicators was excellent although certain pollutant sources were depicted by one group only. For example Pb/Zn mining activity in the Rhenish Massif was only detected by elevated Cd concentration.

Inorganic and organic multiproxy air quality analyses allows for very reliable and independent source allocation even in areas with multiple emission sources.

Constraints on the revision of the K decay constants

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As the accuracy of current K-Ar age calculations is seriously limited by the uncertainties of the 40K decay constants [1,2], a reevaluation is required. 40K has a dual decay to 40Ar and 40Ca with a branching ratio of 10.48/89.52 [1,3] and a total decay constant of 5.543·10⁻¹⁰ a⁻¹ (calculated with data from [3] and a 40K/K ratio of 0.01167% [4]). Thus for conventional K-Ar and Ar-Ar dating (where the age calculation depend on mineral standards dated by conv. K-Ar technique) all three values are needed in the age equation.

To revise the decay parameters for 40K, the systematic offset of Ar-Ar and U/Pb mineral ages of rapidly cooled rocks were determined [e.g. 5]. Using the H chondrite parent body cooling history [6,7] it is possible to calculate the age offset of U/Pb and Ar-Ar ages for c. 4.6 Ga old rocks – it is c. 30 Ma [8], significantly smaller than 1% which is noted in [5] or [9]. A biotite from the Great Dyke Intrusion in Zimbabwe/Africa with an age of c. 2.5 Ga, lead to an age discrepancy of c. 20 Ma. The age data for the c. 2.0 Ga old Vrededorp impact structure from [10] recalculated for a new NL25 standard age [11] lead to a difference of c. 17 Ma.

These new age data lead to a decay constant of c. 5.520·10⁻¹⁰ a⁻¹, only a little smaller than that defined by [1] - this result will not change including the available literature data [e.g. 5,9]. It is slightly different from the determination of the total decay constant of 5.545·10⁻¹⁰ a⁻¹ via LSC by [12] and [13], but different 40K/K and branching ratios were used for these calculations. Using the geochemical data and the age equation for K-Ar dating is not possible (though not important for calulating ages) to decide whether the branching or the 40K/K ratio is wrong by about 1%. Assuming a 40K/K ratio of 0.01167% would lead to the decay constant to 40Ar of c. 0.575·10⁻¹⁰ a⁻¹ and thus a branching ratio of c. 10.42/89.58. Nevertheless an independent redetermination of the 40K/K and the branching ratio is desirable.

References
The AsO$_6$ polyhedron in arsenates, statistics and the novel compound Ti$^{1+}$Ti$^{3+}$As$_4$O$_{12}$

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Inorganic arsenates comprise a large number of compounds, demonstrated by 1145 entries in the ICSD (version 2006/2), however, only 23 compounds ($R < 8\%$) contain the rare AsO$_6$ octahedral unit.

Hydrothermal synthesis (Teflon-lined stainless steel autoclave, 7 d, 493 K) using the starting materials Tl$_2$CO$_3$ and arsenic acid led to the growth of hexagonal platelets of the novel compound Ti$^{1+}$Ti$^{3+}$As$_4$O$_{12}$ (single-crystal X-ray diffraction, $P$=31m, $Z$ = 1; $a$ = 4.848(1), $c$ = 11.091(2) Å, $V$ = 225.75(8) Å$^3$). The new compound is closely related to the following three structure types: $M^6$As$_6$O$_{18}$ ($M^6$ = Ca, Mn, Co, Ni, Cd, Hg, Pb), $H_2$As$_2$O$_6$, and LiAsO$_4$. All of these, as well as the novel compound, are built of layers of edge-sharing AsO$_6$ octahedra, which are connected by the usually octahedrally coordinated metal cations. In the case of Ti$^{1+}$Ti$^{3+}$As$_4$O$_{12}$, Ti$^{1+}$ is octahedrally coordinated whereas the coordination polyhedron of the larger Ti$^{3+}$ can be described as a trigonal antiprism.

![Image of Ti$^{1+}$Ti$^{3+}$As$_4$O$_{12}$ structure]

Considering the scarce data available for AsO$_6$ polyhedra a statistical analysis of bond lengths in AsO$_6$ groups was conducted. A total of 40 AsO$_6$ polyhedra in 38 different compounds were analysed. The bond lengths in the AsO$_6$ octahedra range between 1.736 and 1.918 Å, with a mean value of 1.827(29) Å. The individual bond lengths are very strongly influenced by the next nearest neighbours. As-OH bond lengths are considerably shortened to a mean value of 1.767(14) Å, which gives the perfect bond valence contribution of 1.00 for this As-O bond. Exactly the opposite effect is found in protonated AsO$_4$ tetrahedra, where the As-OH bond lengths are elongated to a mean value of 1.719(27) Å. As-O bond lengths to other AsO$_4$ and AsO$_6$ polyhedra are very close to the mean value with 1.834(33) and 1.824(20) Å, respectively. The longest mean distances are to edges of other metal octahedra with 1.846(23) Å. No clear correlation between the bond-length distortion and mean bond lengths of individual polyhedra could be established. Financial support by a DOC-FFORTE Fellowship of the Austrian Academy of Sciences (ÖAW) is gratefully acknowledged.

Detector strategies to measure Osmium isotope ratios in small samples by NTIMS

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Negative Thermal Ionization Mass Spectrometry (NTIMS) is the method of choice for high precision Osmium isotope ratio measurements of small sample sizes. Because of its high selectivity and high ionization efficiency optimum sample utilization as well as low backgrounds are achieved.

One of the limiting factors when analyzing small samples with Faraday detectors, is the noise level of the current amplifiers. The noise level is reduced as the resistor value and the gain of the current amplifier is increased. Today’s instruments use 10$^{12}$Ohm amplifiers as a standard. Larger resistor values maybe used to reduce the noise level, however there is a practical limit due to the limited insulation resistance of the PCB as well as the insulation resistance of the Faraday cup and the feedthroughs itself.

Single collector ion counting or even multicollector ion counting detectors overcome the noise problem and promises higher precision touching the limit of counting statistics. Today’s multicollector instruments are equipped with a single ion counting channel as a standard and very small samples can be measured in single collector by peak jumping procedures. The laminated magnet of the TRITON instrument from Thermo Fisher Scientific allows fast peak jumping sequences with short settling times between peak jumps. Nevertheless, this still is a sequential method, whereas the Multi-Ion-Counting (MIC) aproach allows a simultaneaous measurement of all isotopes of interest and thus maximises sample utilization and also eliminates the effect of signal fluctuations on the isotope ratio measurement.

In this experimental study, the performance of all three different detector strategies are compared on the basis of measured data of Osmium samples with different ion beam intensities ranging from >1 Mcps to a few Kcps. The different detector strategies are: (i) Faraday detectors combined with 10$^{12}$ Ohm amplifiers, (ii) fast peak jumping single collector ion counting using an SEM, and finally (iii) multi-ion-counting using multiple channeltron detectors. The best operation range and the pros and cons of each detector strategy for different signal intensities are discussed.
Experimental study of the Na-in-cordierite thermometer at different fluid compositions (NaOH-H$_2$O; NaCl-H$_2$O)

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Orthorhombic cordierite, (Mg,Fe)$_2$Al$_4$Si$_5$O$_{10}$*(Na, H$_2$O, CO$_2$ etc.), a characteristic mineral phase of medium to high grade metapelites, has thermometric properties. A previous study in the model system Mg-cordierite – 1n Na(OH) (Mirwald, 1986) showed that the Na-content is inversely related to temperature, is largely pressure independent, and stabilises cordierite by about 75MPa relatively to the upper stability boundary according to the reaction (1) Crd + H$_2$O = Tc + Q + Ky (Mirwald, 1984).

In this study we investigated the Na-incorporation in Mg-cordierite using different NaCl solutions (X$_{H_2O}$= H$_2$O/(H$_2$O+NaCl; X$_{H_2O}$: 1, 0.8, 0.6, 0.4 and 0.2) which implies, in addition, different H$_2$O activities covering the P-T range 0.2 – 1.1GPa and 650 to 750°C. Thus, the present experiments were conducted in a slightly acidic fluid milieu. The experiments were carried out in a piston cylinder and a hydrothermal apparatus. Microprobe and X-ray diffraction were used for sample characterisation.

The preliminary data confirm the inverse temperature relation without a significant pressure dependence. Previous Na-T relation: Na(apfu) = 0.406+/-0.003 –0.000471*T(°C); this study: Na(apfu) = 0.398+/-0.015 – 0.000466*T(°C). Again, the Na incorporation stabilises cordierite by about 75MPa, varying H$_2$O activities have no significant influence on the position of reaction (1).

Further experiments performed on quartzphyllite samples and application of the Na-in-cordierite thermometer to high-grade rocks are presented by Wyhlidal et al. (2007) at the same meeting.

References

Water-rock interactions at the new Gotthard rail base tunnel, Switzerland

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In Switzerland the new 57 km long rail base tunnel traversing the Central Alps is currently under construction. From the 11.35 km long Amsteg-Sedrun section in the northern part of the tunnel 110 water samples from fractures and open fissures have been collected and analyzed. Geologically this section lies completely in the steeply dipping crystalline basement of the Aar massif.

Depending on the lithology the tunnel water samples show different compositions and the total of dissolved solids is varying from 171 to 4014 mg/l. The most prominent cation is sodium. Magnesium is in most samples close to or below the detection limit of 0.02 mg/l. The majority of the waters has also a very low calcium content. Only a few samples have elevated Ca-concentration, which can be related to the dissolution of fracture anhydrite. The major anions represent a mixture of bicarbonate, chloride and sulphate with varying concentrations. Chloride together with an equivalent amount of sodium is contributed to the waters from leaching of crushed fluid inclusions and grain boundaries. Sulphate originates mainly from the oxidation of sulphide minerals and to a minor extend from the dissolution of anhydrite locally present in fissures.

One striking feature of the tunnel waters is their surprisingly high fluoride content of up to 29 mg/l. In low-TDS waters the fluoride concentration can even exceed the chloride concentration. Fluoride is contributed by fluorite dissolution, which can be found both as secondary fracture mineral and in the granite matrix. The low calcium content of the fluoride-buffered waters leads to the observed extremely high fluoride concentration.

The other remarkable feature of the tunnel waters is their very high pH throughout all lithologies with values up to 10.4. It results from dissolution of calcite under closed system conditions, which leads to a strong decrease of the partial pressure of CO$_2$. Calcite was found frequently in the granitoid host rocks. Calcite dissolution is also the source of bicarbonate in the waters. The dissolved calcium is then removed via a combination of plagioclase alteration and formation of zeolites. The hydrolysis of albite (anorthite content of the plagioclase is below 5 mole%) releases sodium as major cation into the water. Zeolites, especially laumontite, are present as thick mats on fracture surfaces in the tunnel. Zeolite formation is then responsible for the removal of calcium from the water.
Rare earth elements as natural tracers in the Thau basin karst system (Southern France)

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Rare Earth Elements (REE) have been more frequently used as natural tracers in hydrogeology (Smedley, 1991; Johannesson et al., 1996), with the analytical progresses for their determination at very low concentrations (ng/L). These elements cannot be considered as perfect conservative tracers, but REE patterns of groundwaters are mostly inherited from aquifer rocks through which they flow. As a consequence, REEs can be useful to study flow pathways and water mixing processes at different scales.

Because of the few REE studies realized in karst environment, the method was applied to the karst system of the Thau basin (southern France), which is characterized by a high complexity of water mixing processes (Aquilina et al., 2002). Three endmember water bodies (hydrothermal, karstic and sea or brackish waters) are present. The Vise submarine spring constitutes one of the main permanent outlet of the aquifers.

Rain, surface and ground waters were sampled from 2005 to 2007 over the Thau basin karst system. Major elements were determined by ionic chromatography. Trace elements and REE, after preconcentration, were analyzed by ICP-MS. Characteristic REE profiles enable to differentiate several types of water and to follow the hydrodynamics of the submarine spring. The study allowed to individuate the different concerned aquifers and to illustrate their possible temporal connections in function of the hydrologic cycle. Further studies are under progress to investigate REE complexation with organic matter.

References

Diverse active microbial communities in a tidal flat sediment as deciphered by a multidisciplinary approach

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Up to six meter long sediment cores were recovered from a backbarrier tidal flat area of the island of Spiekeroog in the Northwest German Wadden Sea and analyzed by a combination of complementary geochemical, molecular biological and microbiological methods to investigate the activity and composition of microbial communities.

One of our analytical approaches is the analysis of intact polar lipids (IPLs) using HPLC-ESI-MS. These diagnostic membrane lipids are rapidly degraded after cell lysis and thus are considered suitable biomarkers to trace viable microorganisms.

The quantities of the detected IPLs decreased only slightly with depth and correlate well with the total cell counts obtained by DAPI staining.

Furthermore, phospholipids with alkyl diether and mixed alkyl-acyl side-chains become dominant with increasing depth. In accordance with the molecular biological results this may indicate a substantial proportion of sulphate-reducing bacteria (SRB) in the microbial community even in deeper sediment layers because these lipids were detected in mesophilic SRBs (Rütters et al., 2001).

Whereas in the uppermost layers phospholipid-type diethers of archaeal origin were absent, archaeol-containing phospholipids were detected throughout the deeper part of the sediment column. In layers with low contents of methane high numbers of ANME-2 and ANME-1 archaea were found using molecular biological methods.

The major IPLs detected in a deep sulphate-methane transition zone were phospholipids with archaeal and hydroxyarchaeol cores which support the identification of ANME-2 consortia. The isotopic composition of these diethers is currently examined to show whether they are constituents of cell membranes from archaea mediating AOM.

References
Concentrations and signatures of stable isotopes of methane and hydrogen in hydrothermal fluids of the Mid-Atlantic Ridge

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Introduction

We have measured concentrations of dissolved methane and hydrogen in a set of fluid samples recovered by ROV from hydrothermal systems located on the Mid-Atlantic Ridge (MAR) at 15°N and between 4° and 10°S under the auspices of the German SPP 1144 project. Fluids investigated originate from different settings comprising peridotitic to basaltic host rocks, hot and diffuse vents, and water depths between 1500m and 3000m.

Results and discussion

Fluid endmember concentrations calculated based on the Mg content were up to 3.5 and 19 mmol/L for CH\(_4\) and H\(_2\), respectively, for fluids from the Logatchev hydrothermal field. Similar exceptional high concentrations with 1.4 mmol/L of CH\(_4\) and 11.6 mmol/L of H\(_2\) were also found in fluids of the recently discovered smoking crater Drachenschlund located at 08°18’S and characterised by ultramafic host rocks alike the Logatchev hydrothermal field.

Much lower gas concentrations were found in the fluids of basalt hosted systems. Among these, a black smoker of the Turtle Pits field (4°49’S) emanating vigorously boiling fluids with temperatures of up to 407°C at 3000m depth showed the highest fluid endmember concentrations of 0.3 mmol/L H\(_2\) and 0.018 mmol/L CH\(_4\). Black smoker fluids with no indication of phase separation revealed significantly lower gas concentrations.

Signatures of stable C isotopes for CH\(_4\) covered a range from \(\delta^{13}C\) -9.2 to -13.7‰ for all fluids sampled from vents at about 3000m water depth with no systematic difference between the various settings. Only CH\(_4\) in fluids of the Lilliput hydrothermal field (9°33’S) emanating at 1500m water depth with temperatures < 20°C revealed \(\delta^{13}C\) values of about -32‰. This might be attributed to distinct p/T conditions during abiotic CH\(_4\) generation or to a significant microbial contribution. \(\delta^2H\) values of H\(_2\) were used to estimate temperatures of emanating fluids.

Conclusion

Hydrogen dominates over methane among reactive gases within black smoker fluids. Host rock composition and phase separation processes strongly affect the gas concentrations in hydrothermal fluids but not the stable isotope distributions within the gases.

Evaluation of geothermometers for a zircon-rutile-corundum intergrowth

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A corundum megacryst (7x5 mm) from residues of an alkali basalt from SE Saxony (Germany) includes zircon and rutile. It provides a suitable specimen to test recently published geothermometers (“Ti-in-zircon” and “Zr-in-rutile” (Watson et al., 2006), and may be revealing about the origin of this mineral paragenesis, which is uncommon for basalts.

Rim-core-rim traverses of the trace elements Ti and Zr in zircon and rutile, respectively, were performed using an electron microprobe JXA-8500F under different analytical conditions (see figures below, detection limits in brackets).

Calculated temperatures are about 1100 °C for zircon (distance of analysis points to rutile >60 µm), but about 1015 °C for the core of rutile and 940 °C for the rim of rutile.

The shape of the traverses are discussed in consideration of secondary fluorescence, temperature, and chemistry of the crystallizing medium.

Reference

Lithium isotopes of the early solar system and terrestrial planets

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Despite large mineralogical, textural and chemical differences between carbonaceous chondrites, ordinary chondrites and achondrites, the range of δ⁷Li is restricted from +0.5 to +5.4‰. Hydroxide alteration and metamorphism are extremely variable in chondrites but Li isotopes show no obvious correlation with petrological types. Neither carbonaceous or ordinary chondrites, nor achondrites exhibit a correlation between their Li abundances and δ⁷Li, suggesting that Li isotopes did not fractionate during early stages of our solar system nor during magmatic differentiation on smaller asteroidal bodies.

Based mainly on the composition of basaltic and ultramafic rock types from Earth, Elliott et al. [1] and Magna et al. [2] suggested a δ⁷Li-value for BSE (bulk silicate Earth) of ~ +4‰. Elliott et al. [3] derived a weighted average of +3.4‰ for unmetasomatised mantle peridotites. Seitz et al. [4] and [3] concluded that a δ⁷Li of ~ +4‰ should also be the value for the inner planets, because rocks from the Moon and Mars give average values. McDonough et al. [5], on the other hand, suggested a δ⁷Li-value of 0‰ for the solar system, an average of a restricted number of measurements on chondrites. More recent work by McDonough et al. [6] revealed a slightly heavier average composition (δ⁷Li = +1.3‰). However, such low values are not supported by our measurements which comprise a much wider range of chondrite types. We find an average of +3.3‰ for carbonaceous chondrites. Ordinary and enstatite chondrites give a lighter average of +2.3‰.

The previously suggested ‘BSE’ value of ~ +4‰ by [1,3,4] was based mainly on basaltic rock types. The average δ⁷Li-value of unmetasomatised peridotites [3,7] and of olivines from relatively pristine spinel peridotites [1] is +3.3‰, indistinguishable from carbonaceous chondrites.

We therefore suggest, in agreement with Elliott et al. [3], that the δ⁷Li-value for BSE and also for the inner planets is +3.3‰. In turn, the different isotope signatures of carbonaceous chondrites on one side and of ordinary chondrites on the other are interpreted to reflect distinct reservoirs in the early solar nebula.

References

Re-Os isotope systematics of kimberlites from SW Greenland: Implications for an isolated lithospheric mantle during 500m.y.

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Kimberlite magma is well known to entrain many xenoliths and diamonds, which suggest that the magma originated from a source at the depth deeper than 200km. However, the nature of this source material is still highly debated. Here, we report the Re-Os data for kimberlite dykes from the Sarfartoq area, SW Greenland. In this area, the alkaline ultramafic dykes intrude into the boundary between the Archean craton and the Palaeo-proterozoic orogen. The kimberlites were erupted around 600Ma with a large carbonatite complex, which is located at the center of a widely distributed kimberlite swarm (Larsen et al., 1983; Larsen and Rex, 1992).

The Re-Os whole rock reference age of 1100 Ma is significantly older than the eruption ages of the Sarfartoq kimberlites, determined by K-Ar and U-Pb methods (Larsen et al., 1983; Bizzaro et al., 2002). It implies that the kimberlite source mantle was separated from convecting mantle at the time of the Re-Os reference isochron age and remained isolated until eruption. The Re-Os TMA ages of the kimberlites, however, are similar to the eruption ages. Thus, in this case it appears that Re-Os TMA ages record the eruption. The initial 187Os/188Os ratio of the kimberlites, 0.113, is in the range of the continental lithospheric mantle. The 187Os/188Os values of the kimberlites at 1100 Ma are also similar to those of the lithospheric mantle xenoliths from Somerset Island (Irvine et al., 2003), rather than the primitive upper mantle estimated by Meisel et al. (1996), supporting the isolated source hypothesis.

References
Numerical simulation on the thermal evolution and differentiation of iron meteorites’ parent body

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According to Hf-W chronometry, the parent bodies of iron meteorites had experienced silicate-metal separation within the first a few myr since CAI formation (e.g., Markowski et al., 2006). In this case short-lived radioisotopes such as $^{26}$Al and $^{56}$Fe may have been survived and played a key role in thermal history of parent body (Urey, 1955). However the thermal history and the mechanism of silicate-metal separation have been unclear so far. Thus, in this study, we developed a numerical model on the thermal evolution and differentiation of planetesimal-sized (from a few km to about 100km-sized) celestial body to clarify the timing and mechanism of the formation of metallic core, which is one of the most plausible candidate of the origin of iron meteorites.

Our model takes into account the internal heating due to short-lived radioisotopes, radiative cooling from the surface, the porosity effect on the thermal conductivity, sintering of silicate media (pores shrink due to the effect of pressure and temperature), and silicate-metal separation due to permeable flow of molten metal through silicate media. Since the melting temperature highly depends on the sulfur content, we also consider the change in sulfur content along the phase diagram in Fe-FeS system (Kullerud, 1967).

According to our numerical results, there are two conditions for the planetesimal-sized body to form a metallic core. At first, the parent body should form within the first 2 myr from CAI formation, otherwise it would have insufficient heat source. Next, the radius of the body should be larger than about 7 km, otherwise the body would be cooled rapidly. Once these conditions are satisfied, molten metal, into which sulfur preferentially dissolves, migrates toward the center of the body to form metallic core. Afterward, as the core cools down precipitation of pure iron takes place in accordance with the phase diagram in Fe-FeS system. Finally a pure iron ‘inner core’ forms at the center of the metallic core, which would be the origin of iron meteorites. Resulting cooling rate of metallic core at 800 K is slower than several 100 K/myr depending on the planetary size, which is consistent with the cooling rate of iron meteorites obtained from the analytical study, from 1 to 500 K/myr (e.g., Wood, 1964).

References

Syn-plutonic dykes and magma mingling: An example from the Alvand plutonic complex, Sanandaj-Sirjan metamorphic belt, Iran

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The Alvand plutonic complex is composed of various mafic to felsic plutonic rocks (gabbro-diorite-tonalite-granite) formed by repeated injections of magmas of crustal (anatectic) and mantle origin. Two extreme end-members of magmas in the complex include: 1) M-type magmas generating gabbro-diorite-tonalite suite and mafic-intermediate dykes and 2) crustal anatectic magmas generating S-type granites and related rocks. There are many NE-SW trending microdioritic-microtonalitic syn-plutonic dykes in the complex which in the some places they are disaggregated to mafic microgranular enclaves (MME). Their appearance, mineralogical and geochemical affinities are similar to other dioritic rocks of the complex but they are finer grained, richer in quartz-ocelli and mafic clots and they are more silicic than their coarse grained equivalents. Regarding to field, petrographic, mineralogical and geochemical features a suite of pure anatectic to hybrid and to mantle type plutonic rocks can be distinguished in the Alvand plutonic complex. The dioritic-tonalitic rocks are hornblende-rich (30-50 %) but anatectic monzogranites-granodiorites are hornblende-free. The evidence of hybridization due to magma mingling in the region is better understood by characteristics of mafic end member than felsic one. This is due to volumetric abundance of two original magmas so that felsic magma has been more abundant than mafic one at the time of hybridization, and therefore, the mafic magma has been surrounded by the felsic magma, so that, solidified parts of the felsic magma have been disintegrated into mafic magma. Since that the felsic magma has been near the end of its crystallization (solidification) history its mixing with mafic magma has been limited. The geochemical properties of both of the felsic and mafic rocks of the region have been slightly affected by hybridization process.
Geochemistry and petrogenesis of the Tamuteh leucogranites in SW Saqqez, northwestern Iran

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The Tamuteh area is located in the southwest of Saqqez in the north of the Kurdistan Province, western Iran. The Tamuteh leucogranites are situated in the Sanandaj-Sirjan Metamorphic Belt, Zagros Orogen and are composed of various granitic rocks including syenogranite, monzogranite, granodiorite, tonalite and microtonalite. They are cut by lamprophyric dykes and silicic veins. Geochemically, these leucogranites are subalkaline (calc-alkaline), metaluminous and weakly peraluminous and their characteristics resemble the I-type granites. According to the geochemical classification scheme of Frost’s et al. (2001), Tamuteh leucogranites are magnesian to weakly ferroan and calc-alkalic to calcic. They contain low concentrations of Rb, Y, Zr, Th, U, Ce, FeOt+MgO and high concentrations of SiO2, Ba and high Sr/Y and Ba/Rb ratios. They show general trends of decreasing contents of Al2O3, Fe2O3, MgO, P2O5 and TiO2 with increasing SiO2 but CaO, Na2O and K2O amounts show no regular patterns. According to tectonic discrimination diagrams of Pearce et al. (1984), Tamuteh leucogranites were generated in a volcanic arc setting. Behaviour of trace elements in the Tamuteh leucogranites is similar to those of well-known volcanic arc granites from Chile and Jamaica. Normalized trace element patterns show enrichment in LILEs (Rb, Ba, K, Th and Ce) relative to HFSEs (Nb, Zr and Y) and similar to calc-alkaline subduction related rocks from orogenic belts, including that they have had much interaction with crustal materials. The Tamuteh leucogranites also have high Sr and low Y and Rb contents, therefore can be related to mantle-derived magmas. The calc-alkaline, I-type leucogranite or syenogranitic to tonalitic composition and the presence of lamprophyric dykes indicate the formation of two magmas experiencing subsequent mixing/mingling processes. Therefore, these leucogranites may have resulted from contamination of mantle-derived magmas by continental crust during an ancient subduction event.

References

Large 14C age offsets between fine aragonite fraction and coexisting planktonic foraminifera in shallow Caribbean sediments

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14C is a widespread dating tool in paleoceanography. Age models are usually derived from coarse fraction planktonic foraminifera (>150 µm), but many proxies used in paleoclimatic research such as fine aragonite or organic components belong to the fine fraction (<63µm). Several studies have shown time-lags between records from various granulometric fractions (Paull et al., 1991; Thomson et al., 1995; Mollenhauer et al., 2005) due to different processes such as changes in sediment sources or abundances, sedimentation rates, bioturbation, reworking...

We studied the temporal phasing between the coarse and the fine fractions from sediments retrieved in the Northern Caribbean Sea. Detailed stratigraphies over the past 40 kyr of δ18O and 14C of aragonite fine fraction and planktonic foraminifer Globigerinoides ruber, and their respective abundances were performed on core MD032628 (Walton Basin, 17°21N, 77°42W, 846m water depth).

δ18O records are nearly in phase for both fractions, with a slight lead of the fine fraction during the last deglaciation. 14C ages are identical within errors over the past last 5 kyr. The age difference increases through time with a fine fraction being younger than G. ruber. The discrepancies range between 1.33 kyr at the end of the last deglaciation up to 5 kyr during the LGM.

Bioturbation and variations in accumulation rates are likely causes for the observed discrepancies (Bard et al., 1987; Wheatcroft, 1992; Bard, 2001). Indeed, G. ruber abundance is highest during the LGM and decreases over the last deglaciation. Inversely, the fine fraction is minimum during the LGM and reaches its maximum during the Holocene. Bioturbation has probably mixed a “lighter δ18O-younger 14C” fine fraction of the last deglaciation downward with “heavier δ18O-older 14C” G. ruber. The relative influence of various mechanisms (size-dependant bioturbation, sedimentation rates, abundances) has been tested by using a numerical model (Bard et al., 1987).

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The geochemistry of Ni isotopes in mafic-ultramafic layered complexes

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Introduction

For better understanding the natural processes involved in the formation of Ni ore deposits in igneous layered complexes, we analyzed Ni isotopes in a section through the 2.45 Ga Burakovsky layered mafic-ultramafic massif (NW Baltic Shield, Russia). In order to constrain the mechanisms of Ni isotopic fractionation, we also analysed Ni isotopes in samples that have undergone Ni-enriching by the Mond process, where synthesis gas (95-97% CO and H) is used for highly effective Ni extraction involving metal-carbonyl formation.

Analyses were made on whole-rock (WR) samples and on separated pyroxenes and Ni-rich sulphide minerals with a Neptune MC-HR-ICP-MS. The measuring precision achieved for δ62Ni/60Ni was at ±0.1‰ with a maximum observed fractionation value for Δ62Ni/60Ni of 5‰.

Results

1) WR samples from the section through the Burakovsky Massif (BM) (from -700 to -50m) show a clear fractionation trend of enrichment of light Ni isotopes from the base towards the roof of the massif (change of δ62Ni/60Ni of +0.3‰ at the base, towards -1.5‰ at the top).

2) Ni-rich sulphide secondary minerals, which are forming the upper layer of the intrusion, have the lightest measured Ni isotope composition in the natural samples, in particular those which are associated with carbon minerals (δ62Ni/60Ni = -2‰).

3) The Ni isotope ratios in pyroxenes changes independently of their position in the section. This may indicate the importance of a secondary, low temperature process.

4) Materials from the technological process of metallic nickel production show the most intensive 64Ni/60Ni and 64Ni/60Ni fractionation (δ62Ni/60Ni from +0.5 to -4.5‰). Lighter isotopes accumulate in the chamber’s top, where the gas phases condense.

5) Gas analyses from the BM WR samples show up to 41.5 vol% of (N2+CO) component.

Interpretation

The observed trends of Ni isotopic fractionation in the BM rock, similar to those observed in the technological Mond process, as well as the presence of trapped (N2+CO) gasses, suggest a model of natural kinetic Ni fractionation involving reducing gasses and natural metal-carbonyl formation. Such gasses may either have a juvenile origin or may be formed from heating (intrusion contact, metamorphism) and water vaporization of carbon-bearing geological units.

Development of a mosaic-like micro-pattern during Mg-calcite crystal growth

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In natural calcium carbonate precipitation systems, Mg2+ ions play a major role due to their inhibiting effect on calcite growth and the formation of CaCO3-MgCO3 solid solutions, resulting in the modification of precipitation kinetics and rates, thermodynamic stability of the precipitate, as well as in changes of crystal morphology. Marine sedimentary and biomineralized Mg-calcite crystals have been reported to contain up to about 20 mole% MgCO3, although such high-Mg-calcite crystals are considered to be metastable under seawater-like conditions. These natural Mg-calcite crystals usually show micro-morphologies different from pure calcite crystals.

To explore deeper into the conditions of high-Mg-calcite formation, Mg-calcite growth under different solution conditions has been directly observed using atomic force microscopy. Within a certain range of solution conditions, dependent on the Mg/Ca ratio in solution, on the saturation state, as well as on the presence of other ions in solution, an intriguing observation of crystal restructuring has been made: After fast crystal growth by step advancement as well as by two-dimensional nucleation and spreading of monolayer-islands on calcite cleavage faces, straight ridges of sub-nanometre height appeared at the crystal surface. These ridges do not grow on the crystal surface, but they pop up by bulging of the newly precipitated crystal layers. Ridge formation starts at one point and usually proceeds in one direction until they connect to another ridge or stop at a major crystal defect. Ridges occur in three crystallographically defined directions, which probably correspond to the equivalent planes of the prismatic {110} form. Through progressive development of new ridges, the growing crystal becomes subdivided into mosaic blocks that can be reduced down to a few hundreds of nanometres in diameter. When advancing steps stop at ridges, they pile up to form multilayer steps that separate the mosaic blocks from each other, which may finally lead to crystal growth as aligned fibres.

EDX analyses yielded a bulk content of about 8-10 mole% MgCO3 in the mosaic calcite, which should increase its solubility in water. However, dissolution of a mosaic takes place preferentially along the ridges, which may suggest a shift of the bulk strain and possibly exsolution-like dislocation of magnesium ions towards preferential crystallographic planes, where the accumulated strain gives rise to the ridges.

The described mechanism of crystal restructuring may have implications for the formation kinetics of CaCO3-MgCO3 solid solutions, and it may play a role in the formation of crystal ultrastructures, such as in biominerals.
Metal sulfide complexing – What we know and what we should know

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Reduced sulfur occurs ubiquitously in aqueous fluids within and on the Earth’s crust over a wide range of conditions extending from ambient to high temperatures and pressures. In all these environments, metal ions may be complexed to varying degrees by simple inorganic ligands such as HS-, S2-, and SxS2- (polysulfide) as well as by thio-organic electron donors. Metal sulfide complexes and clusters play an important role in element sequestration and transport and biogeochemistry in aquatic (e.g. wetland) systems as well as in the ocean water column and in particular, in anoxic marine environments (e.g. the Black Sea dead zone). In seafloor and subaerial hydrothermal systems, metal-sulfide complexing (i.e. transport) and precipitation are in important not only in ore formation but also in defining many aspects of biodiversity in seafloor and surface discharge environments. At more extreme conditions within the Earth’s crust, metal sulfide complexes are considered to partition into volatile rich fractions during phase separation of saline, magmatic (hydrothermal) fluids. In volcanic gas environments, volatile metal sulfide complexes account significantly for the transition metal transport budget to the atmosphere.

Despite the overall importance of metal sulfide complexing in understanding many geo(bio)chemical phenomena, the stability and stoichiometry of many aqueous metal sulfide complexes are not well known, particularly at ambient temperature where the experimental determination of reliable equilibrium constants is fraught with problems. A few metal-sulfide complex are quite well defined over a range to supercritical conditions such as with the formation of silver and gold hydrosulfide/sulfide complexes. Both Ag and Au are soft Lewis acids and thus form very stable molecular moieties with reduced sulfur. Reliable equilibrium thermodynamic data also exist for sulfide complexes of Cu, Zn, Cd and Hg and some other elements (e.g. As, Mo) but there is a dearth of information available for many other metals with respect to the stability of the complexes as well as their related clusters and their structures. Our current state of knowledge will be discussed together with an assessment of the crucial gaps in our knowledge in metal-sulfide interactions under a variety of conditions.

A geochemical scenario for evolution of the Nain-Baft back arc basin

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The Nain-Baft ophiolitic complex is categorized as an oceanic back arc basin, opened during the middle Cretaceous in the active continental margin of the Central Iranian continental block (the Sanandaj-Sirjan zone), due to the oblique subduction of the Tethys Ocean beneath the Iranian block. This extensional basin is behind the Mesozoic magmatic arc of the Sanandaj-Sirjan zone but crosscutting by the Eocene magmatic rocks of the Urumieh-Dokhtar magmatic belt. The Upper Cretaceous is believed to be the time of crystallization or metamorphism of the rock units in this oceanic basin based upon the K-Ar age determination. Clinopyroxene grains in the basaltic rocks of the Nain-Baft ophiolitic complex are characterized by low content of TiO2 content, similar to those of basalts, erupted in arc related environments. The basaltic-gabbroic rocks and the more acidic terms of this belt are of both tholeiitic (IAT) and calc-alkaline affinity. Depletion in HFSE and enrichment in LILE are the more distinctive features. Fractional crystallization and various degrees of depletion/enrichment in the mantle source associated with different degrees of partial melting are the main mechanisms, responsible for the geochemical evolution of the rock series in these ophiolitic complexes.
An experimental approach to high-temperature iron isotope fractionation

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There is considerable variation in $^{57}$Fe/$^{54}$Fe among igneous minerals but the cause is uncertain. A central problem in interpreting natural iron isotope data is that equilibrium fractionation factors among coexisting minerals are poorly known. We performed experiments to establish the iron isotope equilibrium partitioning between fayalite and magnetite at a range of temperatures. These minerals are surrogates for mantle spinel and olivine. Experiments were performed in a piston cyldiner apparatus at 1 GPa and at 600, 700, and 800°C. Starting synthetic magnetite was spiked with $^{54}$Fe to track the approach to equilibrium (e.g., Matsuhisa et al., 1978). The experiments were conducted with added quartz to ensure that oxygen fugacity was fixed at the quartz-fayalite-magnetite equilibrium.

The results show that there is a resolvable fractionation between the fayalite and magnetite and that it decreases with increasing temperature: at 600°C $\Delta_{\text{mgt-fa}} = 0.45$‰, at 700°C $\Delta_{\text{mgt-fa}} = 0.31$‰, and at 800°C $\Delta_{\text{mgt-fa}} = 0.28$‰ +/- 0.017‰. The figure below shows our data compared with the predicted fractionation factors (Polyakov and Mineev, 2000). At higher temperatures the theory and experiments are in fair agreement, but as temperature decreases there is a more substantial difference. This study has experimentally determined for the first time inter-mineral $^{57}$Fe/$^{54}$Fe equilibrium fractionation at high temperature. The results show that the magnitudes of these fractionations are large and require consideration when interpreting iron isotope ratios observed in natural igneous samples.

References

Coeval Pan-African granitization and migmatization of the north Sudan Basement

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We have carried out geochronological and isotopic investigations (zircon U-Pb and Pb evaporation and Nd isotope analyses of North Sudan Basement granitoids and migmatites to characterize sources and to find comprehensive answers to the apparently misleading field chronology, where granitoids (quartz-monzonite, granodiorite, tonalite and granites) intrude (quartz-monzonite, granodiorite, tonalite and granites) migmatite-gneisses; thus suggesting post migmatization emplacement. Whole rock and biotite separates were also analysed for Rb and Sr isotope composition, to determine migmatization-reheating and/or cooling ages.

Zircon U-Pb isotope dilution analyses for representative granitoid that intrude or form lenses and pods interbeded with migmatites, yield ages of 602 ± 3.1 Ma and 602 ± 28 Ma, while zircon $^{207}$Pb/$^{206}$Pb evaporation data give similar mean ages of 602 ± 3.5 Ma and 599 ± 3.8 Ma. U-Pb analyses for migmatic zircon fractions from representative samples yield ages of 599 ± 12 Ma to 606 ± 7 Ma and zircon $^{207}$Pb/$^{206}$Pb evaporation analyses give similar mean ages of 603.8 ± 2.1 Ma and 603.5 ± 3.7 Ma. We interpret these identical zircon age data as crystallization ages for the North Sudan basement granitoids and migmatites Both rock types have crustal signatures ($\varepsilon$Nd = -3.5 to -4.8 for migmatites and $\varepsilon$Nd = -2.4 to -8.9 for granitoids). These basement rock types are different from the older (717.6 ± 0.61 Ma and 707.3 ± 0.97 Ma) mantle sourced ($\varepsilon$Nd = +5.6 to +6.9) granitoid Ring complexes. Rb/Sr whole rock isochron for migmatites give an age of 583 ± 21 Ma, being identical within error limits to basement rock zircon ages. Biotite Rb/Sr cooling ages for both migmatites and granitoids are younger and very similar, (566 ± 11 Ma to 570 ± 17 Ma) with a mean age of 567.5 ± 2.8 Ma and are interpreted as the metamorphic-cooling ages.

While isotope data indicate crustal sources for North Sudan basement migmatite and associated granitoid melt, their similar Pan-African zircon age data and identical biotite cooling ages suggest concomitant crystallization, with inference for coeval indicate coeval crystallization, which together with identical biotite cooling ages, suggest concomitant granitization and migmatization of the North Sudan basement.
Amino acids in shungite matter of Precambrian sedimentary rocks of Karelia

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Amino acid composition of Karelian shungites (Shunga, Zazhogino and Nigozero deposits) of the Onega area from Palaeoproterozoic with various carbon contents (from 3 up to 98 %) was investigated.

It was established, that the general contents of amino-acids in calculation on percentage of organic matter increase with concentration decrease of organic carbon. The lowest concentrations of amino-acids were established in rocks with the migratory organic matter (0.0005 mg·g<sub>org</sub>). In shungite rocks containing sedimentary organic matter, amino acid contents were increased by 1–2 order (0.002–0.02 mg·g<sub>org</sub>).

In the area of Shunga deposit the group composition of amino acids for sedimentary and mixed organic matter look as follows: aliphatic ≈ hydroxil. In migration organic substance the relation varies: aliphatic > hydroxil. In sedimentary shungite of Zazhogino deposit the group composition of amino-acids is submitted substantially by aliphatic differences (60 %), and in migratory-elastic shungite substance of Nigozero deposit the concentration of amino acids containing acid groups is increased: aliphatic > acid > hydroxil. Among individual amino acids increased contents of serine, glicine and alanine are characteristic. In a sample with the least content of organic carbon (lidite, Shunga deposit) was established high tyrosine quantity and presence of lisine (basic amino acid) which is absent in high-carbon shungite.

Additional researches of sedimentary shungite remains (Zazhogino deposit) after bitumoid extraction have shown that more than 60% of amino-acids were removed from a sample as a result of extraction by chloroform and methanol-benzene. Content of amino acids up to extraction is 0.075 mg·g<sup>-1</sup>, after extraction – 0.029 mg·g<sup>-1</sup>. This fact allows us to believe that the significant part of amino acids in shungite structure includes in bitumoid organic matter.

Our results well coordinate with previous data about distribution of bitumoids in shungite rocks (Solov’eva et al., 2000). The more content of carbon in shungite, the less amount of bitumoids it contains, and accordingly amino acids. Amino acids in shungite matter of sedimentary origin are the best kept; with increase of carbon contents the quantity of amino acids sharply decrease, but does not disappear totally. That is connected with originality shungite structure formed nanoporous fullerene-like carbon particles.

References

Fluid composition in veins of the Outokumpu drilling site, Finland

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The Outokumpu drilling site is located in the vicinity of the Outokumpu ore deposit in SW Finland. The Proterozoic Outokumpu formation, consisting of mica schist with black schist interlayers, serpentine, skarn rocks, and pegmatitic gneisses, is thrust over an Archaean basement. The borehole (2.5 km deep) transects the Outokumpu formation and was intended to encounter the Archaean basement.

Core samples with quartz and carbonate veins were taken in order to study fluid inclusions. The wallrocks were metamorphosed in the amphibolite facies. Three different vein types can be discerned: (i) quartz-filled with a biotite-rich alteration halo, (ii) quartz-filled without alteration zone, and (iii) carbonate-filled with an Mg-Hbl alteration zone. The quartz veins show variable sizes in length and thickness ranging from a few mm to several cm, which range from lenses and thin to relatively large veins. The type (iii) veins have a smaller thickness of a few mm.

The investigated fluid inclusions in the quartz veins are primary and pseudosecondary showing one to three phases containing vapor and/or liquid. These inclusions occur together on intragranular trails, in clusters, or as single inclusions in quartz. Locally, pure gas inclusions form intragranular trails. Transgranular trails which indicate secondary inclusions are rare. They also consist of mixed aqueous and carbonic inclusions.

The lowest measured homogenization temperature (Th) is at about 250°C but most of the measured Th are in the range of 300-400°C. The eutectic temperatures (Te) have values of about –22°C and final melting temperatures (Tm) of about –12°C which indicate a salinity of 15–19 wt.% NaCl eq. in the aqueous solution. The Te for gas inclusions have values of about -56°C and a Th of 26°C which points to a CO<sub>2</sub>-rich composition.

The minimum formation temperatures around 300-400°C and the alteration mineralogy (Hbl, Bt) suggest a formation of the hydrothermal quartz veins at conditions of the lower amphibolite facies. This saline and carbonic fluid composition is typical for metamorphic rocks.

The investigation of the fluid inclusions provides a documentary of the fluid development and the possible hydrothermal mobilisation/remobilisation of the Outokumpu ores during later metamorphism.
How well do we know the initial Nd isotopic state of the Earth?

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As is evident from the extensive studies of CAIs and presolar grains in meteorites, the material in the Solar System is a mixture of debris from widely different nucleosynthetic sources. The differences in isotopic composition of bulk meteorite samples may therefore reflect variations in the mixing ratio of various components in different “planetary” materials. It would then follow that models of planetary evolution that are based on small shifts in isotopic ratios due to radioactive decay (Boyet and Carlson, 2005) are strongly dependent on the initial isotopic state and a “bulk solar” value that cannot be properly assumed. A key issue to understand the evolution of early Earth has been whether the available samples of meteorites accurately reflect the Nd isotopic composition of bulk Earth (Andreasen and Sharma, 2006; Ranen and Jacobsen, 2006). We have addressed this question using high precision Sr, Ba, Nd, and Sm isotopes in large samples of chondrites and a eucrite (Andreasen and Sharma, 2006; 2007).

High-precision barium isotopic compositions of large samples of St. Severin (LL6) and Juvisn (eucrite) are identical to the terrestrial values. In contrast, Murchison and Allende (carbonaceous chondrites) reveal excesses in $^{135}$Ba and $^{137}$Ba of around +39 and +22 parts per million, respectively; no anomalies are resolvable in $^{130,132,136}$Ba. High precision Sr isotopic compositions of all meteorites are identical within error. The data are consistent with carbonaceous chondrites having an excess in r-process $^{135,137}$Ba with respect to Earth, Eucrite Parent Body, and ordinary chondrites. The carbonaceous chondrites, however, display no variation in the r- and s-process Sm and Nd isotopes suggesting that the r-process sources of Ba and the lanthanides were decoupled. The homogeneity of Ba and Sm isotopes in the Earth, Eucrite Parent Body and ordinary chondrites indicates that the Solar Nebula that fed planetesimals between ~1 to ~2.4 AU was well mixed with respect to these elements. It was heterogeneous beyond ~2.7 AU where carbonaceous chondrite parent bodies formed. These observations also indicate that the best estimate of the Nd isotopic composition of the Earth is obtained from ordinary chondrites and not from carbonaceous chondrites, as is normally assumed. Since the terrestrial upper mantle shows a $^{142}$Nd anomaly of +18±6 parts per million with respect to the ordinary chondrites, this is further evidence that the upper mantle retains a memory of early Earth differentiation and sequestration of a reservoir with an average Sm/Nd ratio lower than that of chondrites.

References


Remediation of heavy metals with species and green vegetables

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The common spices and green vegetables (i.e. Amaranth, Anise, Coriander, Methi and spinach) grown in the contaminated soil of the pyrite belt area, Mandala, central India has been studied for remediation of heavy metals (HMs) i.e. As, Cr, Mn, Fe, Ni, Cu, Zn, Hg, Pb. These plant have remarkable accumulation capacity for these elements. The total mean soil contents of metals i.e. As, Cr, Mn, Fe, Ni, Cu, Zn, Hg and Pb were found to be 53.0, 1380, 1832, 8900, 667, 743, 153, 4.8 and 387 mg kg$^{-1}$, respectively. The total mean contents of HMs i.e. As, Cr, Mn, Fe, Ni, Cu, Zn, Hg and Pb in these plants were 0.48-2.81, 107–5869, 76–1700, 716-53381, 56–8837, 19.9-165, 59–196, 0.9–11.2, 4.6-54 mg kg-1 of DW respectively. The species: Anise, Coriander and Spinach were found to be hyperaccumulator for Cr (> 0.1); Cr (>0.5), Fe (> 5%), Ni (> 0.8%) and Cr (>0.4%), Ni (>0.2%). A sequential extraction procedure was used to fractionate heavy metals in highly contaminated soils into the conceptual metal pools: exchangeable; carbonate bound; bound organically; bound in Fe-Mn oxides; and residual. The leachable and total contents of metals in soil, total metal contents in six plant species and their correlations are discussed. Among five plant leaf tested, Anise, Coriander and Spinach showed the extremely high accumulation tendency towards the heavy metals (i.e. Cr, Fe, Ni), may be due to micellization with essential oils, and sequestration with dibasic acids i.e. oxalic, succinic, etc. The species: Anise, Coriander and Spinach accumulated Cr, Cr, Fe and Ni; Cr and Ni at extremely high levels and considered as hyperaccumulator. These spices provide new plant resource for exploring the mechanism of metal hyper accumulation to use in the phyto remediation of the heavy metal contaminated soils.
Subduction of hydrated lithosphere: 300 ppm H₂O in subducting olivine would eliminate the metastable olivine wedge

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In subducting slabs, where temperatures may be low enough to inhibit equilibrium transformation of olivine, the persistence of metastable olivine into the earth’s transition zone would reduce subduction rates and possibly result in deep focus earthquakes through transformational faulting. Several studies have used experimental transformation kinetic data to model the depth range of metastable olivine persistence under subduction zone conditions (Kirby et al. 1996; Mosenfelder et al. 2001, Marton et al. 1999, 2005). H₂O in olivine has been shown to enhance growth rates in the olivine-wadsleyite and olivine-ringwoodite phase transformations (Kubo et al. 1998, 2004) Recent modeling of the depth range of metastable olivine persistence has included a power law dependence of water concentration (Hosoya, 2005). Here we present new experimental results on the transformation of hydrous San Carlos olivine (300 wt-ppm H₂O) to ringwoodite at 18 GPa. Our experiments show that 300 ppm H₂O greatly enhances ringwoodite growth rates, resulting in an activation enthalpy of 186 kJ/mole. Even at temperatures as low as 700 °C, we obtain measurable growth rates, implying that rapid ringwoodite growth at temperatures corresponding to the interiors of cold subducting slabs. Combining our kinetic data with thermal modeling of subduction zone shows that even for very old and fast subduction zones, 300 ppm H₂O would eliminate the metastable olivine wedge. Alternatively, if deep-focus earthquakes are triggered by olivine-transformational faulting in cold subducting slabs, then the olivine in such slabs cannot be significantly hydrated.

References

Chlorine isotope distribution on Earth

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With our ability to analyze ³⁷Cl/³⁵Cl ratios (δ³⁷Cl values) of small amounts of solid materials, it is now possible to use chlorine isotope geochemistry of low Cl-concentration solids as a tracer of fluid movement in the subduction process. Cl is a hydrophilic ion that should faithfully track aqueous fluids throughout the crust and mantle. The δ³⁷Cl values of primitive carbonaceous chondrites, pristine MORB glasses and samples of sub-continental mantle origin are all close to 0‰, equal to average crustal values (Sharp et al., Nature ’07). Notable variations do exist, however. Primitive sodalite inclusions from Allende (CV chondrite) average -1.3(±0.6)%o, and MORB glass from 12°N, EPR have δ³⁷Cl values of -1.0‰. The sodalite may represent a separate nebular Cl reservoir or have low δ³⁷Cl due to an equilibrium isotopic fractionation. The 12°N, EPR data may represent mantle heterogeneity, as is seen in other geochemical systems. The overall homogeneous δ³⁷Cl value of 0% for Earth means that even small deviations from this value require a distinct source or fractionation process to explain the non-zero values.

Chlorine isotope fractionation between phases is generally very small, and cannot change the δ³⁷Cl of a system by more than ~0.5‰. Two mechanisms which cause appreciable fractionation have been identified. The first is vaporization of NaCl, where liquid-vapor fractionation at 800°C is ~0.7‰. While not large, fractionation in a Rayleigh distillation process in the solar nebula could easily exceed 2‰, even at high T, if 90% of a sample is vaporized. Far more remarkable is the fractionation between hydrochloric acid and vapor, where fractionations in excess of 8‰ are observed in simple boiling experiments. This fractionation process explains extremely variable δ³⁷Cl values (covering a range of 16‰) found in high temperature, acidic volcanic fumaroles in Central America (Barnes et al., this meeting). Excepting these unusual fractionation processes, chlorine isotope ratios should maintain fidelity throughout subduction and return in arcs. Non-fractionated samples from Central America and the Izu Bonin arcs have values clustering around -2‰, presumably recording the value of their source.

References
How well do trace element proxies predict slab fluid behavior?
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We present volatile, major and trace element data for olivine-hosted melt inclusions from a suite of cross chain seamount samples extending across the Mariana arc from Guguan volcano to the Mariana Trough. H2O, CO2, S, F and Cl abundances, as well as trace elements, have been determined by SIMS [1]. Our results show that there is a strong decoupling of water and slab fluid tracers such as Ba/La and B contents, beyond the main arc system. As might be anticipated, trace element enrichments generally associated with the subducting slab show a systematic decrease across the arc into the back-arc. However, water contents in cross-chain samples, 230 km above the subducting slab, show similar values to the arc-front samples, implying that water release is a continuous process across the arc. This finding is consistent with experimental results [2] and melt inclusion studies across the Central American arc [3]. In contrast to H2O contents, we observe significantly higher CO2 contents in the cross chain samples (up to 820 ppm) as compared to the arc samples (max CO2= 550ppm), suggesting either enhanced decarbonation at depth, or that the cross chain samples have experienced less degassing. Our observations show that fluid release can be substantial behind the main volcanic front and that a re-evaluation of the common use of slab-fluid tracers is clearly needed.

References

An experimental study of the origin of reaction textures in mantle xenoliths
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Sieve-textured clinopyroxene and spinel are common in mantle lherzolite and harzburgite xenoliths. Various interpretations have been put forward to explain the origin of this texture, including partial melting, mantle metasomatism and host magma – xenolith reaction during transport. Shaw et al. (2006) suggested that sieve texture was a result of a two stage process involving breakdown of orthopyroxene with generation of a secondary Si-Al-alkali-rich melt, followed by migration of this melt along grain boundaries where it dissolved clinopyroxene and spinel in an incongruent reaction. In this study, we have performed a set of time series experiments to test the above hypothesis. The experiments were performed under both reducing and oxidized conditions at 1200 and 1156 °C at one atmosphere, using a synthetic leucitite melt and discs of natural herzolite. Experiment durations ranged from 1 to 15 days.

Sieve texture was developed on clinopyroxene and spinel in all experiments, but only on grains in direct contact with melt derived from symplectic reaction zones around orthopyroxene. Reaction zone thickness does not show a simple relation to experiment duration, however reaction zones developed at 1156°C are narrower than those formed at higher temperature.

Our results show that sieve texture development on clinopyroxene and spinel in orthopyroxene-bearing mantle xenoliths is the result of a multistage reaction process. In the first step, orthopyroxene undergoes incongruent dissolution to produce a silica and alkali-rich melt together with olivine and clinopyroxene. As this melt migrates along grain boundaries it causes incongruent dissolution of clinopyroxene and spinel. The incongruent dissolution reactions involve complete dissolution of the reacting mineral followed by nucleation and growth of the secondary phases once the reacting melt is saturated with them. These secondary phases have a smaller volume than the primary grains leaving behind a reaction zone with interstitial melt, i.e. a sieve textured zone. The reaction of orthopyroxene, clinopyroxene and spinel with infiltrated host magma results in a range of melt compositions that are indistinguishable from those interpreted to be due to very small degrees of partial melting.

References
Geochemical and microbiological controls on the corrosion and transport of depleted uranium in soil

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Assessment of the environmental impact of depleted uranium (DU) from munitions in oxic soil is hampered by limitations on information regarding uranium mobilisation and transport. Soil geochemistry, mineralogy and microbiology have been shown to have a significant effect on the behaviour of uranium within many natural environments.

The aim of this study is to determine the relative influence of geochemical and microbiological factors within the context of the overall biogeochemical processes, including the speciation and mineralogy of the uranium present during the DU metal breakdown.

In this study 2 soil columns were collected from field sites (Kirkcudbright and Eskmeals) in the UK where DU metal samples had been buried for ≈8 years. The Kirkcudbright soil is organic and clay rich, whereas the Eskmeals soils is a quartz-rich dune sand. Samples of soil up to 50cm from the DU metal were analysed by Sequential Extractions (SE), Sampling Electron Microscopy (SEM), mini-focus X-ray Adsorption Spectroscopy/ X-ray Fluorescence (XAS/XRF), X-ray Diffraction and pore water analysis (ICP-MS). The microbial population in the soil was also characterised using culturing and Biolog techniques.

The SE and XAS data indicate that within the soils the uranium is only present as U(VI). In the Eskmeals site the contaminated soil is dominated by schoepite \((\text{UO}_2)_3\text{O}(\text{OH})_6\cdot6\text{H}_2\text{O}\) coating the quartz grains (fig. 1). In the Kirkcudbright soils mini-focus XAS and XRF analysis indicate the U is more dispersed and associated with ferric oxyhydroxide minerals. The contaminated zone around the corroding metal is relatively small in the Eskmeals soil, with total [U] <10ppm within 10cm of the DU metal. The bacterial community counts from the soil are not affected by the U concentration, but there is a significant decrease in the metabolic diversity within the contaminated zone. The pore water in the contaminated zone also contains high concentrations of oxalic acid indicating a significant biological response.

The distribution pattern study of rare earth elements in Choghart iron ore mine, Bafq area, Iran

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From the metallogenic points of view, Iran is divide into several provinces and belts out of which, metallogenic province of Saghand-Golpayegan-Bafq has a special importance. The presence of rare earth elements along with the elements such as Fe, P, U and Ti is known only in this province. Metallogenic province of Saghand-Golpayegan-Bafq is made of the different mines, out of which, the Choghart iron ore mine is one of them. This mine is one of the most important iron ore mines of Iran which could be important due to presence of the REE. The Choghart iron ore mine is situated in central Iran plateau and its geographical coordinate is as: 55°28'02" longitude and 31°42'00" latitude. In order to study the behaviour of REE in Choghart mine, samples from magnetite and apatite have been analysed by NAA. Aquired results show that, as a whole, magnetites from this mine are not much enriched from the REE. All magnetites show less LREE enrichment and only the aquired sample from the borehole with degree of high purity of iron shows more enrichment in LREE. \((\text{La/Lu})_{in}\) ratio shows that the fractionation between LREE and HREE occur nearly in all magnetites but magnetite with degree of high purity of iron shows more extent of fractionation between LREE and HREE in Choghart mine. Also these conclusions show that Choghart mine apatites are enriched from REE in such away that the percent of REE in these apatites is about 1.54%. The great slope of spidergrams and amount of \((\text{La/Lu})_{in}\) ratio show intense fractionation between LREE and HREE, depletion of HREE and enrichment of LREE in these apatites. Therefore apatites from this mine have very high values in order to obtain LREE or Ce group. We come to know that in mineral processing stage of iron ore of Choghart mine, if the apatite concentration with degree of high purity produces, then the extraction of these elements will be considerable.

Keywords: Rare earth elements, magnetite, apatite, Choghart mine, metallogenic province.

References
Cretaceous-Cenozoic exhumation of Dabashan from apatite fission track thermochronology and its implication for growth of the northeastern Tibetan plateau margin

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As a part of Qinling collisional orogenic belt, Dabashan located at the northeast margin of Sichuan craton basin and closely adjacent to the eastern Tibetan plateau margin, is an ideal region for better understanding the tectonic evolution of Qinling orogeny roundly and stepwise migration of the northeastern Tibetan plateau margin. Apatite fission track dating and time-temperature thermal history modeling were carried to analyze on 10 samples in the Dabashan. The new data yield ages ranging from 73±8 to 33±4 and mean track lengths between 11.4±1.6 to 12.7±1.6. Thermal history models based on the AFT data taken together with published K-Ar data (Zheng et al., 2006) indicate that the cooling and exhumation process of Dabashan can be divided into three stages since Cretaceous. The three stages are identified as (1) a phase of rapid uplifting cooling at 120-110 Ma, (2) following by a period of relative thermal stability during which rocks remained at temperatures with in AFT partial annealing zone (∼60-110°C), (3) ending with a new stage of accelerated uplifting during ∼10Ma to resent. The first rapid uplifting cooling phase has been suggested to reflect the large-scale transtensional deformation of Qinling orogeny belt, which is attributed to the Cretaceous eastward tectonic escape and Pacific backarc extension (Hu et al., 2006). Following the transition phase the subsequent slow cooling phase pattern implies a net reduction in horizontal compressional stress corresponding to increased extension rates along the continental margin due to the decrease in plate convergencce. The last accelerated uplifting event is response to eastward growth of Tibetan plateau uplift and lateral growth, which continues today. Numerous studies of Tibetan Plateau suggest that the onset of deformation in eastern and northern margin of Tibetan Plateau occurred in the latest Miocene (Tapponnier et al., 2001; Kirby et al., 2002; Zheng et al., 2006; Enkelmann et al., 2006).

Pedogenic origin dolomite developed within calcium concretion of Tertiary red clay at Loess Plateau, China

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Previous research has shown that the land-origin dolomite was almost deposited at the high salinity environments. Only a few researches reported the un-salina origin dolomite was existed in the paleosol of Hawaii for a particular geologic reason and not any data regarding the authigenic dolomite in Chinese Loess has been recorded.

The carbonate concretions are widely existed in Tertiary red clay layers developed at the Xifeng area of Loess Plateau, central China. With application of the XRD and the high-resolution SEM and TEM, lots of dolomite in rhombohedron in company with palygorskite has been detected, distributing along the dissolved interspaces within the calcium concretion. The morphological characters of those minerals indicate they are authigenic origin and come into being during the pedogenic period of the red clay. The former appearance needs enough Mg2+ in environment. In this case, Mg2+ is thought from the condensation of the outcome of the thorough weathering of the carbonate and silicate after the action of the heavy precipitation during the pedogenic period. The latter is widely considered only formed under the extremely dry climate. Electron Microprobe analysis farther testifies that the dolomite is with low Mg concentration and the lower ratio of Mg/Ca. Moreover, the cations such as Mg2+, Sr2+, Na+ etc. in dolomites at the different carbonate concretions are in a wide range, indicating the dolomites don’t come into being in the unitary soil solution, but at the dividable micro-environments with different salinity.

It can be concluded that, when the red clay come into being, the climatic condition was characterized as the alternation of heavy precipitation-high temperature and dry-high temperature. The result has also provided an example to explain the cause of formation of dolomite in terrigenous fresh-water environment.

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References
Surface complexation of Uranium(VI) on Fe/Mn (hydr)oxides

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The fate and mobility of U in oxic soils, groundwater and the marine environment is controlled by sorption of UO$_2^{++}$ onto nanocrystalline iron and manganese (hydr)oxides. Thermodynamic models for such reactions are needed before we can understand the aqueous geochmistry of U. However, we cannot develop useful thermodynamic models until we have a molecular-level understanding of U sorption and complexation. Previous EXAFS studies of UO$_2^{++}$ sorption on FeOOH have been interpreted as indicating an inner-sphere >Fe(OH)$_2$UO$_2$ surface complex formed by edge sharing with FeO$_6$ polyhedra (2E complex). However, this complex is at odds with the known surface site densities of FeOOH phases. On goethite, for example, 2E complexes can only occur on the {210} and {010} planes (space group setting Pnma) which comprise only a small fraction of the surface area. Here, we show that previous EXAFS spectra have been misinterpreted owing to the neglect or incomplete inclusion of multiple scattering. The dominant UO$_2^{++}$ surface complex on FeOOH is >Fe(OH)$_2$UO$_2$(H$_2$O,OH)$_3$ and >Fe(OH)$_2$UO$_2$CO$_3$ (2C complex) resulting from bidentate corner-sharing with two adjacent FeO$_6$ surface polyhedra. Ab initio calculations of U-O and U-Fe distances in the 2C complexes are consistent with the EXAFS results. On goethite, 2C complexes can form on the {101} planes which comprise nearly all of the reactive surface area; the 2C complex explains the high sorption capacity (>2 wt%) for U(VI) on goethite and, apparently, ferricydrite.

We developed a surface complexation model to fit a series of sorption experiments of U on goethite and ferricydrite. Using a 1pK formalism and Basic Stern model for electrostatics, we found we could fit our data using >Fe(OH)$_2$UO$_2$(OH) and >Fe(OH)$_2$UO$_2$CO$_3$ (2C complexes) consistent with EXAFS results. An analogous model for U sorption onto hexagonal birnessite was developed using the >MnO$_2$UO$_2$OH and >MnO$_2$UO$_2$CO$_3$ complexes assuming that UO$_2^{++}$ complexes over vacancies in the phyllosilicate layer. Implications of our models for the fate of U(VI) in soils and aquatic environments will be discussed.

The Os isotope heterogeneities in the mantle sequence of the Bangong Lake ophiolite, northwestern Tibet

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Two type harzburgites occur in mantle sequence of the Bangong Lake ophiolite, NW Tibet. Type I is Cpx-bearing harzburgite with Cr$^2$ = 20–25 of spinel reflecting 10–15% degrees of partial melting; Type II is Cpx-free harzburgite with Cr$^2$ = 69–73 of spinel representing 35–40% degrees of partial melting formed in the suprasubduction zone (SSZ) [1]. In Type I, the $^{187}$Os/$^{188}$Os ratios (0.12446 to 0.12853) are chondritic and the $^{187}$Re/$^{188}$Os ratios (0.44 to 1.77) are suprachondritic reflecting that Re gain recently by basaltic melt percolating during the formation of the Bangong Lake crust 167 Ma ago [2], while in Type II, part of $^{187}$Os/$^{188}$Os ratios (0.12166 to 0.12896) are subchondritic, this can be explained by Re depletion during ancient partial melting. The old Os isotope model age (>950 Ma) of one Cpx-free harzburgite in a young ophiolitic mantle show that ancient Os isotopic heterogeneities can survive in the Earth upper mantle.

Osmium concentrations tend to decrease from Type I (Cpx-bearing harzburgites, 5.25-5.45ppb) to Type II (Cpx-free harzburgites, 4.4-4.45ppb, one sample is 1.32ppb) indicating that Os does not behave compatibly during melt percolation as it is observed during partial melting, but becomes dissolved and mobilized by the percolating melt [3]. But the heavy serpentinization likely caused the Os loss by the sulphide decomposition in a SSZ environment with high fO$_2$.

This study shows that Type I and II harzburgites of the Bangong Lake ophiolitic mantle have complex and different evolution. However, the Os isotopic features are consistent with a model where the two type harzburgites belong to the same melting regime producing the Bangong Lake oceanic crust. This scenario is also observed early in Troodos ophiolite [3].

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References

Genesis of tholeiitic and calcalkaline series of Zao volcano, NE Japan arc, Japan

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Genesis of co-existing tholeiitic series (TH) and calcalkaline series (CA) in island arc and their relationship has been a focus of attention because it is critical to understanding magma genesis in island arc. The Zao is Quaternary volcano situated on the Tohoku Backbone Ranges, Northeastern Japan arc, and both of TH and CA co-exist in continuous volcanic activity (Sakayori, 1991). We investigated the Sr, Nd, Pb isotope and trace element compositions to discuss the genesis of TH and CA from Zao volcano.

The trace element compositions of the studied samples show the typical characteristics of island arc magma in the diagram of MORB normalized pattern, such as enrichment of LILEs and negative Nb spike. Positive Pb and Sr spikes are also apparent. The LILEs enrichment and negative spikes of Nb are relatively larger in CA than TH. Although abundance ratios of Cs/Nb of TH are restricted to 0.09 - 0.20, those of CA can be divided into two ranges, such as 0.20 – 0.25 and 0.42 – 0.57.

The isotopic compositions of TH are more enriched compared to CA. In all the diagrams presenting the relationship of the isotope compositions, TH and CA make different linear trends, which indicate the mixing relation. Furthermore, Pb isotopic compositions suggest that two depleted endmember is necessary to explain the trend of TH and CA. The depleted endmember of TH is relatively enriched than that of CA. On the other hand, tow enriched endmembers are required from the relationships between parent/daughter and the isotope ratios, because TH and CA show different linear trends in these relation and the linear trends are diverse in the direction of isotopically enriched side. The both of the enriched direction of TH and CA is differ from the mixing trend of mantle wedge and recycled materials form subducting slab observed from Northeastern Japan (Shibata and Nakamura, 1997). From the observations in the above, it can be concluded that four components are necessary to explain the chemical characteristics of TH and CA from Zao volcano and the different two enriched components are derived from different crustal materials, although the sources of those are not obvious yet.

References

Anthropogenic contamination of bivalves revealed by Cd isotopes

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We are studying Cd isotopic compositions in bivalves to assess their natural and anthropogenic variability and sources. Oysters (Crassostrea gigas) from BC were collected from Desolation Sound (BC coast) and Barkley Sound (west coast of Vancouver Island). For comparison, we analyzed bivalves collected off the coasts of France, oysters (C. gigas) from the Gironde estuary and northern Brittany and mussels (Mytilus galloprovincialis) from the Gulf of Lion.

Cd isotopes were measured by dynamic multi-collection using a Nu Plasma MC-ICPMS and sample-standard bracketing technique together with external normalization to correct for instrumental mass bias. Results are reported in del notation (δ), normalized to a mass difference of one atomic mass unit. Our reference Cd standard (High Purity Standards, Inc., lot 291012) has the same Cd isotopic signature as JMC Cd [1,2]. Reproducibility is estimated from repeat analysis of a secondary Cd standard (High Purity Standards, Inc., lot 502624), 0.37 ± 0.03 permil/amu (2SD; n=31).

BC oysters have Cd isotopic signatures consistent with those reported for seawater from the N Pacific [3,4] suggesting that the high Cd concentrations (4.8-15.8 ppm tissue dw) found in bivalves along this coast result from natural coastal upwelling. Oysters from the BC coast have a slightly lighter signature than those from the west coast of Vancouver Island, potentially resulting from a larger anthropogenic contribution consistent with this geographical location. Mediterranean mussels have Cd isotopic signatures within the range of NW Mediterranean seawater values [3]. Oysters from northern Brittany and the Gironde estuary have signatures significantly lighter than the literature value for the Atlantic [4]. The Gironde oysters have the lightest signatures consistent with pollution resulting from industrial evaporation-condensation processes, as documented by the shift to δ = –0.16 permil/amu for two dust samples from a Pb-Zn refinery plant in northern France [2]. These results demonstrate the ability of Cd isotopes to trace anthropogenic pollution.

References
**Geochemical variation and residence time of groundwater in Mt. Fuji area, central Japan**

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Many groundwater samples were collected from Mt. Fuji area, central Japan which is totally composed of basaltic materials. The samples were analyzed for Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Si, Al\(^{3+}\), Fe\(^{2+}\), Fe\(^{3+}\), TC (total dissolved carbon), Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\) and TP (total phosphorus). Analytical data plotted against altitude indicate that alkali and alkali earth element (Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Ca\(^{2+}\)) and Si concentrations increase with decreasing altitude, indicating that the dissolution of silicates in basaltic materials control the trends. Ca and Mg concentrations positively correlate with each other and the correlation coefficient is 1.64. This is consistent with CaO/MgO molal ratio of basalt which is 1.47. Therefore, it is inferred that Ca and Mg in groundwater were derived mainly from the congruent dissolution of basalt. Ca/Si concentration ratio determined by the dissolution reactions of basalt accompanied by the precipitation of allophane is 0.29 which is lower than 0.48 estimated from the analytical data on groundwater. This lower value could be due to the precipitation of silica mineral (SiO\(_2\)). The agreement between theoretical and analytical results indicate that Ca, Mg and Si concentrations of groundwater are governed by dissolution and precipitation reactions. In order to interpret groundwater chemistry and estimate residence time of groundwater in southeastern part of Mt. Fuji area (Kakitagawa site) was estimated to be several years to 30 years. This estimated residence time is consistent with isotope data (herium isotope and tritium concentration).

**CO\(_2\)-water-basalt interactions: Experimental and mineralogical study**

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**Introduction**

Development of a better understanding of fluid-rock interaction is important in many areas of applied science and basic research. Investigation of reaction of basalt with H\(_2\)O and CO\(_2\) at different P-T-fO\(_2\) conditions is important both for planetary processes including processes in subduction zones of the Earth and mineral storage of CO\(_2\) including the problem of reducing the anthropogenic CO\(_2\) emission into the atmosphere. We have carried out experimental, mineralogical and carbon stable isotope study of this reaction.

**Experimental Method**

Carbonation experiments were run by exposing natural basalt powders (100-200\(\mu\)m grain size) to CO\(_2\) and H\(_2\)O under various conditions in a hydraulic press (total pressure 1 kbar and 400-500\(^\circ\)C). Oxalic acid (H\(_2\)C\(_2\)O\(_4\)) was used as a source of CO\(_2\) and H\(_2\)O. Additional amounts of H\(_2\)O were added in the platinum capsules. The thus produced CO\(_2\) and H\(_2\)O were then reacted with the basalt powder at high pressure and temperature. Gas phase and solid products of experiments were analyzed by manometry, step heating and mass-spectrometry techniques. Mineralogical study of the products of experiments by Scanning Electron Microscopy allowed the identification and observation of carbonates and water-bearing minerals.

**Discussion and Conclusions**

Our experimental results document the effect of the H\(_2\)O-CO\(_2\) medium on basalts under these P-T conditions and that calcite forms during the carbonation of plagioclase. We observed that carbonation reaction in basic rocks is different from that in ultrabasic rocks. Pressure, temperature and molar fractions of H\(_2\)O and CO\(_2\) are important parameters whose influences were quantified. Measured \(\delta\)\(^{13}\) C of gas and solid phase allowed to discuss kinetic and thermodynamic factors of carbon isotope fractionation in such reactions and are discussed in terms of mass balance.
A study on the formation mechanism of Temagami Iron-Formations, Canada

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In order to elucidate systematically the formation mechanism of BIF (Banded Iron-Formations), a BIF sample collected at Temagami, Canada was characterized by optical microscope, EPMA, Xray microscope, SIMS, and chemical analysis. This BIF can be divided into three layers visually; black layer, white layer, red layer. Main minerals in the three layers were magnetite, dolomite and quartz with fine hematite particles respectively.

To estimate the formation temperature of each three mineral and the formation environment (especially oxidation-reduction conditions), the oxygen isotope ratios (¹⁸O/¹⁶O) and contents of rare earth elements were measured by SIMS and chemical analysis. The isotope equilibrium temperature of dolomite and magnetite located in the white layer were 250-350°C. In the rare earth elements patterns for all the layers, a positive Eu anomaly appeared suggesting contribution of the anoxic submarine hydrothermal fluid for the formation of the BIF. On the other hand, a negative Ce anomaly, which indicates a character of oxic sea water, was observed for a part of samples of the red layer. These dolomite and magnetite may be formed under reduction conditions at high temperature, that is, from mixed water of the large amount of anoxic hydrothermal water of 250-350°C and the small amount of oxic sea water. While magnetite and dolomite located in the black layer shows lower formation temperature of 100 °C than that of magnetite and dolomite in the white layer. The latter magnetite and dolomite may be formed from hydrothermal water with high mixing percentage of seawater.

As mentioned above, each mineral in the layers might be precipitate from the fluids formed by mixing of large amount of anoxic submarine hydrothermal fluid with high temperature and small amount of oxic seawater with low temperature. The mixing degree may be different among minerals in the BIF.

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High-grade Ag-Cu-Sn-In mineralization in the Nishizawa-Ashio area, Tochigi Prefecture, central Japan

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Mineral Identification and Observation

Polymetallic (Au-Ag-Cu-Pb-Zn-Fe-As-Sb-Bi-Sn-In-W) vein-type mineralization in the Nishizawa-Ashio area occurs in strongly altered late Neogene felsic volcanic rocks. Recently Ishihara (2006) and Ishihara et al. (2006) reported that indium had been exploited in ore concentrates (e.g., 1200 tons In at Ashio). At Nishizawa, roquesite and “sakuraiite” (CuZnInS₄) were identified as discrete In minerals, associated with Pb,Se-bearing matildite, electrum (Au:Au ≒ 5:5–7:3), chalcopyrite, sphalerite (1-2% FeS), cassiterite and quartz. Canfieldite-argyrodite, Se-bearing acanthite, proustite-pyrrargyrite, Ag-bearing tetrahedrite-freibergite (Cu:Au=5.4:6-4.2:5.7), smithite and ferbeite (Fe:Mn=9:1) are also observed. Roquesite frequently occurs as radiating prismatic crystals (up to 0.5 mm), and sometimes as intergrowths with “sakuraiite”.

Conclusions

In-bearing sphalerite as solid solution between sphalerite and roquesite has been previously reported (e.g., Burke and Kieft, 1980). The roquesite-“sakuraiite” intergrowths at Nishizawa reveal no solid solution between roquesite and sakuraiite, and instead imply that In-bearing sphalerite represents solid solution between sphalerite and incompletely defined “sakuraiite” (with petruke as an intermediate phase?).

References

Geochemical study on Bousei, Hotta and Smetanin Seamounts near the Japan Trench in Northwestern Pacific Ocean

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The Northwestern Pacific plate is characterized by existence of a large number of seamounts (Koppers et al., 1998). It is widely accepted that these seamounts were produced by extensive magmatic activity during the Cretaceous in the South Pacific that is considered to be one of the largest volcanic events in Earth’s history. As this magmatism would represent large-scale mantle upwelling, the magmatism could provide a key constraint to understand chemical evolution of the Earth. Due to this importance, many researches have been conducted on the south Pacific islands, and thus present-day magmatism in the South Pacific is well constrained. In contrast, little constraint has been given to the past volcanic activity in this region.

It has been reported that there are two peaks in the volcanic activity in the South Pacific during the Cretaceous (after Winterer, 1976). As the volcanic peaks should be essential to understand the large mantle up-welling, an investigation on the volcanism during the Cretaceous should be important. The Cretaceous age seamounts near the Japan Trench (e.g., Takagi et al., 1989) are thus suitable examples to study the magmatism in the South Pacific. For the evaluation of the origin of these seamounts, we collected samples from these seamounts during Geological Survey of Japan Daini-Hakureimaru cruise. Drilling and dredging were conducted at 12 sites and fresh samples, alkali basalts and andesites, were recovered from three Seamounts; Bousei, Hotta and Smetanin Seamounts. The phenocrysts are mainly plagioclase and pyroxene with/without hornblende. The geochemical character of the rocks from the Bosei and Hotta are HIMU-type. In contrast, those from the Smetanin show less HIMU signature. In this presentation, we will discuss the origin of Seamounts along Japan Trench and constrain the volcanic activity in the South Pacific.

References

The influence of Philippine Sea Plate on the composition of mantle beneath Kyusyu, SW Japan arc: Along-arc variation of B data

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Volcanism in Kyusyu island is associated with subduction of Philippine Sea Plate (PSP) under Eurasian plate. Kyusyu-Palau Ridge, which subducts nearly at right angles to central part of Kyusyu, marks the boundary between young (15-26 Ma) PSP in the north and old (37-115 Ma) PSP in the south. Thus volcanic rocks from Kyusyu are good samples to test the compositional difference resulting from the subduction of oceanic plates with different ages.

We studied the difference in subduction component using boron element, As boron is enriched in altered oceanic crust and ocean sediment, it is one of the best indicators to show the contribution of fluid phase coming from the subducting plate to the mantle beneath volcanic arc. The release of the fluid phase from the oceanic plate is believed to occur in two manners. One is by aqueous fluid at high temperature, and the other is by the dehydration process, i.e. the breakdown of hydrous phases at high pressures. In this case, fluid is continuously released from the plate with increasing pressure, because various phases were involved in producing boron-rich fluid at different pressures.

The ratio of B/Nb was used to see the contribution of the subducting plate. It eliminates the influence of different degrees of partial melting in the mantle and fractional crystallization and crustal contamination in the crust.

The across-arc variation as observed by B/Nb ratios in volcanic rock is almost absent in the northern Kyusyu (NK), whereas it shows a gradual decrease in B/Nb from the volcanic front to the back-arc side in southern Kyusyu (SK). In addition, the B/Nb ratio of rocks from the volcanoes at the volcanic front is relatively high in the SK (~7.5), whereas it is relatively low in the NK (~3.5).

The lack of lateral variation in subduction component in volcanic rocks from the NK indicates a possibility that the release of fluid phase is completed before the oceanic plate reaches the volcanic front. The relatively low number in B/Nb ratio also supports this hypothesis. The young age of oceanic plate suggests a high temperature gradient in the depth profile of the subducting plate. In contrast, the volcanic rocks from the SK show a normal across-arc variation of subduction component typically related with the subduction of relatively old and cold oceanic plate.
Oxygen and sulfur isotope characteristics of the Salmagora Complex, Kola Peninsula

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Introduction
Oxygen and sulfur isotope study on the rock of dunite-wehrlite-mellitolite (type 0) from the early stage of magma differentiation and on the rock of pyroxeneite-ijolite (type 1 and type 2) from the later stage, which are classified based on the mineralogical and geochemical characteristics, is performed for the contribution to the petrogenetic model of the Salmagora ultramafic-alkaline-carbonatite complex in the Kola Peninsula.

Experimental Method
25 bulk rock samples were analyzed for oxygen isotope using silicate oxygen preparation line and Finnigan MAT 252 mass spectrometer in Indiana University and splits of the samples used for oxygen isotope were also analyzed for sulfur isotope composition by CF-mass spectrometer.

![Graph showing variations of oxygen isotope compositions of the Salmagora Complex.]

Results and Discussions
In Figure 1, we can observe that oxygen isotope composition systematically increases from type 0, type 1 and to type 2. Especially each rock type of pyroxenite, melteigite, ijolite and urtite in type 2 has higher value than that in type 1 by +0.6 to +2.4‰. Sulfur content was below analytical limit in type 0. The isotope composition varies from -9.3 to -4.8‰ for only melteigite in type 1 and from -4.2 to +1.0‰ in type 2. The increases in oxygen isotope composition from type 0 to type 1 can be explained by common magmatic differentiation process [1] with the influence of crustal contamination, while type 2 seems to indicate another highly evolved magma. Similarly, the low sulfur isotope values in type 1 may also be the effect of crustal contamination and the higher values of type 2 indicates the effect of more evolved magma.

Reference

Inorganic arsenic speciation in contaminated soils, in Korea

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Materials and method
The selected site for this study is an area of arsenic contaminated region (abondoned mine) and near land. Total arsenic concentration in soil samples and reference materials were as follows. 0.1g of sample was accurately weighed into acid washed digestion vessels containing 9ml of HCl and 3ml of HNO₃, and the resultant solution was heated at 140°C for 1hr in a digestion block. The solutions were allowed to cool and then diluted to 100ml with deionized water. The extraction of the arsenic species for speciation analysis were as follows. 0.1g of soil sample and 15ml of extractant (1M of phosphoric acid + 0.1 M of ascorbic acid) were reacted in a microwave system (Milestone 1200 Mega, power 60W, 15min). This solution is then cooled at room temperature and centrifuged at 2500 rpm for 30min. Total arsenic and arsenic speciation of the supernatant solution was analyzed by ICP-AES and SPE-HG-ICP-AES respectively.

Result and discussion
Total arsenic concentration in samples were measured between 109.97 and 11758.31ppm. In all samples, the majority of arsenic was present as AsV, while AsIII only account for < 3% of the total arsenic. The extraction efficiency, relative to the total arsenic concentration, varied from 25 – 108%. Most of the samples - except to one samples – showed recovery efficiency of above 86%. Only one samples exist both AsIII and AsV and recovery efficiency is not good (respectively 3.18% (AsIII) and 22.18% (AsV)). This sample is tailing which is mostly composed of calcite mineral. Concentration of the Ca is about 24%. AsIII of the tailing sample is presumed to be adsorbed on the calcite surfaces.

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Minor and trace element geochemistry of a branching coral *Acropora sp.* skeleton

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Incorporations of chemical elements and isotopes, into coral skeletons are influenced by ambient water conditions which may provide important information on past climate in the tropics. The geochemistry of *Acropora* is significantly important for the past-temperature reconstruction because *Acropora* is one of the main genera constituting the coral reefs. *Acropora* may also provide unique opportunity to evaluate the effects of physiological processes on the elemental incorporation. Branching coral *Acropora* consists of fast-growing axial corallite and slowly growing radial corallite at the visible scale. On the other hand, at the micro-scale, there are several types of skeletal elements precipitated under different biological mechanisms. However, geochemistry of branching corals has not been well understood. To investigate the mechanisms of elemental incorporation into *Acropora* skeletons, chemical and isotopic compositions in the skeleton were analyzed at various spatial resolutions.

The chemical profiles of both axial and radial corallite along with growth axes were measured by conventional ICP-MS and Stable Isotope Mass Spectrometry. The tip and basal parts of *Acropora* skeletons were also analyzed at micro-scale. The Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca ratios were measured in ~5μm diameter spots by using NanoSIMS, and Mg, Sr, Ca, and S distributions were analyzed by Electron Probe Micro Analyzer (EPMA), with a spatial resolution of ~2μm.

Based on the elemental distribution obtained by EPMA, we found that the *Acropora*’s skeleton is composed of more than three types of the skeletal elements, “Framework”, “Infilling” and “High-Mg Low-S” skeletons. Observation of skeletal structure revealed that the skeletal porosity decreased with distance from the tip, because “Infilling” skeletons possibly filled the space between “Framework” skeletons. Micro-scale elemental analyses (EPMA and NanoSIMS) revealed that “Infilling” skeletons have lower Mg/Ca and higher Sr/Ca and U/Ca than “Framework” skeletons. Since the “Infilling” skeletons were probably formed under the slower calcification rate than “Framework” skeletons, the elemental fractionation pattern between two skeletal elements is consistent with the model of elemental incorporations dependent on calcification rate. The chemical profiles of axial corallite along with the growth were significantly affected by the proportions of “Infilling” skeletons.

Mantle and crustal processes in the Hadean and Archean: Evidence for the onset of subduction at 3.8 Ga

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Considerable geochemical evidence supports initiation of plate tectonics on Earth shortly after the end of the Hadean. The present upper mantle retains old heterogeneities, some of which likely derive from subduction in the early Eoarchean. Nb/Th and Th/U ratios of mafic-ultramafic rocks from the depleted upper mantle begin to change from 7 to 18.2 and 4.7 to 2.9 (respectively) at 3.6 Ga. This signals the appearance of subduction-altered slabs in general mantle circulation from subduction initiated at 3.8 Ga. Juvenile crustal rocks begin to show derivation from progressively depleted mantle with typical igneous ε Nd: ε Hf = 1.2 after 3.6 Ga. Cratons with stable mantle keels that have subduction imprints begin to appear at 3.5 Ga. These changes all suggest that extraction of continental crust by plate tectonic processes was progressively depleting the mantle from 3.6 Ga onwards. Neoarchean subduction appears largely analogous to present subduction except for the production of large cratons with thick mantle keels. The earliest Eoarchean juvenile rocks and Hadean zircons have compositions that reflect the integrated effects of separation of an early enriched reservoir and fractionation of perovskite from the Mars-sized, impact-derived magma ocean, rather than separation of voluminous continental crust or oceanic plate tectonics. Hadean zircons most likely were derived from a continent-absent, initially mafic to ultramafic protocrust that was multiply remelted between 4.4 and 4.0 Ga under wet conditions to produce more evolved (felsic) rocks. If the protocrust was produced by global mantle overturn at ca 4.4 Ga, then the transition to plate tectonics resulted from radioactive decay-driven mantle heating. Otherwise, such protocrust would have been the typical product of mantle convection and the transition to plate tectonics resulted from cooling and stabilization of lithospheric plates.
The influence of neutron irradiation and thermal annealing on helium diffusivity in apatite

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Accurate extrapolation of helium diffusivity over temperature and time is essential for quantifying long term erosion rates and the topographic evolution of Cenozoic orogens using (U-Th)/He thermochronometry. Naturally occurring radiation damage was recently shown to influence helium diffusion in apatite, such that the kinetics is controlled by the parent nuclide concentrations as an evolving function of time [1]. This implies that apatite helium ages are sensitive to lower temperatures and shallower depths than indicated by the diffusion kinetics presently observed in a given mineral. Here, we present results of controlled experiments to quantify the effects of (a) synthetic irradiation and (b) thermal annealing on helium diffusion kinetics in both synthetic and natural apatites. Exposure to a 1 MeV equivalent neutron fluence ($\Phi_{eq}$ [MeV, Si]) of $2\times10^{18}$ n/cm$^2$ (90 hours in the cadmium lined in-core irradiation tube, CLICIT, facility of the Oregon State University TRIGA reactor) caused the helium closure temperatures ($T_c$; 10 °C/My) to increase by up to $+27$ °C. The $\Delta T_c$ negatively correlates with the initial $T_c$, where apatites with higher initial $T_c$ were less perturbed by the neutron irradiation than samples with lower initial $T_c$. Conversely, simply heating natural apatites to 550°C for 1 hour caused $T_c$ in all cases to decrease to $47\pm7$ °C regardless of the initial $T_c$ (the maximum observed $\Delta T_c$ = -44 °C). The resulting $T_c$ agrees well with diffusion parameters constrained [1] for radiation damage-free apatite, $T_c$ = 52 °C.

These results clearly demonstrate that exposure to radiation causes the retentivity of helium in apatite to increase, whereas exposure to temperatures at which thermal annealing occurs causes the retentivity to decrease. The experiments suggest that after 1 hr at 550°C, effectively all natural radiation damage was annealed in each sample to yield a common $T_c$. This closure temperature ($\sim47$ °C) would correspond to the diffusion kinetics in the damage-free apatite structure. From radiation damage theory we estimate the damage caused by the 90 hr neutron irradiation to be roughly equal to the alpha recoil damage corresponding to [4He] $\sim10^{-8}$ mol/g, or roughly the present 4He concentration of Durango apatite. This implies that Durango apatite should presently have $T_c$ $\sim27$°C above the completely annealed state, or $\sim74$°C, which is in excellent agreement with observations. This study highlights a need to quantify the kinetic effects of damage accumulation and annealing on helium diffusion in minerals used for (U-Th)/He thermochronometry.

Reference


Geochemistry of Late Cretaceous tholeiitic volcanism and oceanic island arc affinities of the Chagai arc

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The major part of the Chagai arc occur in the western-north part of Pakistan and a small part of it also extends towards north in Afghanistan and west in Iran. The Late Cretaceous volcanic rocks which are designated as Sinjrani Volcanic Group, is the most wide spread and the oldest unite of the Chagai arc. This volcanic Group is mainly composed of basaltic to andesitic lava flow and volcaniclastics including agglomerate.

The petrological studies of various lava flow revealed that these are mainly basaltic-andesites (53.27-55.93 wt.% SiO$_2$) with minor basalts (49.57-52.14 wt.% SiO$_2$) and andesites (59.12-59.88 wt.% SiO$_2$). Petrochemical studies based on major and trace elements suggest that these are medium to low K tholeiites. The trace element show variable enrichment in LILE and depletion in HFSE relative to N-MORB. Their primordial mantle-normalized trace element patterns show marked negative Nb anomalies with positive spikes generally on K, Ba and Sr which strongly confirm their island arc signatures. The chondrite normalized REE patterns shows minor but variable enrichment of LREE and positive Eu anomalies. The Zr/Y versus Zr, and Cr versus Y studies, lowers Mg # and lower abundances of Ni and Co suggest that the parent magma of these rock suites was generated by about 15-30 % melting of depleted sub-arc mantle source, and fractionated in an upper level magma chamber en-route to eruption. These volcanics exhibit lower $^{87}$Sr/$^{86}$Sr ratios (0.7038-0.7049), which are consistent with a depleted mantle source and closely correlate with oceanic island arcs rather than continental margin type arcs. On the basis of these studies it is concluded that the Chagai arc was initially developed as an oceanic island arc which was formed due to the intra-oceanic convergence in the Ceno-Tethys during the Late Cretaceous rather than constructed on the southern continental margin of Afghan block, as previously claimed by several workers.
The age of the Danube fault, 40 years after W. Schreyer

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As a result of his PhD study, Werner Schreyer published several papers about petrographic work in the Bavarian Forest where he investigated Variscan basement rocks close to the Danube valley. He also addressed the age of the Danube fault based on his observation from Natternberg, geological map sheet Deggendorf, and finally (in 1967) concluded that the Danube fault was formed during late-Variscan times and not, as suggested earlier (1961), during the Tertiary period.

The Danube fault stretches for about 200 km and is one of the most impressive fault lines in central Europe. As revealed by our recent field mapping, ancient motion along this fault has produced intensive cataclastic deformation along the Donaustauf segment of the fracture zone. The strain localised in this zone resulted in pervasive brittle deformation of the primary rock type, K-feldspar dominated granite. The cataclastic material was ultimately subjected to argillic alteration and K-feldspar was almost completely transferred into illite and other phyllosilicates. The crystallization age of the granite (known as “Kristallgranit”) derived from an unaltered sample is 325 Ma (Pb-evaporation method) whereas the age of argillic alteration is constrained by K-Ar dating of illite fine-fractions (<2 µm) at 266 and 255 Ma. The new ages bracket the time of deformation and imply near surface exhumation of the fault rocks already during the Permian period, confirming Werner Schreyer’s conclusion from 1967. Post-Cretaceous movement along the Danube fault, as indicated by offset of Mesozoic and Tertiary strata, did not re-open the K-Ar illite system. The illite ages also suggest that hydrothermal fluorite mineralization, genetically connected with the Danube fault, was an early Permian process.

References
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Peat deposits from Central Europe to the East European Plains investigated by uranium-series dating

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Interstadial and interglacial peat deposits are widespread in a transection between Central Europe, Lithuania, Russia, and Siberia, and enable us to reconstruct the vegetation history of the Northern Hemisphere. Multidisciplinary studies including lithostratigraphy, palaeontology, and palynology were performed by partners all over the transect. The reliable chronological frame for the reconstruction of climate and vegetation history was investigated by uranium series dating. The suitability of the peat layers for dating strongly depends on two essential prerequisites: (1) during the initial formation process any thorium was absent and (2) a geochemically closed system behaviour excluding uranium and thorium migration after deposition. However, peat may contain varying amount of admixed thorium by dust and clay minerals, while water passing through the peat layer can cause migration of uranium. Therefore, dating has to be carefully checked for the fulfilments of the prerequisites. Uranium series dating was performed on peat and organogenic deposits applying the thermal ionisation mass spectrometry (TIMS). Coeval peat samples were burned to ash and prepared by the leachate/leachate technique, spiked, and chemically separated for measurements of the isotopic composition. Once isotope activities are determined, age calculation depends on the evaluation techniques used to obtain reliable ages. The evaluation procedure includes (1) estimation of the thorium index by the isochron method to (2) correct the activity ratios for admixed detrital thorium, (3) calculation of corrected single 230Th/U ages, (4) checking corrected ages with the Chi-square test, and (5) calculation of weighted mean of isochron derived detritally corrected age for the deposit. The study of a variety of sections of burial peat on the transect gave a widespread overview on the suitability of peat deposits. Several case studies were investigated by uranium series dating. At the Netiesos section located in Lithuania, the age determination for the peat failed owing to the impossibility of determining an isochron to correct the single ages for the admixed detrital thorium. Furthermore, the investigation of the peat section of Gröbern, Germany, failed due to wide spreading activity ratios clearly demonstrating open system behaviour. Comparisons with radiometrically investigated uranium series ages retrieve the possible reasons. An isochron derived detritally corrected age of 219 ±8 ka was successfully determined for the peat layer from Krivosheino in Siberia, which is in excellent agreement with independent age control.


210Pb-226Ra disequilibrium in basalts from Surtsey Island (Iceland) and implications for magma transport time

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Primitive basalts with radioactive disequilibrium between isotopes of the 238U decay chain may provide constraints on the timescales of mantle melt migration. Few results still exist on the 210Pb-226Ra disequilibria. Due to the short half-live of 210Pb (22.3 years), only basalts significantly younger than 100 years old can be studied for 210Pb-226Ra disequilibria generated in the magma pluming system or the mantle. Most lavas measured so far show either 210Pb-226Ra equilibria or 210Pb-deficit which have been attributed to the degassing of 222Rn in shallow magma chambers. Excess 210Pb has also been observed in a few cases and explained by accumulation of 222Rn that decays to 210Pb. Icelandic tholeiites from the last century are in radioactive equilibrium with (210Pb/226Ra) equal to unity. These basalts are fed from shallow magma chambers having residence time exceeding 100 years. In contrast, primitive alkaline basalts (MgO =7-12 %) from Surtsey island had (210Pb/226Ra) ranging from 0.45 ±0.04 to 0.82 ±0.06 at the time of eruption. These large 210Pb deficits are unlikely to result from shallow magma degassing since no magma chamber existed beneath this volcanic island which was born during the 1963-67 eruption. The 210Pb-226Ra disequilibria increase from the beginning towards the end of the eruption when the most primitive basalts were produced, and decrease systematically with increasing Th content. These same basalts show a negative correlation between Pb and Cu abundances which are inconsistent with exsolution of sulfur rich liquid or crystallisation of sulphides as a fractionation mechanism of 210Pb and 226Ra.

The large deficit of 210Pb in Surtsey lavas were thus most likely generated during mantle partial melting. In such a case, the time of melt transport from the source region to surface is constrained to be significantly shorter than 100 years.

Climate changes and volcanic signals during the Bronze Age: A stalagmite record

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In this study we present high-resolution and multi-proxy records of a Holocene stalagmite showing volcanic signals detected the first time in a stalagmite by REE analyses. Stable oxygen and carbon isotope data profile along the speleothem deposited during the last 5000 years in the Mecsek Mts. (S-Hungary) suggest relatively stable conditions in most of the studied period. However, a significant d18O decrease (>2 %o) between approx. 3800 and 3500 years BP occurs in the record. Fluid inclusion water shows also significant D-depletion, supporting cooling. Combined isotope and trace element measurements indicated coupled temperature and precipitation quantity changes occurring in the above period. Rare earth elements (REEs) were also measured by LA-ICP-MS technique, and unlike the longer trends shown by C and O isotopes, the REE and Y distributions indicate sudden changes at the beginning of the cooling period. The La/Y ratio of this segment shows similarities with the volcanic rocks of of the Thera (Santorini) eruption that occurred at about 3650 years BP. As an independent indicator, 87Sr/86Sr ratios show slight decrease at the REE peak, supporting the inferred volcanic signal.

The climatic conditions ameliorated rapidly (within ~100 years) to close to present day conditions as reflected by the C, O and H isotope compositions. However, some of the trace elements show marked changes following the recovery. Elements indicating detrital material within the carbonate matrix (e.g. Si, Al, Th) show marked elevations, along with 87Sr/86Sr increase, suggesting increased amount of silicious material transported by dripwaters. However, the Mg content is also higher at this section part, thus, the increase of detrital material amount may be related to lower carbonate precipitation rate, rather than to stronger weathering of silicate rocks.

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A geochemical gradient along the North Mid-Atlantic Ridge revisited: New Hf and Pb isotope data

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Basalts dredged along the Mid-Atlantic Ridge north of the 15°20’N fracture zone and the so-called 14°N anomaly (Bougault et al., 1988), from 15° 44’ to 17° 28’ show a well-documented gradient from enriched to depleted chemical characteristics (Dosso et al. 1991) where Sr isotopic compositions vary from 0.70288 to 0.70217, respectively.

We will present new Hf and Pb isotope data for this region of the MAR. Preliminary results show that the Hf and the Pb isotope ratios range between the ambient local MORB mantle source that defines the 14°N bathymetric and C-like (Hanan and Graham, 1996) geochemical anomaly and an extremely depleted mantle source unlike any other so far recognized along the North Atlantic ridge. The results will be discussed in terms of the regional tectonic framework.

Detection of biomarkers in oils using ToF-SIMS

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To identify biological traces in geological samples molecular biomarkers are widely used. Traditionally GC-MS (Gas chromatography-mass spectrometry) has been used for the analysis. In recent years when concentrations of target compounds were low surface sensitive ToF-SIMS (Time of Flight – Secondary Ion Mass Spectrometry) analysis has been applied. We present the results of a study using GC-MS and ToF-SIMS for the characterization of biomarkers in oils and oil extracts, aiming to prepare for the analysis of smallest quantities in oil samples recovered from fluid inclusions.

The biomarkers steranes and hopanes were characterized using polyatomic primary ion source (Bi⁺) ToF-SIMS. These compounds were present in hexane extracts from natural oil samples by GC-MS analysis. The same extracts were analyzed by ToF-SIMS, allowing identification of individual biomarkers in this complex sample extract. This information was then used to interpret ToF-SIMS spectra derived from the crude oil by direct analysis. Although these spectra show the presence of a vast variety of components and compound fragments, the target biomarker components could be identified.

This initial study was done in preparation for the investigation of oil-bearing fluid inclusions in rocks from different environments and of different ages. Fluid inclusions may provide a wealth of yet undiscovered information due to their isolation from the environment. The capability to characterize smallest biomarker quantities from oil-bearing fluid inclusions contributes to the understanding of the environment in which the oil was formed and could provide insight into the biodiversity of early Earth.

References

Arsenic contamination of drinking water in some localities of Vila Real – Northern Portugal

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The occurrence of problems resulting from arsenic contamination of drinking water in Vila Real (Northern Portugal) was recognized by the Supplier Company of domestic water itself. One of the most significant water quality problems that will be present for a long time to come is the Rebordolongo site, which has arsenic contamination far in excess of any other area.

This preliminary study discusses the geological occurrence, the origin, the environmental impact and the health risks of arsenic in drinking water of the public water supply of Rebordolongo. The approach taken by this study was to compare the water quality were from boreholes and wells with the water quality in the homes of the consumers. Hydrochemical analyses have confirmed the presence of dissolved arsenic in drinking waters, with concentrations exceeding the current WHO potable water guideline. The total arsenic content of all these waters varies between <10 µg/L, and 28 µg/L.

The field work have confirmed placed near the one of the wells an abandoned wolfram mine, the waste from which is typically rich in arsenopirite. The mineralogical composition of quartz-veins and waste samples from the mining site were undertaken to assess their potential as a subregional source of arsenic contamination. Tailings from the site are predominantly composed of quartz detritus with abundant arsenopyrite. The sulphides are mainly arsenopyrite and pyrite, with some galena and chalcopyrite.

The relatively high arsenic concentrations in the waters from the mine site may reflect the oxidation/weathering of arsenopyrite and other sulphide-bearing mine tailings. This allows for the solubilization of metals. Arsenic concentrations in domestic water were higher than those in the water from boreholes, probably suggesting direct mixing of effluent from mining area. Meanwhile, the domestic waters do not contain more than 14 µg As/L. However, arsenic is highly concentrated in the iron oxyhydroxides sampled in the bottom of the water reservoir. Upon contact with air, these waters locally form oxyhydroxides deposits, sorbing effectively arsenic. These deposits contain 0.83% As. Therefore, one can conclude that the environmental and health impact of these waters in Rebordolongo is not negligible.

A complementary phase that is in progress intends to characterise arsenic and heavy metals speciation more clearly and determine the link with iron oxyhydroxydes.

Global Ca-isotope signatures in post-Snowball Earth cap-carbonates

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δ44/40Ca(seawater) values of Neoproterozoic cap-carbonates in NW Canada and NE Brazil overlying glacigenic units are reported. While cap-carbonates (Rapitian and Jaccoca Fms) overlying ca 0.74 Ga Rapitian diamictites display δ44/40Ca(seawater) values increasing from −1.9‰ to −0.7‰, cap-carbonates (Raventhroat-Hayhook and Acaua Fms) overlying ca 0.635 Ga Marinoan diamictites display δ44/40Ca(seawater) values decreasing from -0.9‰ to –1.8‰, followed by a progressive up-section increase to values near 0‰. The δ44/40Ca(seawater) values displayed by the post-Marinoan cap-carbonates are undistinguishable from those of their correlative Kailber and Maiberg Fms (NW Namibia, Kasemann et al., 2005). We suggest that changes in the δ44/40Ca(seawater) values of the studied cap-carbonates reflect changes in the Ca-isotope composition of their coeval seawater. The similar δ44/40Ca(seawater) values displayed by coeval carbonates from a deep to shallow marine profile (lower Hayhook Fm) suggest a homogeneous Ca-isotope composition of oceans. Differences in the degree of diagenetic overprint of these samples along with the sub-greenschists facies of metamorphism of the Brazilian cap carbonates suggest preservation of the sedimentary Ca-isotope compositions even after diagenesis and burial. The global nature of the δ44/40Ca(seawater) values, along with varying Ca-isotope compositions with stratigraphy displayed by the post-Marinoan and Post-Rapitian cap-carbonate indicate that Ca-isotope stratigraphy can be used to correlate cap-carbonate successions worldwide.

Reference
Macroscopic and infrared spectroscopic investigation of the synergistic effect between small organic ligands and desferrioxamine-B on the dissolution of goethite

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In several recent papers, Kraemer et al. [e.g. 1-2] have suggested that the dissolution of goethite by desferrioxamine-B (des-B) is enhanced in the presence of small organic ligands such as oxalate that actively shuttle iron from the goethite surface to bulk solution. The goal of the present study was to further an understanding of this phenomenon in both the oxalate- and malonate-goethite-des-B systems using macroscopic and spectroscopic methods. All experiments were performed at 25 °C in the absence of visible and ultraviolet light. The amount of oxalate and malonate adsorbed and the concentration of Fe(III) dissolved were studied after a reaction time of one week at total ligand concentrations of both 0.1 and 1 µmol/m² and covering the pH range 3 to 9.5. Several different types of in situ infrared spectroscopic experiments were performed at constant pH values of both 4 and 6, total oxalate and malonate concentrations of 1 µmol/m², and des-B concentrations of between 0.1 µmol/m² and 1 µmol/m². First, spectra were collected to monitor the adsorption and surface speciation of oxalate and malonate on the goethite surface in the absence of des-B as a function of time, and the desorption of these ligands was followed spectroscopically to clarify the relative stabilities of the different types surface complexes. Second, spectra were collected as a function of time after the simultaneous addition of 1 µmol/m² concentrations of both oxalate or malonate and des-B to identify the complexes present at the goethite surface. Third, oxalate and malonate were reacted with goethite in the absence of des-B, and then spectra were collected as a function of time after repeated 0.1 µmol/m² additions of des-B every 24 hours. These experiments have revealed the type of surface complex responsible for the synergistic effect between these small organic ligands and des-B on the dissolution of goethite. The results are also discussed with respect to their broader implications toward mechanisms for ligand-promoted mineral dissolution.

References

Variable Calcium isotopic fractionation factor in natural carbonated water

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Carbonates precipitated inorganically under laboratory conditions are fractionated relative to the coexisting solution by up to about -1‰ in their 44Ca/42Ca ratio [1,2]. Such Ca isotopic fractionation (44/42α_carb) is dependent upon the rate of carbonate precipitation with a temperature dependency as a knock-on effect [2] and has been attributed to kinetic effects. The mechanism by which Ca gets enriched in the light isotope in carbonate is rather controversial [1,2] but the experimental approach can be reconciled with the data obtained for biomineralisation. Evidence for a kinetic effect behind the preferential incorporation of light isotopes in inorganic carbonate is more elusive since studies at catchment scale [3-5] are complicated by the role of the vegetation and the incorporation or release of Ca by the biomass.

Here we report 44/42Ca for paired dripping water and speleothems previously studied for Mg isotopic fractionation [6]. The 44/42α_carb ranges from 0.9998 to 0.9988 while the 44/42Ca of the dripping water are either indistinguishable from the values of the country rock or enriched toward heavier values by up to 0.22‰. The largest 44/42α_carb is found in a slow dripping speleothem while fast dripping stalagmites precipitate carbonate weakly fractionated. Qualitatively, our data support Lemarchand et al. [2] model but with a much greater 44/42α_carb value for very low rate of carbonate precipitation. While this data is not direct evidence for an equilibrium fractionation of Ca isotopes, it is worth noticing that the incorporation of O and Mg isotopes in all of these speleothems occurs at equilibrium [6] and clearly suggests that the mechanisms responsible for Mg and O isotopic fractionations are distinct from those responsible for Ca isotopic fractionation.

References
Lithospheric geodynamics with thermo-chemical density anomalies and mineral phase transitions switched on

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Density is an important physical property of rocks, which e.g. determines the isostatic response of the lithosphere to deformation. The density of a piece of mantle depends on pressure, temperature and composition. These three parameters inevitably change during geological processes such as rifting, but can also vary in apparently passive settings, e.g. at the lithosphere-asthenosphere boundary. The density distribution of the shallow mantle is non-linear and discontinuous due to complex mineralogy and, most importantly, phase transitions. The two shallow phase transitions that have the strongest effect on density are the plagioclase-in transition above ~50 km and the garnet-in reaction below ~40 – 100 km. The depth of these phase transitions strongly depends on the bulk composition of the mantle. The depth of the plagioclase-in boundary is mostly pressure dependent and predominantly controlled by bulk Na2O/Al2O3, whereas the garnet-in transition has a steep and curved Clapeyron slope with a strong depth-dependence on bulk Cr2O3/Al2O3.

In an extending lithosphere, the density changes in the lithospheric column due to phase transitions can cause significant deviations from purely thermal subsidence. The amount of subsidence depends on the composition of the mantle, in addition to classical parameters such as the thickness of the crust, the initial geotherm and the amount of stretching. The phase-transition effect is most pronounced for thin crust, strong mantle thinning/upwelling and relatively fertile mantle compositions rich in aluminum and sodium, and can match the effect of thermal expansion. This could explain the pronounced syn-rift uplift and accelerated post-rift subsidence observed in some basins. The incompatible nature and strong mobility of sodium may lead to large changes in bulk Na2O, and therefore density, during minor melting (Na extraction) or metasomatism (Na addition).

Densification of portions of the mantle, e.g., due to melt infiltration and shifts in the location of phase boundaries, might also contribute to the formation of gravitational instabilities and small scale convection, e.g. at the lithosphere-asthenosphere boundary. The combination of 2-D finite element deformation modeling and thermodynamic phase diagram calculations allows us to evaluate and quantify the feedback between geochemical variations and lithospheric deformation.

Elemental and Sr isotope investigations of human tooth enamel by laser ablation-(MC)-ICP-MS: Successes and pitfalls

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Sr isotope analysis of human tissue has proven to be an important tool for examining ancient human migration. Previous studies have typically conducted Sr isotope measurements by TIMS; however, Sr isotopic measurement by solution mode MC-ICP-MS greatly increases sample volume throughput with little (if any) detriment to the quality of individual analyses (e.g. Buzon et al., in press). Recent studies have also reported reliable Sr isotope measurements and elemental concentrations within geologic and biologic samples at high spatial resolution using various LA-(MC)-ICP-MS instrument configurations. The relatively rapid nature of an individual laser ablation Sr isotope analysis (i.e. minutes) could possibly revolutionize (if successful) the manner in which migration studies of ancient civilizations are conducted in the future.

We investigated the elemental and Sr isotope ratios of tooth enamel from remains at the New Kingdom period Egyptian colonial site of Tombos (Sudan) by both laser ablation and solution mode-(MC)-ICP-MS analysis. Elemental abundances for both solution and laser ablation modes of analysis were obtained using a ELAN6000 quadrupole ICP-MS. Sr isotope measurements obtained in both solution and laser ablation modes were acquired with a NuPlasma MC-ICP-MS instrument. Laser ablation analyses were conducted using a UP213 system (New Wave Research).

Elemental abundances determined by both solution mode and laser ablation-ICP-MS analysis yield comparable values; however, 87Sr/86Sr values obtained by laser ablation are higher compared to their solution mode counterparts. This discrepancy is related to the production of a molecular interference- Ca+P+O (overlaps 85Sr); hence the higher 8Sr/86Sr values recorded during ablation analyses. Laser ablation studies of enamel may provide relatively precise 8Sr/86Sr values rather quickly but cannot be used for accurately deciphering historical population migrations (Simonetti et al. in press).

References

Characterizing degassing and magma recharge from measurement of short-lived U-series isotopes in volcanic gases and lavas

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Magma recharge and degassing are directly linked to volcanic activity. Determining the timescales of these shallow level processes is fundamental to our understanding of physical eruption dynamics and hazard assessment.

At many quiescent but potentially dangerous volcanoes, persistent degassing is the most common manifestation of volcanic activity. While it is generally agreed that these gas fluxes are mostly sustained by the exsolution of volatiles that were initially dissolved in the magma at depth, it has been unclear whether these gases originated from small ascending magma batches (ultimately recycled at depth once degassed) or large magma reservoirs beneath active volcanoes. Setting constraints on magma residence times in shallow degassing reservoirs and/or feeding systems is critical to distinguish between these two end-member models. Measurement of radioactive disequilibria between short-lived ²²²Rn, ²¹⁹Pb, ²¹⁸Bi, and ²¹⁰Po in gases and tephras collected from inside the Santiago Crater of volcano Masaya (Nicaragua). To our knowledge these are the first measurements of ²²²Rn from magmatic gases. Masaya’s (²¹⁸Po/²¹⁰Pb) and (²²²Rn²¹⁰Pb) are best explained by ²²²Rn enrichment and subsequent decay in gas bubbles of a magma body having a residence time between 3 and 150 years. Our measurements of radioactive disequilibria in Masaya's gases also display significant variability through time (periodically since 2000) that are correlated with observed variations in activity and gas fluxes at the surface. Taken together, these observations suggest that degassing occurs in a large magma reservoir beneath the active Santiago crater and that input of deep pristine magma into this reservoir controls the eruptive activity at the surface.

Anthropogenic signatures in sediments of the fast growing urban area of Natal (NE-Brazil) – A study of heavy metals and organic components

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In this study the effect of anthropogenic discharges on the composition of sediments in the Potengi – Jundiaí river system near the fast growing city of Natal, NE-Brazil, is investigated.

In general, the sediments of the Rio Potengí – Jundiaí river system in the studied area are not severely polluted. Rather they represent an incipient stage of anthropogenic accumulation. A previous study (Sindern et al. 2006) has shown that heavy metals such as Zn, Pb, Cu, Cd and in part also Sn, Hg and Ag have enhanced values relative to reference elements such as Al and Fe. Sources are domestic and animal waste, combustion products and hydrocarbons. These heavy metals are mainly bound to organic matter.

The elements Cr, Ni and V are characteristic of weathering heavy minerals in crystalline rocks exposed in the catchment area of the river system and are not significantly added from anthropogenic sources.

Additionally, a comprehensive spectrum of organic compounds was identified in sediment as well as water samples of the Potengi-Jundiaí river system. Individual organic components were characterized dominantly to be of biogenic origin. However, huge amounts of indicative substances, e.g. fatty acids, suggest a significant emission of natural organic matter as the result of anthropogenic waste discharge. This might reflect incomplete of insufficiently working waste water treatment. Further on, well known xenobiotics, such as plastiziers, pharmaceuticals or pesticides, were detected only to a minor extend, although this type of anthropogenic contamination has frequently been found in riverine systems. The anthropogenic impact on the organic emission within the riverine system differs significantly from the organic signature of rivers from other regions, e.g. Europe or North America.

References

Geochemistry and PGE potential of Bangur Gabbro from the Baula-Nuasahi Mafic Ultramafic Complex, Orissa (India)

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Geological set-up
The Baula-Nausahi mafic ultramafic complex comprises (1) Gabbro-Anorthosite unit, (2) Peridotite unit (with three chromite bands Ganga, Lakshmi and Sankar), (3) Pyroxenite unit and (4) Bangur Gabbro (~3.1 Ga) (Auge et al. 2003).

Geochemistry
The Zr/TiO\textsubscript{2}*0.0001 vs Nb/Y diagram shows these gabbros in the field of basalt. SiO\textsubscript{2}, Na\textsubscript{2}O and Al\textsubscript{2}O\textsubscript{3} show negative trend while MnO and Fe\textsubscript{2}O\textsubscript{3} show positive trend with MgO which indicates the differentiation trend of magma and is reflected in mineralogy. Trace element pattern of Bangur gabbro shows the positive Rb and Y anomaly and negative Nb anomaly. The positive anomaly of Rb and Y can be attributed to the development of secondary amphiboles due to alteration.

The metal ratio diagram shows the PGE potential of Bangur Gabbro as almost all the samples plots in the field of Layered complex. So the samples plotted above the extrusive rocks field also show enough potential as the chrome-spinel in Bangur gabbro may have affected the ratio.

Discussion and Conclusion
The hydrothermal processes have lead to the formation of secondary minerals as well as remobilization of Base metal sulphide. The metal ratio diagram shows the potential for PGE and supports the further investigation to delineate the mineralized zone within Bangur gabbro.

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The Alteration Mineralogy and Mass Change of Volcanics from Zigana (Gümüşhane, NE-Turkey)

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The Late Cretaceous volcanic rocks around Zigana Mountain (Gümüşhane) at the eastern part of Black Sea Region (NE-Turkey) belong to the east Black Sea metallogenic province, and have intensive hydrothermal alteration although weathering alteration is limited. The basement of the study area is formed by the Late Cretaceous basalt, andesite and their pyroclastics. These rocks are overlaid by the Late Cretaceous aged dactic rocks, namely Dacite-I and Dacite-II described by [1] and [2]. These volcanic rocks are bimodal in character and have tholeitic to calc-alkaline affinity, and have developed in volcanic arc environment. The Late Cretaceous rocks are the host of VMS and vein type deposits in the study area and region.

Volcanic rocks in the study area have been altered to the sericite/illite-chlorite facieses, and contain sericite/illite, chlorite, quartz, carbonate minerals (ankerite and calcite), iron-oxide, and rare kaolinite, smectite and epidote as the alteration products. Sericitization/illitization is the most common type of the hydrothermal alteration associated with the Zigana Volcanics, and chloritization is the second. Pyritisation is seen all volcanics, and the most commonly in dacites. In some fields, limonitisation is occasionally present. Epidotization is rare, and especially seen at basalt and andesite. Isocon method was applied to estimate the mass gains and losses of the Zigana Volcanics as a result of hydrothermal alteration. According to this, basalt and andesite, Dacite-I, and Dacite-II have 2-61 % mass gain, 71 % mass gain and 42 % mass loss, and 44 % mass gain and 32 % mass loss, respectively. Namely, both mass gain and mass loss have occurred in volcanics during the hydrothermal alteration of the parent materials. Illitization-chloritization-kaolinitization increase generally from least altered rock to highly altered rock, whereas carbonatization decreases. The relation between metals such as Cu, Pb, Zn and sericitization/illitization, chloritization and silisification shows that fluids which cause sericitization and chloritization did not increase the amount of these metals and, in fact, it can be said that this fluids are poor in these metals. This also shows that they developed under different hydrothermal conditions.

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References
Results of FTIR studying microdiamonds from gneisses and calc-silicate rocks from mine Kumdi-Kol, Northern Kazakhstan

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Statistically representative selection of microdiamonds from gneiss and calc-silicate rocks of the Kumdy-Kol deposit was first time studied by means of FTIR spectroscopy. Grayish yellow diamonds of the calc-silicate rocks are about 10-90 mkm in size and have cuboidal morphology. The morphology of microdiamonds from gneiss is more versatile. The crystals of octahedral, cuboctahedral and cuboidal morphologies were found there. They also have yellow color with grayish tint. The size of the gneiss microdiamonds varies between 15 and 150 mkm. The size of studied diamonds were about 60-150 mkm.

The selected diamonds have been studied with Bruker VERTEX-70 FTIR spectrometer equipped by Hyperion IR-microscope. IR spectra demonstrate that all of the studied diamonds contain nitrogen defects, which are manifested through the absorption at 1135 cm⁻¹ (C-defects) and 1282 cm⁻¹ (A-defects). Concentrations of nitrogen in the diamonds from different rocks are similar and vary from 700 to 2500 ppm (+20%). The nitrogen aggregation in the studied crystals varies from 30 up to 50% (+6-18%). The absorption at 3107 cm⁻¹ indicates the presence of hydrogen defects. The intensity of absorption at 3107 cm⁻¹ in gneiss diamonds is 5-20, while in calc-silicate rock diamonds - 2-10. Our data indicate that the studied microdiamonds belong to the Ib-IaA type.

IR spectra of diamonds from gneiss and calc-silicate rocks differ from each other in additional absorption lines. The spectra of calc-silicate rock diamonds testify to the presence of carbonate (1430 cm⁻¹) and silicate (1090 cm⁻¹) inclusions, water (banding vibrations at 1630 (1650)+5cm⁻¹ and stretching at 3420 cm⁻¹). The spectra of the gneiss diamonds do not demonstrate the presence of carbonates, silicates and/or water.

The differences of inclusion assemblages in microdiamonds from gneiss and calc-silicate rocks are the evidence of the extremely low mobility of the fluids/melts in the course of UHP metamorphism.

“Blood Coltan”: Fingerprinting of columbite-tantalite ores

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The term “Blood Coltan” was coined for columbite-tantalite ores in the Congolese civil war, as their sale supported the conflict, especially in the eastern provinces of the DRC. Following the United Nations initiative to fingerprint the origin of conflict materials, the German Ministry for Economic Cooperation and Development decided to fund this pilot study on fingerprinting coltan ores.

So far about 160 samples have been obtained from the world’s major coltan producing areas. Special attention is directed toward the Ta-Nb-Sn provinces in Africa: DR Congo, Rwanda, Mozambique and Namibia.

Using state of the art analytical tools, we are investigating a wide range of mineralogical and chemical parameters obtained from columbite-tantalite ores, in an attempt to distinguish between different ore provinces, down to the individual deposit scale.

Methods employed include XRF (bulk major and trace elements), XRD (structure), ore microscopy, fully automated electron microscopy (Mineral Liberation Analysis), electron microprobe analysis (major and minor), laser ablation-ICP-MS (trace elements, isotopes), and TIMS (U-Pb dating).

Elevated concentrations of U, and low amounts of common Pb in columbite-tantalite, facilitate the application of the U-Pb system to date columbite-tantalite. Consistent results of TIMS and LA-ICP-MS analyses in three different laboratories prove that columbite-tantalite yields concordant and reliable ages. In the samples analyzed so far from Africa, four age populations are evident: Archaean (>2.6 Ga), Palaeoproterozoic (1.9-2.1 Ga), early Neoproterozoic ("Kibaran"; 0.98-0.93 Ga), and early Palaeozoic (ca. 0.5 Ga). The bulk of the current Central African columbite-tantalite production is from Kibaran pegmatites associated with late “G4” tin granites. Trace element concentration patterns, mineral assemblages, and zoning characteristics in these pegmatites are clearly different from rare element pegmatite-hosted Ta mineralization in Alto Ligonha, Mozambique.
Study of trace elements reactivity in polluted soils: Measure of Cd, Zn, Cu and Pb lability by using DGT and isotopic dilution methods

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Industrial production and more precisely the metallurgy led to the dissemination of chemical contaminants in the environment. According to the metallurgical processes, this contamination can be more or less strong and induce, locally, grounds, water and plants pollutions.

In this study we try to quantify the labile pool of various trace elements in cultivated gardens, located around an industrial area.

The concentrations of heavy metals (As, Cu, Zn, Cd and Pb) measured in various cultivated vegetables are significatively higher than the european reference values (EC466/2001). The accumulation in plants differs in leaf, roots and fruits vegetables and is clearly correlated with the pH of the soils. In order to describe the heavy metal soil/plant exchanges, we tried to determine the concentrations of metals in the labile pool of the soils and to relate it to phytoavailability.

An isotopic dilution method (ID) using spiking with stable isotopes [1] and [2] has been performed in these polluted soils to determine the labile pool whereas a Diffusive Gradient in Thin film (DGT) method realised in the same soils permitted to mimic the heavy metal uptake by the roots of the plants [3]. The comparison between these two complementary methods allowed to describe the soil-solution transfer and demonstrated the different behaviours of the measured metals: relationships between labile pool measured by DGT and phytoaccumulation are observed for some of them, such as cadmium or zinc, but not for lead.

The kinetic aspects of the soil/solution exchanges were also described by performing ID and DGT, from 1h to 2 weeks. Modelization of these kinetiks gave us the parameters describing the exchange properties and the desorption of the metal from soil to solution. These parameters varied with metal concentration, pH or organic carbon content in the soils.

References

Organic microanalysis by time-of-flight secondary ion mass spectrometry

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Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is based on the analysis of positive or negative secondary ions emitted from a solid surface during bombardment by energetic ions. The technique has during the past decades become a well established surface analysis technique in materials science, in particular in the field of semiconductors and polymeric materials [1]. This is due to the attractive combination of high analytical sensitivity (in terms of absolute detection limits) and excellent imaging capability, with lateral resolution in the ~100 nm range. The application of the technique to more complex materials and molecular analysis was, however, for a long time hampered by the fact that the ionization process on which the technique is based lead to extensive fragmentation of and low yields (sensitivities) for organic anlyte molecules of masses higher than a few 100 u. This was in turn due to the properties of the primary ions used for accomplishing the sputtering and ionization of the sample under study.

During the last few years, there has been a strong development around TOF-SIMS for the analysis of organic materials and molecules. In particular, the development of new cluster primary ion sources (e.g., Au3+, Bi127+, C60+) have lead to dramatic improvements (typically by a factor 100-1000) in the detection sensitivity for organic molecules in the range from a few 100 u to 2000 u [2]. Due to the developments in instrumentation, in combination with a rapidly growing data base of reference spectra and the use of multivariate statistical tools for spectrum interpretation, TOF-SIMS is now emerging as a highly useful analytical tool for organic microanalysis, for example, in the field of biomedicine.

The presentation will give an introduction to TOF-SIMS, and illustrate the capabilities of the technique to more complex materials and molecular analysis was, however, for a long time hampered by the fact that the ionization process on which the technique is based lead to extensive fragmentation of and low yields (sensitivities) for organic anlyte molecules of masses higher than a few 100 u. This was in turn due to the properties of the primary ions used for accomplishing the sputtering and ionization of the sample under study.

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References
Fluid inclusions, REE and sulfur isotope geochemistry of the Lavrion carbonate hosted ore deposit, SE Attica, Greece

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The Pb-Ag-Zn sulfide mineralization of the ca. 3000 year old mining district of Lavrion, comprises mainly mantos and skarn-type massive sulfides. The area is a part of the Attico-Cycladic Belt (ACB). Late Miocene granitoid dykes and a granodiorite stock intruded the footwall of the detachment fault that separates the Basal Unit from the overlying Cycladic Blueschist Unit. Late Miocene porphyritic S-type granitoid rocks occur as sills along or within the hangingwall close to the detachment fault. The manto-type ores are spatially associated with the detachment fault, shear bands within marbles, and the shear contacts between marbles and the intercalated metaclastics of the Basal Unit, indicating that the most important structural control of the Lavrion mineralization is related to the large-scale back-arc Miocene extension in the Aegean. The mineralizing event postdated the mylonitic deformation stage of the marbles, as proved by the alignment of ore bodies with the mylonitic foliation planes or by their crosscut relationship. Wall-rock alteration is characterized by carbonatization and minor silicification. Ore deposition involved mainly marble dissolution and replacement, and open space filling.

Fluid inclusion studies provide evidence for deposition of sulfides of the manto-type mineralization at temperatures of about 280°C from fluids having salinities between 14 and 17wt% NaCl eq. Quartz and fluorite deposition occurred at lower temperatures (250 to 125 °C) from fluids having highly variable salinities (1-19 wt% NaCl eq.). The δ34SCTD values of galena, sphalerite and pyrite range between -4.8 to +3.99 per mil. Most paired samples of sphalerite-galena, sphalerite-pyrite and galena-pyrite show either reversed fractionations or unreasonably high temperature values, indicating either sulfur isotope disequilibrium or noncontemporaneous precipitation of sulfides. Chondrite-normalized REE patterns in fluorites show slightly increasing LREE and decreasing HREE contents. All fluorite samples possess weak negative Ce and pronounced positive Eu anomalies. A meteoric water influx late into the granodiorite stock is documented by the fluid inclusions in quartz of widespread extensional quartz veins. There is no clear evidence whether a direct genetic link exists between the manto-type massive sulfides and the Late Miocene igneous activity in the footwall of the detachment or along the detachment fault. Ag-rich sulfide mineralization forming tension gashes within hydrothermally altered hornfelses postdates contact metamorphic phenomena.

Adsorption energy trends on UO2 and ThO2 surfaces

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Determining the interaction of adsorbates such as water and oxygen with surfaces of uranium and thorium dioxide is important for the long-term storage of these isostructural nuclear fuel materials. The semi-conducting versus insulating nature of UO2 and ThO2, respectively, makes comparison of surface-adsorbate interactions with these materials possible as a function of electronic structure in addition to surface structure. Previously, the quantum mechanical code CASTEP was used to calculate surface energies for UO2 and ThO2, and the (111) surface was found to be the most stable relative to the (110) and (100) surfaces in both cases (Skomurski et al., 2006). In this study, CASTEP was used to investigate the interaction of water and oxygen with UO2 and ThO2 slabs of finite thickness representing each crystallographic orientation. The effect of model set-up on adsorption energy trends is discussed for single versus double-sided models in a periodic setting.

On a defect-free (111) surface, the adsorption of molecular water is found to be more favorable than dissociated water for both UO2 and ThO2. On the more reactive (110) surface, however, the opposite trend is favored. The adsorption of molecular and atomic oxygen is investigated as a function of spin configuration to determine the very first steps of oxidation on UO2 surfaces. On both the (111) and (110) surfaces, the adsorption of atomic oxygen leads to oxidation of near-surface uranium atoms. Investigations into possible transition state spin configurations for oxygen interacting with the substrate are discussed. A co-adsorption case for water and oxygen is tested on both UO2 and ThO2 surfaces. On the UO2 (111) surface, the presence of water is found to enhance the oxidation of near-surface uranium atoms, a phenomenon attributed to the semi-conducting nature of UO2 as this trend is not observed on the insulating ThO2 surface. Finally, the distance dependence of this “surface proximity effect” (Rosso and Becker, 2002) is tested as a function of distance between adsorbates on the (110) surface. By using quantum mechanical methods to investigate the very first interactions of oxygen and water with actinde oxide surfaces, we start to develop a mechanistic understanding of processes that ultimately affect oxidation and dissolution rates on the macroscopic scale.

References
Garnet growth in the Zermatt-Saas Fee eclogites

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Different approaches have been used to infer the growth-limiting mechanism. The radius rate relations of e.g. Kretz (1973) rely on major element compositional zoning as time markers assuming that all porphyroblasts are precipitating the same chemical composition at any point in time. Comparison of chemical contour lines in variably sized garnets is used to distinguish between the different rate laws. A second approach is based on the 3-D spatial distribution of porphyroblasts. It assumes that depletion halos developing around early porphyroblast in the diffusion-controlled case will inhibit nucleation within the halos. This is supposed to lead to an ordered distribution while a random distribution is to expect for the interface-controlled case.

Application of the radius-rate concept to garnets of the eclogites of the Zermatt-Saas Fee ophiolite (ZSF, Western Alps, Switzerland/Italy) suggests that all garnets precipitated the same amount of radius per time interval, hence were grown limited by an interface-controlled growth mechanism. Approximately bell-shaped crystal size distributions suggest continuous nucleation and growth throughout the garnet growth history. Preliminary 3-D spatial distribution data using the nearest neighbour method is used to distinguish between the different rate laws. A second approach is based on the 3-D spatial distribution of porphyroblasts. It assumes that depletion halos developing around early porphyroblast in the diffusion-controlled case will inhibit nucleation within the halos. This is supposed to lead to an ordered distribution while a random distribution is to expect for the interface-controlled case.

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References

Investigation of the interaction between green rust sodium sulfate and aqueous selenium

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Selenium is an important trace nutrient in the body at low concentrations but becomes toxic at high concentrations. It is a natural compound in many rocks and sediments in various concentrations, but selenium is also produced as a decay product in radioactive waste. It exists in various redox states of which the higher, selenate (VI) and selenite (IV) are mobile in the aquatic environment. Inorganic reduction to elemental, insoluble selenium is one pathway to minimize the bioavailability of selenium in areas of increased levels.

Green rust is an Fe(II)-containing compound, known for its capability of reducing a large number of oxidized elements and compounds. It belongs to the family of layered double hydroxides (LDHs) with layers of Fe(II)-Fe(III) hydroxide, separated by interlayers of water, anions and for some types also cations (poster by Christiansen et al.). The reduction of selenate and selenite by green rust has been studied during the last decade. We have focused our investigations at the nanoscale level to understand the mechanism of the reactions. We use transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) to observe the particles at various times during the reactions.

Our results suggest that the mechanism of reaction is dependent on the type of green rust as well as the oxidation state of selenium. We used a green rust type which had SO42- incorporated in the interlayers. When SeO42- was added, we observed signs of intrusion into the interlayers. However, when SeO32-, which has a different steric nature, was added, interlayer exchange was not observed. In both cases, the oxidised species were reduced to insoluble elemental selenium. Previous studies on chromate (Skovbjerg et al., 2006) showed that the reduction mechanism is important for the mobility of the reduced contaminant, but in the case of selenium it appears not to be of relevance.

References
REE distribution in volkhovites – New type of the tektite-like glasses

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Volkhovites are the tektite-like glasses of mafic and ultramafic composition; for the first time we have discovered them among fluvial-glacial sediments of Valday glaciations (10-65 thousand years) at the right side of the river Volkhov (North-West Russia). Volkhovite particles are characterized by small size (0.1-3.0 mm), varied microtektite aerodynamic (spherules, drop-shaped, dumbbell-like) and irregular forms, and the perfect safety indicating their postglacial age (Skublov et al., 2007).

Volkhovites can be separated into four groups: Ca-enriched, Mg-enriched, Mn-enriched and K-enriched. REE distribution was studied in volkhovites locally by ion microprobe Cameca IMS-4f (IMI RAS, Jaroslavl, Russia). REE patterns for K-volkhovites and Australasian microtektites are very similar.

We suggest that volkhovites were formed as a result of outburst of the fluidisite slag-stone-melt-mud-gas mixture from the crust deep levels up to surface (Skublov et al., 2007).

Figure 1: Chondrite-normalized REE patterns for mean values for different types of volkhovites. Dotted line indicates the mean value for the normal Australasian microtektites (Glass et al., 2004).

References


Plešovice zircon – A new natural standard for U-Pb and Hf isotopic microanalysis


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Increasing number of geological applications requires the use of well-characterized and widely available reference materials for in situ analysis. We have established a new natural zircon standard (“Plešovice”) for U-Pb dating and Hf isotopic analysis by laser ablation ICP-MS.

The ID-TIMS U-Pb age of the Plešovice zircon has been determined to 336.9±0.2 Ma (95% confidence limits; mean 206Pb/238U age). The U-Pb ages obtained by LA ICP-MS (3 labs) and SIMS techniques show larger spread but within their analytical uncertainties they are consistent with the TIMS age. Hafnium isotopic composition of the Plešovice zircon appears to be homogenous within and between grains. Combined laser ablation and solution MC ICP-MS analyses gave a mean 176Hf/177Hf value of 0.282481±0.000013 (95% confidence limits, 87 analyses). Cathodoluminescence and BSE imaging and chemical analyses revealed that discrete zones in the Plešovice zircon are enriched in trace elements and especially in U and Th. Raman spectroscopy suggests that these highly radiation-damaged areas have not undergone any annealing. However, our LA ICP-MS analyses did not indicate any Pb-loss but the high intensities of measured U signal require that these areas are avoided during routine U-Pb isotopic analysis.
Constraining carbon sources and growth of microbialites in Pavilion Lake, BC using $^{14}$C

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The morphologically varied freshwater carbonate microbialite structures in Pavilion Lake, B.C. Canada represent an opportunity to investigate the processes leading to their formation and potential associated biosignatures that will contribute to our understanding of geo-microbe interactions and to our ability to interpret the geologic record. A primary question in such systems is determination of the primary carbon sources and cycling. In some systems, such as Mono Lake, carbonate structures are proposed to be the result of abiotic precipitation due to supersaturation resulting from groundwater-surface water mixing. Alternatively, modern stromatolites such as those in Shark Bay and the Bahamas are proposed to form via significant biological influence using bulk DIC.

Determination of the $\Delta^{14}$C of dissolved inorganic carbon (DIC) sources and mid-depth microbialite carbonate demonstrated that microbialite carbonate was significantly depleted in $\Delta^{14}$C with respect to bulk surface water indicating either contributions of geologically derived carbon or significant time since precipitation. Assuming surface carbonate was recently precipitated, comparison to local and regional groundwater $\Delta^{14}$C indicates that regional $\Delta^{14}$C depleted groundwater DIC sources provide 12% of carbonate carbon.

$\Delta^{14}$C of the detrital wood sample resulted in an estimated constant growth rate of 3 to 6 cm/thousand years, approximately double a previous U/Th based estimate.

The $\Delta^{14}$C of a deep water carbonate sample was highly depleted indicating that either groundwater was making a larger contribution to this carbonate or that this carbonate was precipitated significantly earlier than the mid-depth carbonates.

Modeling marine Carbon and Phosphorus cycling during Cretaceous Oceanic Anoxic Events

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Phosphorus (P) is a key nutrient and may control rates of primary productivity and organic carbon (C) burial in the oceans. Changes in phosphorus (P) availability thus may have played an important role in the initiation, formation and termination of Cretaceous oceanic anoxic events (OAEs). Besides redox-dependent changes in the recycling efficiency of sediment P, as deduced from elevated organic C/total P ratios in black shales, the marine P cycle can be affected by variations in sealevel, oceanic circulation and chemical weathering.

In this study, we use a model for the coupled marine cycles of P and C to examine the relative role of these various factors in determining changes in P availability and organic C burial during OAEs. We focus on OAE-2 (~94 Myrs BP; 500 kyr duration) and specifically study (1) possible triggers for the OAE, such as enhanced weathering and reduced oceanic circulation, (2) factors leading to its termination and (3) the relative role of the continental shelves and open ocean.
Abiotic Nitrogen reduction in Hadean hydrothermal systems

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One of the outstanding questions in Astrobiology is the source and formation mechanisms of NH\textsubscript{4}\textsuperscript{+} which presumably was required for reactions of prebiotic synthesis and origin of life. The uncatalyzed reduction of abundant N\textsubscript{2} to NH\textsubscript{4}\textsuperscript{+} is prohibitively slow due to the strong triple bond in the molecule. However, NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-} present in the Hadean Ocean as result of atmospheric reactions may have been more susceptible to reduction. We have experimentally tested the hypothesis, which suggests that Ni, Fe metals and alloys formed as a result of hydrothermal (HT) serpentinization processes in the Hadean oceanic crust could have acted as catalysts and/or reactants in reactions leading to abiotic NH\textsubscript{4}\textsuperscript{+}.

Our results show NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-} were converted into NH\textsubscript{4}\textsuperscript{+} more rapidly than N\textsubscript{2}, and the reduction process had a strong temperature dependence. Metals, especially Ni were found to be more effective than alloys in reducing N\textsubscript{2} with yields usually not exceeding few percent. Based on the experimental results we have estimated NH\textsubscript{4}\textsuperscript{+} yield of Hadean HT systems from to be approximately $10^{10}$-$10^{12}$ mol.yr\textsuperscript{-1} which is comparable to values estimated by Brandes et al., 1999 ($10^{10}$-$10^{11}$ mol.yr\textsuperscript{-1}) and Schoonen and Xu (2001) ($10^{9}$-$10^{10}$ mol.yr\textsuperscript{-1}) in HT systems as well as Summers and Chang (1993) for NO\textsubscript{2}\textsuperscript{-} reduction by Fe\textsuperscript{2+}. Our estimate only includes N\textsubscript{2} to NH\textsubscript{4}\textsuperscript{+} reaction yield and therefore if NO\textsubscript{2}/NO\textsubscript{3}\textsuperscript{-} were present in the advected seawater, the yields would have been proportionally higher considering their high conversion rates to NH\textsubscript{4}\textsuperscript{+} in the presence of metals/aleys.

We have also considered iron meteorites as possible sources of N since they commonly coain reduced N species such as nitride (N\textsuperscript{3-}) which could have reacted to form NH\textsubscript{4}\textsuperscript{+} during dissolution in the Hadean Ocean. When compared, however, with HT production, the meteoritic NH\textsubscript{4}\textsuperscript{+} flux during the Late Heavy Bombardment is approximately 6 orders of magnitude smaller.

References

Melt segregation and near source fractionation: Examples from small scale basaltic systems

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Basaltic magmatic systems, expressed at the earth’s surface as volcano fields, are characterised by very low rates of magma production (< 1.0$^4$ km\textsuperscript{3} /year) over relatively long time scales (up to 10\textsuperscript{7} years); these are tiny igneous provinces contrasting with Large Igneous Provinces that represent the other extreme in the spectrum of mantle derived magmatism. Tiny igneous provinces are the result of very small degrees of partial melting from a mantle source. In the Auckland volcanic field of Northern New Zealand, sampling of stratigraphically defined eruption sequences typically shows compositional trends in small magma batches that cannot be accounted for by fractionation involving low pressure mineral assemblages in a shallow pre-eruption environment. Detailed study of several individual volcanic centres in the Auckland field has defined two styles of compositional variation. 1). Least evolved compositions (as defined by geochemical parameters such as Mg-number and incompatible element content) are erupted first followed by more evolved compositions. This is interpreted to reflect magma extraction from a source in which a thermal gradient has produced a range of melting proportions with the greater proportion melt leading the extraction process. 2). The eruption sequence is initiated by relatively evolved compositions followed sequentially by progressively less evolved compositions. This trend is interpreted as the result of high pressure fractionation immediately above the source in a part of the conduit where melt is thermally connected to its surroundings and side wall crystallisation controls fractionation. The fact that these well defined compositional variations can be observed in stratigraphic sequence shows that the fractionated magma column rose very rapidly and without mixing once it left the source region. Further, such subtle compositional trends are probably only preserved because of the extremely small volumes of melt involved. In the Auckland volcanic field there is evidence for these extraction/fractionation processes occurring in both garnet and spinel peridotite facies giving rise to a range of alkaline to sub-alkaline basalt compositions. There is also evidence for compositionally distinct small magma batches coexisting independantly and rising simultaneously to the surface demonstrating the inherent instability of small scale mantle based magmatic systems.
Purification of sterols and alkenones for compound specific hydrogen isotopic analysis using HPLC

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Here we present two variations of a method for purifying sterols and alkenones out of total lipid extracts using an HPLC-MS coupled to a fraction collector. The presented methods reduce the amount of work needed and simplify the procedure to obtain fractions pure enough for compound specific irm-GC/MS analysis, compared to traditional wet chemical techniques. This allows a higher throughput of samples so that high-resolution paleoclimatic or paleoenvironmental proxy records based on compound-specific isotope measurements can be obtained more efficiently. The presented method was developed for hydrogen isotope analysis, and introduces no isotopic fractionation. The method could also be used in other cases where purification of lipid biomarkers out of total lipid extracts is required.

Figure 1: Gas Chromatograms of:
A) Total lipid extract of a Chesapeake Bay sediment and fractions as purified by semi-preparative HPLC. Individual alkenones are separated from notoriously co-eluting alkenoates.
B) Neutral fraction of a sediment from Palau (West Pacific) and collected fractions containing various alcohol classes.

Continental temperatures from the Paleocene-Eocene boundary in the Big Horn Basin, WY from carbonate clumped isotope thermometry

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We used carbonate clumped isotope thermometry to constrain growth temperatures of paleosol carbonates and fossil unionid bivalves collected from the Big Horn Basin (Wyoming) from sections that span the Paleocene-Eocene boundary. Long-term global warming of ~10°C occurred from the Late Paleocene to the Early Eocene. The Paleocene-Eocene Thermal Maximum (PETM) is an extreme thermal event of short duration (< 200 ky) superimposed on the long-term warming trend, and has been identified globally in the ocean sediment record and on the continents in sedimentary basins. The Big Horn Basin is one such basin that has been extensively studied with multiple climatic and biotic proxies in an attempt to characterize the PETM. Therefore, it is an ideal case study for the new paleothermometry technique we use here.

Temperature estimates for the paleosol carbonates capture the pattern of temperature change through time suggested by other paleotemperature proxies, but are consistently higher than previous estimates. Temperature estimates from the fossil mollusk shells, however, are too high to reflect original climatic conditions and do not mimic the stratigraphic change in temperature seen in other proxies. These samples were buried to > 1 km and subsequently exhumed. Our results suggest the paleosol carbonate samples were not dramatically reset by burial metamorphism, whereas the mollusk fossil carbonate was reset by re-crystallization or other processes. We speculate that carbonate that originally forms as calcite is more resistant to resetting during burial metamorphism than carbonate initially formed as metastable aragonite. Although X-ray diffraction analyses detected primary aragonite and no calcite in these fossil mollusks, trace metal analysis and more detailed SEM and/or XRD studies may be required to identify sufficiently unaltered fossil mollusks, if they exist (Came et al., in revision, 2007). We conclude that the soil carbonate data constrain continental climate across the Paleocene to Eocene transition. In addition, the contrast between soil carbonates and fossil mollusks provides an important first case study of the relative ability of different forms of carbonate to retain primary temperatures as measured by clumped isotope thermometry.

Reference
Melt inclusions and host olivines: What do they tell about mantle processes and sources?
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Host olivines and magmatic (melt and fluid) inclusion studies have had significant impact on petrology and geochemistry of mantle-related igneous processes in recent years. This includes better understanding of melting processes, source heterogeneities, and volatile contents of parental melts. At the same time, new results have shown possible processes (such as magma mixing and interaction with crustal materials) which appear to compromise the idea that melt inclusions represent simple primary liquids (e.g. Danyushevsky et al., 2003). Here I present a summary of last 5 years studies of our group concerning compositions of melt inclusions and host olivines from the mantle plume, LIP and MOR environments.

Melt inclusions in olivines are likely trapped during relatively fast growth of crystals in the environments of significant temperature and (or) compositional gradients such as magma mixing. Compositional variability of melt inclusions far exceeds variability of lavas representing end-members commonly present in bulk rock in highly attenuated form. Melt inclusions of variable compositions coexisting in a single olivine phenocryst are often trapped sequentially at different depths. This suggests complicated multistage crystallization and trapping process rather than nearly simultaneous trapping of locally heterogeneous melts.

Data suggest that each volcanic plumbing system or particular lava represents dynamic mixing of numerous parental melts and products of their fractionation and (or) interaction with crystal mashes and melts in shallow conduits. Some inclusions approach primary melt compositions much better then any studied rocks. These inclusions show extreme compositional ranges far exceeding those of bulk surface lavas. They are usually trapped in the earliest crystals formed in the deepest parts of plumbing system. The compositional and isotopic ranges of the recovered parental melts suggest highly efficient open system melting; fast melt transport and compositional heterogeneity of mantle sources in all volcanic environments studied so far. In particular the concentrations of Mn, Ni, Ca, Zn and Sc of early olivine phenocrysts from wide range of mantle derived melts are not consistent with common peridotitic source and suggest significant amount olivine-free hydride pyroxenite source formed by melting and reaction of recycled crustal component in the convecting mantle (Sobolev et al., 2005, 2007).

References

Recycled oceanic crust as a source of Siberian flood basalts
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Recent study (Sobolev et al., 2007) has shown that Gudchikhinskaya suite (Gd2) from the base of Siberian flood basalts in Norilsk region likely formed by melting of olivine-free hybrid pyroxenite, produced by reaction of melts from recycled crust and peridotite. Here we present new data on major and trace element compositions and volatile contents in parental melts for Gd2 basaltic suite recovered from the study of homogenised melt inclusions in olivine phenocrysts by EPMA, LA-ICP MS and SIMS. We show that the composition of trapped melt varies from similar to tholeiitic OIB (e.g. Mauna Loa, Hawaii) with notable depletion in Pb, U, Th and Rb to those enriched in these elements (Fig.1). Abundances of these elements correlate with concentrations of Si, K (positively) and Nb, Ti (negatively). This suggests significant contamination of melt by continental crust during magma fractionation. All melts are severely undersaturated by S and contain low water concentrations.

The composition of melts unaffected by crustal contamination indicate oceanic crustal component. This suggests that the recycled oceanic crust was a major source of Siberian flood basalts at the initial stage of LIP formation.

Figure 1: Average compositions of melt inclusions in olivine from Gd2 picrites (2 samples) compared with continental crust (Rudnik, 2003) and typical Mauna Loa melt (Sobolev et al., 2005) normalized to primitive mantle (Hofmann, 1988).

References
Evidence for correlation of late CFBs from East Greenland and the Faeroe Islands (North Atlantic Igneous Province)

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The Faeroe Islands formed early as part of the North Atlantic Igneous Province (NAIP) and is composed of a 4-5km thick basaltic lava sequence erupted before and during continental breakup ~56-55 Ma ago (Storey et al. 2007). The present dataset represents the syn-breakup part of the sequence and comprises both enriched high-Ti plume related basalts and depleted MORB-like low-Ti basalts. The Faroese lavapile has earlier been correlated geochemically with the East Greenland Paleogene lavaseries from Kangerlussuak and Blosseville Coast by Larsen et al. (1999), where the Faroes Middle and Upper Formations were correlated with the Milne Land Formation (MLF) from East Greenland. New data from the southern island of Søndøy on the Faroe Islands shows that thin counterparts of the East Greenland Geikie Plateau Formation (GPF) and Rømer Fjord Formation (RFF) are present on the Faeroe Islands in the very top of the sequence. The correlation is based on variations in Zr/Nb and 206Pb/204Pb and is also consistent with petrological observations that GPF and RFF lavas are mainly aphyric and RFF lavas have lower depleted MORB-like low-Ti lavas can be modelled as mixtures between a MORB source and a component identical with the NAEM composition of Ellam and Stuart (2000). The proposed Icelandic depleted plume end-member ID1 (Thirlwall et al. 2004) does not seem to be present in the Paleogene lavas which is an argument against its existence.

References

Occurrence and origin of igneous fragments in chondritic breccias

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The ordinary chondrite breccias Adzhi-Bogdo (LL3-6) and Study Butte (H3-6) contain igneous-textured inclusions that are best described as alkali-granitoids in Adzhi-Bogdo (Bischoff et al., 1993) and andesite in Study Butte (Fredriksson et al., 1989). Both the granitoids and the andesite appear to have been formed by melting and magmatic differentiation on a parent body and indicate mixing of achnodratic fragments with chondritic components.

Al-Mg isotope data for these igneous-textured clasts reveal no evidence for radiogenic 26Mg and indicate that the formation of these igneous clasts, the incorporation into the parent body regolith, and the lithification must have occurred late, after almost all 26Al had decayed (Sokol et al., 2007).

Oxygen isotope ratios of plagioclase, quartz and pyroxene in the fragments were measured in situ with the CRPG-CNRS Cameca IMS 1270 ion microprobe. On a three-O isotope diagram all fragments fall in the range of ordinary chondrites (Fig 1). These results imply that the fragments derive from an ordinary chondrite precursor and that the granitic fragments may have formed on the same parent body as the surrounding host rock material. The andesite seems to derive from a LL chondrite in contrast to its host rock (which is H3-6). This in turn indicates that melt formation and extreme differentiation occurred on ordinary chondrite parent bodies in the early stage of solar solar system formation. Alternatively, the fragments may have formed on another parent body but within the same oxygen isotope region of the solar nebula. In this case, they may represent projectile fragments within the chondritic breccias.

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New approaches to geochemical exploration for deep-seated and covered mineral deposits

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At present, because of the urgent need to carry out exploration for deep-seated mineral deposits, as well as deposits within areas covered by drifts, it is necessary to create and develop new geochemical techniques which are deep-penetrating ones and enable revelation of such concealed ore deposits. Routine geochemical prospecting surveys are not effective enough in such terrains due to low contrast or absence of geochemical anomalies related to ores.

Among the deep-penetrating geochemical methods based on the phenomenon of jet-flow vertical migration of chemical elements from the deep to the surface resulting in superimposed dispersion halos formation, is the Method of Analysis of Superfine Fraction (MASF) developed in VSEGEI that uses extraction and analysis of superfine fraction of soils (<3-10 μm) where superimposed dispersion halos occur. These halos are predominantly created by the process of secondary fixation of mobile forms of elements due to the sorption of metals from the gaseous and water upward flows by clays, Fe and Mn hydroxides, and other natural substances. MASF surveys use sampling of definite horizons of soils and/or stream sediments, extraction of superfine fraction from samples by means of special technology, determination of contents of indicator elements using ICP-AES, ICP-MS, AAA with specific sample preparation, and geochemical data processing and interpretation with the help of original algorithms.

Another perspective technique is the geochemical prospecting using water-extractable and weak-acid-extractable forms of chemical elements (mobile ions) from soils and stream sediments. Results of our survey carried out in the Far East region has shown that most reliable prediction of gold mineralization can be distinguished by getting together data obtained by both mentioned deep-penetrating geochemical techniques.

Nisa granitic massif: SHRIMP zircon U-Pb age and source constraints

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The Nisa granitic massif crops out over an area of 1000 km² in SW Iberia. It is a zoned batholith dominated by a rim consisting of very coarse-grained porphyritic two mica S-type monzogranite-syenogranite and a discontinuous core of very fine-grained 1-type tonalite-granodiorite. To constrain the age relationships and petrologic processes responsible for this zonation, SHRIMP 206Pb/238U zircon ages were obtained for the monzogranite and tonalite. Zircons from the monzogranite are typical of granitic rocks and can be broadly classified into three texturally and chemically distinct types: 1) high-U, low Th/U overgrews (307.4 ± 4.0 Ma); 2) moderate U and Th/U zircon with concentric zoning occurring both as inner overgrowths and whole grains (305.4 ± 6.2 Ma) and 3) texturally discordant cores (309.0 ± 4.6 Ma and inherited). It was impossible to identify in advance, on any textural basis, which cores were ‘young’ or inherited. Despite textural and compositional contrasts the three “young” zircon types have mutually indistinguishable ages. Zircons 1) and 2) represent different stages of igneous zircon growth and zircon 3) must represent an earlier stage of growth. Either the protolith of the monzogranite contained some zircon slightly older than the monzogranite itself or zircon grew in two stages, separated by a period of zircon undersaturation. The former hypothesis seems to be unrealistic in the regional geological context. The latter would be possible if the magma was reheated soon after cooling to the point of zircon saturation. This is consistent with the dissolution features found in some of both older and younger cores. There is a very marked chemical contrast between zircons 1) and 2), as Th/U in 1) is almost 10x lower than in 2), which is compatible with saturation of monazite at a late stage of crystallization and/or the presence of U-rich fluid soon after the monzogranite was intruded. The inherited old cores fall broadly into Neoproterozoic, near concordant ages (506–661 Ma), and Paleoproterozoic and older, mostly discordant ages (1.85–2.55 Ga). There is a noticeable absence of Mesoproterozoic ages, which is significant in a regional geodynamic context. In contrast, zircons from the tonalite have banded zoning that is typical of zircon from mafic igneous rocks, and inherited cores were not found. Further, their Th/U is generally >1, higher than in zircon from the monzogranite. Their age, 306.2 ± 3.0 Ma, overlaps the ages of the three generations of zircon from the monzogranite, but zircon features suggest different sources for these two granitoids. The tonalite protolith might have been a more refractory level that melted soon after the crystallization of the “young” zircon cores from the monzogranite due to an increase in temperature (causing zircon dissolution). Tonalite in the core of the batholith probably intruded immediately after the dominant monzogranite rim.
Land ocean interactions in a coastal embayment, Kaneohe Bay, Hawaii: Nutrient dynamics, productivity, and CO$_2$ exchange between seawater and atmosphere

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Human activities throughout the past two centuries have generated large increases in the atmospheric content of greenhouse gases, leading to higher global mean surface temperatures. The warming of oceans may increase the frequency of storms, which facilitate the transfer of nutrients, sediment, and pollutants from rivers into coastal ecosystems. Increased oceanic CO$_2$ concentrations attributable to anthropogenic input lower the saturation state of seawater with respect to carbonate minerals, can cause “ocean acidification” and have been argued by some to negatively impact calcification (e.g., Kleypas, 1999; Orr, 2005). Coastal areas and estuaries, however, may be either net annual sources or sinks of atmospheric CO$_2$ (-41 to 7.3 Mole C m$^{-2}$ yr$^{-1}$, Mackenzie and Lerman, 2006).

We present here results from 18 months of observations at CRIMP-CO$_2$, a collaborative effort in Kaneohe Bay, Hawaii between UH Manoa and NOAA/PMEL. This buoy was the first coastal buoy of the NOAA/PMEL-CO$_2$ program. CRIMP-CO$_2$ has documented the response of bay waters to pulsed inputs throughout a La Niña winter season (2005-06) and the much drier winter of 2006-07. The evolution of bay waters following storm-derived inputs was studied, along with the impacts of blooms and physical forcing on the air-sea exchange of CO$_2$. Physical forcing strongly influences system response, in particular stratification and mixing, hence controls both the duration of blooms and attendant changes in CO$_2$ concentration. Southern Kaneohe Bay often becomes a CO$_2$ sink following storm inputs (0.2-0.7 m Mole C m$^{-2}$ hr$^{-1}$), but remained a net source of CO$_2$ to the atmosphere (-1.06 Mole C m$^{-2}$ yr$^{-1}$) throughout our study period. This result is similar to estimates from Hog Reef flat in Bermuda and from the Scheldt Estuary plume (-1.2 and -1.1 to -1.9 Mole C m$^{-2}$ yr$^{-1}$, respectively, Mackenzie and Lerman, 2006).

Diamonds, xenoliths and kimberlites:
A window into the Earth’s Mantle.

UNESCO IGCP 557

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The principal aim of this study is to develop a dynamic process based understanding for the formation of the e- and p-type diamonds. A joint study of the petrology and geodynamics of diamond bearing rocks is thus understood as a space-time window for unravelling deep processes in the Earth’s Upper Mantle. Our assessment aims particularly at the migration paths of hydrogen in nominally OH-free minerals in xenoliths, their geological/geodynamic setting as well as their petrological evolution. Recently, a 3-D dimensional modelling tool for understanding the geometry of a subduction zones was developed (Morra, et al., 2006). The new method comprises a novel Finite-Element/Boundary Element method (FEM/BEM) coupled to a thermodynamic solver (PERPLEX). The primary target of the code was to give a quantitative tool for modelling mantle tomography and geodynamics using the constraint of phase equilibria. Although the simulations are mainly geared at subduction/collision environments, both methods can be used in a much broader sense and thus provide a unique opportunity to test geodynamic settings for diamond formation in a truly quantitative manner. The strength of the FEM-BEM method of Morra and Regenauer-Lieb (2006), lies in the fact that the physical parameters derived from thermodynamic calculations provide a robust tool for predicting a geodynamic processes. In our approach, density contrasts and mineral chemical compositions are used for driving geodynamic processes occurring in a subduction zone. Material parameters, are equally derived and complemented by the best of our knowledge on rheological properties of rocks from laboratory data. We propose to compare the predicted phases with in situ observations using multi-scale laboratory analyses complemented by a high resolution synchrotron based FT-IR analysis to derive passage of aqueous fluids through the lithosphere. This latter technique has proven to be very powerful to map the formation of mineral inclusions in mantle minerals such olivine. The project is carried out under the auspices of an international UNESCO IGCP557 collaboration involving a large group of international scientists.

References
High sea bed methane emission rates at Hikurangi margin (New Zealand) associated with extremely dense populations of ampharetid polychaetes

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Occurrence of gas hydrates and gas seepage from Hikurangi margin sediments has been inferred from BSR structures, methane derived carbonates, gas flares in the water column, and the presence of chemosynthetic bivalve mollusks. Apart from these geophysical indications and sporadic observations by fishermen and scientific dredge samples, detailed biogeochemical studies are missing. We determined the in situ sea bed methane emission and associated fluxes of oxygen, nitrate, sulfate and sulfide at 3 different locations along the Hikurangi margin in water depths ranging from 662 to 1104 m using GEOMAR lander technology. Highest sea bed methane emissions of up to 203 mmol m⁻² d⁻¹ were associated with extremely high abundances of ampharetid polychaetes (10³20 ind. m⁻²), highly elevated total oxygen uptake rates (up to 98 mmol m⁻² d⁻¹) and steep pore water gradients of methane, oxygen, sulfate and sulfide. Although members of the family Ampharetidae have been also reported from other cold seep sites and whale falls, this is to the best of our knowledge the first record where these polychaetes constitute key organisms of a cold seep environment. The distribution of the ampharetids was restricted to spatially highly confined patches of darkened sediment at the fringe of extended carbonate concretions. Close to these sites expulsion of free gas from the sea bed has been observed. They live in tubes of organic material that penetrate about 3 cm deep into the sediment. Density and spatial arrangement of their tubes, that extend a few millimeters into the water column, likely affects the current regime of the bottom contact water and therewith physical sediment properties and in consequence the exchange of solutes across the sediment-water interface. Micro gradients of oxygen and sulfide indicate further solute transport along the tubes. Both mechanisms might largely affect methane carbon turnover and release from this particular environment.

Sequential oxidation of arsenite by both permanganate and the reaction byproduct

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Arsenic contamination of soil, surface- and groundwater is of serious concern over the world because of its toxicity and carcinogenicity. One of the most effective ways to remove As from water is to oxidize it to less mobile and less toxic As(V), which can be subsequently immobilized by sorption to various sorbents. This study investigates the effects of permanganate on the oxidation of As(III) at pH 4 and 8 at varying doses of As(III) (10 or 100 µM) and permanganate (1 – 170 µM) in 0.01 M NaNO₃. The solution pH was adjusted to the desired values using 10 mM of either monobasic or dibasic phosphate buffer with 10 mM HNO₃.

The oxidation of As(III) by permanganate at the stoichiometric ratio of As(III) to Mn(VII) (i.e., 3:2 for As(III) oxidation to As(V) with an assumption of Mn(VII) reduction to Mn(IV)-oxide) or at excessive Mn(VII) concentrations is instantaneous at both pH's. In addition, the ratio of oxidized As(III) to reduced Mn(VII) is ca. 2:1, indicating the reaction product is probably Mn(III)-oxide/oxyhydroxide. When As(III) dose exceeds Mn(VII) concentration at pH 8, the excess As(III) is further oxidized by the primary reaction product, which is thereby reduced to dissolved Mn(II). This subsequent heterogeneous reaction between the excess of As(III) and the manganese solid byproduct is slower than the primary reaction. These results indicate that permanganate may be an effective and efficient reagent for As(III) oxidation in water treatment processes.
Study on 3-D crustal structure in the area along Yangtze River: The significance to multi-metal mineralization
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Introduction
The complex structure characteristics of the area along the Yangtze River in Anhui Province is located in the convergent collision belt formed by two big tectonic plates, which are North China Plate and Yangtze plate. Plenty of mineral sources were generated in the duration of the frequent magmatic activities in this area. Therefore, it has a significant meaning in the exploring mineral sources to get a comprehensive view of the 3-D crustal structure. Based on the inversion and integrated interpretation of six geophysical profiles across this area, we obtain the 3-D characteristics about the crustal structure in Anhui Province along Yangtze River.

Data Processing and Results
Taking the crustal structure of Yangtze Plate as the frame, and combining with the geological strata or tectonic units, the initial model containing the different blocks was designed. Taking the exsisting partially seismic profile interpretation as the constraint condition, gravity and magnetic robust iterative inversion and the 3-D crustal structure integrated interpretation are carried out in the six geophysical profiles across the entire area. Several conclusions were obtained as follows: (1) The crustal structure has the obvious three layers overally, namely the upper crust, the mid-crust and the lower crust. (2) The upper crust, with a violent changing structure, has deposited the relative thicker cap rock. The partial area may hit 10km, with the character of the low velocity, low resistivity, low density and low magnetism (V: 5.7~5.8 km/s, \( \rho_s: 1000~1500 \)Ωm, \( \sigma_s: 3.0~3.2 \times 10^3 \)kg/m\(^3\), J: 10\(^{-8}\)~10\(^{-7}\)A/m). (3) The mid crust has the top depth generally below 10 km and the bottom depth generally about 20 km, with the characteristics of high velocity, high resistivity, high density and high magnetism (V: 6.0~7.0 km/s, \( \rho_s: 1000~1500 \)Ωm, \( \sigma_s: 2.9~3.0 \times 10^3 \)kg/m\(^3\), J: n×A/m), differently from the upper crust. (4) The lower crust, with an average of 12 km depth, has the character of high velocity, high resistivity and high density (V: 6.8~7.6 km/s, \( \rho_s: 10^3~10^4 \)Ωm, \( \sigma_s: 3.0~3.2 \) kg/m\(^3\)). The Curie surface is in this layer. This study has significance to multi-metal mineralization.

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Historical variations in zinc stable isotope compositions of smelter polluted sediments
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Two case studies were carried out to investigate the use of zinc stable isotopes as tracers for industrial smelter sources and processes: 1) two organic sediment cores obtained 800 m from the former pyrometallurgical zinc smelter of Lommel (Belgium), which received exclusively atmospheric inputs, and 2) two dam lake sediment cores taken 15 km downstream and 30 km downstream of the former pyro/hydro-metallurgical zinc plant of Viviez (France), which received predominantly riverine dissolved Zn and particulate Zn inputs. Zinc isotopic compositions were measured on the LMTG Thermo-Finnigan Neptune MC-ICPMS in Toulouse and expressed as per mille deviations from the JMC 3-0749L standard. In case 1 atmospheric pre-industrial deposits have \( \delta^{66}Zn = +0.31\pm0.09 \)‰ (2sd). Deposits dated from 1900-1930 have \( \delta^{66}Zn = +0.29\pm0.06 \)%o (2sd), and sediments dated from 1956-1995 shift to lighter isotopic compositions of \( \delta^{66}Zn = +0.13\pm0.08 \)%o (2sd) in 1968. 42 ZnS minerals from ore import dominating Australian and African mines yield, together with literature ZnS data, a grand average of \( \delta^{66}Zn = +0.16\pm0.07 \)%o 2se, n=83 for ZnS. Emission control since 1955 is a likely cause for the \( \delta^{66}Zn \) sediment shift. In case 2 the polluted riverine sediments dated from 1952-2002 have elevated \( \delta^{66}Zn \) of +0.75 to +1.32‰ relative to the geochemical background \( \delta^{66}Zn = 0.33\pm0.06 \)‰ (2sd). Mine tailing slag samples also had elevated \( \delta^{66}Zn \) ranging from +0.18 to +1.49‰. In summary we show that 1. Bulk ZnS ore minerals have homogeneous \( \delta^{66}Zn \). 2. Zinc refinery processes fractionate Zn isotopes: slags are enriched in heavy isotopes. 3. near-field (<1 km) atmospheric deposition resembles ZnS ores, far-field carries isotopically light Zn, and mine tailing drainage carries heavy Zn.
**Diffusion profiles of Li in plagioclase/clinopyroxene and plagioclase/olivine intergrowths**

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Diffusion in magmatic systems occurs during crystal growth, magma mixing and ascent. In some magmatic crystals diffusion profiles are preserved. These profiles provide information about the timescales of magmatic processes. It is known that Li diffuses very rapidly in plagioclase and clinopyroxene (Giletti and Shanahan 1997, Coogan et al. 2005, Parkinson et al. 2007) and that Li diffuses in plagioclase two to three times faster than in clinopyroxene (Coogan et al. 2005).

This study is focused on the diffusion of Li between intergrown plagioclase/clinopyroxene and plagioclase/olivine. These intergrowths are observed in andesitic and dacitic rocks from the volcanic island Nisyros (Greece). Plagioclase phenocrysts in the andesitic lavas are cloudy zoned with slightly higher An content in the cores, while olivine and clinopyroxene phenocrysts are not zoned. In the dacitic lavas plagioclase phenocrysts have complexly zoned (‘splotchy’) cores and low An rims, while clinopyroxene phenocrysts show nearly no zoning. Both intergrowths of phenocrysts were analysed for Li concentration. Concentration profiles across the minerals were measured using a Cameca ims3f ionprobe with ~ 5 µm lateral resolution.

Li concentration in the dacitic sample jumps at the border of the intergrowth from 10 µg/g in the plagioclase to 44 µg/g in the clinopyroxene and then drops steadily over a distance of 100 µm to 5 µg/g in the clinopyroxene core. Similar patterns are observed for plagioclase/clinopyroxene pairs in other dacitic and andesitic samples. In intergrowths of plagioclase and olivine in andesitic samples, the same Li increase on the border of the crystals is found (7 µg/g in the plagioclase to 13 µg/g in the olivine rim and a slow decrease to 5 µg/g in the core). Preliminary Li isotope measurements reveal negative δ⁷Li values (~ -26‰) in clinopyroxene rims to zero values in the core. Isotope and concentration profiles are estimated to be caused by diffusion at ~ 1000°C and on timescale of only hours.

**References**


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**Jadeitite, lawsonite eclogite, and related rocks, Guatemala: Fluid-rock histories from a cold subduction zone**

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Jadeitite (jadeite rock) occurs rarely in a few serpentinite bodies from worldwide subduction complexes. Geochemical and CL-textural data show that such jadeite crystallizes directly from multiply sourced Na-, Al, and Si-bearing fluids. Both jadeite and lawsonite eclogite occur together in a few serpentinite-matrix mélanges of Guatemala. Also a rare rock, lawsonite eclogite forms under wet, extreme P/T conditions.

Each rock type shows complex fluid-rock interactions. Relationships of jadeite-forming fluids and host rocks are all but unknown—such contacts are rarely preserved. In the Sierra de las Minas, a 3 m-wide pit exposes such a contact, with jadeite and serpentinite respectively altered to albite and meta-ultramafic rocks. At the paleocontact, Zr, U, Hf, Pb, Ba, Sr, Y and Cs are greatly enriched in albite relative to the other rocks. Enrichments coincide with the appearance of and/or increase in abundance and/or grain size of zircon, titanite, celsian and REE-rich epidote in albite. All contain albite inclusions—many appear poikiloblastic—suggesting nucleation/growth of “trace-element-rich grains in albrite.”

Lawsonite eclogite records another fluid-rock system. For example, sample 2-14 (Jalapa dept.) is LREE-rich, with La 50× and Sm 30× Chondrite. It contains lawsonite grains as: 1) 100-300 µm, subidiomorphic inclusions in cores of 3-5 mm garnet; 2) 200-400 µm, irregular grains in garnet; 3) 100-300 µm idiomorphic matrix, partly consumed by amoeboid titanite; 4) 100-300 µm, idiomorphic matrix, with 100-200 µm garnet; and 5) 300-600 µm idiomorphic late veins. Each textural type shows distinct LREE abundances and fractionations, as well as Sr contents and zoning (all by LA-ICPMS). Mass balance suggests only lawsonite (1) reflects “protolith” LREE values. The others manifest LREE redistribution, or deposition of exotic REE.

These data show that Guatemalan serpentinite-matrix mélanges yield field examples of the mobility of “immobile” elements under low-T (300-450°C), high to very high-P (~8-~23 kbar) conditions, in chemically distinct fluids.
Improved in situ measurements of lead isotopes in silicate glasses by LA-MC-ICPMS using multiple ion counters

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A new technique that improves the spatial resolution and detection limits of the measurement of lead isotope ratios in silicate glasses with < 15 ppm total Pb by laser ablation-multicollector magnetic sector-inductively coupled plasma mass spectrometry (LA-MC-ICPMS) is presented. The method allows for the concurrent, static measurement of 206Pb, 207Pb, 208Pb, along with 204Hg and 235U, in six Multi-Ion Counters (MICs) fitted on a Finnigan NEPTUNE MC-ICPMS. Use of a collector array consisting only of MICs eliminates the need for cross calibration between Faraday cups and ion counters, as employed in previous methods reporting 204Pb values by LA-MC-ICPMS. Standard-sample-standard bracketing using BCR-2G as the calibrant is used to correct for instrumental mass bias. Accuracy and precision of the method was evaluated by replicate analyses of various MPI-DING reference glasses, with low Pb concentrations (1.38 to 11.6 ppm total Pb) and well-determined isotopic ratios. Typical spot sizes for in situ analyses ranged from 40-69 microns, providing better spatial resolution than previous LA-MC-ICPMS reporting 204Pb. Ablations for all analyses were carried out using a 193 nm ArF GeoLas laser at a repetition rate of 10 Hz and a pulse energy of 5 J/cm². Mercury derived from argon gas is a chronic problem for ICPMS measurements of the minor 204Pb isotope because of the isobaric intereferece by 204Hg. Due to the high sensitivity of the MICs, the Hg-correction of the measured 204Pb mass was significant, especially for samples with < 5 ppm total Pb. Two different methods were used to correct for Hg on the 204Pb mass with the results agreeing within error for each method on all lead isotope ratios. Measured lead isotope ratios for the MPI-DING KL2G (2.07 ppm Pb) and ATHO (5.67 ppm Pb) agree within 0.10% and 0.16% respectively of the accepted values. For MPI-DING KL2G (2.07 ppm Pb) and ML3B (1.38 ppm Pb), measured Pb ratios involving 204Pb agree within 1% of the accepted values with typical precisions of < 2.9% RSD (2 sigma). Measured 208Pb/206Pb and 207Pb/206Pb ratios for KL2G and ML3B are within 0.40% of the accepted values with typical precisions are < 0.75% RSD (2 sigma). The results for KL2G and ML3B demonstrate improvement over previous LA-MC-ICP-MS data in terms of both detection limits and spatial resolution, while retaining similar levels of accuracy and precision. The new method provides the capability of making quantitative in situ lead isotope measurements on tiny objects of geologic interest such as mineral growth bands, melt inclusions, and accessory minerals, even where they are lead poor.

Mineral phase identification of coral skeletal microstructure

K. SOWA, T. WATANABE, Y. SETO, S. MOTAI AND T. NAGAI

Mineral phase identification of the coral skeletal microstructure is important for reconstructing the paleo-climate. Especially, Porites sp. is widely used a paleo-climatic proxy. To reconstructing the paleo-environment, those chemical compositions have been studied as coral thermometry. For example, Sr/Ca ratio in coral skeletons is sensitive to the paleo-environment variant so that Sr/Ca ratio has the possibility as the accuracy archive. However, there are one assumption is that trace elements in coral aragonite originate from solid solution. Gregor et al. (1997) reported that the as much as 40% of strontium (Sr) in coral aragonite existed as a strontianite which was not the solid solution by using X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). On the other hand, Finch et al. (2003a, 2003) and Allison et al. (2005) showed no evidence of the presence of strontianite or its intermediate state in coral aragonite. They attempted to seek out the strontianite in coral samples using EXAFS. However, XANES and EXAFS could not identify the mineral phase directly. In addition, few studies have referred to mineral phase in coral skeletons with micro scale. X-ray diffraction analysis (XRD) with synchrotron radiation plays a role in detecting the mineral phase identification of coral skeletal microstructure for their strong energy, which enables phase identification with small range of X-ray spots: X-ray spot sizes of this study are 15µm and 40µm.

We performed XRD analysis with synchrotron radiation for coral, Porites sp., living/fossil microstructure. The experiment conducted with imaging plate (IP) on BL-18c at Photon factory, KEK (HIGH ENERGY ACCELERATOR RESEARCH ORGANIZATION), Tsukuba, Japan. A monochromatic incident X-ray beam with a wavelength of 0.616Å was used and was collimated to a diameter of 15µm or 40µm. The two-dimensional IP data were integrated and conducted to one dimensional intensity data.

The size of the centre of calcification (COC) is approximately 30µm in diameter in the samples of this study. That size corresponds to the X-ray spot sizes of this study in 15 or 40µm in diameter, so we got the different mineral structural information between the COC and fibres. All diffraction peaks of COC and fibres can be explained as aragonite, and no significant difference of cell parameters can be observed. This indicates that COC and fibres consist of aragonite: this study could not detect calcite phase.

Reference

Survival times of anomalous melt inclusions; Constraints from REE diffusion in olivine and chromite

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It is widely assumed that incompatible element diffusion through olivine and chromite is very slow and hence melt inclusions (MI) hosted in these minerals do not experience diffusive re-equilibration with the external magma. However, at present there are no data on diffusion coefficients for most trace elements in olivine or chromite.

We have conducted experiments at one atmosphere to determine diffusion coefficients for REE in forsteritic olivine and chromite. Clean samples of olivine and chromite that contain well-characterized MI suites were annealed with REE-doped (Pr, Ho, Tb, Lu) synthetic melts for up to 25 days at 1300-1450°C and under controlled fO2. Diffusion profiles were measured across sections of the crystal/synthetic melt boundary by laser-ablation ICP-MS and by electron microprobe. Element concentrations were then fitted to the diffusion equation to obtain diffusion coefficients. Calculated diffusivities for REE are relatively fast (D = 10-15 m²/s at 1300°C), whereas P and Al diffusion appears to be very slow (D <10-18 m²/s at 1300°C).

MI in the olivine and chromite crystals have distinct enrichments in the REE that were doped in the external melts. The systematic degree of enrichment of Lu>Ho>Tb>Pr and correlation between degree of enrichment and MI size and/or experiment duration are all consistent with re-equilibration of these inclusions via lattice diffusion through the host crystal.

Applying our diffusion coefficients to the equations of Qin et al. [1], we calculate that the REE compositions of olivine- or chromite-hosted MI will completely re-equilibrate with external magma in years to decades. These timescales are consistent with the REE enrichment observed in the experimental MI, and are significantly shorter than the times estimated for magma extraction from the mantle or residence in the lower crust. Therefore, anomalous MI must be trapped in the upper crust shortly before eruption. Our results show that the assumption of chemical isolation of incompatible elements in olivine and chromite-hosted MI is not valid, and hence calls for re-evaluation of the popular interpretation that anomalous MI represent preserved samples of unmodified mantle melts.

Reference

Biogeochmical insight on the origin of carbonaceous matter in metalliferous lowest Cambrian black shale, South China

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Early Cambrian black shale deposits in the Yangtze Platform in South China are, in places, strongly enriched in Ba (~470 Mt barite and witherite), Ni, Mo, V, Co, Cr, Au, U, As, Pb, Zn, Cu, Re, and PGE. Several models have been put forward for explaining the extreme metal enrichment of the ~0.50-0.52 Ga old black shale. These include enrichment by diagenetic fluids, hydrothermal exhalation, extraterrestrial impact, synsedimentary enrichment from seawater, and discharge of petroleum into the basin. This communication presents the first results of a molecular and isotopic organic geochemical study of the metalliferous carbonaceous shale. The new biogeochemical data provide further insight into the source of the hydrocarbons and the formation of the organic matter-metal association.

The TOC content of the analysed samples is between 0.7 and 8.2 wt%. The Rock-Eval parameters were not reliable in most samples because of the low S1 and S2 peaks. The massive aspect of the samples without altered surfaces and coating of metal oxyhydroxides suggest indigeneity of the organic extracts. The δ13C and δ15N ratios of the kerogen range respectively from –31.5 to –35.4‰ V-PDB and from –1.4 to 0.6‰ V-Air. The δ34S values of the organic-solvent soluble molecular sulphur of black shale samples range between 13.9 and 15.8‰ V-CDT, similar to the values obtained for sulphides.

The distribution of saturated HC is characterized by: n-alkanes in the C11–C31 range (maximum at C16) with bimodal distribution with further maxima at C22 or C26 in some samples, slight even-over-odd dominance), moderate to large i-C18 to i-C21 isoprenoid peaks, pronounced unresolved naphthenic humps in the n-C15-22 range, generally pristane and phytane in roughly equal proportion, and alkylcyclohexanes in the range C11 – C26. Some bitumens contain C25-C35 hopanes and C27-C29 steranes, with the latter dominating over the former. Aromatic HC such as alkylbenzenes, naphthalene, and alkynaphthalenes were detected only in very minor concentrations. The δ13C values of n-alkanes and isoprenoids vary between –33 and –25‰. In all samples pristane and phytane are depleted in 13C by up to 6‰ compared to C17 and C18 n-alkanes. All these results are best explained by derivation of hydrocarbons from algal and bacterial mats that were deposited in a saline, anoxic marine environment.
**Chlorine Partitioning: The behavior of Cl in the presence of sulfide-silicate melts and aqueous fluid**

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Can sulfide melts exsolve halogen rich fluids? Several ore deposits around the world (eg. Broken Hill, Stillwater, Sudbury and Bushveld) have occurrences of halogen-rich minerals in association with the ore. To help better understand these occurrences, piston cylinder experiments were performed to investigate the partitioning behavior of Cl between coexisting haplogranite and Pb-Fe-Zn-sulfide melts at 0.5 GPa pressure and 810ºC temperature.

In water undersaturated experiments where a Cl doped haplogranite glass was used as the silicate starting material, the Cl was found to partition strongly into the sulfide melt. Here Cl may be acting as a flux within the sulfide melt resulting in lowering its eutectic temperature. Not only is Cl dissolved in the sulfide melt, but as the sulfides crystallize the residual sulfide melt progressively enriches in Cl. In water saturated experiments where Cl was doped into the sulfides, Cl was noticeably absent from both quenched sulfide melt and silicate glass, suggesting strong partitioning into the coexisting aqueous fluid. The results indicate that the partitioning preference of Cl, when in equilibrium with sulfide-silicate melts and aqueous fluid, decreases in the order aqueous fluid - sulfide melt - silicate melt.

These experimental results can be applied to understand the cooling of sulphur- and chlorine-bearing magmatic systems. Initially, Cl will partition into a sulfide melt that coexists with a hydrous silicate melt. Once an aqueous fluid exsolves from the silicate melt – due to decomposition or crystallization at the solidus – Cl will partition into the newly formed fluid causing the sulfides to freeze and crystallize rapidly. The escaping Cl-rich fluid might lead to extensive halogen alteration in the country rocks of the intrusion. The concepts investigated in this study may have significant implications for understanding the evolution of magmas giving rise to copper porphyry deposits and aid in our understanding of halogen-alteration and halogen-rich minerals in major sulfide deposits.

**Planktonic foraminifera: Calcifying microenvironments, diffusive boundary layers and a peek at the event horizon**

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The planktonic foraminifera, *Orbulina universa*, should be considered the proverbial white rat for researchers studying biomineralization in the marine realm. This protozoan produces a spherical test in a single brief (several hours) calcifying event, that involves organic matrix secretion, rapid calcite precipitation and spine elongation. Chamber thickening in subsequent days is intimately linked to diurnal physiological oscillations related to symbiont photosynthesis and host assemblage respiration which controls large shifts in microenvironment pH (7.8 – 8.8) and [O\(_2\)] (~80-220% air saturation) (Rink, et al., 1998). Interestingly, microelectrode measurements of Ca\(^{2+}\) at the chamber surface show concentrations that are 10% higher than ambient seawater, while [CO\(_2\)] measurements on *O. universa* under dark and light conditions suggest \(\Sigma\)CO\(_2\) varies between ambient (~2 mMol/kg) and ~5 mMol/kg respectively in the boundary layer near the calcifying shell (Köhler-Rink and Kühl, 2005). Together these data point to an active calcium and carbon concentrating mechanism in this species, and may help explain how *O. universa* can calcify in seawater at pH between 7.4 and 8.8 (Bijma, et al., 1999).

Laboratory experiments and stable isotope and trace/minor elemental analyses of *O. universa* demonstrate that shell geochemistry is influenced by physiologically-controlled boundary layer chemistry. Elemental ratio banding, possibly related to the diurnal cycle, as well as observations of non-equilibrium calcite precipitation, provide insight into aspects of calcification that were previously poorly constrained. Together, these observations may provide clues for novel applications of foraminifera geochemistry for paleoenvironmental reconstructions.

**References**


Trace elements in garnets of diamondiferous xenoliths from the Nurbinskaya pipe, Yakutia

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Rare earth elements (REE) and other trace elements were analyzed by LAM-ICPMS in garnets of about 150 mafic and ultramafic diamondiferous xenoliths from the Nurbinskaya pipe. Most garnets are homogeneous in terms of major- and trace-element contents. Garnets from ultramafic xenoliths define two groups, one with sinusoidal REE N (chondrite normalised) patterns (10 harzburgites, two lherzolites) and one with flat MREEN (lherzolites, some websterites).

Most eclogitic garnets have LREE-depleted patterns (Ce N as low as 0.1), and no Eu anomalies. Heavy rare earth elements are variably enriched; most LuN varies 20-50. Most websteritic garnets show REE patterns similar to this but they are typically enriched in LREE with Ce N (0.2-0.5). Garnets with nearly flat HREE and small positive Eu anomalies are common in coesite-bearing eclogites and those containing kyanite and/or corundum [1]. Another group of garnets (n=9) from eclogites and websterites have small negative Eu anomalies. These types of pattern commonly are interpreted as evidence of the reaction of plagioclase to garnet and used to support the origin of mantle eclogites by subduction of oceanic crust [1, 2], but may be simply a redox feature. Garnets from highly aluminous eclogites show convex REE patterns enrichment in LREE and strong depletion of in HREE (YbN<5). Garnets of corundum-bearing eclogites commonly have positive slopes within the LREEN, peaking at Sm and then slowly decreasing to about chondritic abundance for Lu. LAM-ICPMS analysis could be used to show how different populations within an eclogite xenolith series can document the heterogeneous evolution of the lithospheric mantle beneath cratonic areas.

References

Latest-stage exhumation history of the Central Alps

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The European Alps, like many other Cenozoic orogens, show a pronounced increase in erosion rages since ~5 Ma. In a recent paper, Willett et al. (2006) proposed that this accelerated erosion was due to enhanced precipitation subsequent to the Messinian salinity crisis and marked the transition from orogenic construction to orogenic destruction.

In this study, the latest-stage exhumation history of the Central Alps was investigated by using zircon fission track (ZFT), apatite fission track (AFT) and apatite (U-Th)/He (AHe) thermochronology along the eastern margin of the Lepontine Dome. The study area covers basement nappes east and west of the Forcola fault, a major Alpine normal fault bordering the Lepontine Dome to the east.

ZFT ages from both east and west of the Forcola fault range between 25 and 16 Ma, with youngest ages occurring close to the fault system. These ages reflect a period of enhanced exhumation related to the onset of orogen-parallel lateral extension of the Alps. The area east of the Forcola yielded AFT ages between 17 and 5 Ma and AHe ages between 7.5 and 6 Ma, whereas the area west of the Forcola yielded AFT ages between 9 and 4 Ma and AHe ages between 6.6 and 3.4 Ma. The age difference between basement nappes east and west of the Forcola normal fault indicates that the fault system has been active (or re-activated) during the Latest Miocene to Pliocene, much later than previously assumed. Late Neogene reactivation, however, has also been observed for the Simplon normal fault west of the Lepontine Dome, which is supposed to be conjugated to the Forcola fault. Age-elevation relationships reveal that the area west of the Forcola fault experienced a period of rapid exhumation between approximately 5.5 to 4 Ma, and that exhumation rates slowed down after ~4 Ma. The period of rapid exhumation is temporally consistent with the increase in deposition rates in the foreland basins, whereas the end of rapid exhumation coincided with the end of deformation in the Jura mountains. These temporal relations support the idea of a Pliocene shift from orogenic construction to orogenic destruction and thus to a decrease of the actively deforming area of the Alps.

Reference
Spatial record of recent anthropogenic changes in the sedimentary soils of the Netherlands; Opportunities for a knowledge-based soil legislation framework

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Much of our knowledge about recent environmental changes – such as the increased anthropogenic emission of various metals – has been inferred from sedimentary records. These paleorecords, however, mainly focus on environmental changes through time. To generalize such changes in a spatial context, geochemical baseline surveys are required.

Using the data from the Geochemical Soil Survey of the Netherlands (Van der Veer, 2006), a geochemical baseline model was developed. The baseline model, based on covariability in pristine sediments, revealed a substantial overall enrichment of metals including Cd, Cu, Hg, Pb and Zn. These enrichments reflect the accumulation of metals in the topsoil compartment as a result of ongoing diffuse input from various anthropogenic sources. The enrichment, generally a factor 2-3 above natural concentrations, varies on a local as well as a regional scale.

Besides tracking environmental changes in a spatial context, the model furthermore offers unique possibilities to derive soil quality standards for a knowledge-based soil legislation framework. In this presentation we will show how the model can be used to derive soil quality standards, and how to take the natural variation of soils, as well as the diffuse enrichment, into account.

Reference

Bionergetics of the buried seafloor

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Major questions in subsurface biosphere research are related to bioenergetics. How much energy is required to support a given amount of biomass? And what is the minimum energy yield of reactions that are biologically utilized? Beyond these, there are related issues, such as, the energetic rules that govern the distribution of subsurface life, in particular, the controls on the distribution and rates of the various energy producing metabolic reactions and the possibility that some buried marine ecosystems rely on radiolytic H2 as their principle electron donor.

In situ metabolic rates and energy yields of diverse microbial activities in sediments of the eastern equatorial Pacific have been determined based on sedimentary pore fluid chemical profiles. Fe and SO42- reduction, and methanogenesis co-occur. These are energetically favorable throughout the sediment column with relatively constant energy yields. Based on this, minimum biologically utilizable energies of reaction can be inferred and it appears that this ecosystem operates as a thermodynamic homeostat.

When combined with reaction rate estimates, based on a numerical solution to the diffusion/reaction continuity equation, these data allow the calculation of an average maintenance energy that is orders of magnitude lower than observed in the laboratory. Based on this, it is inferred that in marine sediments, radiolytic H2 could support approximately 105 while approximately 104 could be supported in a water-saturated sediment that has a U, Th, and K similar to that estimated for the Martian crust.
Plate-tectonic controls on intraplate volcanism in New Zealand

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Cretaceous to recent intraplate volcanism in the New Zealand microcontinent provides an ideal case to explore possible factors that exert control on this type of volcanism. Located in the vicinity of the active Australian-Pacific plate boundary, the New Zealand microcontinent exhibits intraplate volcanic activity that is associated with various tectonic regimes: behind an active arc, in domains with predominant strike-slip motion, and in areas that are virtually unaffected by recent plate-tectonic activity.

Based on major-, trace-element-, and Hf-Nd-Pb-Sr isotope compositions of a representative set of near-primitive samples, distinct end member compositions corresponding to different tectonic regimes can be recognized: (1) HIMU-like signatures (206Pb/204Pb up to 20.57, “decoupled” Hf-Nd systematics; e.g., Chatham Islands), (2) dilute HIMU-like trace element signatures and depleted, asthenospheric isotope compositions (εHf: +9.9, εNd: +7.0; North Island), and (3) compositions having affinities to subducted sediments (87Sr/86Sr: 0.7037, 206Pb/204Pb: 18.99, 207Pb/204Pb: 15.67; South Island). The HIMU- and sediment-like signatures are interpreted to originate from a veined lithospheric mantle, reflecting a variable overprint by an ancient, possibly Cretaceous mantle plume and by Phanerozoic subduction zone enrichment.

Variations in the average melting depths of the magmas are manifested in a variable impact of residual garnet (e.g., Gd8/Yb8: 1.84 - 4.74). Changes in relative melting depths reflect variations in lithospheric thickness [1]. The geodynamic setting (lithospheric thickness, heat flow, degree of extension) controls the proportions of asthenospheric and lithospheric source components. For the South Island, magma compositions provide “snapshots” of a decreasing lithospheric mantle plume and by Phanerozoic subduction zone enrichment.

The Podili alkaline complex, Prakasam alkaline province, Andhra Pradesh, southern India

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The Podili alkaline complex in Prakasam alkaline province of Andhra Pradesh, in the southern India, is one among the cluster of alkaline complexes with a near NE-SW disposition pervading the cratonic corridor that is terminated by intracratonic sedimentary Cuddapah Basin in the west and Eastern Ghat Mobile belt in the east.

This N-S trending complex (12 km²) has a close spatial and temporal association with granites and gabbros that represents the manifestations of basic, acidic and alkaline magmatism.

Alkaline syenite, and subordinate quartz syenite constitute the important lithounits of the complex. The syenites are leucocratic dominated by microcline mesoperthite, plagioclase feldspar, quartz. The mafic minerals are alkali pyriboles and biotite with subordinate magnetite, sphene and apatite. The mafic minerals attribute to the alkaline and hydrous nature of parental liquids.

The syenites are of different degrees of silica saturation, and alkali syenites in particular carry normative nepheline and acmite, an indication of the peralkaline trait possibly inherited from the parental alkaline magma, either by prolonged differentiation or lowest degree of partial melting of an enriched/fertile mantle source.

References

Soil contamination due to heavy metals from tannery industries: A case study of Jajmau (Kanpur) and Unnao industrial areas, Uttar Pradesh, India

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Environmental geochemical studies were carried out in and around Jajmau (Kanpur) and Unnao industrial areas, to find out the extent of chemical pollution in soil due to waste disposal from tannery industries. There are more than 2500 tanneries in the country and nearly 80% of them are engaged in the chrome tanning process. In Uttar Pradesh, Jajmau (Kanpur) and Unnao (80°18’ – 80°30’ E longitude and 26°25’ – 26°34’ N latitude) are prominent centers for leather processing and there are two clusters of tannery industries (about 450) along the banks of river Ganga. Geologically the study area is covered by alluvium of Quaternary age consisting of older alluvium of middle to upper Pleistocene and newer alluvium of Holocene and the climate of the study area is semi-arid type.

Fifty-three soil samples were collected from Jajmau (Kanpur) and Unnao industrial areas from top 10 cm layer of the soil and were analyzed for heavy metals by using Philips PW 2440 X-ray fluorescence spectrometer. The data reveals that the soil in this area is significantly contaminated, and shows very high concentrations of chromium ranging from 162 to 60819 mg/kg (14535 mg/kg average). Other heavy metals such as Ba ranges 44-781 mg/kg (295.7 mg/kg average), Cu 1.7-126 mg/kg (42.9 mg/kg average), Pb 22-68 mg/kg (40.4 mg/kg average), Sr 47-151 mg/kg (105.3 mg/kg average), V 1.3-209 mg/kg (54.4 mg/kg average) and Zn 44-688 mg/kg (159.9 mg/kg average). High concentrations of these toxic/heavy metals are contributors for the degradation of human health in the study area and people suffer from occupational diseases such as asthma, chromium ulcers and skin diseases. Distribution and correlation of heavy metals in soil along with possible remedial measures are discussed.

New constraints on the origin of short-lived radioactive nuclides in the early solar system

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The presence of several short-lived radioactive nuclides (10Be, 26Al, 26Cl, 41Ca, 53Mn, 60Fe) in the early solar system is established from the presence of their decay products in constituents of primitive meteorites such as Ca-Al-rich inclusions (CAIs). These nuclides are either (i) the products of stellar nucleosynthesis (as demonstrated by the presence of 60Fe) and were injected in the protosolar cloud before or during its collapse or (ii) the result of interactions of energetic particles (as demonstrated by the presence of 10Be) with gas and dust either in the protosolar nebula or in the presolar cloud. As shown by X-ray observations of young stellar objects, one obvious source of an intense flux of accelerated particles in the protosolar nebula is the young active Sun. CAIs being the oldest solids formed in the solar system, they may have formed close to the young Sun and may contain a record of these irradiation processes. Understanding the origin of short-lived radioactive nuclides is thus fundamental not only for early solar system chronology but also for deciphering the astrophysical context of the formation of the first solids in the early solar system.

We report Li, B and Mg isotopic analyses by ion microprobe ( Cameca ims 1270) of a set of various CAIs from the CH chondrite Acfer 182 and CV3 chondrite Efremovka, including some hibonite-rich CAIs which because of their refractory composition are considered to be among the earliest CAIs. The hibonite-rich CAIs have lower 26Al/27Al ratios (<1.1±0.5×10-5) than the classical type B CAIs from Efremovka (e.g. CAI E66 which has a 26Al/27Al ratio of 5.49±0.15×10-5). The 10Be/9Be ratios are lower by a factor of two in hibonite-rich CAIs compared to Efremovka type B CAIs (e.g. 10Be/9Be=1.2±0.3×10-5 in E65). These data show that 26Al and 10Be are likely decoupled in the early solar system. The low 26Al/27Al ratios in hibonite-rich CAIs may reflect the steady state abundance of 26Al in the local interstellar medium. The hibonite-rich CAIs show a systematic slight but significant 6Li enrichment indicative of the presence of a component produced by spallation. This can be used to put a higher limit on the amount of 10Be which could have been produced in the presolar molecular cloud by trapping of galactic cosmic rays.
Water structure and exchange kinetics are important to a number of fundamental geochemical processes. For example, the rate of dissolution of isosstructural materials often correlates with the rate of water exchange on the aqueous cation. However, thus far most computational studies have focused on structure of the mineral surface. Water structure and kinetics are less often studied, yet are necessary to understand such basic properties of the interface such as adsorption energy. In this work, we use an existing molecular dynamics potential model [1] to estimate the water structure and exchange kinetics of aqueous barium ion on the barite \{001\} surface.

Water exchange kinetics were using a correlation function as well as the potential of mean force and a reactive flux. The latter methods involve calculating a transition state theory rate constant through integrating a free energy of activation estimated from a radial distribution function and a transmission coefficient estimated via a reactive flux. It was found that using only the barium-oxygen distance to constrain the reaction coordinate resulted in unphysical results and a solvent organization parameter is necessary. Using these methods, water structure and exchange kinetics surrounding aqueous barium ion fall within the range of experimental estimates. Water-barium distances for the surface ions on the \{001\} barite surface are very close to those of the aqueous ion, yet the rate constant is significantly faster. This increase in exchange rate is attributed to a relatively hydrophobic, high energy interface.

The calculated water structure of the overall interface is relatively complicated, with up to five distinguishable oxygen positions interacting with both surface sulfates and bariums. This complex structure contrasts to the fit of experimental X-ray reflectivity data, which can only justifiably include a single ordered layer of water that matches unsaturated barium-oxygen bonds. It is unclear at this point how to reconcile of this discrepancy, but there are substantial uncertainties in both the experimental and computational water structures.

This study is the first time the kinetics of water exchange on aqueous barium ion and barite surfaces have been examined using a reactive flux method and as such, represent a significant expansion of this new and hitherto relatively unexplored method to systems of geochemical interest.

References

Continental erosion averaged over space and time

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Matching rates of denudation at all temporal scales have been used to infer erosional steady state in various mountain belts. What variation in erosion rates is significant or expected from one temporal and spatial scale to another and over a range of tectonic regimes?

Under ideal conditions, the cosmogenic nuclide flux out of a basin can be used to measure the denudation rates that average over millennia for the entire drainage area. Erosion rates measured over shorter timescales (e.g. sediment yield, reservoir infill) show greater variance due to the stochastic nature of erosion and surface process interactions. Short-term measurements miss rare events in a predictable way and because of this property, rates of surficial processes measured over increasingly longer time intervals can incorporate longer intervals of process inactivity, thus producing a different apparent rate of deposition and erosion (Sadler, 1981; Gardner et al., 1987).

We use a new (available from the author) compilation of all previously published and new cosmogenic nuclide-derived denudation rates and sediment-flux measurements for the same basins to evaluate this variability. Despite anthropogenic effects, the majority of sediment fluxes are less than long-term rates of erosion, contrary to that predicted by Gardner et al. (1987).

References
What controls Sulfur isotope fractionation in modern estuarine sediments?

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Sulfur isotopes are a promising tool for tracing sulfate reduction in sedimentary rocks, and for providing constraints on one of the oldest metabolic process on Earth. However, the relationship between isotopic fractionation and parameters such as sulfate reduction rate, temperature and availability of organic matter remains unclear, with conflicting results from pure culture and natural population studies [1,2,3]. Here, we use flow through reactors that contain undisturbed slices of sediment to measure sulfate reduction rate under quasi-steady state conditions. Flow through experiments were run to investigate the control of temperature, sediment depth, organic matter content, sulfate concentration and the effects of inhibitors on sulfate reduction rate and sulfur isotope fractionation. Samples were collected at a brackish location of a temperate estuarine sediment (Western Schelde, The Netherlands).

Our results indicate an inverse relation between sulfate reduction rate (SRR) and sulfur isotope enrichment factor under optimum temperatures (20 and 30°C). This trend disappears at low rates (<10 nmol cm⁻³ h⁻¹) and for non-optimum temperatures (10 and 50°C). Large fractionations (>20‰) were observed only at low SRR (<10 nmol cm⁻³ h⁻¹). Sediment depth as well as organic matter content did not significantly affect isotope fractionation.

This study demonstrates that the degree of isotope fractionation can be used to infer SRR in natural populations as well as in pure cultures providing that the bacterial population is thriving under optimal conditions.

References

History of seafloor hydrothermal activity in the SW Pacific Bare Zone using fish teeth strontium isotope dating of metalliferous sediments

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A 2 million km² region virtually devoid of sediment has been identified in the remote SW Pacific Basin (February/March 2005 drill site survey cruise - Rea et al., 2006). This region, informally termed the "South Pacific Bare Zone" comprises ocean floor dating back to the Late Cretaceous. Seismic profiling, piston cores and gravity cores reveal the full extent of barren crust – an area nearly the size of the Mediterranean Sea. Within the Bare Zone, a small (1km²) abyssal valley with 24 m of sediment was identified and sampled with a large diameter piston core, leading to recovery of 8.35 meters of metalliferous sediment at 5082 m water depth. Fish-teeth Sr-isotope stratigraphy reveals a continuous record of sedimentation 31Ma to present, with an average linear sedimentation rate at this site of 0.27 mm/kyr. However, the fish teeth age-depth profile and INAA geochemistry show an exponentially decreasing hydrothermal flux, with sedimentation rates approaching <0.05 mm/kyr between 17 Ma and the present. The origin of the main pulse of hydrothermal activity is uncertain, but may be related to a series of late Eocene/early Oligocene ridge jumps and propagating rifts that accompanied large-scale plate tectonic reorganization of South Pacific seafloor. The fish teeth Sr isotope age-depth profile and pelagic clay geochemistry also reveals that the terrigenous component at this site registers a very low eolian flux, increasing in proportion to the hydrothermal component upcore. Primary dust sources were likely Australia and New Zealand, consistent with Nd-Sr-Pb isotopes of detrital extracts. The unusual conditions of Cenozoic non-deposition that characterize this area of the South Pacific make this the first record of its kind, providing unique insight into hydrothermal activity and eolian sedimentation since the early Oligocene. The utility of the fish teeth Sr isotope method for dating marine hydrothermal cores should be explored further.

References
No role for discrete, depleted high \(^3\)He/\(^4\)He mantle

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Recently, several studies have shown an apparent link between high \(^3\)He/\(^4\)He and depleted mantle (Stuart et al., 2003; Class and Goldstein 2005) which is inconsistent with prevailing orthodoxy where high \(^3\)He/\(^4\)He reflects a lack of mantle degassing and depletion. Here we present 28 new \(^3\)He/\(^4\)He analyses from Tertiary picrites of Baffin Island and West Greenland and have identified 21 samples with \(^3\)He/\(^4\)He >35\(^R\) (the highest value observed in recently erupted basalt). Whole rock \(^{143}\)Nd/\(^{144}\)Nd for these samples show a significant peak at depleted values (mean of 0.513024), as observed in an earlier study (Stuart et al., 2003), but an interesting feature of the new data is the scatter in \(^{143}\)Nd/\(^{144}\)Nd down to 0.512876, a value which although not chondritic is certainly less depleted than observed in Baffin Island and West Greenland picrites. Whole rock Pb isotope data show significant variations which are consistent with incorporation of radiogenic Pb of crustal origin but critically there is no relationship between Pb and Nd isotopes. Thus, if crustal contamination is the cause of Pb isotope variation, it was not responsible for the range in \(^{143}\)Nd/\(^{144}\)Nd.

In addition, major and trace element compositions of olivine hosted melt inclusions allow us to compare melt inclusion compositions from olivines of various sizes, that record different stages of magma evolution, to provide better resolution on the effects, if any, and timing of potential crustal contamination. We conclude that variations in \(^{143}\)Nd/\(^{144}\)Nd are likely to derive from heterogeneity in the mantle sources tapped by the Baffin Island and West Greenland picrites and that these new data do not support the concept of a discrete depleted-high \(^3\)He/\(^4\)He end-member in the mantle.

References

What controls iron isotope fractionation in an acid mining pile?

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This study explores the potential use of Fe isotope analysis in long-term risk assessment of acid mine drainage generating mining piles. Balci et al. (2006) have demonstrated the enrichment of heavy Fe isotopes in Fe oxidation products with respect to Fe(II)\(_{aq}\) during growth of Acidithiobacillus ferrooxidans in batch culture-experiments. They argued that inorganic equilibrium fractionation between Fe(III)\(_{aq}\) and Fe(II)\(_{aq}\) is the controlling reaction as described earlier by Welch et al. (2003). These authors have shown that in equilibrium the isotopic difference is \(\Delta^{56}\)Fe\(_{Fe(III)-Fe(II)}\) ~ 2.9‰. Here, we present Fe isotope ratios measured on sequentially leached tailings material sampled from a 25 m drill core into an active pile at Selebi-Phikwe, Botswana, and of an additional analog column bio-leaching experiment in the laboratory. Throughout the drill core, reactive solid Fe(III) is enriched in the heavy isotopes (average \(\delta^{56}\)Fe = −0.15‰) with respect to pyrrhotite (average \(\delta^{56}\)Fe = −0.40‰). This is in general agreement with the batch experiments of Balci et al. (2006). The fraction of exchangeable and soluble Fe shows very low \(\delta^{56}\)Fe values down to −2.4‰. Such extreme values can only occur in a small residual pool after the majority of dissolved Fe has been removed by precipitation. Our results can best be explained if the total reaction is broken down as follows. Fe dissolved from pyrrhotite is partitioned by microbial Fe(II)-oxidation into a mixed Fe(III)\(_{aq}\) and Fe(II)\(_{aq}\) pool which quickly equilibrates isotopically. Precipitation of solid Fe(III) occurs with perhaps additional fractionation from the Fe(III)\(_{aq}\) in the mix. Our data suggest that the mixed reservoir initially consisted mostly of Fe(III)\(_{aq}\) whose \(\delta^{56}\)Fe would be close to the initial pyrrhotite. The strongly fractionated residual derives from the remaining small pool of Fe(II)\(_{aq}\). However, low \(\delta^{56}\)Fe values cannot be sustained unless resupply of unfraccionated, freshly dissolved Fe from pyrrhotite is sluggish. Although showing complex results, the bio-leaching experiments appear to confirm that the ratio of Fe(II)\(_{aq}\) to Fe(III)\(_{aq}\) in the fluid, and thus the overall metal sulfide oxidation activity in the pile, is the main factor that controls the isotopic composition of soluble Fe.

References
The hydrothermal Wenzel deposit, South Germany: Implications for the formation of Kongsberg-type silver deposits

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The post-Variscan Kongsberg-type Wenzel deposit near Wolfach, Schwarzwald, Germany, the type locality of the Ag-Sb alloy dyscrasite, was investigated by ore microscopy, electron microprobe analysis, stable isotope and fluid inclusion analysis. Three mineralization stages could be distinguished in the vein. Whereas the first stage is a typical sulfide mineralization including galena and tetrahedrite, the second and third stage show a sulfide-poor association of Ag-Sb alloys with Fe-, Co- and Ni-arsenides and -sulfarsenides in a calcite matrix. The main ore minerals of this stage are allargentum and dyscrasite.

Seven distinct generations of calcite were distinguished. The δ¹³C (V-PDB) and δ¹⁸O (V-SMOW) values of these generations show a positively correlated trend that evolves from -13.0 to -4.0 ‰ and from 12.3 to 23.6 ‰, respectively.

Fluid inclusion data of stage I fluorite and quartz show homogenization temperatures of 100-180 °C at salinities of 17-26 wt.% NaCl eqv. Fluid inclusions in stage II calcite display similar, but more restricted values of 110-150 °C and 25-28 wt.% NaCl eqv., respectively. The stage III fluid inclusions of calcite show similar homogenization temperatures, but different salinities. Earlier Ag-Sb-alloy bearing calcite of this stage contains inclusions with salinities of 27-30 wt.% NaCl eqv., whereas later ore-free calcite crystals show lower salinities of 3-10 wt.% NaCl eqv. The initial ice melting temperatures of most fluid inclusions range between -45 and -60 °C and are typical of an H₂O-NaCl-CaCl₂ fluid.

Based on all available geochemical data and phase equilibrium constraints in the system Ag-Ca-Na-C-Si-Cl-O-H, we favor a model in which basement-derived near-neutral-pH hydrothermal fluids remobilized older Ag-Sb-bearing mineralizations. Mixing of these fluids with more alkaline formation waters from the Mesozoic cover rocks resulted in the precipitation of the silver alloys in an enrichment zone at P-T conditions of 120-150 °C and approximately 200 bars. A significant pH shift from near-neutral to alkaline is able to explain the abundant association of silver alloys with calcite gangue and the general absence of quartz in the enriched ore zone. This conceptual model can be applied to similar ore deposits world-wide, where rich ores of native silver and silver alloys are hosted by calcite-rich and quartz-poor gangue mineral assemblages.

Interpreting reaction rates at the field scale

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Interpreting reaction rates and associated rate formulations (rate constants, catalytic and inhibitory effects, reaction affinity) at the field typically requires explicit consideration of transport. This is because overall rates may be either locally transport-controlled in the case of heterogeneous systems, or even globally transport-controlled if sufficiently large length scales for reaction are considered. The potential role of physical and chemical heterogeneity has been discussed, but is still not routinely evaluated at the field scale. Heterogeneity may introduce a scale dependence to field-scale rates even in the case where the pore fluids remain far from equilibrium due to either transverse concentration (and therefore rate) gradients, or as a result of longitudinal gradients that develop where the extent of reaction is large. These two effects can be quantified in models of the field-scale system respectively by 1) comparing results from 2D or 3D representations with those from 1D continuum models, and 2) by comparing results from 1D models with those from well-mixed flowthrough reactor models. The analysis indicates that well-mixed reactor models, implicit in the so-called “Inverse Models” to the extent that they are used to determine rate constants, should be used with considerable caution at the field scale.

Another effect associated with the presence of heterogeneities that complicates the interpretation of field-scale rates has to do with the determination of hydrologically accessible reactive surface area. Some regions within the reactive domain may be largely inaccessible because of their low permeability, or mass transfer from the low to high permeability regions (where the bulk of the flow occurs) may be rate-limited. An approach that uses the retardation of a reactive tracer to quantify the hydrologically accessible reactive surface area is presented and is combined with an example involving the weathering of smectite to kaolinite at the Shale Hills site in Pennsylvania, USA.

The complexity of many multicomponent reaction networks presents another significant obstacle to the interpretation of rates at the field scale. Problems are usually manifested when an incomplete data set has been collected at the field scale, in which case potentially important pathways may be neglected altogether. In this regard, combining major and minor element aqueous and solid phase chemical analyses with isotopic analyses offers a powerful approach for delineating all of the important pathways within a field-scale reaction network. Successful examples of such an approach will be provided.
Magma sources in the Icelandic Western Rift Zone (WRZ): Crustal and mantle input

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Low δ18O Icelandic rift basalts have been interpreted as a result of contamination by low δ18O crust, or as derived from an unusual, low δ18O mantle source. In the Reykjanes Peninsula (RP) δ18O values ≥ +4.2 ‰ have been interpreted as mantle derived, while lower values were thought to reflect contamination [1]. (230Th/238U) disequilibrium has also been used as an indicator of crustal contamination in both rift, and off-rift zones in Iceland [2]. Since the magnitude of (230Th/238U) disequilibrium varies radially with proximity to the proposed centre of the Iceland plume [3], variations in this sample.

The WRZ is an ideal area to study the extent to which low δ18O and (230Th/238U) disequilibrium indicate crustal contamination, due to their eruption during post/last-glacial time minimizing the need for an age correction. Further, the rift zone is orientated tangentially to the assumed location of the centre of the plume, and thus variations in extent of disequilibrium cannot be strongly controlled by distance to the plume.

A study of new O-Sr-Nd-Pb data from the WRZ demonstrates δ18O as low as +3.79 ‰ in primitive lavas (9.5 % MgO, 143Nd/144Nd 0.513046). The WRZ data appear compatible with varying degrees of crustal contamination in terms of δ18O and 143Nd/144Nd. However, assuming the WRZ assimilant has a δ18O OL of +1.2 ‰ [1] then 35 % bulk assimilation is required to produce the lowest δ18O OL sample of 3.79 ‰ from the mantle mean of 5.2 δ18O OL. This is difficult to reconcile with the relatively low degrees of fractional crystallization, shown by the 9.52 % MgO found in this sample.

Isotopic data from Hengill central volcano, located at the triple junction between the WRZ, RP, and the south Iceland seismic zone (SISZ), plot at the enriched end of WRZ Nd-Sr-Pb trends, showing the sources are isotopically linked. δ18O OL from Hengill is 3.83 - 4.5 ‰, with 5.91 - 8.73 % MgO. This range is present in rocks with homogenous Nd-Sr isotope ratios, showing that Hengill is much more consistent with assimilation producing the low δ18O signature.

References

The hydrolysis and cloro complexation of iron(III) in hydrothermal solutions

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A knowledge of the stability of iron(III) hydroxide and chloride complexes in hydrothermal solutions is important for quantitative interpretation of the transport and precipitation of iron by crustal fluids. It is generally accepted that iron is predominantly transported as iron(II) species in reduced hydrothermal fluids in the Earth’s crust. However, boiling (phase separation) occurs ubiquitously in hydrothermal systems with the partitioning of hydrogen into the volatile (less dense) phase. The redox state of the residual liquid (or denser phase) and pH changes, such that iron(III) may become the predominant oxidation state of iron. A knowledge of the complex equilibria involving Fe3+ is therefore important in understanding the transport and precipitation chemistry of iron by fluids in the crust at high temperatures and pressure.

The complexation of iron(III) with hydroxy and chloride ligands has been studied as a function of solution composition (salinity and pH) in hydrothermal solutions to 300°C at saturated water vapour pressure. Two experimental methods have been applied, uv-vis spectrophotometry using a high-temperature, flow-through gold-lined optical cell and hematite solubility using flow-through and static autoclave systems. The strong ligand-to-metal charge transitions of the uv-vis spectra of iron(III) hydroxy and cloro complexes at wavelengths below 400 nm were used to obtain molar absorptivities, ε, and equilibrium formation constants using principle component analysis and non-linear least squares treatment of the hematite solubility measurements were used to obtain solubility constants. Based on the experimental result iron(III) was found to hydrolyse to form FeOH2+, Fe(OH)3(aq) and Fe(OH)4+ with increasing pH and FeCl2+, FeCl3+, FeCl4-(aq) with increasing chloride concentration in acid solutions. Iron(III) hydroxide complexes were found to predominate in dilute and alkaline hydrothermal solutions whereas with increasing chloride concentration and temperature iron(III) chloride complexes become increasingly important species in oxidised acid solutions.
A 3.3 Ga Mo-Cu porphyry-style deposit at Spinifex Ridge, East Pilbara, Western Australia: Re-Os dating of Paleoarchean molybdenite

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Here we show that the Re-Os chronometer is robust for Paleoarchean molybdenites. Prior to this study, AIRIE’s oldest dated molybdenite was from the 3128 ± 13 Ma Sergeevske porphyry Au-Cu-Mo deposit, Ukraine. The youngest is from the 2.120 ± 0.007 Ma Boyongan porphyry Cu-Au deposit, Philippines. Thus, molybdenite chronology can be readily used across the full span of geologic time [1].

The Spinifex Ridge (Coppins Gap) Mo-Cu deposit is located immediately north of the variably deformed Mount Edgar batholith in the 3.52-2.85 Ga East Pilbara granite-greenstone terrane. Mo-Cu mineralization, estimated at 481 million tons carrying 0.06% Mo and 0.08% Cu, is associated with high-level quartz-plagioclase porphyry intruded into Warrawoona Group basalts and rhyolites, and porphyritic granodiorite bodies [2]. Quartz veins with molybdenite and chalcopyrite are most abundant where both granodiorite and quartz-plagioclase porphyry are present.

Two molybdenite samples ascertain the timing of porphyry-style Mo-Cu mineralization at Spinifex Ridge. The drill core samples (SRD053, 227.2 and 227.6 m) represent main-stage stockwork ore hosted in potassically altered porphyry. Molybdenite was analyzed by NTIMS using a Carius tube digestion and double Os spike. Re-Os ages are 3298 ± 11 for a 1.5 cm quartz vein with irregular molybdenite selvages and 3284 ± 11 Ma for a 0.2 cm molybdenite clot adjacent to a similar vein. Ages are indistinguishable within their 2-sigma uncertainties, and agree with SHRIMP U-Pb zircon ages [3] for the Mount Edgar batholith (3314 ± 13 Ma, Coppin Gap suite; 3304 ± 10 Ma, Boodallana suite).

Ore zone geometry inclusive of silicified, brecciated borders to the quartz-plagioclase porphyry suggest that the entire intrusive-mineralization system was strongly tilted by regional listric faulting that accompanied uplift of the batholith. The Re-Os dates present a maximum age for that faulting and a minimum age for the hosting quartz-plagioclase porphyry. The geology supports formation of the Spinifex Ridge Mo-Cu deposit in a weakly extending brittle regime at ~3.3 Ga, similar to magmatic-tectonic conditions that produce Mo-Cu porphyry-style deposits today.

References
UV femtosecond laser ablation applied to stable Fe isotopes in BIFs

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Here we present in situ stable Fe isotope measurements in Precambrian banded iron formations (BIFs) using our in-house built laser ablation system which consists of a frequency-quadrupled fs laser operating at a wavelength of 196 nm and a multicolonlector-ICP-MS. The short pulse length turns the ablation process away from thermal pathways preventing artificial fractionation and minimizing matrix dependency (Horn and von Blanckenburg, 2007). The accuracy of this method has been verified for different types of matrices giving a reproducibility of 0.1‰ (2SD) for the $^{56}$Fe/$^{54}$Fe ratio (Horn et al., 2006). BIFs are fine-grained chemical sediments which are the product of initial precipitation from seawater and subsequent diagenetic and metamorphic processes. All of these processes involve redox reactions, dissolution and precipitation of Fe resulting in fractionation of Fe isotopes. In order to investigate these processes, we have determined the Fe isotope composition of single Fe-oxide and Fe-carbonate crystals by spot analyses at 30 microns resolution in different thin sections of low-grade metamorphosed BIFs. Small-scale isotopic variations of up to 0.9‰ in $\delta^{56}$Fe within single layers exist for hematite as well as for magnetite. Furthermore we detect isotopic zonation in magnetite crystals as small as 30 microns which becomes heavier in their Fe isotope composition towards the rim. These heterogeneities suggest variable relocation of Fe on a sub-millimeter scale during diagenesis and metamorphism. Fe-carbonates have also been investigated. Although crystal sizes are often less than 25 microns and Fe contents are low giving only low Fe signal intensities, we have found that variations in chemical composition have little influence on the Fe isotopic composition. Both, Fe-oxides and Fe-carbonates show constant average Fe compositions over all layers within a thin section. Since also magnetite and Fe-carbonate exhibit a constant relative difference of ca. 0.9‰, either a diagenetic process with the same precursor material must have established these isotope equilibrium fractionations or, alternatively, fluid sources were distinct but pathways to the Fe-carbonate and Fe-oxide were steady with time. These results illustrate that the study of stable Fe isotopes at high spatial-resolution have the potential to gain a better understanding on the mechanism of BIF formation and the Precambrian Fe cycle.

References


Potassium partitioning in the lowermost mantle from ab-initio computations

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Partitioning of radioactive isotopes in the Earth’s interior is of great importance to the thermal and dynamic state and evolution of the Earth as radioactive decay provides an important source of energy for mantle dynamics. As a consequence, enriched (or depleted) reservoirs in the mantle can influence the energy balance in geodynamics. The recently discovered phase transition in MgSiO3 from perovskite (pv) to post-perovskite (ppv) in the lowermost mantle provides the possibility for an enriched or depleted zone at the base of the mantle. Therefore, the partitioning of radiogenic isotopes among the phases of the lower mantle is of central importance in geochemistry and geodynamics of the deep Earth. Here we take a first step in addressing this issue by considering the partitioning of potassium between pv and ppv by performing ab-initio computations.

We have set up computations for a coupled substitutions of K and Al or Fe$^{3+}$ (M ion) for 2 Mg on the A site, and evaluate the energetics of a (Mg$_{30}$K,M)$_{Si_{32}O_{96}}$ composition in the pv and ppv structure. We compare the energetics of the following reactions for both pv and ppv to compute the enthalpy of formation:

\[
(Mg_{30}K,M)_{Si_{32}O_{96}} + 2MgO \rightarrow Mg_{32}Si_{32}O_{96} + 1/2 K_2O + 1/2 M_2O_3.
\]

The computations are performed with the VASP package using the projector augmented wave method for the static lattices of the high pressure phases in the reaction above. We use the generalized gradient approximation to the exchange and correlation potential. Structures are optimized for internal and external degrees of freedom at constant volume, and we assume that the M and K ions are at A positions directly adjacent to one another. Computations are performed for a wide compression range, reaching pressures of the CMB.

Slightly above 100 GPa we predict that $D_{K}<1$, implying that K partitions preferably into the ppv phase. Increased temperatures would decrease the magnitude of preferred differentiation. This makes a K enriched layer at the base of the mantle a possibility. It is clear, however, that the effect of other phases stable in the lower mantle (Ca-pv and mw) must be considered in a full assessment of K distribution in the lower mantle.
Biogeochemical cycling of rare earth elements in surface soils

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Stille et al. (2006) have suggested in a study on the Strengbach catchment in the Vosges mountains (eastern France, http://ohge.u-strasbg.fr) that preferential absorption of light REE (LREE) by vegetation may contribute to LREE depletion of stream water. New REE data on soil solutions recovered on the same site from 10 to 70 cm depth show similar to vegetation an enrichment of the LREE. Strontium and neodymium isotope data from these solutions indicate that up to 90 % of Sr and Nd are derived from vegetation litter. This origin of the REE in the surface soil is in strong contrast to the underlying regolith, where the mobile REE essentially originate from the dissolution of apatite derived from the granitic bedrock (Aubert et al., 2001). The Sr isotope record from tree rings of 3 spruce specimens planted 90-100 years ago on the study site yields valuable information on the formation of these different REE pools. The data demonstrate that the spruce mainly absorbed Sr from granite-derived minerals during the first years after plantation. But rapidly the isotopic compositions of the tree rings are shifted to values typical for atmospheric deposits. We interpret this evolution by transformation of the initial mineral soil into a surface soil rich in organics issued from the decomposition of vegetation litter. This new surface soil contained in the beginning mainly regolith-derived Sr inherited from vegetation. This initial Sr was then continuously removed by soil water runoff and replaced by atmospheric Sr. We are actually analyzing Nd isotopic compositions on the same spruce samples in order to confirm this hypothesis for the REE. This scenario thus suggests that vegetation and surface soil form an almost closed biogeochemical cycle for the REE, accumulating preferentially LREE issued from vegetation litter. This cycle is modified by inputs from atmospheric sources and leaching of remaining soil minerals, and outputs by surface and soil water runoff. Local stream water is in contrast to surface soil and vegetation depleted in LREE indicating that surface soil water is not the dominant source for stream water. This is in agreement with Nd-Sr isotope data from Stille et al. (2006) showing that stream water REE are mainly derived from alteration of apatite within the mineral soil. We suggest that the formation of a LREE enriched reservoir in the surface soil has together with preferential scavenging of the LREE by adsorption and precipitation during groundwater flow contributed to the formation of a LREE depleted groundwater pool within the underlying regolith. This groundwater is the main source for stream water at low stream flow.

References

The mobility of actinides and ⁹⁰Sr from bomb test fallout in a karstic area, Jura Mountains (Switzerland)

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The presence of artificial radioisotopes of plutonium, americium and strontrium is mainly due to the atmospheric tests of nuclear bombs before 1964. Present day inventories of these radionuclides in soils of the Jura Mountains (Switzerland) are often less than expected. Apparently, there has been leakage from the soils (especially the thin soils) into the karst of this region of carbonate rocks.

With the goal to assess this possible long-range migration in a natural setting we analyzed the radioisotopes - in upland soils (soil profiles and soil solution profiles near Col de Mollendruz, Switzerland, 1200 m a.s.l.), - in a karstic source at a distance of ca. 5 km (water and aquatic mosses, 660 m a.s.l.), and - in cave deposits from the same area. The mean soil inventories (0-25 cm) for thick soils are 1.3 kBq/m² and 0.12 kBq/m² for ⁹⁰Sr and Pu, respectively. These radioisotopes have significantly diffused towards deeper soil layers (40 cm depth or more) and they are also present in measurable amounts in the soil solution (< 0.22 µg/m, i.e. dissolved and colloidal). These findings highlight the potential of long-range transport in colloidal form. The calculated distribution coefficients K₄ are on the order of 10⁰⁰⁰; 3'000; and 1'500 for Pu, Am, and Sr, respectively.

The radioisotopes appear in the waters of the karstic source and in aquatic mosses collected close to the source. The plutonium activity found in the filtered (<0.45 µm) source water is 4 and 22 µBq/l for ⁹⁰Sr and Pu, respectively. The radioisotopes have significantly diffused towards deeper soil layers (40 cm depth or more) and they are also present in measurable amounts in the soil solution (< 0.22 µ, i.e. dissolved and colloidal). These findings highlight the potential of long-range transport in colloidal form. The calculated distribution coefficients K₄ are on the order of 10⁰⁰⁰; 3'000; and 1'500 for Pu, Am, and Sr, respectively.

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Taken together our results demonstrate the long-range transport (km-scale) of Pu, Am, and ⁹⁰Sr in a natural karstic environment with no radioisotope contamination other than "global fallout".
Solute exchange across the sediment water interface in an acidic pit lake

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Solute exchange across the sediment-water interface affects the water quality in mining pit lakes. Fluxes are supposed to be affected by advective groundwater flow. However, benthic solute fluxes in such lakes have mostly been determined by sediment core incubations in the laboratory or by calculation from pore water profiles.

In the present study direct solute flux measurements were carried out in situ in acidic Mining Lake 111 in the Lausitz lignite mining area, Germany. Three sites were chosen to represent A) groundwater inflow conditions B) the lake profundal and C) a reference littoral site. A volume of lake water and the sediment below were enclosed using an opaque benthic flux chamber. Oxygen decrease in the chamber was directly measured using an optode, whereas parameters such as total inorganic carbon (TIC) and dissolved Fe$^{2+}$ were analyzed in a series of water samples withdrawn from the chamber.

Sites B and C showed oxygen consumption rates between 5 and 15 mmol m$^{-2}$ d$^{-1}$ while oxygen loss from the chamber at site A equaled rates between 19 and 35 mmol m$^{-2}$ d$^{-1}$. TIC fluxes from the sediment varied closely around 5 mmol m$^{-2}$d$^{-1}$ at sites B and C, but reached up to 100 mmol m$^{-2}$d$^{-1}$ at site A. Further a distinct increase of ferrous iron in the chamber was detected only at site A, i.e. in the groundwater inflow area.

Our results reveal significant differences in benthic solute fluxes depending on groundwater inflow and setting in the lake. The groundwater inflow area is characterized by high oxygen consumption and high inflow of TIC and dissolved iron. To our knowledge these are the first measurements of this kind, providing valuable practical experience for the use of benthic flux chambers in pit lake research.

FTIR water observation in minerals from diamond inclusions and matrix of diamondiferous eclogite

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The series of recent observations have recovered that nominally anhydrous minerals (NAM) in the Earth’s mantle may contain significant amount of water. There are some evidences that water plays an important role in diamond formation. Here we present the first data on water content in clinopyroxenes (Cpx) in the matrix and diamond inclusions (DI) from diamondiferous eclogite xenolith from Udachnaya kimberlite pipe (Yakutia, Russia, description in [1]).

The water content has been estimated from unpolarized FTIR spectra of slices of the rock and polished plates of diamonds with DI. Spectra from individual DI have been obtained by subtraction of diamond absorption in the point near inclusions. The thickness of rock slices was measured by micrometer and thickness of inclusions was determined by up and bottom focusing under microscope with reference to refractive index.

The strong band at 3450 cm$^{-1}$ and two weaker bands at 3620 and 3740 cm$^{-1}$ are observed in FTIR spectra of Cpx from the matrix of eclogite. Most Cpx inclusions in diamonds show single absorption band at 3450 cm$^{-1}$ and only one inclusion has additional band with the maximum at 3600 cm$^{-1}$ (may be attributed to OH band in chlorite [2]). Water content in Cpx has been estimated by using calibrations from [3]. Water concentrations are 60-90 ppm in Cpx from the matrix and 80-150 ppm in Cpx from diamond inclusions. Neither Grt DI nor Grt from the matrix do not show any water absorption in their FTIR spectra.

Specific results of this study are: (i) the major phase containing water in the eclogite is Cpx; (ii) water content in the matrix and DI from eclogite is not significantly different. It may testify that water content in eclogite did not change during period between diamond formation and ascent of xenolith to the surface by kimberlite magma.

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References
Towards improved accuracy of SHRIMP zircon $^{207}$Pb/$^{206}$Pb measurements

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SHRIMP and other ion probes are routinely utilized to determine $^{207}$Pb/$^{206}$Pb ratios of zircons, but only in special cases can the accuracy of the measurements be claimed to be better than a few %. A great deal of attention is placed on calibrating $^{206}$Pb/$^{238}$U ratios, yet for $^{207}$Pb/$^{206}$Pb this is seldom the case. Any systematic bias in $^{207}$Pb/$^{206}$Pb of zircon is considered insignificant relative to the low precision of the individual spot analyses, a reasonable assumption based upon the generally well-known characteristics of the large ion probe. Nevertheless, as several individual $^{207}$Pb/$^{206}$Pb measurements are typically pooled to improve overall precision to the ±1-5 ‰ level for Paleoproterozoic or older zircons, the accuracy of the composite ratio should be a concern.

There are several potential sources of bias in ion probe $^{207}$Pb/$^{206}$Pb measurements of zircon, including instrumental mass fractionation, peak shape, detector performance, isobaric interferences, common Pb correction, and the method of data processing. Although it is important to understand and potentially control these individual factors, it is critical to be able to measure the overall bias. Unfortunately, there appear to be no ion probe zircon reference materials developed expressly for $^{207}$Pb/$^{206}$Pb calibration. Our data obtained from analyzing the Proterozoic U-Pb zircon QNG suggest that systematic errors of several ‰ may exist between sessions on the same instrument and between different instruments. However, this zircon is not a suitable Pb-isotope standard for several reasons, and the validity of the results is uncertain. We have developed an Archean (ca. 3.5 Ga) $^{207}$Pb/$^{206}$Pb zircon reference material, and TIMS data indicate homogeneity. The goal is to incorporate analyses of this material as a routine part of SHRIMP zircon sessions in order to monitor and potentially correct for any systematic error in the $^{207}$Pb/$^{206}$Pb ages.
Fungal transformation of lignite in overburden dumps

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Acidity in overburden dumps of open cast lignite mines poses a considerable environmental threat. Despite the persistence of the dump organic material (lignified organic matter), microbial acidity attenuation processes such as iron sulphide formation by microbial sulphate reduction were observed within several dumps (Storch et al.; 2007). Fungi are known for their ability to liquefy lignite (Ward; 1985). Therefore, autochthonous acidotolerant fungi may provide bacterial substrates by transformation of lignite into water soluble organic matter.

Methods

Autochthonous fungal strains were isolated from dump material of the Plessa field site (Lusatia, Germany). The sediment was placed on Sabouraud glucose agar and incubated at 20°C. After formation of a thick hyphae mat identical dump material was placed on this mat. A few days later bioliquefaction of lignite particles started.

Results

The autochthonous fungi (Mucor hiemalis) transformed lignite particles into black and shiny droplets of very high organic carbon contents (~15 g/L). The liquid product was analysed by gel chromatography to consist of humic substances (a), building blocks (b), low molecular weight substances (c), neutral substances (d), and polysaccharides (e). The liquefied organic matter is highly polar and water soluble. HPLC analysis (Schmalz et al.; 2002) of the water dissolved droplets revealed the predominance of carboxylic and carboxylic functional groups. Carbonic acids are well known substrates for sulphate reducing bacteria (Widdel; 1988).

References


Isotopic fractionation of Uranium in low-temperature environments

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Uranium is the heaviest naturally occurring element and mass-dependent isotopic fractionation between 235U and 238U, which scales with δM/M2, is not normally considered significant given the small ~1% difference in mass. It is therefore usual to assume that 238U/235U is constant in the terrestrial environment and equal everywhere to 137.88 at the present day. Importantly, isotopic fractionation of the very heavy elements has recently been investigated for mercury and thallium in the context of mass-independent nuclear field shift effects1, which do not scale with δM/M2, and are predicted to have permil-level effects on the heavy masses, including uranium.

We have developed experimental protocols for the precise measurement of 238U/235U and 238U/234U by multiple-collector ICPMS (MC-ICPMS) to investigate potential isotopic fractionation in uranium. Using multiple-Faraday protocols and a high-purity 238U:236U double spike to internally monitor instrumental mass bias effects, we are able to resolve variations in 238U/235U and 238U/234U at the 0.4 and 0.3 epsilon level (2σ, 1 epsilon = 1 part in 10,000), respectively. Measurements for samples formed in a range of low-temperature environments reveal sizeable, permil-level natural variability in 238U/235U2. Present experiments are focussed on the isotopic fractionation of uranium during the biologically-mediated reduction of U(VI) to U(IV).

Our new observations indicate that uranium isotopic fractionation of 238U/235U may offer the potential to monitor biological pathways and redox processes occurring during mineralization, weathering, and the transition between the U(IV) and U(VI) oxidation states, offering new insight into the processes at work. Moreover, variability in 238U/235U will have a direct bearing on the U-series and U-Th-Pb chronometers, when applied to samples formed in low-temperature environments, as these chronometers currently assume an invariant 238U/235U equal to 137.88.

References

Rivers of North Rhine Westphalia – Revisited

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In the early nineties of the last century rivers of North-Rhine Westphalia were examined by Veizer and members of his working group (Flintrop et al., 1996). Their motivation for having a close look on these – and on other more eminent – rivers was primarily the search for the missing carbon-dioxide sink. In addition, they provided a documentation of the pollution situation. We revisited some of these rivers, looking for possible changes that occurred during the past 15 years, and visited additional rivers with the focus not on the carbon budget but more on the pollution state.

In order to isolate occuring in-river processes and to identify sources of river constituents we analysed the isotopic compositions of $\delta^2$H and $\delta^{18}$O of water, $\delta^{13}$C of dissolved inorganic carbon, $\delta^{34}$S and $\delta^{18}$O of sulphate, and $\delta^{15}$N and $\delta^{18}$O of nitrate. Isotopic work was supplemented with measurements of common physical parameters and concentrations of major anions and cations.

The different geographic settings of the rivers are mirrored by their isotopic composition of water. Respective regional trends are affected by processes as evaporation and mixing of different water masses. Compared to previous work, salt pollution (i.e. ions commonly attributed to an anthropogenic origin) has decreased. This holds true especially for potassium and nitrate, but also for sodium and chloride. The isotopic composition of nitrate in the river Ruhr identifies organic fertilizers and sewage as the main sources, with some evidence for denitrification processes. Compared to 1991, sulphate concentration has increased in the downstream part of the Lippe. Low $\delta^{34}$S values suggest a higher contribution from pyrite oxidation as the likely cause. This could indicate changes in mining activity and related groundwater hydrology. For dissolved inorganic carbon we found higher concentrations characterized by lower $\delta^{13}$C-values in all rivers compared to results from the early 1990s, caused by differing meteorological situations and in-river carbon cycling.

Reference

Cosmogenic nuclide calibration – A progress report from the CRONUS project

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One goal of the overall CRONUS project (CRONUS-Earth, CRONUS-EU and contributors from countries outside the US and EU) is to derive cosmogenic nuclide production rates from well-characterised geologic sites. We aim to generate a network of natural calibration data that span a wide range of altitudes, latitudes and exposure periods, including as many nuclides and target minerals as possible at each site. This talk will provide a status report on geological calibration of $^{10}$Be, $^{26}$Al, $^{36}$Cl and $^{3}$He production rates, reviewing published data and presenting initial CRONUS results from sites in North America, Scotland and Antarctica.

The geological calibration effort is closely integrated with work on altitude-latitude scaling schemes, which provide the framework for comparing production rates between different latitudes, altitudes and exposure periods. All published scaling schemes can reconcile existing $^{10}$Be calibration data to within approximately 10% (1 sd). Assigning appropriate scaling errors is more complicated, however, because examination of the misfit between scaled production rate estimates and calibration data shows that there are systematic effects (biases in latitude and/or altitude) for all calibration schemes, as well as random error. The systematic component is minimal close to calibration sites, but may be large (and is unknown) at latitudes and altitudes far from calibration data. Additional calibration sites are needed to provide denser coverage, especially in latitude and exposure duration. Low latitudes are poorly represented in the data so far, and old sites are required to test the predictions of time-dependent scaling schemes which attempt to correct for paleomagnetic variations.
Age of magnetite–apatite deposits and geochemistry of host rocks, Bafq District, Central Iran

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Major hydrothermal/metasomatic Kiruna-type REE-apatite-magnetite ores (2x109 t) of the Bafq district in East Central Iran are hosted by Early Cambrian rhyolitic rocks and occur locally also in late spilitic basalts. This intimate association within a 150 km N–S striking structural zone, bordered by crustal faults, suggests a genetic link between magma generation and ore formation. The exact age of the mineralization, however, has not yet been determined. The tectonic setting of granitoids and rhyolites has been controversially discussed (rift setting versus magmatic arc environment) with Ramezani and Tucker (2003) favoring a collisional setting based on the chemical signature of the felsic magmatic rocks and paleogeographic reconstructions.

Our current study deals with the age of the mineralization and the geochemistry of the host rocks.

Petrographic investigations indicate that the rhyolites have been subjected to a broad-scale alkali metasomatism and an ore-related metasomatism that have modified their original composition, thus complicating the interpretation of geochemical data. Indeed, our major and trace element data do not yet permit an unambiguous interpretation of the geotectonic environment. However, we note that volcanism in the southern sector of the Bafq District is essentially bimodal with intermediate (andesitic) rocks being rarely encountered and mafic rocks being subordinate to felsic ones.

Clear apatite crystals were separated from three apatite-magnetite deposits. The nine analyzed samples yield apparent 206Pb/238U ages between about 527 and 539 Ma and thus fall entirely within the age range of the felsic magmatic rocks dated by Ramezani and Tucker (2003) [525–547 Ma]. This confirms field evidence that the ore formation was closely related to the Early Cambrian magmatic event (Daliran, 2002).

References


Tracing the mineralogy of oceanic basalt sources

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Subduction of oceanic crust has introduced considerable quantities of basalt into the Earth’s mantle, which, in the form of eclogite or pyroxenite, have often been proposed to constitute part of oceanic basalt sources. Isotopic evidence for mafic constituents in oceanic basalt sources remains ambiguous because their inferred isotopic composition is highly model dependent. Identification of pyroxenite derived melts on the basis of their major element composition is complicated by second order processes, i.e., fractional crystallization. Incompatible trace element compositions, however, are less affected by small extents of fractional crystallization. In addition, the higher modal abundance and different composition of garnet and clinopyroxene in pyroxenite compared to peridotite can lead to different partitioning behavior of the incompatible trace elements, which may be a useful tracer of pyroxenite versus peridotite derived melts. On the basis of recent partitioning experiments, bulk D values for pyroxenite are, on average, about factor of 3-6 higher than for garnet peridotite. The relative compatibility of the lithophile trace elements, however, is broadly similar. The main differences are an order of magnitude higher Ba/(Th, U, Nb, La), and about a factor of 2-3 lower Nb/(Th, U, La) and Sr/(Nd, Hf, Zr, Pb) bulk D ratios in pyroxenite compared to peridotite. Owing to the extremely low bulk D values of the most incompatible elements Ba, Th, U, Nb and La, however, even large differences in their bulk D ratios result in no resolvable differences in derivative melt compositions at melt fractions ≥ 5%. For the more compatible elements Sr, Nd, Hf, and Zr, partition coefficient induced differences (higher Sr/(Nd, Hf, Zr) and Nd/Hf ratios) persist up to melt fractions of 20-30%.

Whether differences in melt composition owing to the different partitioning behavior of garnet-peridotite and pyroxenite can be identified therefore depends largely on the style of melting and melt aggregation, i.e. how do melts form, what degree of melting is reached before separation from the solid (melt extraction) and how and to what extent do melts pool to form the aggregate melts erupted on the surface. Owing to its lower solidus temperature, pyroxenite starts melting deeper than peridotite. Key parameters for being able to resolve partitioning induced differences in melt compositions are therefore the extent of melting of pyroxenite before the onset of peridotite melting and the extent to which early pyroxenite melts can be extracted, if at all, without being significantly mixed with melts from the ambient peridotite. Regardless of the exact melt extraction scenario, the large extents of melting expected for pyroxenite (>20%) suggest that any partition coefficient induced differences between peridotite and pyroxenite melts are likely to be subordinate to initial compositional differences.
Mineralogical and ore-petrographic investigation of the iron ore occurrence of Ano Valsamonero, Rethymno (Crete)

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Numerous iron ore occurrences appear within the Phyllite-Quartzite-Series (PQS) of Crete, some of which were occasionally mined. The PQS forms the lower part of the Phyllite nappe, which with Gypsum-Rauwacke-Formation, composes the Phyllite nappe of Crete that includes the metamorphic rocks between the Plattenkalk-Series underneath and the Tripolitza-Series above. The PQS contains mainly phyllites and quartzites, in addition to metaconglomerates, marbles, calcareous phyllites and metabasalts.

The examined occurrence is located about 15 km southwest from Rethymno next to Ano Valsamonero and occurs in the form of lenses within the phyllite and quartzite of the PQS. Sampling took place along a 10 m thick profile, in distances approximately 1 m in vertical arrangement. X-ray diffraction and ore microscopy were used for determination of the mineralogy and structure of the iron ore, while the chemical composition was determined by X-ray fluorescence.

The iron ore consists predominantly of hematite, goethite and quartz, and subordinately of chlorite and muscovite. Hematite occurs in the form of radial, or more rarely in punctate aggregates between the quartz grains of ferruginized quartzite, especially in those samples, which originate from the above layers of the profile. In the samples from the middle and lower parts of the profile, hematite and goethite form a ferruginized front, which replaced largest part of the groundmass of quartzite. The Fe-rich solutions penetrated quartzite and precipitated as goethite, which forms concentric textures. The goethite changes gradually by dehydroxylation into hematite. The replacement by the Fe-rich solutions takes place from hair-cracks of the existing quartz grains. The composition of the iron ore along the profile varies regarding the Fe2O3 and SiO2 contents within a wide range.

According to the microscopic investigation of the ore, it is concluded that the processes, which have caused the massive replacing ferrugination of the ore occurrence of Ano Valsamonero are of epigenetic origin and can be classified to the continental ones.

Multiple sulphur isotopes reflecting compositional changes in Earth’s early atmosphere

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Pyrite extracted from more than 120 samples collected from Archean and Paleoproterozoic siliciclastic sedimentary units in southern Africa, western Australia, south-central Canada as well as in southwest Greenland and ranging in age from 3.8 to 2.1 Ga display nonzero Δ34S and Δ36S values. Based on empirical and experimental data as well as respective modeling results, non mass-dependent sulphur isotope fractionations are considered to result from photochemical reactions of different sulphur-bearing compounds in the atmosphere under low atmospheric oxygen abundances (e.g., Farquhar et al., 2000; Farquhar and Wing, 2003; Pavlov and Kasting, 2002).

The record of newly obtained non mass-dependent sulphur isotope results displays distinct temporal variations in their magnitude. High-magnitude Δ33S values for the Paleoarchean are followed by a somewhat attenuated Δ33S signal in the Mesoarchean, while the Neoarchean and early Paleoproterozoic show extremely variable Δ33S values (total range of 11.5‰). Post-2.3 Ga old sediments do not show a non mass-dependent sulphur isotope signal.

In addition to the temporal change in Δ33S, distinct temporal differences also exist considering relationships between δ34S and Δ33S as well as between Δ33S and Δ36S. This suggests variations in the respective photochemical reactions (e.g., different sulphur-bearing compounds involved) and/or reflect differences in atmospheric composition with respect to effective UV-shielding. However, we clearly rule out transient oxygen abundances as possible cause. Instead, potential alternatives include variations in the atmospheric abundance of methane and/or in the ratio of carbon dioxide to methane.

References
Molecular characterization of Selenium in the environment

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Selenium in the environment is an important element for ecosystem nutrition, but also can be toxic when present at slightly elevated concentrations. Selenium has similar chemistry as sulfur, and thus has multiple oxidation states and molecular forms in the environment. Availability of selenium for uptake by organisms or leaching to ground and surface waters is a function of its speciation. Thus understanding Se speciation and biogeochemistry in the environment is critical for evaluating risks and developing best management practices.

In this presentation results on speciation of Se in rocks, soils, plants, and stream waters located in an active mining region in southeastern Idaho will be presented. Phosphorus-ore in the region comprises the Western Phosphate Resource Area. The affected samples have elevated concentrations of Se relative to background levels, resulting from distribution of an ore interbed-shale (middle-waste shale) throughout the surficial environment during mine-site reclamation.

Speciation of Se in the samples was investigated using microscopically focused X-ray absorption spectroscopy. This technique utilizes focused synchrotron-generated radiation to excite core electrons in Se atoms within a sample, and fluorescence or transmission can be monitored either spatially or as a function of impinging energy. It is ideally suited for speciation in natural samples because it is element specific, and has a resolution of a few microns, thus allowing for speciation in heterogeneous samples to be investigated.

In the middle-waste shale, Se existed as reduced Se(0) or Se(II-) species. Three end-members were identified in the shale: Se-substituted pyrite, an iron selenide mineral, and an organic Se phase. Within the soil, both reduced and oxidized Se phases were detected, with the oxidized phases primarily Se(IV) (selenite); very little Se(VI) (selenate) was detected. In the plant materials both reduced organic Se and Se(VI) were identified. Finally, in the stream sediments, reduced Se, and selenite and selenate were identified.

Using the speciation information together with known ecological and biogeochemical processes, we are developing a better understanding of reaction processes, sources, and sinks for Se in the Western Phosphate Resource Area. This detailed information will facilitate a better understanding of the biogeochemical cycling in the system.

Origin of sulfur rich apatite in silicic, calc-alkaline magmas

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We have investigated volcanic apatite from a well-known center of calc-alkaline magmatism – the Oligocene Central San Juan Caldera Complex (CSJCC), Colorado, USA – to constrain the origin of sulfur rich (> ~0.6 wt.% SO3) apatite found in dacitic to rhyolitic, calc-alkaline magmas. Allapatites are small (typically 20-100 μm) and apatite from most units investigated (Fish Canyon Tuff, tuffs and lavas of the San Luis caldera complex) yield SO3 contents ranging from ≤0.2 wt.% to values of 0.8–2.0 wt.%; the bulk of apatite, however, indicate SO3 contents of 0.3–0.5 wt.%.

We performed laser-ablation ICP-MS analyses on apatite with a range in sulfur concentrations from selected units to correlate variations observed in sulfur with variations in trace elements (e.g REE) to find evidence for melt compositional changes during crystallization of S-rich vs. S-poor apatites. Apatite among units indicates characteristic compositional changes but within single units, apatite tends to form tight compositional clusters in parameters like Eu/Eu* and Sr contents, while REE concentrations may vary by a factor of two. Exceptions are a few distinct apatites. REE concentrations are typically ≥50-60x of bulk rock and/or of interstitial glass in keeping with other natural systems (e.g. Dempster et al., 2003) and suggest partition coefficients several times the ones of experimental studies.

To constrain actual melt composition from whichapatites grew, we find the combination of REE, Sr concentrations and Eu/Eu* most useful. Based on the trend of decreasing Sr towards more silicic compositions of bulk rock & glass for the CSJCC (this study and Lipman, 2004) and a DSr ≥ 3, all apatite grew from melts more silicic than ~68 wt.% SiO2 at the exclusion of the most evolved melt composition (~6 ppm Sr, 77 wt.% SiO2) that is too depleted in Eu to yield a DSr consistent with those of neighboring REE.

Our study suggests that apatite with low to high S concentrations grew in hydodacitic/rhyolitic melt requiring either 100’s of ppm of sulfur in the melt or alternative mechanisms to explain upper end of S range in apatite. One such alternative explanation may involve some sort of interaction of S-rich fluids (which could be largely derived from an underplated, degassing mafic magma) with crystallizing apatite.

References

**Climate change in the southern central Andes at 8 Ma**

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Being situated in a subtropical high-pressure region with atmospheric subsidence and cold upwelling along the western coast of the continent, the southern central Andes are extremely arid between about 15°S and 27°S. About 20mm/yr rainfall and low erosion rates characterize the Atacama Desert on the western flank of the orogen. With hyper-aridity in this region and less than 200mm/yr rainfall on the adjacent intra-Andean Puna-Altiplano plateau and in the intermontane basins E of the Puna, the southern central Andes thus comprise the most arid sector of the orogen. Despite this inherently arid character, the eastern flanks of the ranges intercept moisture-laden, easterly winds that result in up to 3000mm/yr precipitation. The cause and the timing for the establishment of this pronounced asymmetry is not known, however. Here, we report on stable C-isotope data obtained from paleosols developed in foreland-basin strata of S Bolivia that serve as proxies for paleoclimatic conditions along the eastern flanks of the Andes. Tephra in these sediments provide the chronostatigraphy for the paleoenvironmental evolution. In two sections our preliminary data show delta $\delta^{13}$C values that both decrease from -7 to -8‰ to -11 and -13‰ between about 12.5 and 8 Ma, before they become less negative with an average of -10‰ in the remainder of the profiles. The relatively rapid ~4‰ change in $\delta^{13}$C is attributed to a greater availability of moisture and increased climatic variability in this inherently dry area of the Andes. Our data suggest that the climate was characterized by a mixed C3/C4 vegetation cover since approximately 8 Ma. Moisture availability must have been similar to the present humid conditions with a dry winter season. Holocene $\delta^{13}$C values are between -9 and -10‰, thus indicating the dominance of a moisture stressed C3/C4 vegetative cover. Thus, present-day atmospheric circulation patterns and the distribution of rainfall are similar to the conditions during late Miocene time. Based on these observations we suggest that precipitation in the southern central Andes was associated with the South American Monsoon and increased at about 8 Ma. We suggest that enhanced precipitation in this region was closely linked to uplift of the Puna-Altiplano and its adjacent eastern orographic barriers that forced the southward displacement of easterly moisture-bearing winds via the Low Level Andean Jet.

**Gabbroic bodies in the Trinity Ophiolite**

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The Trinity Ophiolite (N. California) displays discrete silurian to devonian gabbroic bodies hosted by mantle rocks. It might be a good on-land analogue to test the applicability of current accretionary models for slow spreading systems. We report here first results from a mapping campaign in a northern (China Mtn.), central (Bear Creek) and southern gabbroic body (Bonanza King). The central body contains the most regular vertical lithological sequence: mantle peridotite; a shallow dipping transition zone with thick pyroxenitic layers; foliated gabbro; varly-textured gabbro. The northern body displays a disrupted transition zone separated from varly-textured gabbro by plastically deformed amphibolitized gabbro. The strain is potentially related to extensional ridge tectonics. The southern body exhibits small exposures of wehrlitic and pyroxenic rocks overlying mantle peridotite; gabbro and gabbronorite with a mineral foliation subparallel to the local dykes; varly-textured gabbro; doleritic dikes and sills. Two kinds of lateral contacts are observed. (1) Xenolithic margins, described by Cannat et al. (1991), demonstrating brittle behavior during emplacement into a cold lithosphere. (2) Dyke-like pyroxenites intruded between mantle peridotite and gabbro. No magmatic strain is obvious. We interpret this as a reactivated contact because of the sharp, sheet-like marginal zone. An inhomogeneous succession of rare peridotite; pyroxenite; doleritic dykes and varly-textured gabbro occurs at the topographic highest parts of two bodies and might represent a roof position. The disrupted character of the transition zones in the northern and southern body suggests the presence of multiple intrusive events which probably caused displacement of existing rock units. Specifically, it is our impression that the abundance of pyroxenites and primitive gabbros is too low relative to the exposed volume of evolved gabbro if a regular, mantle-derived magma is assumed.

**Reference**

Helium and neon isotopes as mantle tracers

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Noble gas isotopes, especially He isotopes, are widely used tracers for the formation and evolution of the Earth’s mantle and atmosphere. Basic concepts on mantle structure and evolution are primarily based on the interpretation of mantle ³He as reflecting primordial, undegassed mantle material. In general, the relative enrichment of ³He observed in MORBs and OIBs, compared to atmospheric values, is interpreted in terms of the retention of primordial He by the mantle throughout the history of the Earth. Primordial He isotopic ratios in terrestrial matter are largely thought to be solar-like, with the deviation from those solar-like ratios increasing during Earth’s history caused by the production of radiogenic ⁴He. Thus high ³He/⁴He ratios are interpreted to represent deep mantle material, whereas ratios around 8 RA (RA stands for the atmospheric ³He/⁴He ratio of 1.39 × 10⁻⁶) are thought to be representative for the upper mantle. Based on He, Ne and Ar fusion data of fresh, submarine volcanic glasses of a number of Mid-Atlantic Ridge off-axis seamounts we show that melt formation and evolution can have a larger impact on He than on e.g. Ne resulting in a decoupled behavior of He from other elements, such as e.g. Ne or Pb. All obtained He data are indistinguishable from the MORB range. In contrast, Ne isotopic compositions are much more primitive than MORB. Combined He, Ne and Ar systematics show that the source region of these seamounts experienced a preferential loss of He compared to Ne and Ar. This He loss, combined with subsequent ⁴He production, resulted in the decoupling of the He isotope systematics from Ne and Pb. Thus, among He and Ne only Ne has preserved the evidence that a primitive mantle component contributed to the formation of the investigated seamounts. As these seamounts are not fed from a mantle plume being derived from the deep mantle, the primitive Ne component resides within the upper mantle, implying that primitive noble gases are not necessarily indicative for deep mantle material. Our studies point out the necessity of obtaining Ne data in addition to He for the modeling of mantle formation and evolution and correct source characterization.

He-Ne-Ar isotope constraints on the nature and origin of high ³He/⁴He mantle

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Olivine phenocrysts from early Tertiary picrites from Baffin Island (BI) and West Greenland have ³He/⁴He = 38-50 Ra (n=24). The high ³He/⁴He are consistent with derivation from a mantle reservoir that is relatively undegassed compared to the depleted upper (MORB-source) mantle. Although Ne and Ar concentrations are typically 2 orders of magnitude lower than in basaltic glasses a low blank crusher is allowing Ne and Ar isotope determinations of high-³He/⁴He olivines. On a conventional 3-isotope plot, the BI picrites are indistinguishable from the Iceland and solar trends; the highest ²⁰Ne/²²Ne is 11.3. ⁴⁰Ar/³⁶Ar are typically less than 1,000. ³⁸Ar/³⁶Ar are indistinguishable from air values providing no evidence for solar Ar in the high-³He/⁴He mantle. Most samples define a trend in ²⁰Ne/²²Ne-⁴⁰Ar/³⁶Ar space that is consistent with mantle end-member with ⁴⁰Ar/³⁶Ar of 6,000-8,000. ⁴He*/²¹Ne* and air-corrected ³He/²²Ne imply the magmatic noble gases have suffered intense fractionation. This is supported by co-variation of ⁴He*/⁴⁰Ar* and ³He/³⁶Ar. The elemental fractionation is consistent with recent magmatic degassing and provides no evidence for an ancient degassing event necessary if the high-³He/⁴He mantle was a residue of early Earth depletion. The BI picrites plot on a trend in ⁴He*/²¹Ne*-³He/²²Ne space defined by basaltic glasses from Iceland. This is distinct from samples of Kola intrusives and we tentatively propose different degassing/depletion histories for the high-³He/⁴He mantle domains.
Structural incorporation of Eu(III) into calcite: Process understanding on a molecular level

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Demonstrating the geochemical aspects of the long term safety of a nuclear waste repository can significantly be improved by a molecular level understanding of the actinides behavior in the geosphere. In particular the interaction of radionuclides with minerals (adsorption, structural incorporation) strongly affects their mobility and retardation. In this presentation we will focus on the interaction of trivalent actinides and lanthanides with calcite, with special focus on the structural incorporation.

Calcite (CaCO3) is an omnipresent mineral in many rocks which are discussed as potential host for a nuclear waste repository. Furthermore, many waste repository designs include cement based components. Calcite is one of the major secondary alteration products formed during the degradation of cement over geological timescales. Actinide and lanthanide partition data derived from co-precipitation experiments indicate a high sorption affinity of these elements to calcite but a comprehensive understanding of actinide and REE uptake by calcite is not yet available. From a geochemical perspective the molecular level substitution mechanism is of key interest. Trivalent actinides and lanthanides have a similar ionic radius compared to Ca, the charge compensation mechanism upon substitution is unclear despite various recent studies. We have studied synthetically doped calcite crystals with Time Resolved Laser Fluorescence Spectroscopy and Extended X-Ray Absorption Fine Structure Spectroscopy. The focus has primarily been on Eu(III), due to its fluorescence properties. The structural parameters of Am(III) doped calcites obtained by EXAFS confirm the substitution of Ca2+ within the calcite structure. Site-selective TRLFS measurements at temperatures < 20 K show the presence of various incorporated molecular species. The incorporation into calcite involves several structurally distinguishable “sites”. These sites may be due to local lattice distortions/relaxations around the metal ion in the calcite structure. These investigations give a mechanistic understanding of the incorporation process and show that the incorporation of trivalent metal ions is not a simple coupled substitution mechanism but involves complex substitution mechanisms.

Bugs in stress: Microbial control of surface reactivity in a stress field

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The reactivity of a solid surface is strongly affected by the imposition of non-hydrostatic stress: the resulting strain rate is a driving force for mass transfer during pressure solution. Previous work [1,2] has shown that bacteria (e.g., *Shewanella oneidensis* MR-1) recognize and modify crystal surfaces through apparent recognition of surface energy, and are thus potentially sensitive to the distribution of surface stress as well. Here we present the results of a novel integration of vertical scanning interferometry (VSI) with the means to control and measure stress distribution on a solid surface, through controlled deflection of a cantilever beam. These deflection data, measured with VSI at (sub-)nanometer vertical and sub-micron lateral resolution, yield a high resolution map of surface deformation. These data can be compared with Euler-Bernoulli beam bending theory and elastic constants to yield a quantitative prediction of material response. This controlled system can be immersed in a fluid cell inoculated with MR-1 (or other microorganisms) and thus permits the study of bacterial interaction with a stressed surface.

This new technique can be used for abiotic systems as well and has a large potential for applications in earth, environmental, and material sciences.

References

Duration of metamorphism in the eclogite type locality

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The eclogite type locality is located in the Kor- and Saualpe region of the Eastern European Alps. The region also hosts one of the largest shear zones of the orogen: The Plattengneiss shear zone. Peak metamorphism occurred around 15 kbar and 700°C and the duration of its metamorphic cycle is loosely constrained by peak ages around 80 Ma and fission track ages around 50 Ma.

Despite the high temperatures of peak metamorphism, equilibration of both, major elements and radiogenic isotopes is extremely heterogeneous so that metamorphic conditions and the absolute timing thereof are not very well constrained. The lack of pervasive equilibration suggests that the highest grade metamorphic conditions were only achieved for a very short time and/or at very dry conditions.

In a series of projects over the last 10 years we have attempted to constrain both, the water content of the rocks and the time scales of metamorphism using petrological rather than geochronological methods. Although we generally obtain very short time scales and dry conditions, our studies are plagued by the inherent problems of petrological methods.

Nevertheless, on the largest scale, we have determined a metamorphic field gradient from north to south across the Koralpe range that shows that metamorphic conditions increase by less than 20°C per kilobar. We suggest that this shallow field gradient may be interpreted in terms of a non-lithostatic pressure gradient. This in turn implies that these conditions prevailed only very briefly.

Fractional crystallization of monosulfide solid solution from sulfide liquids lead to the PGE enrichment in the Jinchuan Ni-Cu sulfide deposit, western China

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Discordant lenses of Pt-Pd enriched zones (ores bearing up to 1.0 ppm of Pt or Pd) have recently been identified in the sulfide-bearing peridotite of the Jinchuan Cu-Ni-PGE (Platinum group element) sulfide deposit, China. Chalcopyrite, pyrrhotite, and pentlandite occur in both Pt-Pd enriched zones and normal ores, but Cu-bearing minerals such as cubanite and Bi-, Te-, and As-bearing minerals are more abundant in the Pt-Pd enriched zones. Sperrylite is the major Pt-host minerals in the Pt-Pd enriched zones interstitially and occurs mainly as euhedral grains within base-metal sulfides which occur among the cumulates of olivine. PGE-enrichment is found only in sulfide-bearing samples. In orebody 1 and orebody 24, Rh, Ru, and Ir are positively correlated, but a negative Ir-Pd and Ir-Pt correlation. However in orebody 2 Rh, Ru, Pt, Pd and Ir are positively correlated.

Taken together, the elemental correlations and mineralogical data support a model for the origin of Pt-Pd rich ores in Orebody 1 and Orebody 24 of the Jinchuan deposit are consistent with fractional crystallization of monosulfide solid solution from sulfide liquids on cooling; The origin of Orebody 2 involves variable magma/sulfide liquid mass ratios (R-factors).
New $^{40}\text{Ar}/^{39}\text{Ar}$ and K-Ar ages from Macolod Corridor, SW Luzon, Philippines: Implication for its volcanic history

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Macolod Corridor, southwestern Luzon, Philippines, is an extensive Quaternary volcanic field including Taal caldera and many monogenetic/polygenetic volcanoes. Recently reported K-Ar or $^{14}\text{C}$ ages (Listanco, 1994; Sudo et al., 2000) suggest that several volcanoes have younger ages than e.g., 0.14 Ma. However, the history of the possible caldera, located at the central lobe of the lake Laguna de Bay, at the north of Macolod Corridor has not been well understood. Radiometric dates remain few other than the K-Ar age, 1.84±0.07 Ma (error: 1σ), from an essential scoria (sample name 013006; Sudo et al., 2000) with a size of ~30 cm in the pyroclastic (scoria) flow at the northeastern rim, or the $^{14}\text{C}$ ages of 5000 to 47000 yBP, from pyroclastic materials between Laguna de Bay and Metropolitan Manila.

In this study, the essential scoria (sample name P4-2), smaller than 10 cm, included in the pyroclastic (scoria) flow near Teresa city located at the north of Laguna de Bay, and the scoria, 013006, have been dated at the new $^{40}\text{Ar}/^{39}\text{Ar}$ chronology laboratory in the University of Potsdam. The system used consists of a continuous CO$_2$ laser, Micromass 5400 noble gas mass spectrometer and the ultra-high vacuum tubes adopting SAES getters and a cold trap. The prepared samples were irradiated for 96 hours at the reactor in the Geesthacht Neutron Facility (fast neutron flux: $1\times10^{12}$ n/cm$^2$/s) together with the Fish Canyon Tuff sanidine and crystals of CaF$_2$ and K$_2$SO$_4$.

The obtained $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages are 1.85±0.01 Ma and 1.83±0.02 Ma from P4-2, while 1.92±0.03 Ma from 013006. With the K-Ar age, 1.82±0.05 Ma (unpublished), obtained from the scoria in the same outcrop for 013006, all the ages show agreement within 2 sigma error. These ages would be the constraints for solving the history of the caldera at Laguna de Bay.

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Gabbros drilled by IODP Leg 305, 30°N, Mid-Atlantic Ridge

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IODP Hole 1309D (Legs 304/305) penetrated 1415 m into the core-complex of the Atlantis Massif at 30°N, Mid-Atlantic Ridge. Of the 75% recovered rock, 96% is gabbroic. Possibly, a larger-scale magmatic cycle is preserved between 600 und 1240 mbsf, as marked by olivine-rich troctolites at the base and more common gabbro-norites near the top. In detail, however, internal magmatic contacts are numerous with more evolved rocks intruding into less evolved ones. Here we present an overview of the 800-1200 mbsf interval and a detailed study of the transition from evolved rocks below 1235 mbsf to overlying primitive gabbros.

Geochemically, there is a good correlation between the REE in cpx, the Mg#$^+$ in cpx, and lithological evolution. The data can be modeled as increments of batch fractionation ranging from 5 to >80% from a primitive N-MORB. There is no immediate need for magma replenishment. The rims of nearly all clinopyroxenes were overprinted by an evolved melt. A three stage model is required to explain the data set: (1) a cumulus phase; (2) displacement of residual melt and formation of new cumulate bodies from it. These two processes can explain the presence of well-equilibrated, but differently evolved cores of clinopyroxene. (3) Compaction of residual melt and differentiation of it as it migrates through the cumulus pile. This stage explains the late overprint of the clinopyroxene rims.
‘Green’ geosequestration: Secure carbon sequestration via plant silica biomineralisation

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Phytoliths form via biomineralization processes as microscopic grains of silica in plants, especially grasses. During plant growth a proportion of the organic carbon produced by plants is encapsulated by silica within the microscopic phytoliths. This phytolith occluded carbon (PhytOC) usually comprises much less than 1% of the dry weight of plants, and less than 10% of the total carbon pool in grassland topsoils (with ages of < 200 years). However, data from soil chronosequences shows that the high resistance of the PhytOC fraction (relative to the other soil carbon fractions) against decomposition processes results in PhytOC comprising ~70% of the total carbon pool in grassland topsoils that have been isolated for >3,000 years from fresh plant material addition by burial. Therefore, unlike most plant matter, which readily decomposes returning CO\(_2\) to the atmosphere, the organic carbon occluded in phytoliths effectively sequestrates carbon in soils and sediments in a very secure manner. This ‘green’ geosequestration process (i.e. occlusion of carbon in phytoliths) is currently responsible for the secure sequestering within soil of ~300 million tonnes of CO\(_2\) equivalent per year globally.

More over different plant types biomineralise silica and yield PhytOC at greatly different rates. Some major crops produce over 100 times more PhytOC than other major crop types. Furthermore, varieties within a single major crop type, such as sugar-cane and sorghum, have been found to produce widely differing quantities of PhytOC. This suggests that crop/cultivar choice decisions by farmers and foresters etc have a considerable impact on the amount of soil carbon sequestered and are a significant contributing factor affecting the global carbon cycle. It follows that the management of PhytOC in crops, pastures, forests etc has the potential to greatly enhance the current rates of secure terrestrial carbon sequestration. 

Subducted noble gas and halogen preserved in wedge mantle peridotite from the Sanbagawa belt, SW Japan

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Water-rich fluids released from subducting slabs play an important role in arc volcanism. Indeed, subduction volcanism is thought to efficiently return volatiles contained in subducting material back to the Earth’s surface. Less than 100% removal of the volatile component may result in volatile recycling into the deep mantle [1]. The volatile composition of subducting fluids is however, not well characterised. The Higashi-akaishi peridotite body in the Sanbagawa metamorphic belt, southwest Japan, is possibly a unique example of a km-scale sliver of a former mantle wedge exhumed from depths of at least 100 km. Serpentine dominated micro-inclusions in olivine grains in the peridotite are regarded as relics of former water-rich inclusions developed in the wedge mantle above a subducting slab. Thus, it is expected that these micro-inclusions should preserve characteristics of slab-derived fluids. Determination of their compositions could provide important geochemical constraints on subduction zone processes.

Noble gas and halogen determination of the micro-inclusions has been carried out using noble gas isotope analysis of both neutron-irradiated and unirradiated samples. The following isotopic characteristics have been determined: (1) \(^3\)He/\(^4\)He ratios of 1.4-1.8 Ra represent a mixture of mantle and radiogenic He; (2) \(^40\)Ar/\(^36\)Ar ratios up to 470 are close to the atmospheric ratio with a small contribution of mantle and/or radiogenic Ar; (3) Seawater-like noble gas elemental ratios enriched in heavy noble gases; and (4) halogen (Cl, Br, and I) composition is similar to marine pore fluids and brines. These characteristics imply that noble gases and halogens with compositions little different to marine pore fluids are injected into the mantle wedge just above the subducting slab.

The subducted halogen and noble gas elemental ratios are clearly distinct from those of arc volcanic gases. This implies that the Higashi-akaishi peridotite body has frozen in and preserved an inferred but previously unseen part of the volatile recycling process. Return of these volatiles to the atmosphere via arc volcanism requires the addition of a mantle component and fractionation during degassing. A small proportion preserved in the downgoing slab can explain the heavy noble gases observed in the convecting mantle.

Reference

Using reflectance spectroscopy for the reconstruction of penguin palaeoecological process in Antarctic ornithogenic sediments

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The present study explored the application of the rapid, cost-effective, non-destructive and simultaneous technique of reflectance spectroscopy within visible-near-infrared region to infer penguin palaeoecological records in the maritime Antarctic. A total of 106 samples taken from four sediment cores (Y2, Y2-4, Y4, AD3) on the Ardley Island were measured by both chemical and spectral methods. These cores were previously reported to be influenced by penguin guano, and nine elements including sulfur (S), phosphorus (as P\(_2\)O\(_5\)), calcium (as CaO), copper (Cu), zinc (Zn), selenium (Se), strontium (Sr), barium (Ba), and fluorine (F) were identified as bio-elements; their concentrations could be used as inorganic geochemical indicators for tracking historical penguin population change. The reflectance (r) and its derived indexes were employed to develop calibrations for predicting nine bio-element concentrations, using stepwise multiple linear regression (s-MLR) and principal component regression (PCR) approaches. R between optimal spectra-predicted and chemically analyzed concentrations were Ba: 0.894, all the other eight elements >0.954 for s-MLR; Ba: 0.926, all the other eight elements >0.963 for PCR.

Furthermore, principal component analysis (PCA) was performed on all the reflectance spectra data and the results showed that the first two factors were able to account for 98.9% of the variance of the data. The first PCA factor(PC1), accounting for 95.8% of the total variance, could be explained to bear the information of the content of penguin guano, and thus the PC1 score against depth of the samples (curve A) indicated the fluctuation of historical penguin population. In addition, by using spectra of pure guano and pure soil, these absorbance spectra data (log1/r) of ornithogenic sediments were linearly separated to guano part and soil part. The penguin population change inferred from the separated guano proportion (curve B) was consistent with curve A, and both curves showed similar historical change trends as inferences from inorganic elements and isotopes. Overall, this study demonstrated that using reflectance spectroscopy to infer palaeoecological information recorded in Antarctic ornithogenic sediments is feasible.

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The coupling between plate subduction and intraplate evolution in eastern China

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Plate interactions along subduction zones usually cause deformations ofoverlaying crusts as shown in the Andes. Numerical modelling shows that plate interaction during plate subduction is of critical importance for intraplate tectonic evolutions of the American continent [1].

Eastern China was an active continental margin related to the subduction of the paleo-Pacific plate under Eurasia from Jurassic to Cretaceous. This continent is well known for the removal of subcontinental lithosphere mantle with complicated geological evolutions, which leads to different models, ranging from extension to subduction-related compression and crust delamination etc. We find that the Cretaceous tectonic evolution in eastern China matches remarkably well with the drifting history of the paleo-Pacific plate. The most pronounced phenomenon is that the eastern China large-scale orogenic lode gold mineralisation occurred at about 125 Ma [2], concurrent with the major shift in the drifting direction of the subducting paleo-Pacific Plate [3] and the formation of the Ontong Java Plateau. Given lode gold deposits usually formed onset of compressional or transpressional deformations, the lode gold deposits dated the major tectonic change from extension to transpression in eastern China [4], consistent with the subduction regime and other geological records in the region. The Early Cretaceous drifting history of the paleo-Pacific also matches with other tectonic and magmatic evolutions in eastern China, suggesting that the major geological events in eastern China in the Early Cretaceous have been mainly controlled by the subduction of the paleo-Pacific plate, and that plate interactions are important driving forces for intraplate tectonic evolution in general. This provides a new angle of view to understand the tectonic evolution of the eastern Eurasian continents, e.g., the mechanism behind lithosphere thinning in eastern China as well as the evolution of the Tan-Lu Fault.

References

40Ar/39Ar dating of muscovite from the Maofeng Granite, N-Guangdong Province, China

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The Maofeng Granite, located in the Guidong granite composite, N-Guangdong Province, China, has been paid much attention to by geoscientists because of its hosting several big uranium deposits. Two muscovite concentrates have been prepared from representative samples collected from the outcrop of the granite body. They were analysed using incremental-release 40Ar/39Ar method. The 40Ar/39Ar apparent ages of the two samples are shown in Fig. 1.

The plateau ages ranging from 131.2±0.5 to 136±0.9 Ma are much different from the single grain zircon U-Pb ages varying from 207.6±3.2 to 219.6±0.9 Ma of the Maofeng Granite reported by previous researchers. The plateau ages of the U ore-forming hydrothermal activity.

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Oxygen isotopic zonality at the Iultin Sn-W Deposit (Chukotka, North-East of Russia)

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The oxygen isotope composition of host rocks and main vein minerals was studied at the large well known Sn-W Iultin deposit with application to the role of mixing fluids of different origins in the deposition of Sn-W ores in granite-related hydrothermal systems.

The deposit is located in the exo- and endocontact of leucogranite stock (K2) and is formed by the seria of the proximate quartz veins in hornfelsized sandstone-schist rocks (T1-2). The veins and greisens are largely composed of the productive mineral assemblage (quartz, muscovite, cassiterite, wolframite, arsenopyrite, subordinate beryl, scheelite), formed from sodium chloride boiling solutions enriched in CO2 and CH4 at T 270-350°C, P 0.5-1.0 kbar as it followed from fluid inclusion data. The postore sulfide and fluorite-carbonate assemblages are poorly developed.

The oxygen isotope composition of the rocks was examined in: a) metamorphosed sedimentary rocks of outer part of hydrothermal system, b) the contact part of the leucogranite cupola, c) the altered wall rocks in the central part of the deposit across the large ore body (62/50) and d) the wall rocks of the veins (7,10), poor in Sn-W ores. It was found that large (hundred meters) low-18O zones have been formed in the central part of the Iultin hydrothermal system. The δ18O values decreased monotonously from the initial 12‰ (1km from the contact) to 3-5‰ at the contact with granite. Substantial 18O decrease in the contact zone, formed by greisenized granites, is the result of active movement of hydrothermal solutions and is explained by higher permeability in comparison with metamorphosed sedimentary rocks (Spasennykh et al., 2002). During the development of vein ore bodies the wall rocks were altered insignificantly in oxygen isotope composition. The high δ18O values of minerals of productive association bore witness to magmatogenic source of the fluids. The notable depletion of the wall rocks in 18O took place during the final stage, when meteoric waters dominated in the hydrothermal system. That time no significant ascending fluid flows were focused within the veins. The initial picture of oxygen isotope zonality, connected with ore deposition, had been wiped away by active interaction of exogenic waters with host rocks.

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Synchrotron-based studies of fluids, mineral-water interfaces and glasses

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Synchrotron-based analytical methods have proved to be valuable in a wide variety of studies of fluids, glasses and mineral-water interfaces. This presentation is an overview of experiments of this nature being conducted at the GSECARS facility at the Advanced Photon Source (USA).

X-ray absorption fine structure (XAFS) spectroscopy is one of the principal methods used in these studies. One such microbeam application involves the determination of valence states for multivalent elements in igneous glasses, which in turn are used as proxies for oxygen fugacity inferences for both terrestrial and extraterrestrial magmas (e.g., Sutton et al. 2005). MicroXAFS is also used in ore-relevant studies to establish the speciation of metals in hydrothermal fluids. These applications involve measurements on fluid inclusions (both natural and synthetic) where the samples are analyzed in situ above their homogenization temperature using a heating stage (e.g., Berry et al. 2006).

Mineral-water interface studies aim to establish the atomic-scale structures of mineral surfaces, the structural and reactivity changes that occur during hydration and the resultant metal sorption properties of these surfaces. These in situ experiments typically involve combinations of x-ray reflectivity, crystal truncation rod, x-ray standing waves and grazing-incidence XAFS methods. A focus of this work is the determination of structural and reactivity changes of hydrated metal oxide surfaces (e.g., Eng et al. 2000).

Fluids can be imaged within objects using x-ray computed microtomography (CMT). One aspect involves the determination of the distribution and flow properties of multi-phase fluids in soil columns (e.g., Culligan et al. 2006). CMT methods can also reveal transport paths of metals in plants (e.g., McNear et al. 2005).

References

Raman spectroscopy of organics in Antarctic micrometeorites

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Introduction
Micrometeorites are expected to be the major source of the C flux from extraterrestrial materials delivered to the earth and might represent a major contribution to the pre-biotic organic matter on the early earth (Maurette 2006). On the other hand, organics from carbobaceous chondrites have been characterized non-destructively by means of Raman microspectroscopies (Raynal, 2003; Matrajt et al., 2004).

Methods
Raman spectra have been measured on 73 points of 11 unmelted Antarctic micrometeorite (AMM) grains pressed on aluminum foils under a Raman microscope. Peak positions, full widths at half maximum (FWHM), band intensity ratios (I(D)/I(G) and band area ratios (A(D)/A(D+G)(%)) for D (defect: ~1360 cm⁻¹) and G (graphite: ~1600 cm⁻¹) bands were determined for the AMMs and compared with the literature data on carbonaceous chondrites and other cosmic materials.

Results and Discussion
The peak position and FWHM of G band of the AMMs are ranging from 1581 to 1593 cm⁻¹, and from 87 to 133 cm⁻¹, respectively. These value ranges are almost the same as those for CM2 carbonaceous chondrites. The peak position and FWHM of D band for the AMMs are from 1357 to 1379 cm⁻¹, and from 66 to 271 cm⁻¹, respectively. This region for the AMMs mostly overlaps with the region for C11s. The D peak position range of the AMMs is similar to those for CM2 and CR2 chondrites. The I(D)/I(G) and A(D)/A(D+G)(%) are ranging from 1.1 to 1.7 and from 65 to 78, respectively. These distributions of the AMMs are close to Orgueil carbonaceous chondrite (CI1). A(D)/A(D+G) band area ratios (%) of the AMMs are in the similar range to those for CR2 and Tagish Lake carbonaceous chondrites.

These Raman features of macromolecular carbonaceous materials in the AMMs are similar to those in C1 and C2 chondrites. The AMMs studied here might have the aqueous alteration level higher than 2 and have possibly delivered useful organic components to the early earth.

References
Raynal P. I. (2003), Ph. D. Thesis, Université Peirre et Marie Curie, Paris, France
Osmium behavior in a subduction zone setting elucidated from Cr-spinel sands of boninites and tholeiite in Bonin islands

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Osmium (Os) isotope is a sensitive tracer of crust and sediment as its eroding form, because of significant contrast between a high Os isotope ratio of crust and sediments ($^{187}\text{Os}/^{188}\text{Os}>0.5$) and a low ratio of mantle ($^{187}\text{Os}/^{188}\text{Os}<0.13$). Therefore, Os isotope provides information on slab components contribution to the mantle source of island arc lavas (Brandon et al., 1999; Borg et al., 2000; Alves et al., 2002). Radiogenic Os isotopic compositions are commonly found in volcanic lavas and peridotite xenoliths in a subduction zone setting. Though most of the authors had attributed these high $^{187}\text{Os}/^{188}\text{Os}$ to the input of the slab component to the mantle source, some pointed out that assimilation of crustal materials during magma ascent possibly reproduce the elevated Os isotope ratios of the arc lavas (Lassiter and Luhr, 2001; Woodhead and Brauns, 2004). Since then, whether the high Os isotope ratios of arc lavas are caused by contribution of slab component or by assimilation of the overlying crust has long been highly debated.

Here we report the unradiogenic Os isotopic ratios of Cr-spinel sands from Chichi-Jima and Yome-Shima boninites and the significantly high $^{187}\text{Os}/^{188}\text{Os}$ of Cr-spinels of the Mukoo-jima tholeiite, Izu-Bonin arc. As Cr-spinel is resistant to later alteration and weathering and, more importantly, is the early stage crystal in the fractional crystallization, it preserves the chemical and isotopic compositions of very primitive magma in its melt inclusion and spinel itself without any later stage crustal contamination. Therefore, extremely high $^{187}\text{Os}/^{188}\text{Os}$ of 0.1429 of Mukoo-jima tholeiite is most likely caused by inputs from slab component, not by assimilation of the overlying crust. As a result, we demonstrate that Cr-spinel is the most useful mineral to decode the Os isotopic compositions of primitive arc magmas.

References

Reduction of U(VI) by Shewanella putrefaciens in the presence of organic acids

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Introduction
The oxidation state of uranium is one of the important factors that affect its migration in the environment. Although microbial reduction of U(VI) has been extensively investigated, limited information is available of the effects of organic acids. We examined the reduction behavior of U(VI) by Shewanella putrefaciens in the organic acid solutions.

Experimental
Shewanella putrefaciens was incubated in anaerobic medium at pH 7 that contained 1mM UO$_2^{2+}$, 50 mM lactic acid and 100 mM organic acids (acetic, oxalic, malonic, succinic, adipic, malic, tartaric, citric acid or EDTA). Aliquots of medium were periodically withdrawn, and filtered. Dissolved uranium concentrations and UV-vis spectra of the aliquots were measured. Precipitates generated were analyzed by XANES and SEM. The medium without organic acid (except for lactic acid) was examined as a control.

Results and Discussion
In the control medium and the media containing acetic or adipic acid, dissolved uranium decreased with time, and precipitates were observed. The XANES spectra of the precipitates showed that the precipitates contained U(IV). The SEM analysis showed that the precipitates was uraninite (UO$_2$). In the other media, dissolved uranium was almost constant. The UV-vis spectra showed that dissolved U(VI) was reduced to U(IV), and it was present as U(IV) organic complex in the medium containing oxalic, tartaric, citric acid or EDTA. No evidence of U(VI) reduction was observed in the media with succinic or malic acid. These results suggest that the reduction behaviors of U(VI) by S. putrefaciens are categorized into three cases depending on organic acid.

References
**Provenance and post-sedimentary low-temperature evolution of the James Ross Basin sediments (Antarctic Peninsula) based on zircon and apatite fission-track analysis**

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James Ross Basin contains one of the thickest and most complete Jurassic-Paleogene age sedimentary successions anywhere in the Southern Hemisphere. The basin is filled by a sequence of arc-derived clastic and volcaniclastic marine sediments through the Late Jurassic to Late Eocene. In order to reconstruct thermal history for basin low-temperature evolution of potential sedimentary resources and post-sedimentations succession, we dated detrital zircons andapatites from the sequence of sandstones collected from the James Ross and Seymour Island using fission-track (FT) thermochronology. All zircon FT ages are older than apatite FT ages provided in the identical individual rocks. Provenance of individual FT zircons and apatites ages varies in wide spread of Carboniferous to Early Paleogene ages between ~60 to ~350 Ma. Jurassic-Cretaceous ages of northwest James Ross Island are probably compatible with derivation of sediment from western lying Mt. Reece and Mt. Bradley region, where the rocks of the Antarctic Peninsula batholith appears.

Sediments from Seymour Island are probably originating from Trinity Peninsula Group and Antarctic Peninsula Volcanic Group. Shortening of tracks was due to subsequent volcanic/magmatic activity before transport of rocks and deposition into the James Ross Basin or alternatively, due to volcanic reheating after deposition.

Time-temperature modelling of the apatite fission-track samples from Seymour Island (Marambio and Seymour Island Groups) shows a similar thermal history style, involving a period of total thermal annealing and subsequent cooling (erosion/denudation). The samples were above 120°C until about the Upper Triassic (220 – 210 Ma) age and then followed by the period of relatively quick Neogene and Quaternary exhumation (since ~30 – 40 Ma) to the present erosion surface.

**Isotopic and trace element evidence for groundwater discharge in the coastal zone**

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Determination of the relative importance of freshwater discharge from surface and groundwater sources into coastal estuaries and lagoons is important in making assessments regarding water control policies. In this study, variations in δD, δ18O, δ13C, and concentrations of Sr, Ba, and Mg relative to Ca have been used to distinguish the input of fresh groundwater from rainwater and surface discharge into coastal ecosystems of South Florida (Biscayne Bay and Florida Bay). These tracers are able to distinguish between these various sources, because rainwater has relatively negative δ18O and δD values and low concentrations of cations. Groundwater also has depleted δ18O and δD, but low Sr/Ca, Mg/Ca, and Ba/Ca ratios. In contrast, surface waters have relatively positive δ18O and δD values, intermediate concentrations of Ca, high concentrations of Ba, and negative δ13C values (Swart and Price, 2002). The differences in the geochemical parameters arise because (i) surface waters in South Florida are highly evaporated thereby enriching δD and δ18O values, (ii) surface waters are highly influenced by surface organic activity which produces waters depleted in δ13C and elevated in Ba, (iii) groundwaters dissolve the local carbonate rocks which contain high concentration of Ca, but relatively low concentrations of Ba, Sr, and Mg; these waters also contain relatively positive δ13C values. Our results indicate that within Florida Bay, the input of fresh groundwater contributes an insignificant amount to the hydrological balance. Instead the salinity is controlled by runoff and precipitation. In contrast in Biscayne Bay, groundwater, surface water, and direct precipitation all contribute equally to the salinity balance.

**Reference**

In situ U/Pb geochronology of baddeleyite by LA-ICPMS

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Baddeleyite (ZrO$_2$) is a useful U-Pb chronometer for determining magmatic crystallization ages of silica-poor rocks that failed to form zircon. In situ baddeleyite dating has been plagued by analytical problems, however, limiting its application. Crystal orientation effects produce unacceptably large variations in $^{206}$Pb/$^{238}$U ratios measured by ion microprobe so that ages must be determined from $^{206}$Pb/$^{206}$Pb ratios alone. Laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) analyses have produced $^{206}$Pb/$^{238}$U and $^{207}$Pb/$^{206}$U ratios that plot in arrays extending far above concordia, suggesting severe laser-induced Pb/U fractionation. Correction procedures for instrumental mass bias, in particular the extent of matrix effects between baddeleyite and common zircon standard reference materials (SRMs) used for calibration of measured isotope ratios, are poorly defined. We have dated two baddeleyites of known (TIMS) age using a Finnigan ELEMENT-XR magnetic sector ICPMS coupled to a GeoLas 193 nm ArF excimer laser ablation system. The baddeleyites are from carbonatite in the Phalaborwa Complex in South Africa (PHB; 2059.8± 0.8 Ma) and gabbroic anorthosite of the Duluth gabbro complex at Forest Center, Minnesota (FC-1; 1099.0± 0.6 Ma). Two methods commonly used for LA-ICPMS U-Pb dating were tested. The first involved spot analysis (40 micron beam, 5 Hz, 5 J/cm$^2$) and calibration of isotopic ratios by standard-sample-standard bracketing with zircon 91500 as the calibrant. The second employed raster analysis (10 micron beam, 10 Hz, 5 J/cm$^2$), making a 40 by 40 micron box pattern and Pb/U determinations by the “intercept” method. Mass bias corrections are made by reference to a tracer solution of Tl-Bi-$^{231}$U-$^{237}$Np (with a composition defined by reference to zircon SRMs) aspirated into the argon plasma at the same time as sample ablation. Both spot and raster analyses exhibited laser-induced U/Pb fractionation during analysis, but the degree of fractionation was much more severe for the spot analyses. PHB baddeleyite exhibited much more fractionation than FC-1 baddeleyite. The reason is unclear but may be related to polysynthetic twinning on {100} being less well-developed in FC-1. Pb and U are heterogeneously distributed in the PHB baddeleyite: there is much less scatter on Pb/U ratios when it is drilled perpendicular to the {100} planes than when drilled parallel to them, suggesting that Pb/U ratios are more homogeneous at the scale of laser sampling in this orientation. Both zircon SRM and tracer solution calibration methods produced inadequate mass bias corrections for measured Pb/U and $^{206}$Pb/$^{206}$Pb ratios and erroneous ages for analysed baddeleyites. LA-ICPMS U-Pb ages with accuracies comparable to those determined for zircon can be attained using raster analyses, intercept corrections, and a tracer solution calibrated for baddeleyite.

Efficiency of Cl recycling during subduction of oceanic crust: Constraints from melt inclusions in HIMU lavas

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The amount of chlorine that is recycled into the deep mantle through subduction processes is poorly constrained. Estimates of the chlorine content in recycled, dehydrated oceanic crust range from <50 ppm [1] up to ~200 ppm [2,3].

In order to better constrain the Cl content in subducted crust, we have examined Cl concentrations as well as Cl/K$_2$O and Cl/Nb ratios in olivine-hosted melt inclusions in HIMU lavas from the island of Raivavae, Austral Islands. Raivavae lavas span a wide range of lead isotopic values, with $^{206}$Pb/$^{206}$Pb ranging from ~19.3 to 21.3. Previous isotopic and trace element studies suggest that Raivavae lavas derive from a mantle source containing ancient dehydrated oceanic crust.

Chlorine and K$_2$O concentrations range from 40-1070 ppm and 0.22-3.5 wt.% respectively. The majority of Cl/K$_2$O ratios range from 0.01-0.12 and Cl/Nb ratios range from 5-25. Cl/K$_2$O and Cl/Nb ratios are positively correlated with $^{206}$Pb/$^{206}$Pb and negatively correlated with $^{207}$Pb/$^{206}$Pb. In addition, a positive correlation exists between Cl/K$_2$O and Nb/Zr. No correlation exists between host olivine forsterite content and Cl concentration or Cl/K$_2$O ratios.

The lack of correlation between host forsterite content and inclusion Cl/K$_2$O and the correlation between Cl/K$_2$O and Pb-isotopes suggest that Cl contents and Cl/K$_2$O ratios in HIMU lavas are not controlled by shallow assimilation processes. This contradicts the previous suggestion of [1], who argued that elevated Cl/K$_2$O ratios in some Raivavae lavas resulted from assimilation of Cl-rich brine. Instead, the high Cl/Nb and Cl/K$_2$O ratios observed in the HIMU samples suggest that the HIMU source is preferentially enriched in Cl.

Because Nb should be largely retained in subducted oceanic crust during slab dehydration, we can use the average Cl/Nb ratio observed in inclusions from HIMU lavas (~18) to estimate a Cl concentration in recycled oceanic crust. For an average N-MORB Nb content of 5.6 ppm, we estimate ~100 ppm Cl in subducted oceanic crust after slab dehydration, intermediate between previous estimates of [1] and [3].

Given an estimated Cl content in altered oceanic crust of ~157-322 ppm [2], we estimate ~30-65% of the Cl in altered crust is retained in the slab after subduction-induced dehydration and eventually returned to the deep mantle.

References

The occurrences of turquoise in advanced argillic alteration of Darreh-Zerresk and Ali-Abad porphyry copper deposits, Taft-Yazd Province, Central Iran

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The studied area is located in Cenozoic Magmatic Belt of Central Iran. In ali- abad area granitoid rocks which belong to tertiary age are caused the phyllic, argillic and advanced argillic alterations.

In addition to intrusives the red arkosic sandstones and microconglomerates (host rocks) have been subjected to processes of hydrothermal activity too. The following mineral assemblages are distinguished in altered rocks.

Sericite, quartz, kaolinite, epidote, garnet, pyrite, alunite, jarosite, turquoise and iron oxides.

Alunite- jarosite and turquoise occurred as veinlets, encrustations and disseminated nodules mainly in sericitized host rocks. Turquoise genesis are related to oxidation of sulfides and development of advanced argillic alteration in a supergene environment, according to following reactions:

\[\text{alunite} + \text{H}_3\text{PO}_4 + \text{CuSO}_4 + \text{K} = \text{turquoise} + \text{K}_2\text{SO}_4 + \text{H} \]
\[\text{Al(OH)}_3 + \text{H}_3\text{PO}_4 + \text{CuSO}_4 = \text{turquoise} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \]

Reference

Geological and mineralogical studies of hydrothermal alterations (alunitization and kaolinitization) in North of Isfahan (Kesheh Area)

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Northern parts of Isfahan province are included into well known Cenozoic Magmatic Belt of Central Iran. There is extensive Eocene volcanic events. Field observation indicated that, the late intrusion bodies which are belonged to Oligo – Miocene are caused some dispersed hydrothermal alteration in area. On the base of XRD, XRF and SEM data mineralogy and chemical composition of fresh and altered volcanics are determined. Volcanic rocks with chemical composition andesite to trachy- andesite have more extensive in this area. Kaolinite, alunite and jarosite are major minerals in altered pyroclastic rocks. Mineral assemblages of these alterations are characteristic of acid – sulfate or advanced argillic type alterations. With attention to the geochemistry of major and trace element the kaolinite - alunite association are likely from hypogene source in Kesheh area.

Keywords: Cenozoic Magmatism, Uroumieh – Dokhtar Zone, Hydrothermal Alteration, Kaolinite, Alunite
Chondrite volatility trends revisited

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At the Lunar and Planetary Science Conference, we showed that there is complementarity between EH and CK chondrites for certain elements in bulk meteorite patterns [1,2]. In search for more elements showing similar behaviour, we plotted bulk chondrite data (Fig. 1) from [3]. Data are normalized to “volatile-free” CI abundances considering 20% H2O and 3.5% C [4,1].

Fig. 1: Volatility trend for EH and CV/CK chondrites.

A general complementary “mirror-like” trend is observed for elements condensing above 1060 K (Au). CV and CK chondrites are enriched in refractory elements, whereas EH (and EL chondrites, not shown) are depleted. Between 1400 and 1300 K the patterns cross over with EH chondrites becoming enriched over CV/CK. This relative enrichment of EH continues with decreasing condensation temperature.

The temperature interval at which the element patterns cross over corresponds to the transition between refractory inclusion and chondrule formation. EH and EL contain <<1 vol.% refractory inclusions. Removal of a refractory component from the enstatite chondrite forming region has been suggested previously [e.g. 5]. Our observations indicate that this refractory component could have been transported into the CV/CK chondrite forming region before chondrite parent bodies accreted.

References


Spatial and temporal (30 yr.) variations of lead geochemical signature in a macrotidal highly polluted estuary

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Two dated sediment cores (210Pb) were sampled in 2005 on tidal flats of the Scheldt estuary at the vicinity of the heavily industrialized harbour city of Antwerp. Coring was close to the estuarine turbidity maximum and in the reactive 0-10 psu zone. The cores were compared with suspended particulate matter (SPM) and surface sediments (SS), sampled between 2002 and 2006 from the Scheldt river to the southern bay of the North Sea. Pb isotopic compositions measured by MC-ICP-MS were compiled regarding to grain-sized distributions as well as sedimentological, mineralogical and geochemical data. The present study aims at characterizing the sources and the evolution of Pb inputs during last 30 yr. in that complex environment.

As a whole, Pb isotopic data for SPM, SS and cores from the Antwerp area show a narrow range of variations. 206Pb/207Pb data vary of 1.9 ‰ (RSD) from the mean value of 1.1629 (with 1.1630 for SS and SPM, and 1.1628 for cores) suggesting that ~70% of particulate Pb has an anthropogenic origin. A close look at the Pb isotopic ratios highlights systematic variations reflecting different controlling mechanisms. In the SPM and SS samples, the larger Pb isotopic variations (from 1.1582 ± 0.000010 -2sd- to 1.1697 ± 0.000017) are related to daily tidal cycles, where the relative contribution of fluvial and marine waters controls the isotopic signature. In the cores, the relative lower variation range (from 1.1608 ± 0.000011 to 1.1646 ± 0.000007) may result from a larger time-series integration and homogenization of the surface layers by bioturbation. Pb isotopic variations are correlated with grain-sized distributions, that are controlled by changes in deposition modes, mainly related to neap tide/spring tide cycles. In contrast, the decrease in Pb concentration, recorded from the 75-80’s period to 2005, does not imply any significant isotopic answer. Therefore, Pb sources in the Scheldt estuary may remain unchanged, in component and relative contribution, over 30 yr. The water quality improvement, in terms of Pb contents, is not related to the removal of the leaded gasoline, but only to industrial emission control policies and establishment of water treatment plants.
Adsorption of oxyanions on schwertmannite and its post-adsorption behavior

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Understanding of toxic trace metal behavior in the natural environment is important in predicting the long-term effects of human activities. Particularly, the behavior of toxic oxyanions is complex for the prediction. Iron hydroxides have been considered to play an important role for the behavior in nature. In this context, adsorption of toxic oxyanion on schwertmannite (major natural iron hydroxide in acidic condition) and its post-adsorption behavior were extensively investigated.

Synthesized schwertmannite was used in the adsorption experiments for Se, Cr, As, P at room temperature and pH 3.9. The concentration of the reactive fluid for the experiments ranged from 0.0mM-2.0mM. Aging experiments at 50°C were conducted for the schwertmannite exchanged original sulfates with the above oxyanions. The zeta-potential of schwertmannites with various oxyanions were also measured.

From the results of adsorption experiments, As and P selectivity on schwertmannite was higher than Cr and Se and much amount of As and P adsorbed on schwertmannite (Fig.1). XRD patterns of the samples with various oxyanions after aging experiments showed the schwertmannite with oxyanions with higher selectivity such as As and P was more stable than that with other oxyanions. The schwertmannite with lower selectivity was easily tranformed to goethite. The result of zeta-potential measurements suggested that inner-sphere complex would be formed for As and P and outer-sphere complex for Cr and Se with schwertmannite surface. Consequently, inner-sphere complexation with oxyanions would retard the transformation of schwertmannite (metastable phase) to goethite (stable phase).

Effect of volatiles in the partial melting in Earth’s asthenosphere

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Introduction and experimental procedure

Existence of partial melting in the asthenosphere is currently a matter of debate (i.e., Faul and Jackson, 2005). A recent study by Hirano et al. (2006) showed a natural evidence for an asthenosphere-derived magnatism on 140Ma old Pacific plate. The newly found alkalic basalts are less than 1Ma old and show remarkable vesicularity even erupted at 5500 m water depth which indicates high concentration of CO₂ present in the magma. In order to understand the nature of melts present in the asthenosphere, we performed a series of melting experiments on a parental alkalic picritic magma found on the Pacific plate near the Japan Trench (JPT-1 (18.4 wt% of MgO and 2.3 wt% of K₂O) and JPT-1* (~1 wt% each of CO₂ and H₂O were added to the JPT-1)). Experiments were also carried out using a mixture of a natural undepleted peridotite (KLB-1) and a wet alkalic picrite JPT-1* (97:3 in weight ratio). Two types of double capsules (Pt/graphite and Pt/Re) were used and the experiments were conducted at 1300–1500°C and 2.7–3.3 GPa for 40–120 hours using piston-cylinder apparatuses. Experiments are also in progress at pressures >5.0 GPa using multi-anvil apparatuses.

Results and discussion

At 3.0 GPa, dry alkalic picrite (JPT-1) has the liquidus T of 1450°C, whereas, at same pressure, the liquidus of the wet JPT-1* lies at ~1400°C and is multiply saturated with an assemblage of olivine+cpx+garnet. Although the dry solidus of the peridotite (KLB-1) is >1500°C at 3.0 GPa, K₂O-rich partial melts were observed in the run products between 1350 and 1500°C. In experiments using starting material (KLB-1+JPT-1*), cpx is the only phase (as quenched crystals) which represents the location of the partial melt. At ≤1350°C, K resides in isolated granules (most probably phlogopite), whereas at >1450°C, K is more widely distributed in interstitial quenched melt, between the cpx dendrites.

Our experimental results and the findings of Hirano et al. (2006) reinforce the partial melting model for the asthenosphere (Wyllie, 1988). Considering a short horizontal thermal gradient within the asthenosphere (Priestley and McKenzie, 2006) and small amounts of K₂O, H₂O and CO₂ are present, partial melt must be present ubiquitously under the oceanic plate.

References

Hirano et al. (2006), Science 313 1426-1428;
Distribution of helium-3 plumes and deep-sea circulation in the central Pacific Ocean

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Introduction
Helium isotope data have been used to study the circulation of various water masses using the mantle derived helium [1]. In order to clarify the origin of helium and deep-sea circulation in the central Pacific basin, we have collected about 200 seawater samples at 20 stations along about 170°W from 45°N to 70°S at various depths (200m ~ 5500m) on the KH-03-1 and KH-04-5 cruises of the Research Vessel, Hakuho Maru. Observed ³He/⁴He data are compared with those in the eastern Pacific [1] and over the East Pacific Rise at 25°S [2].

Analysis
The ³He/⁴He ratios were measured on a conventional noble gas mass spectrometer after extraction, purification and separation using Ti getters and cryogenic charcoal traps. The observed ³He/⁴He ratios were calibrated against atmospheric helium. The ⁴He/²⁰Ne ratios were measured by on-line quadrupole mass spectrometer before cryogenic separation of He from Ne.

Results and Discussion
Homogeneous excess ³He of ~10% is observed below 1000-m depth over the Antarctic Ridge in the Southern Ocean. The excess is significantly smaller than those observed over the East Pacific Rise at 25°S of ~50% [2]. This may be due to the lower supply of mantle helium from the ridge and dilution by well-mixing of deep seawater by fast current around the Antarctic.

In meridional helium transect along 170°W line in the South Pacific, circulation pattern inferred from salinity and dissolved oxygen distributions is confirmed by ³He/⁴He ratio. Moreover a pattern of two helium-3 maxima at 10°N and 15°S with a minimum on the equator at 2500-m depth is observed, which is similar to those observed along WOCE P16 (152°W) and P17 (135°W) sections [1]. Observed pair of helium plumes may be originated from the EPR based on the lateral distribution of excess ³He at 2500-m depth, which suggests westward flows at 10°N and 15°S in the central Pacific Ocean.

References
Determination of lead isotopic ratios in ferromanganese crust by using MC-ICP-MS and NanoSIMS

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The isotopic compositions of such trace elements as Pb and Nd, which have short residence times in the ocean, are considered to be influenced by fluctuation of deep ocean circulation. Therefore, the isotopic compositions of those elements in seawater could be a sensitive tracer for investigation of deep ocean circulation.

Ferromanganese crusts are regarded as a natural archive of past deep ocean circulation. Because of quite low growth rates of crusts, a long range record of the fluctuation of deep ocean circulation is expected to be preserved in them. By using Pb, Nd and Hf isotopic compositions of crusts, intensive studies have been undertaken to reconstruct the past deep ocean circulation pattern [e.g., 1]. However, in those earlier studies, spatial resolution of determination spots for the isotopic ratios was ~1mm and it is equal to ~1Ma. Therefore, in order to improve the spatial resolution, we applied SIMS (NanoSIMS) analysis for determination of Pb isotopic ratios of crust. For evaluation of the data of NanoSIMS, the Pb isotope ratios were also determined by MC-ICP-MS method described in Tanimizu and Ishikawa [2].

We analyzed a ferromanganese crust collected at 19°N, 138°E in the Northwest Pacific Ocean. By using microdrilling technique (the spatial interval is ca. 1mm), we prepared the samples for MC-ICP-MS. The data obtained by MC-ICP-MS show a good agreement with in surface layer of other crusts collected in the Pacific (206Pb/204Pb ; 18.67 for this study, 18.7 ± 0.1 by Klemm et al. [3]). However, in the bottom of the crust, our data are less radiogenic than those obtained by NanoSIMS, the Pb isotope ratios were also determined by MC-ICP-MS method described in Tanimizu and Ishikawa [2].

NanoSIMS analysis of Pb isotopic ratios of the crust sample was performed by a spatial resolution of 20µm. The data of NanoSIMS are lower than those obtained by MC-ICP-MS for the same layer. A possible cause of the difference between the data of NanoSIMS and those of MC-ICP-MS is the interference of 204Hg on mass number 204 in NanoSIMS analysis. However, Hg concentration of the crusts is much lower than Pb concentration and cannot be a main reason for the discrepancy. Thus, there might be other unknown isobaric interferences or problems about sample preparations or analytical technique.

References

Exsolution texture of alkali feldspar in a granite porphyry

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Microtextures of alkali feldspar are useful tool for petrologists to deduce the thermal history of felsic rocks. Exsolution texture is, for example, closely related to the cooling rate. In slowly cooled rocks the thickness of the exsolution is coarser than in rapidly cooled rocks. The relationship between the cooling rates and the wavelength of exsolution lamellae in alkali feldspars has for a long time been examined by many previous researchers, e.g., for rhyolitic lava flow [1] and for syenitic rock [2]. However, there are few studies on exsolution texture of alkali feldspar in porphyry with an intermediate cooling rate between volcanic and plutonic rocks. To examine the microtexture of alkali feldspar in felsic rock with the intermediate cooling rate, granite porphyry from the Kose granitic body was used in the present study.

The Kose granitic body is composed of cordierite-biotite granite and biotite granite porphyry [3] and located in the northern Omine acid rocks which are one of Middle Miocene granites in the outer zone of Southwest Japan. In the granite porphyry, some phenocrysts of alkali feldspar can be clearly divided into textually-distinct two regions; in a presence and absence of the well-developed lamellar intergrowth in a microscopic scale. The latter regions look like ‘homogeneous’ by a petrographic microscope and SEM, but TEM observation proves a presence of the fine lamellae in a submicroscopic scale (hereafter, the lamellae observed in the former regions with a microscopic scale are denoted as the coarse lamellae). The chemical compositions of the latter regions without the coarse lamellae (Or54-63) are slightly lower Or contents than those of the former regions with the coarse lamellar intergrowth (Or60-64). Coarse lamellar intergrowth (1 µm in average) has an irregular periodicity and its interfaces between adjacent lamellae are straight and sharp, strongly indicating a formation due to the nucleation and growth mechanism. The wavelength of the fine lamellar intergrowth (40 nm in average), in contrast, is one order or more smaller than that of the coarse lamellar intergrowth. The fine lamellar texture has a regular periodicity and the interfaces are slightly waved and branched, indicating a formation due to the spinodal decomposition mechanism. The fact that these distinct types of exsolution lamellae each of which was formed by the different mechanism coexist in the same phenocryst can be explained by taking a kinetic effect into consideration even through the simple cooling process.

References
EA-IRMS: Analysis of graphite and diamond  
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The continuous-flow mass-spectrometry with EA + ConFloIII is widely used for the isotop analysis of organic carbon, oil fractions, coals, kerogens and doesn’t use for measurement of carbon isotope ratios in graphites and diamonds.

The theoretical precondition of complexity of the isotopic analysis of graphite is connected with the increase of order strength in graphite structure from amorphous to hexagonal form and, accordingly, with growth of activation energy for the reaction of carbons nanocluster oxidation using molecular oxygen. It is interesting, that in contrast to the oxidation of amorphous and linear particles of carbon at which formed only CO₂ molecules, in grafen clusters oxidation CO₂ as well as CO may be formed. All these factors finally lead to incomplete combustion of graphite using standard EA-IRMS technique.

Moreover, there is a problem of isotopic zonality of carbon and heterogeneity in diamond crystal. Our experiments have shown, that the 13C/12C ratio of various domains of a diamond crystal can vary within the limits of 0.5-3 ‰. The typical picture of a diamond crystal burning is presented in the table.

<table>
<thead>
<tr>
<th>№ of a oxygen portion</th>
<th>№ of sample</th>
</tr>
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<tbody>
<tr>
<td>-14.9,-13.9,-14.3,-14.4,-14.7</td>
<td>1</td>
</tr>
<tr>
<td>-6.0,-4.3,-4.5,-4.7,-5.2</td>
<td>2</td>
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The technique used for analysis of 13C/12C in graphites and diamond is an adaption of continuous-flow mass-spectrometry with EA + ConFloIII methods that used for the 13C/12C ratio determination in organic compounds.

In our experiments we used submission of several oxygen portions. The temperature of an oxidizing reactor in EA was 1020°C. Molybdenum and tungsten oxides are added do the investigated sample in order do achieve complete combustion.

Reference  

Experimental study on the mechanism of metasomatism in the system between scheelite and huebnerite  
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Experiments on metasomatism were carried out in the tungstates (scheelite and huebnerite) - aqueous solutions (MnCl₂ and CaCl₂) system. We changed duration (1.5 to 1440 hours), concentration of aqueous solution (0.01, 0.1, 1.0 mol/l) and temperature (100 to 170°C) systematically. Reaction mechanism was considered based on the observation of the mineral texture and chemical analysis of experimental solutions.

In the scheelite - MnCl₂ system, huebnerite crystals grow toward the inside of host scheelite accompanying a lot of void space. The texture is categorized into pseudomorphic replacement texture. However, in the huebnerite - CaCl₂ system, small amount of scheelite was precipitated on the surface of host huebnerite. The texture is categorized into rim replacement texture. Since molar volume of huebnerite (41.88 cm³) is smaller than that of scheelite (47.05 cm³), the reaction solution can easily penetrate through the reaction layer to reach the unreacted scheelite in the former system. The progress of the replacement inside the host mineral is dependent on the ratios of the molecular volumes of the minerals. This is why the replacement textures are different in two systems. In the former system, dissolution of the starting material was a rate limiting process. And, in the latter system, precipitation of the product was probably a rate limiting process.

Dissolution rates of scheelite and huebnerite were obtained from the changes in concentration of the solution which was obtained from the dissolution of the product. Activation energies in the three different concentrations (0.01, 0.1, 1.0) were calculated. Activation energies of scheelite dissolution were estimated to be 16.6×10⁻³, 18.5×10⁻³ and 16.9×10⁻³ kJ/mol for 0.01, 0.1 and 1.0 mol/l aqueous MnCl₂ solution respectively. Activation energies of scheelite dissolution were estimated to be 1.5×10⁻⁴, 18.0×10⁻⁴ and 18.5×10⁻⁴ kJ/mol for 0.01, 0.1 and 1.0 mol/l aqueous CaCl₂ solution respectively. The former values were about one order of magnitude larger than the latter.
Silicic magmas in the Izu-Bonin oceanic arc and implications for crustal evolution


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Crustal structure and chemistry of volcanoes

Rhyolite magmas occur to a greater or lesser degree in most volcanoes along the Izu-Bonin volcanic front from Hakone to Torishima, a distance of 550 km. Their origin, together with that of dactitic magmas, in oceanic arcs is a matter of considerable interest and debate (e.g. Tamura and Wysozanski, 2006). Recent studies of along-arc crustal structures show a clear correlation between the average crustal velocity and thickness of middle crust and the average seismic velocity of the underlying arc crust chemistry (basaltic vs rhyolitic) of the Quaternary volcanoes of the Izu-Bonin arc. We will show the complex history of the 50 Ma crust. We will show the relationship between the chemical compositions of rhyolites and the average crustal velocity and thickness of middle crust beneath the volcanoes, and discuss the origin of rhyolites along the Izu-Bonin volcanic front by examining their chemical variations.

Conclusions

A number of conclusions are reached. 1) Remelting of middle crust and the formation of rhyolite magmas may have occurred both in the basaltic and rhyolitic volcanoes. 2) Basalt volcanoes consume newly produced middle crust at higher temperatures to produce rhyolite magmas. 3) Rhyolite volcanoes may have no mantle roots. The melts that feed these volcanoes originate, instead, in the middle crust. Lateral intrusions of basaltic dikes cause low temperature melting in the old (Oligocene?) middle crust, generating the rhyolitic magmas.

References

Elemental and isotopic fractionation in some organs of bamboo

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Chemical and isotopic compositions are useful tracers to assess the growing environment for plant life. Bamboo is one of the plants providing chemical and isotopic fractionation due to its long fibriform organs. Fu et al. (2001) and Ding et al. (2003) reported difference in REE and Si isotope compositions among organs of bamboo.

A bamboo (Phyllostachys nigra Munro var. henonis Stapf) with 7m high was collected in campus of Nagoya Univ. It is cut into lower trunk, middle trunk, upper trunk, lower branch, upper branch, lower spray, upper spray, lower leaf and upper leaf. After the reducing in ashes, elemental abundances and isotopic compositions are measured by INAA, XRF and surface ionization mass-spectrometry with double spikes (Wakaki et al., this vol.).

Samples are reduced to ashes about 0.5wt% (trunk) to 4wt% (leaf) from raw bamboo. The most abundant element in trunk ash is potassium. Potassium abundance is richer in trunk (60wt%) and lower to leaf (17%). The contrasting is silica. Silica is richer in leaf (68wt%) and lower to trunk (16%). No other elements than these two are enriched in bamboo more than 10wt%. Zn and Rb show similarity in trend to K₂O. Iron, Ca, Sc, Cr, Co and Ba abundances are decreasing from leaf to trunk like that of SiO₂. No clear trend is found in REE and Cs abundances. These features are summarized in the figure. The grouping of the elements seems independent on ionic radius, ionic charge or solubility in water. Isotopic compositions of heavy elements will be discussed.

Co-precipitation of Sr²⁺ with calcite from 5 to 40°C

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Trace elements may fractionate during CaCO₃ crystallization. Degree of fractionation can be used as a proxy to reconstruct e.g. precipitation environments. CO₂ Diffusion Technique is used to crystallize calcite. The aim is to decipher temperature, precipitation rate (R), and solution chemistry effects on Sr²⁺ incorporation.

Sr incorporation into calcite was studied at various R values and T = 5, 25, and 40°C. Results show that (1) at constant T elevated R results in less Sr discrimination in calcite, (2) at constant R lower T yields less Sr fractionation, (3) R effect is enlarged at lower T, (4) an upper limit for Sr incorporation exists at 40°C, and (5) besides T and R effect Sr co-precipitation is influenced by solution chemistry (i.e. pH).

Complex Sr incorporation behaviour can be reasonably explained by the surface enrichment model (e.g. Watson, 2004). According to this model, Sr is significantly enriched in a surface layer of the growing calcite. Sr incorporation into the final calcite crystal lattice depends on crystal growth kinetics, value of Sr enrichment factor, and ion diffusion within the proposed surface layer.

Reference
Finding of negative $\delta^{18}O$ zircon from metagranite in eastern Sulu, China: Implications for local paleoclimate

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Since finding of extremely low $\delta^{18}O$ eclogite at Qinglongshan in the western end of the Sulu orogen (Yui et al., 1995; Zheng et al., 1996), much efforts have been devoted to unraveling of not only more lithologies of this $\delta^{18}O$ anomaly surrounding the Qinglongshan outcrop, but also more localities of low $\delta^{18}O$ metamorphic rocks along the Dabie-Sulu orogenic belt (Zheng et al., 2003, and references therein). This study reports our new finding of unusually $18O$-depleted zircons in granitic gneiss in the eastern end of the Sulu orogen. Low $\delta^{18}O$ values as negative as $−7.8$ to $−3.1\%$ occur along a profile of 60 m length at Zuobuzhen. They are close to extremely low $\delta^{18}O$ values of $−9.0$ to $−5.9\%$ for metagranite at Qinglongshan and adjacent areas. CL imaging shows that the low $\delta^{18}O$ zircons at Zuobuzhen are primarily of igneous origin, but underwent different degrees of metamorphic modification by recrystallization and overgrowth. SHIRMP U-Pb dating yield mid-Neoproterozoic ages of 751±27 Ma for the igneous zircons and Triassic ages of 232±4 Ma for the metamorphic zircons. They are respectively interpreted to represent timing of protolith emplacement and ultrahigh-pressure metamorphism.

The variably negative $\delta^{18}O$ values for the zircons indicate considerable $O$ isotope heterogeneity in its granitic protolith. The low $\delta^{18}O$ zircons are interpreted as crystallizing from low $\delta^{18}O$ magma due to melting of meteoric-hydrothermally altered low $\delta^{18}O$ rocks in an active rift setting at the mid-Neoproterozoic. The metagranites at Zuobuzhen and Qinglongshan, about 450 km apart, are two known localities of low $\delta^{18}O$ metamorphic rocks along the Dabie-Sulu orogenic belt (Zheng Y.-F., Fu B., Gong B., Li S.G. (1996) Eur. J. Mineral. 8, 317-323. Zheng Y.-F., Fu B., Gong B., Li L. (2003) Earth Sci. Rev. 62, 105-161).

References

Re-evaluation of the equilibrium Fe isotope fractionation between $Fe^{3+}(H_2O)_6$ and $Fe^{2+}(H_2O)_6$ in aqueous solution

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We have used high level ab initio quantum chemistry methods to re-evaluate the equilibrium Fe isotope fractionation between $Fe^{3+}(H_2O)_6$ and $Fe^{2+}(H_2O)_6$ in water. The calculated equilibrium fractionation $\Delta_{Fe^{3+}-Fe^{2+}}$ is $3.7\pm0.4$ at $22^\circ C$, which is quite different from previous theoretical or experimental results.

Because it is an important and basic fractionation to govern the Fe isotopic fractionation extent between different redox states, many researchers have previously studied this. Schauble et al. (2001) first used a semi-empirical method (MUBFF) to calculate this fractionation as about $5.5\%$. The experimental result suggested by Johnson et al. (2002) and Welch et al. (2003) is a much smaller fractionation ($\sim$2.9\%). Meanwhile, the DFT & PCM calculation result suggested by Anbar et al. (2005) and Jarzecki et al. (2004) is even smaller (i.e. $\sim$2.5\%). Since there are several possible error sources in the experimental process (e.g. possible Fe-Cl or Fe-OH complexation, etc...) and the DFT & PCM calculation also has a weak point (e.g. PCM methods can poorly handle the salvation effects with strong H-bonding situations), we re-evaluate this fractionation by using a larger basis set and a better way to handle the solvation effects other than the PCM method. Our method is using up to 40 water molecules to form various supermolecules or so-called “water-droplets” surrounding the $Fe^{2+}$ or $Fe^{3+}$ ion, then do the geometry optimization and frequency calculations at B3LYP/6-311G* level. This method can treat the interactions between solute and solvent molecules explicitly and hence provides more accurate results when there is strong H-bonding existing. We also check the possible contributions from the complexation of $Fe^{2+}$, $Cl^-$ and $OH^-$ in the solution. It turns out to form the Fe-Cl or Fe-OH species will let the experimental fractionation value become smaller. We conclude that the fractionation between $Fe^{3+}(H_2O)_6$ and $Fe^{2+}(H_2O)_6$ will be larger than 2.9\% and our calculated fractionation ($3.7\% \pm 0.4$) is very reasonable if those previously ignored errors have been included in.
Use of carbon and hydrogen stable isotopic composition to quantitatively assess natural gas generation

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The mechanisms of natural gas generation and migration are distinctly different from those that control oil accumulation, and consequently new tools and strategies must be developed in order to create effective gas exploration programs. Over the past few decades, carbon isotopic composition has been widely integrated with other geochemical tools in order to determine thermal maturity of gas, gas to gas, and gas to source correlation, as well as oil to oil and oil to source correlation. In recent years, interest has increased in the application of hydrogen isotopic composition of hydrocarbons to these essential questions of petroleum geochemistry. In this presentation, we will review the fundamental chemistry of kinetic and thermodynamic fractionations of both carbon and hydrogen stable isotopes in petroleum hydrocarbons affected by thermal alteration processes.

We have conducted an extensive number of pyrolysis experiments on a wide variety of different source rocks and whole oils in order to determine kinetic isotope fractionation constants for different hydrocarbon gas sources. However, without theoretical constraints on these fractionation constants, it is difficult to derive unique kinetic parameters based only on the laboratory simulation results. Consequently, we have performed a substantial number of ab initio quantum chemical calculations of kinetic isotope fractionations (both entropy and enthalpy terms) in order to developed a model for both carbon and hydrogen isotopes that, when coupled with compositional kinetics, allows for the prediction of the stable isotopic response to thermal stress, the gas quality (e.g., wetness), the thermal maturity of the gas source rock, and the gas to oil ratio (GOR).

We have also quantified the thermodynamic equilibrium fractionation constants for both carbon and hydrogen isotopes of methane based on ab initio quantum chemical calculations. Moreover, we have used a similar approach to determine the theoretical abundance of methane molecules containing both a heavy carbon atom (\(^{13}\)C) and a deuterium atom. We will demonstrate that using the abundance of this doubly, isotopically substituted methane (\(^{13}\text{CDH}_3\)), one might be able to predict the paleotemperature of methane generation. In order to measure the abundance of \(^{13}\text{CDH}_3\), we have developed a new, laser-based, analytical technique and have obtained a detailed spectrum of synthetic \(^{13}\text{CDH}_3\). When combined with traditional stable isotope modeling, this new approach will provide an additional dimension for understanding natural gas geochemistry.

Enhanced Uranium Sorption on Alumina through Surface Modification

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Sorption onto mineral surfaces is one of the principal mechanisms that governs the mobility and bioavailability of U(VI) in subsurface environments and in permeable reactive barriers. Although strongly dependent on pH and solution chemistry, U(VI) sorption is rather limited on some mineral and oxide surfaces. Consequently, sorption may not be effective in restricting its mobility. Considering that uranyl phosphates are highly insoluble and stable in geological settings, we explored mechanisms for increasing U(VI) sorption by pre-treating gamma-alumina surfaces with arsenate, which has a high affinity for binding with uranyl ions and is an analog for environmentally abundant phosphate.

Batch uptake experiments were conducted by treating gamma-alumina surface by pre-equilibration with arsenate, followed by addition of uranyl to the suspension at pH ~4. Parallel experiments were carried out with different U concentrations (from moderate to high) and corresponding particle loading and pretreated As concentrations. Results show a positive correlation between U(VI) uptake and [As]soln/[U]ini (defined as the ratio between As solution concentration after pre-equilibration with alumina and the initial U concentration). Compared to ~20% U uptake on untreated gamma-alumina, U uptake by the pretreated gamma-alumina sharply increases to ~70% at [As]soln/[U]ini ~0.1 and ~100% at [As]soln/[U]ini >0.4, indicating the formation of ternary surface complex(es) and/or precipitates. X-ray absorption fine structure spectroscopy (XAFS) was applied at both the U LIII-edge and the As K-edge on selected sorption samples to characterize the local coordination environments of both elements and to identify the sorption products. XAFS fit results show U-As correlation at ~3.7 Å, suggesting the formation of U-As precipitates with a structure similar to UO\(_2\)HAsO\(_4\)-H\(_2\)O. U-U distances at ~3.9 Å and/or ~4.2 Å, likely corespond to formation of dimeric U species and/or schoepite-like uranyl oxy-hydroxide. The ratios between U-As precipitate and these uranyl dimeroxy-hydroxides are dependent on the [As]soln/[U]ini ratio and the absolute U initial concentration.

Results from this work can provide fundamental information for surface chemical processes in well-defined model systems as well as predictive information of U(VI) mobility in complex natural systems. Knowledge gained may also have applications for the selection and design of permeable reactive barriers, which can be used in removing dissolved uranyl from contaminated sites.
Does Tanzawa plutonic complex represent the IBM middle crust? New age constraint from SHRIMP zircon U-Pb geochronology

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The Tanzawa plutonic complex (TPC) is located in the Izu-Tanzawa collision zone, where the northern extent of the Izu-Bonin-Mariana (IBM) arc is colliding with the Honshu arc. The TPC ranges from tonalite to gabbro, and has been regarded as an exposed mid-crustal section of the IBM arc. Such exposures are extremely scarce in active intra-oceanic arcs.

Despite this importance, emplacement and crystallization ages are not well constrained for the TPC. K-Ar hb/bt ages vary widely (11 - 4 Ma, e.g. Saito et al. 1991), and have led to the suggestion that the formation of the TPC predates the collision of the Tanzawa block with the Honshu arc at ~6 Ma. However, more recent Ar-Ar age study suggests that older K-Ar ages are due to excess argon.

SHRIMP zircon U-Pb ages are newly obtained for tonalite and gabbro samples from the six major plutonic bodies of the TPC. Zircon crystallization ages of 4-5 Ma show that the main pulse of TPC emplacement post-dates the collision of the Tanzawa block.

TPC lithologies are characterized by strong depletion of incompatible elements such as K2O, LILEs, and REEs (Kawate and Arima, 1998), which has been considered to be the general characteristic of IBM arc crust. However, in light of the new post-collisional ages, the association of TPC geochemistry with juvenile IBM crust needs to be carefully assessed, through a comprehensive study of the geochemistry and geochronology of silicic plutonic rocks previously collected in the IBM arc. SHRIMP zircon crystallization ages range from 49 Ma to <1 Ma, representing almost the entire magmatic history of the IBM arc, and compositionally range from tonalite to granite. Most do not show strong depletion of incompatible elements as observed in the TPC. Moreover, the rocks of the TPC have significantly higher Th/Nb (<8) than other silicic plutonic rocks of the IBM arc (~2). Elevated Th/Nb ratios are a good indicator of sediment input from mature crust, and in the TPC may represent incorporation of sediments from the Honshu arc during the collision.

New zircon crystallization ages and geochemical data suggest that the TPC may not be the geochemical representative of the IBM middle crust.

References

Determination of magnesium isotopic variation and fractionation in carbonate minerals

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Calcium carbonate is one of the most important biominerals in aqueous environments. Ca, Mg, and other elements are incorporated through various mechanisms into the lattice. Although extensive studies of C and O isotopes and elemental abundances in these CaCO3 minerals are carried out to understand the mechanisms, little attention has been paid to isotope ratios of heavy elements.

In recent years, inductively coupled plasma mass spectrometry (ICP-MS) with multiple collectors (MC) has been introduced for the precise isotope analysis of heavy elements. The time-independent characteristic of the mass spectrometry against the mass discrimination allowed the precise analysis of Mg isotope ratios. Here, Mg isotope analysis technique was independently developed. The technique was applied to seawater and Mg rich CaCO3, and Mg isotope ratios were determined with the reproducibility of 0.02 % for 25Mg/24Mg and 0.05 % for 26Mg/24Mg ratios. The reason of the isotopic variation and degree of fractionation from seawater will be discussed.

The overall natural Mg isotopic variation and related change in Mg atomic weight are compiled to estimate the uncertainty of Mg atomic weight. Present availability of Mg isotopic reference material is also reported.
Intra-reservoir geochemical heterogeneity in the Shixi oilfield of the central Junggar Basin, China

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The Shixi oilfield is located in the central Junggar Basin, northwestern China. Previous geologic and geochemical studies have suggested that the West Pen 1 Well sag to the southwest was the hydrocarbon kitchen, in which there existed mainly two sets of Permian source sequences (the Lower Permian Fengcheng and Middle Permian Lower Wuerhe Formations). Petroleum exploration results show that hydrocarbons have been produced mainly from two sets of reservoirs, i.e. the deeper Carboniferous volcani-clastic and upper Jurassic clastic ones. In this study, we aim to unravel intra-reservoir geochemical heterogeneity within these two sets of reservoirs and tentatively discuss its controlling factor.

According to geochemical analyses, carbon isotopes and maturity of oils from the Carboniferous reservoir are greater than those from the Jurassic one, while density of the oils is lower in the Carboniferous reservoir. This likely implies that the oils in these two reservoirs have undergone different petroleum migration and accumulation process.

To approve this, we carried out artificial oil mixing experiments. After detailed geochemical analysis, we find that the distribution pattern of C20-C21-C23 tricyclic terpanes varies along with oil-mixing ratio accordingly. Based on this, we studied the characteristics of oils in the two reservoirs. It is indicated that in the Carboniferous reservoir, petroleum sourced from Lower Wuerhe Formation have a higher proportion than from Fengcheng Formation, however, this trend is to the contrary in the Jurassic reservoir.

Also, we studied the history of petroleum accumulation. The results show that the petroleum sourced from Fengcheng Formation migrated into the Carboniferous reservoir in Triassic, and then, adjusted into the Jurassic reservoir in Late Jurassic. The petroleum sourced from Lower Wuerhe Formation inptured into the two reservoirs in Late Cretaceous.

According to our research, the key event caused the heterogeneity is the adjuster of the petroleum sourced from Fengcheng Formation in Late Jurassic. Because of this event, the proportions of petroleum sourced from Fengcheng and Lower Wuerhe Formation in two reservoirs are not consistent. As a result, the carbon isotopes, maturity and density of the oils in these two reservoirs are different.

Interactions between carbonate magmas and MARID metasomes: The case of diamondiferous aillikites from the Torngat Mountains, Canada

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Aillikite magmas (a carbonate-rich ultramafic lamprophyre; UML) erupted through the Archean crust of the Torngat Mountains in northern Labrador between 610 and 550 Ma. These dykes are characterized by long-term isotopic depletion (\( ^{87}\text{Sr} / ^{86}\text{Sr} = 0.70323-0.70377 \); \( \varepsilon\text{Nd} = +1.2 \) to \( +1.8 \); \( \varepsilon\text{Hf} = +1.4 \) to \( +3.5 \); \( 206\text{Pb} / 204\text{Pb} = 18.2-18.5 \)), but grade into carbonate-poorer mela-aillikites which show isotopic enrichment (\( ^{87}\text{Sr} / ^{86}\text{Sr} = 0.70388-0.70523 \); \( \varepsilon\text{Nd} = -0.5 \) to \( -3.9 \); \( \varepsilon\text{Hf} = -0.6 \) to \( -6.0 \); \( 206\text{Pb} / 204\text{Pb} = 17.8-18.2 \)). This long-term enriched signature is coupled to distinctively higher Rb/Cs and Zr-Hf-Ti. Increased partial melting involving old phlogopite- and rutile-bearing source material reminiscent of MARID probably imparted this signature to carbonate-rich aillikite magmas, thereby shifting compositions towards mela-aillikites. Channelling of CO2-rich melts into pre-existing MARID vein networks in the lower reaches of the cratonic lithosphere and their varying interactions best explains the aillikite/mela-aillikite continuum. As there is no evidence for independent melting of the low-T fusible MARID veins, temperatures during aillikite magma generation may never exceed 1200°C. Thus, decompression and volatile-fluxing are the principal causes of UML/carbonatite magma generation within rifting cratonic mantle. Strong interactions between CO2-rich melts and lithosphere are unavoidable, explaining the rarity of direct eruptions of primary carbonatite magmas. The degree of interaction controls whether CO2 (i) remains dissolved in UML magmas, enabling separation of carbonatite intrusions at crustal levels, or (ii) largely reacts out at mantle depths resulting in carbonate-poor UML magmas, as in the Torngat examples.
Geochemical variability within the lithospheric mantle beneath the Adelaide Fold Belt, South Australia

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Kimberlites in South Australia

The Adelaide Fold Belt hosts one of the largest kimberlite provinces in Australia. More than one hundred diamondiferous and non-diamondiferous kimberlites have been discovered in the Southern Flinders Ranges region, ~200 km north of Adelaide. The kimberlites, which commonly occur as northwest-trending dykes, sills, or pipe-like structures, contain abundant mantle-derived xenocrysts, including garnets, clinopyroxenes, orthopyroxenes, Cr-spinels, and ilmenites. The major- and trace-element compositions of these minerals have been used to reconstruct spatial variations in the structure and geochemical history of the mantle lithosphere beneath kimberlites in the Eurelia/Orroroo, Franklyn, and Monk Hills areas.

Results

The xenocryst populations from all kimberlites are dominated by peridotitic parageneses; eclogitic minerals are rare or absent. Although compositional ranges of the xenocryst populations are rather similar within each area, variations on a regional scale do exist. Garnets from the Franklyn area, for example, are characterized by more Ti-rich compositions, when compared to the other areas, and a lack of garnets with sinusoidal REE patterns. Regional differences also exist in the compositional ranges of spinel xenocrysts and the absence and presence of ilmenites.

Geothermobarometry based on single clinopyroxenes indicates a regional gethermal gradient of \(-45\) mW/m\(^2\), which is in stark contrast to previous estimates for the lower crust in this region.

Conclusions

The geochemical variations in the lithospheric mantle are likely caused by variable degrees of metasomatism and/or different styles of metasomatism. Regional changes in the thickness of the lithosphere may also exist, and these factors together may explain the diamond potential of the kimberlites.

Variations of the Eocene climate reflected in the isotopic composition of fossil resins from the Northwest Territories, Canada

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Middle Eocene conifer resins have been analyzed for their C and H isotopic compositions, as well as spectral characteristics using FTIR. The resins were recovered from an un lithified peat sequence that forms part of the infill of the Giraffe kimberlite crater in the Lac de Gras field, Northwest Territories, Canada. Based on the presence of well-preserved macrofossils and FTIR spectra of fossil and modern resins, it is believed that the fossil resins were produced by \textit{Metasequoia glyptostroboides}.

Results

The FTIR spectra indicate that all resins are chemically identical with only minor variations in redox history that is unlikely to influence isotopic composition. Throughout the sequence, resins are extremely variable with respect to \(\delta D\) and \(\delta^{13}C\), ranging from -374 to -286‰ (\(\delta D\) vs SMOW) and -27 to -20‰ (\(\delta^{13}C\) vs PDB), respectively. Variability is broadly mimicked by both isotopic systems, implying pervasive biogeochemical changes in the ecosystem. Based on a constant fractionation factor for hydrogen between resin and water (~200 ‰, Nissenbaum & Yakir, 1995), very light H-isotopic compositions are inferred for the Eocene waters accessed by these trees (-174 to -86‰).

Conclusions

Extreme co-isotopic variability of Eocene conifer resins, coupled to highly-depleted \(\delta D\) values, are indicative of short-lived climatic/hydrological variability in the Canadian low Arctic, in keeping with recent results from biomarkers in cores from the Arctic Ocean (Pagani et al., 2005). This challenges the notion of stable Middle Eocene climates at northern latitudes.

References

Natural estuarine particles and their uptake of nitrogen in estuaries

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Globally, total nitrogen (TN) loadings to estuaries are increasing due to changes in urbanisation etc. Organic N (ON) constitutes >50% of the TN input to estuaries, but its speciation, reactivity and fluxes are poorly quantified.

Water Samples were collected from the Tamar Estuary (SW England). Suspended particulate Material (SPM) was fractionated and the water and particles characterised. Incubations using ¹⁴C-labelled amino acids (AA) as ON proxies examined SPM-water partitioning.

The particle concentrations used for incubation experiments were those measured in the estuary. The results under the two conditions employed (‘live’ and ‘dead’ particles) were considerably different. Under dead conditions there was only negligible binding of the AA to the particles and most remained in the water. The results were similar regardless of the AA chemical structure. Under live conditions, uptake of the AAs onto particles was rapid, with 80-90 % removed from solution over 24 hours. This indicates that the AA uptake onto particles was controlled by bacteria, which used the AAs for cell growth. The results were unexpected as the research literature suggests that the compound chemistry controls its attachment to particles and we used a range of compounds to test this. The broad conclusion to be drawn was that bacterial uptake of AAs is much more rapid and quantitatively important than any other type of physico-chemical binding. Our findings contradict the idea that particle-associated ON is protected from bacterial degradation, and it appears that assumptions on the behaviour of ON in aquatic systems will need to be revised.

Volatile budget of the Kamchatka arc

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In this study I estimate the volatile output (C, N, He, Cl) from the Kamchatka volcanic arc using: (1) direct measurements of flow rates and chemical compositions of thermal waters and vapors from more than 100 groups of thermal springs and hydrothermal systems; (2) direct measurements and indirect estimations of the gas fluxes from Kamchatkan volcanoes and (3) volcano-plutonic Holocene productivity of magmas and the corresponding volatile flux. Plank and Langmiure (1998), Hilton et al (2002), Sadofsky and Bebout (2004) Jarrard (2002) are main sources for the accepted here input data for H₂O, CO₂, N₂, S, Cl and He. The main results (fluxes in mole/year) are shown in the table below:

<table>
<thead>
<tr>
<th>Statement</th>
<th>IN</th>
<th>OUT</th>
<th>OUT/IN</th>
<th>OUT global</th>
<th>Kam/Globe</th>
</tr>
</thead>
<tbody>
<tr>
<td>S x 10⁻¹⁰</td>
<td>2.3</td>
<td>1.2</td>
<td>0.52</td>
<td>32</td>
<td>0.037</td>
</tr>
<tr>
<td>H₂O x 10⁻¹²</td>
<td>2</td>
<td>1.4</td>
<td>0.7</td>
<td>80</td>
<td>0.018</td>
</tr>
<tr>
<td>CO₂ x 10⁻¹⁰</td>
<td>7.8</td>
<td>2.3</td>
<td>0.29</td>
<td>230</td>
<td>0.010</td>
</tr>
<tr>
<td>^4He x 10⁻⁴</td>
<td>4.5</td>
<td>45</td>
<td>10</td>
<td>2000</td>
<td>0.023</td>
</tr>
<tr>
<td>^3He</td>
<td>0.45</td>
<td>4.2</td>
<td>32</td>
<td>200</td>
<td>0.021</td>
</tr>
<tr>
<td>Cl x 10⁻⁹</td>
<td>9.2</td>
<td>12</td>
<td>1.3</td>
<td>320</td>
<td>0.037</td>
</tr>
<tr>
<td>Cl x 10⁻⁹</td>
<td>13</td>
<td>7</td>
<td>1.8</td>
<td>380</td>
<td>0.018</td>
</tr>
</tbody>
</table>

Kamchatkan fluxes relative to global fluxes are roughly proportional to the length of the Kamchatkan segment relative the global arc length (700 km vs ~40,000 km). “Arc-Magmatic” ratios N₂/³He, C/³He and Cl/³He for Kamchatka in log-units are 8.7 ± 0.5, 9.8 ± 0.7 and 9.7 ± 0.6 respectively. It looks like the Cl/³He ratio is a stable indicator of the arc magmatism. Its uniform value among different manifestations including volcanic gases suggests an essentially magmatic source of Cl in thermal springs.

References


Experimental re-equilibration of quartz-hosted H2O-CO2-NaCl inclusions under differential stress using a Griggs apparatus

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Little is known about the effects of plastic deformation on the properties of fluid inclusions within deforming host-crystals. Geochemical and petrologic investigations based on fluid inclusion analysis must therefore be confined to samples in which the host minerals are unstrained or at least contain strain-free domains. For want of a clear interpretative framework, the potentially useful information in inclusions within sheared hydrothermal veins and metamorphic rocks remains inaccessible.

To elucidate the basic behaviour of fluid inclusions during plastic deformation of their host crystals we are undertaking experiments using a Griggs-type piston-cylinder apparatus with weak salt as the solid confining medium. In addition to offering higher experimental pressures than conventional hydrothermal autoclaves pressurized by gas, the Griggs device permits experiments under deviatoric stress. A first series of experiments under hydrostatic conditions have been carried out on natural H2O-CO2-NaCl inclusions in large undeformed quartz crystals, obtained from orogenic gold-quartz veins at Brusson, NW Italy. Disks were cut from the samples at 45° to the crystallographic c-axis and polished such that their upper and lower faces were perfectly parallel.

Prior to the experiments numerous inclusions were mapped, photographed and analysed by microthermometry and Raman spectroscopy to determine their initial molar volumes and compositions. The corresponding fans of isochores were calculated to span a range of pressures at 700 °C, the mean internal pressure being approximately 600 MPa. The samples were therefore placed at 700 °C and 500, 600 and 800 MPa (all within the alpha-quartz field) for 16 hours, in order to induce re-equilibration of the inclusions under conditions of internal underpressure and internal overpressure. Following the experiments the inclusions were relocated and reanalysed. In each case, irreversible changes in the shape and composition of the inclusions were observed. Moreover, the initial variation in bulk molar volumes reduced considerably during the experiments, converging on the values expected for the externally imposed P–T conditions. The successful instrumental control attained in these hydrostatic re-equilibration runs is a necessary prerequisite for our on-going experiments involving deviatoric stress.

Feldspars of composition K[(Al,Fe)Si3O8]: Their growth and ordering behaviour

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K-feldspars in the system K[AlSi3O8] - K[FeSi3O8] have been synthesized hydrothermally from oxide mixes together with KOH solution at P H2O = 1 kbar and T = 400 °C, 500 °C, and 600 °C to investigate their ordering behaviour, the extent of Al,Fe substitution, and the influence of oxygen fugacities on the run products.

In the Ni-NiO buffered runs Fe3+ was partly reduced to Fe2+. Abundant growth of Fe-containing mica left the K-feldspar strongly depleted in Fe3+ relative to the starting material. In the Cu-Cu2O runs with their larger oxygen fugacities, growth of delafossite (Cu1+Fe3+O2) took up various amounts of Fe3+ resulting in Fe2+ contents of the K-feldspars ranging from 20 mol% to 100 mol%.

Considering the discontinuous character of the sanidine-microcline transition in both K-feldspar endmembers, a phase diagram has been calculated from known transition temperatures (480 °C and 704 °C, respectively) and known (7300 J/mol; Hovis, 1988) or derived transition enthalpies (11500 J/mol) yielding a narrow two-phase field separating (Al,Fe)-sanidine from (Al,Fe)-microcline. In the Al-rich part of the diagram, metastable monoclinic K-feldspar persisted in the stability field of microcline, whereas Fe-rich compositions attained the triclinic ordered state. No indication of a miscibility gap was detected.

Pure KAl-feldspars, even after long annealing, kept a high degree of disorder in agreement with predictions from the Mueller rate equation, when using an updated calibration of ln(Kd) vs. 1/T: -RTln(Kd) = 4047(668) - 1.80(47)*T + 10955(929)*Q.

Structural incorporation of Fe3+ leads to increasing order, the more so the lower the temperature of annealing. Following the ideas of Graham & Elphick (1991), this is interpreted as a consequence (i) of the proton concentration in the structure having a larger effect on Fe, Si than Al, Si interchanges and (ii) of solution-reprecipitation processes, dominating over solid state diffusion at increasing Fe contents. Solution-reprecipitation becomes the more effective the more the metastable monoclinic K(Al,Fe)-feldspars deviate from their field of stability.

References

A view of Martian weathering from microns to hundreds of kilometers

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Aqueous processes have left indelible marks on the morphology of the Martian surface. The geochemical effects are visible in Martian meteorites, at the landing sites of robotic missions, and from orbit (Thermal Emission Spectrometer on Mars Global Surveyor; Gamma-Ray Spectrometer on Mars Odyssey, OMEGA on Mars Express). The nakhlite meteorites show clear evidence for aqueous alteration: alteration veins with elevated S concentrations, dissolution of phosphates (producing relatively high abundances of REE in alteration veins), dissolution of residual glass (marked by high abundances of Cs and Rb in alteration phases), and incipient alteration in olivine. These observations are consistent with short-duration alteration by acidic fluids. Landing site data show that the secondary mineralogy is dominated by Mg- (with minor Fe- and Ca-) sulfates and iron oxides, not the clay minerals and Al-hydroxides common in terrestrial weathering. Typical terrestrial alteration follows paths like the arrows on diagram. In contrast, on Mars the alteration process is dominated by olivine dissolution and formation of iron oxides, probably in an environment rich in sulfuric acid at low water/rock ratio. Such conditions allow for rapid dissolution of phosphates and olivine, but, if time is short and water/rock is low, inhibits dissolution of pyroxene and plagioclase, not dissimilar to the record in the nakhlites. The global data from TES and GRS show that this process is not unique to the few landing sites: it appears to be a Mars-wide weathering style. The uniformity of K/Th measured by GRS is consistent with little dissolution of plagioclase or formation of aluminous alteration products.

This record reflects conditions from the mid-Noachian. Models of regolith evolution that include impact, volcanism, and aqueous alteration suggest that most alteration material was produced by 4 Gy. The lack of evidence in the highlands for alteration under neutral-pH and high water/rock (GRS and TES global data) suggests that such conditions were rare, even early in Martian history, although the identification of phyllosilicates (e.g., nontronite or chamosite) by OMEGA suggests that more Earth-like conditions prevailed sometimes.

Temporal increase in iron oxide inputs into a shallow marine carbonate sediment system: A sediment, porewater and geomicrobiological study

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Discovery Bay, a carbonate-dominated embayment in north Jamaica, has been subject to inputs for 40 years of iron-rich bauxite sediment associated with the local mining and transport of processed bauxite. As such, this site is an ideal natural laboratory to study the records and impacts of iron oxide inputs upon geochemical, diagenetic, and microbial processes in tropical carbonate sediments.

The iron contents in these sediments vary from 1500 µg/g in shallow (5m) sites to over 6000 µg/g in deeper water (20m) sites as a result of the preferential deposition of fine-grained iron oxide-rich bauxite material in deeper water. Down-core increases in Fe record the increased inputs into the bay. The presence of iron oxides markedly alters the chemical processes taking place within Discovery Bay, with a shift from dominance of bacterial sulphate reduction at non-impacted (Fe-poor) sites, to a dominance of bacterial Fe(III) reduction in Fe-rich bauxite-impacted sediments. These different carbon oxidation pathways results in contrasting styles of CaCO₃ grain dissolution and preservation.

Iron oxides within all impacted sediments display a high potential reducibility, from 40% to 80% dithionite-extractable Fe(III). Experimental analysis of the potential susceptibility to, and rates of, bacterial Fe(III) reduction, utilising Discovery Bay sediment and Shewanella putrefaciens CN32 (a known Fe(III)-reducer) have confirmed the high bacterial reducibility of iron oxides within the sediment. Up to 70% of initial Fe(III) in the sediments was reduced over 15 days. Current research, using molecular 16s rRNA techniques, will determine the shifts in bacterial communities in the sediment as a result of these iron oxide inputs.
Experimental determination of trace element partition coefficients between zircon, garnet and melt

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The problem of relating ages, as calculated by zircon U-Pb geochronology, to processes and hence geological events is central to understanding mountain building and crustal evolution. Accurate P-T-t paths can only be produced if zircon growth can be linked to specific rock and mineral processes used to establish pressure and temperature values for metamorphic episodes.

As a major metamorphic mineral in crustal events, garnet is widely used as a thermobarometric tool, and linking garnet growth to zircon formation could be used to refine the interpretation of U-Pb ages.

Attempts to resolve this issue have focussed on REE partitioning between zircon and garnet, both of which strongly incorporate the HREE into their structure, and so it is possible there is a distinct REE partitioning signature which will highlight whether the two minerals have grown at the same time. There are two complementary methods to obtaining this information, empirical and experimental.

Empirical methods of determining this signature using carefully selected rocks have proved troublesome, with a wide range of partitioning signatures found.

This project has used experimental techniques to produce zircon-melt, garnet-melt and zircon-garnet-melt partition coefficients at a range of P-T conditions in melt compositions relevant to natural rocks. Zircon and garnet are grown in trace element equilibrium with a water-undersaturated granitic melt, which represents partial melts formed in the lower crust during anatexis. Temperature ranges from 850°C to 1050°C at a pressure of 5Kbar were produced using internally heated gas apparatus. Trace element concentrations were measured using SIMS analysis at the Ion Microprobe Facility at the University of Edinburgh.

The experimental data produced will be applied to interpret chemical signatures of zircon in garnet-bearing metamorphic rocks, and will provide an objective basis for interpretation of the timing of growth or recrystallisation of zircon in many high-grade terrains.

New insights into peralkaline magma chamber processes in the Naivasha area, Kenya Dome

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The Naivasha area, located in the central Kenya rift, comprises three quaternary-recent peralkaline salic volcanic complexes: the caldera Longonot volcano, the Great Olkaria Volcanic Complex, and the Eburru Volcanic Complex (EVC) [1].

In order to further constrain the genesis of peralkaline magmas in this area, the most recent EVC peralkaline trachytes and rhyolites have been the subject of an integrated multi-isotope approach (Sr, Nd, Hf, Pb, U/Th, Rb/Sr, Ar/Ar) coupled with major and trace elements. A model is presented in which an OIB-like parental magma undergoes extensive Assimilation-Fractionation-Crystallisation (AFC) in the upper crust. Subsequent feldspar-dominated fractionation in an upper crustal reservoir increases the peralkaline character of the evolved magma, resulting in isotopic disequilibrium between amphibole, clinopyroxene, feldspars and glass. Pb and Sr isotopes show that the feldspar is the first major phase to crystallise, prior to amphibole and/or clinopyroxene. The oldest rhyolites (<400ka) are succeeded by trachytes (150-95ka) and rhyolites (65-7ka). This temporal evolution is associated with decreasing Sr isotopes ratios (0.7089-0.7047), suggesting the establishment of a mature magmatic plumbing system, preventing extensive crustal contamination. In addition, timescales of magma production and residence in the crust will be discussed using combined Rb/Sr, U-series and Ar/Ar data.

References
Beyond the Moho: Plans for a complete penetration of in situ ocean crust into the upper mantle

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2http://www.iodp.org/ocean-lithosphere/#7
3http://www-odp.tamu.edu/publications/206_IR/front.htm
4http://iodp.tamu.edu/publications/exp309_312/30912title.htm

Sampling the upper mantle was the original inspiration for scientific ocean drilling and remains an unfulfilled ambition of Earth scientists. Fundamental questions about the composition, structure, and evolution of the ocean lithosphere, and the magnitude of chemical exchanges between the mantle, crust and oceans remain unresolved due to the absence of in situ samples and measurements. The geological nature of the Mohorovicic Discontinuity itself remains poorly understood.

“Mission Moho” is a proposal with the ultimate goal to drill completely through intact oceanic crust formed at a fast spreading rate, across the Moho and into the uppermost mantle. The “MoHole” will be the final stage of a multi-cruise campaign requiring non-riser and riser drilling, detailed geophysical survey and technological development, including the construction of a +4000 m riser. The initial cruises will harness existing ocean drilling capabilities to sample shallow and deep targets in increasingly hostile conditions in ocean crust formed at both fast and slow spreading rates.

A major step on the “Road to the MoHole” was made with the drilling of Hole 1256D into intact crust formed during a period superfast spreading (>200 mm/yr) on the East Pacific Rise 15-million years ago. This is the first complete penetration of upper oceanic basement through lavas, dikes and into the uppermost gabbros [1, 2]. The first gabbroic rocks were encountered at 1407 m below seafloor. Below this lies a ~100 m complex zone of fractionated gabbros intruded into contact metamorphosed dikes. The first gabbros were recovered from within the depth range predicted by extrapolating the inverse relationship between spreading rate and the depth to low velocity zones, thought to be axial melt lenses, at modern ocean ridge crests (e.g., [3]). Hole 1256D is open to its full depth and future deepening in the next phase of IODP should recover cumulate gabbros that will settle long-standing debates on the mechanisms of accretion of the lower oceanic crust.

References

Reconstructing the Mg/Ca and Sr/Ca history of seawater from ocean ridge-flank hydrothermal carbonate veins

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Calcium carbonate veins formed from low temperature (~100 °C) ridge flank hydrothermal fluids are common in the upper oceanic crust. Carbonate veins from the Juan de Fuca Ridge (<3.6 Ma) record the compositional evolution of seawater-derived hydrothermal fluids as they are heated and react with the basaltic basement. δ18O-calculated fluid temperatures correlate with the proportion of basalt-derived 87Sr. The Sr/Ca and Mg/Ca of the basement fluids, calculated from carbonate trace element analyses combined with suitable partition coefficients, are also temperature dependent [1].

The precipitation of carbonate veins from fluids with a basaltic Sr component precludes the use of the seawater Sr-isotope curve to date individual carbonate veins. However, the Sr-isotopic compositions of suites of carbonate veins in older sections of ocean crust also correlate with temperature and record the chemical evolution of basement fluids from seawater. The age of a suite of carbonate veins can therefore be estimated from the seawater 87Sr/86Sr curve, by determining the 87Sr/86Sr of contemporaneous seawater from the vein δ18O-calculated fluid temperature. Similar to modern carbonate veins, suites of ancient carbonate veins record decreasing basement fluid Mg/Ca and Sr/Ca with increasing temperature, due to fluid-rock interaction. Extrapolation of these trends back to seawater temperatures allows the determination of past ocean Mg/Ca and Sr/Ca.

The fidelity of a particular suite of ocean basement carbonate veins for determining past ocean chemistry depends on the thermal and hydrological history of the site, the duration of fluid circulation and carbonate precipitation, and the variation of ocean chemistry during this period. Analyses of veins from ODP Sites 801 (170 Ma), 1179 (129 Ma), 417 (110 Ma), and 1224 (46 Ma) indicate that ocean Sr/Ca and Mg/Ca were significantly lower than present from the Middle Jurassic to Late Eocene. This approach provides independent corroboration of past seawater chemistry estimates based on foraminifera and sedimentary calcite chemistry.

References
Resolving the emplacement history of syntectonic granites from Carrazeda de Ansiães, N Portugal, by U-Pb

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The Iberian Massif is a large segment of the European Variscan Belt formed during the polycyclic collision between Laurentia-Baltica and Gondwana in the Devonian/Carboniferous. The Central Iberian Zone forms the inner domain of the Iberian Massif and consists mainly of autochthonous Early Paleozoic metasediments, a few pre-Variscan granites and numerous Variscan granitoids, which were emplaced between 340 and 290 Ma, during and after the Variscan continental collision (at ~360 - 350 Ma). Only few granitoids formed during the early stages of the Variscan cycle (D₁ and D₂ deformation phases) with closure of the intervening ocean, crustal thickening and nappe emplacement. By contrast, extensive granitoid activity accompanied the post-thickening and post-collisional extension (D₃ deformation phase). Based on the emplacement ages the granitoid magmatism of Central Iberian Zone has been classified as: 1) pre-D3; 2) syn- to late-D₃; 3) post-D₃. Most syn-D₃ granitoids are aligned along NW-SE vertical folds and subvertical ductile shear zones.

Peraluminous two-mica granites at Carrazeda de Ansiães, northern Portugal, represent successive intrusive events during the D₃ Variscan deformation phase. Based on tectono-magmatic relationships and petrographic criteria, three groups can be distinguished, from older to younger: I (G1, G2, G3, G4, G5 and G6), II (G7, G8 and G9) and III (G10). The granites from Group I show evidence of high-temperature solid-state deformation, such as microfracturing of feldspar, kinks in biotite, flexural bends in plagioclase and S-C structures. Group II granites show a magmatic syntectonic NW-SE foliation, defined by euhedral phenocrysts of microcline, micas and also surmicaceous enclaves, that is continuous with the regionally developed foliation in the wall rocks. The emplacement of granite G10, belonging to Group III, was controlled by late-Variscan NNE-SSW fractures, which explains its brittle deformation. Representative granites from each group (G5, G7 and G10) were selected for a U-Pb (ID-TIMS) zircon and monazite study. The zircon systematics are generally complex because of Pb loss and inheritance, the latter also affecting some of the monazites. Nevertheless, the data combine to yield consistent ages of 320.5 ± 0.5 Ma for G5, 317.8 ± 0.5 Ma for G7 and 316.2 ± 0.7 Ma for G10, and thus tightly constrain the timing of the main D₃ event.

Time series diffusion experiments with natural alkaline melts

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We performed in this work time series diffusion experiments with contrasting alkaline melts obtained from natural volcanic products. The starting materials are the two end-member compositions and rheologies in the volcanic Province of Tenerife (Canary Islands, Spain). They correspond to an alkali basalt (43% SiO₂; υ= 4,412 Pa·s) and a phonolite (59% SiO₂; υ=10³ Pa·s).

The samples were loaded in a platinum capsule and arranged in a buoyantly stable geometry, where the denser material is placed at the bottom (alkali basalt, ρ=2,73 gr/cm³) and the lighter material at the top (phonolite, ρ=2,36 gr/cm³). We run experiments during 4, 25, 49 and 125 hours and we performed three different sets of experiments (with the same time duration) at 1350°C, 1300°C and 1250°C under atmospheric conditions. For every set the temperature has been kept constant during the whole experimental run and with an irrelevant thermal gradient (< 2°C). These temperatures, well above the liquidus for the system, avoid crystallization. No forced convection was applied, so that the diffusion process takes over and the compositional gradient becomes the only parameter enhancing the mixing process.

Microprobe and laser ablation analyses were performed to track major, minor and trace elements. The evolution of the diffusion profiles along a longitudinal section of the resulting products showed that mixing was possible. Diffusivity coefficients of the main elements at every temperature will be calculated in the near future.
Lower crustal material in the source of the Ontong Java Plateau?

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Was an oceanic plateau as large as Ontong Java Plateau (OJP) a product of voluminous melting by a mantle plume or just a consequence of unusual plate tectonic processes during the Aptian time (120 My ago)? Our Os-Hf results on the plateau lavas put further constraints on the origin of the OJP, suggesting that the plateau is a product of a two-component mantle source possessing distinct Os isotope signatures that are both suprachondritic (0.12-0.17 for Kwaimbaita-type lavas and 0.24-0.60 for Singgalo-type lavas) and different from MORB (with an average composition of 0.125, [1]). In contrast, Hf isotope results for the same Central Malaitan and ODP Sites 807, 1185, and 1187 samples show a slight difference between the Singgalo- and Kwaimbaita-type lavas in 176Hf/177Hf, consistent with previous results for the ODP Leg 192 lavas [2]. Both isotopic groups of lavas have Hf isotope compositions that lie on the terrestrial array defined by MORB and OIB data in HF-Nd diagram but have a gentler slope, reminiscent of the Hawaiian data trend. Both the involvement of pelagic sediments and altered, recycled normal oceanic crust do not have the required Pb and Hf isotopic compositions that can explain the Os-Pb and Os-Hf trends of the OJP data. Instead, the Os and Hf isotopic compositions of the OJP lavas both indicate an origin distinct from the shallow mantle tapped by MORB lavas. Our modeling results indicate that the Os isotopic composition of the Singgalo-type lavas may be explained by incorporation of up to 40% lower continental crust material into the Kwaimbaita-type source of the OJP lavas. This is broadly consistent with suggestions by [3] and [4] but differs from previous interpretation in inferring that the entrained recycled crust is lower continental crust. The present interpretation allows for widespread contamination of the OJP mantle source with delaminated lower crust, possibly during continental break-up, that paved the way for the birth of the Pacific ocean in the past.

References

Impact of organic ligands on antimony behavior in aquatic systems

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Although a huge number of studies have been devoted to metal-organic ligand interactions in natural aquatic systems, the effect of dissolved organic matter on the behavior of toxic metalloids like Sb, Se or As is still very poorly known. This is because metalloids are subjected to strong hydrolysis in aqueous solution, by forming neutral and negatively charged hydroxide species. This strong affinity to hydroxide ligands was believed to limit their complexing with organic ligands in comparison to most metals which exist as simple cations in solution. In this study, we combined systematic solubility and potentiometry measurements with in situ XAFS spectroscopy and dialysis experiments to assess structures and stabilities of antimony aqueous complexes formed with organic ligands having functional groups typical of natural organic matter.

Results show that both trivalent (SbIII) and pentavalent (SbV) antimony form surprisingly stable complexes with hydroxy-carboxylic and hydroxy-phenolic functional groups of organic ligands (lactic, oxalic and citric acids, and catechol), with Sb/ligand stoichiometries from 1:1 to 1:3, over a wide pH range (2<pH<9). The key condition for the formation of such complexes is the establishment of a five-membered chelate cycle via Sb-O-C bonds with two adjacent functional groups of the organic ligand. In these species, SbIII and SbV are respectively four- and six-coordinated, as demonstrated by XAFS spectroscopy.

The stability constants determined for SbIII organic-complexes have been used to approximate Sb complexing with natural humic acids which possess the same functional groups as those investigated in this study. Results show in unpolluted organic-rich natural waters up to 60% of total Sb may be complexed with humic and fulvic acids via carboxylic and hydroxy-carboxylic groups, which is also in agreement with dialysis experiments on a commercial humic acid. Thus, organic matter plays an important role in Sb transfer in natural waters than believed. Our findings indicate that because of the high selectivity of Sb to bidendate linkages with two adjacent functional groups of organic ligands, antimony may serve as a proxy for such moieties in aqueous humic and fulvic acids.

Our results imply that natural organic matter may also exert an important effect, largely neglected before, on the transport of analogous metalloids like As and Se in aquatic systems.
Geochemical properties of Miocene basaltic rocks from Yavuzeli-Araban-Narlı region, Southeast Anatolia, Turkey

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Miocene basaltic rocks from northern part of the Arabian plate (Southeast Anatolia, TURKEY) exposed as lava flow and blocky lava flow from the base to the top. The volcanic rocks are basalt-basaltic andesite in composition, and all of them have tholeiitic characteristics. Based on mineralogical and petrographical studies, it is observed that volcanic rocks are composed of mainly pyroxene and olivine phenocrysts. In the Wo-En-Fs classification diagram of Moritomo (1988), pyroxene compositions plot in the augite (Wo 31-41) field. Composition of olivine phenocrysts range from Fo 77 to Fo 84. Plagioclase minerals are generally found as a microlites in the matrix and labradorite-andesine (An43 to An60) in composition. Clinopyroxene and olivine are normally zoned, and MgO composition of the core and rim are virtually similar. Oxide minerals are ilmenite.

Major and trace element versus MgO diagrams indicate that fractional crystallization process is effective on the evolution of these basalts. Basaltic rocks are characterized by slightly LREE enrichment and high 87Sr/86Sr and low 143Nd/144Nd ratios ranging from 0.704574 to 0.705054 and 0.512652 to 0.512720, respectively. Slightly depletion of Nb-Ta on primitive mantle normalized multi-element diagrams, with high 87Sr/86Sr and low 143Nd/144Nd ratios, and Th/Yb-Ta/Yb diagram reveal that crustal contamination could be effective in their generation. La/Nb (≈0.7) ratios are similar to athenospheric mantle source. The trace elements and isotopic values indicate an athenospheric mantle source. Whereas, these rocks were not derived from a single mantle source according to partial melting modeling. The melts are produced probably by mixing of athenospheric and garnet or spinel peridotitic mantle sources.

Reference

Petrogenesis of Delihalil Quaternary basaltic volcanism, South Anatolia, Turkey

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In this study, Delihalil Quaternary basaltic volcanic rocks situated in the southwest of Osmaniye (south Anatolia, Turkey) were studied. Volcanic units are composed of scoria cones and lava flows exhibiting alkaline characteristic. They are basanite (early eruption phase) and basalt (late eruption phase) in composition. Volcanic rocks consist of olivine and clinopyroxene phenocrysts with plagioclase and clinopyroxene microphenocrysts and microlites. Such features as resorbed surface, skeletal textures, glass and opaque mineral inclusions in the olivine phenocrysts of the early eruption phase indicate magma mixing process in the evolution of these volcanic rocks.

Variation diagrams of MgO with major and trace elements are consistent with fractional crystallization process for basanites. However, this process did not play an important role in the formation of the alkaline olivine basalts which are the late eruption phase. Primitive mantle normalized trace- and RE-element spider diagrams exhibit that the early eruption phase (basanites) is more enriched than the late eruption phase. However, because of similar trace element patterns seen in spider diagrams, it can be concluded that they are derived from the same mantle source with different degrees of partial melting. Delihalil volcanism has low Sr and high Nd isotopic compositions. Their Sr and Nd isotopic compositions range between 0.703012-0.703617 and 0.512848-0.512947, respectively. In the Sr-Nd isotopic variation diagram, the early eruption phase samples are located into the HIMU-OIB area, whereas the late eruption phase sample is located into the EM-I field.
Post-collisional Tertiary volcanism in the Ulubey region at the western edge of the eastern Pontides paleo-arc started with sediments in a shallow marine environment in the Paleocene-Eocene time and then continued extensively with sub-aerial andesitic and rare basaltic volcanism during Eocene and Miocene time. The volcanic rocks studied are mainly andesite/trachyandesite and rarely basalt/trachybasalt and pyroclastics, and show porphyric, hyalo-microlitic porphyric and rarely glomeroporphyric, interstitial, intergranular, fluidal and sieve textures.

The volcanic rocks indicate a magma evolution from tholeiitic-alkaline transitional to calc-alkaline, and have medium to high-K in character. Petrochemical data of the rocks suggest a dominant fractional crystallization and less crustal contamination processes in their evolution. Most samples have also low Mg#, Cr, and Ni, which indicates that they have undergone significant fractional crystallization from mantle-derived melts. Generally, major and trace element geochemical variations in the rocks can be explained by fractionation of common mineral phases. E-MORB normalized trace element patterns show that Ulubey volcanic rocks have geochemical patterns with enrichment in LILE and to a lesser extent in LREE, but depletion in HFSE. The rocks have geochemical patterns with enrichment in LILE and normalized trace element patterns show that Ulubey volcanic rocks developed hornblende + plagioclase + clinopyroxene ± titanomagnetite controlled fractionation whereas andesitic rocks developed hornblende + plagioclase + clinopyroxene ± titanomagnetite controlled fractionation and, rare crustal contamination in shallow level magma chamber(s).

The 40Ar/39Ar dating of the basaltic rocks 15.1±0.6 Ma and the andesitic rocks are between 44.6±0.1 and 49.4±0.1 Ma. The rocks evolved from a parental magma derived from a parental magma derived from an enriched source formed by subduction induced metasomatism of basaltic rocks formed clinopyroxene ± titanomagnetite controlled fractionation whereas andesitic rocks developed hornblende + plagioclase + clinopyroxene ± titanomagnetite controlled fractionation and, rare crustal contamination in shallow level magma chamber(s).
The absence of magnesium isotope fractionation during basalt differentiation

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In order to understand Mg isotope geochemistry during basalt differentiation and characterize the Mg isotopic composition of the mantle, we present high-precision Mg isotopic data measured by MC-ICP-MS for a set of well-characterized samples from Kiluaea Iki lava lake, Hawaii, U.S.A. Samples from the Kiluaea Iki lava lake, produced by closed-system crystal-melt fractionation, range from olivine-rich cumulates to highly differentiated basalts with MgO content ranging from 2.37 to 26.87 wt.%. Our results demonstrate that although these basalts have diverse chemical compositions, mineralogies, crystallization temperatures and degrees of differentiation, their Mg isotopic compositions display no measurable variation within the limits of our external precision (average δ26Mg = -0.36 ± 0.10 and δ25Mg = -0.20 ± 0.07; uncertainties are 2SD). This indicates a lack of Mg isotopic fractionation during crystal-melt fractionation at temperatures of ≥ 1055 °C. Calculations based on these observations suggest that at near-magmatic temperatures the maximum fractionation in the 26Mg/24Mg ratio between olivine and melt is 0.07‰. These results are in contrast to those for lunar basalts, which exhibit significant Mg isotopic variation that has been attributed to fractionation during magmatic differentiation in the lunar magma ocean (Wiechert and Halliday 2007).

Continental basalts (BCR-1 and BCR-2), two mid-oceanic ridge basalts and two chondrites (Allende and Murchison) analyzed in this study have Mg isotopic compositions similar to the Kiluaea Iki lava lake samples. These compositions are additionally similar to those reported recently for several ordinary and carbonaceous (including Allende and Murchison) chondrites (Wiechert and Halliday 2007). This indicates that the terrestrial mantle may have a chondritic Mg isotopic composition. This obviates the need for a model such as that of Wiechert and Halliday (2007), which would be required to explain a non-chondritic Mg isotopic composition for the Earth.

Reference

Two views of initial Pb of early Earth

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A Mixi-chron (Fig. 1), is a line by isochronous samples having a singular K = Th/U and a range in μ = U/Pb. The correlation allows calculation of initial 208Pb. The twin-mixichrons of Barberton intersect the Y-axis in 2 places whose ratio yields the age, t. From t ± intercepts, K of crystallization is calculated (see values in Fig. 1). Assuming a 4.56 Ga source, one obtains from a Pb/Pb isochron (not shown), initial 206/204 = 12.05, and 207/204 = 13.88. The resulting 207/206 = 1.152 is used to define 206/208 and 207/208 endpoints in Fig. 1 (filled circles). These yield initial 208/204 = 31.75. From the isotopic ratios one calculates μ = 8.30 and K = 4.0, for the first stage. Applying this method to three other terrains resulted in μ ranging from 7.8 to 8.9, and K ranging from 4.0 to 4.65. These results appear in general accord with the prevailing view of a Silicate Earth having μ ~ 9 and K ~ 4.

A counter view is that a two-stage model for Earth is a gross approximation that results in a false image, with invalid parameters (1). Also, all models of bulk isotopic composition of silicate Earth, plot to the right of a 4.56 Ga geochron, in the conventional Pb/Pb diagram, thus indicating enrichment in 206Pb. That this is erroneous (1), is further indicated in Fig. 2, where the plotted data are for nine, widely separated terrains [sources of data are in (1)]. Primordial Pb was subtracted. The results indicate excess radiogenic *(207Pb), even for data plotting below the geochron (all are < 4.0 Ga old). Conclusions: The prevailing view of 206Pb-enriched ‘Bulk Earth’ is invalid. The methodology of Pb-isotope planetary evolution is inadequate.

Reference
Modeling of Zn sorption onto clayey sediments using a multi-site and multi-component ion-exchange model

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In literature, many sorption models have been proposed to interpret experimental sorption data onto complex mineralogical assemblages, such as sediments and soils. Nevertheless, these models are often empirical and cannot interpret data obtained in a wide range of physico-chemical conditions (pH, ionic strength, initial trace element concentration, solid/solution ratio…).

The aim of this study is (1) to elaborate a model of multi-site and multi-component cation exchange capable to describe the retention of transition metal on pure clay-minerals (2) to test the ability of this approach to reproduce the retention of these elements on natural material (soils/sediments) in various chemical conditions.

This study is focused on the behaviour of Zn in presence of clayey sediments. Considering that clay-minerals behave as a multi-site cation exchanger, it is possible to describe the retention of metals as well as the competitor cations, including the protons, by ion-exchange equilibria with the surface minerals. This approach was applied with success to interpret the experimental data obtained by Bradbury and Baeyens (1997) in the Zn-Na-montmorillonite system. Behaviour of Na, K, Ca and Mg versus pH was already studied in previous studies on pure montmorillonite (Gorgeon, 1994; Nolin, 1997) and permitted us to elaborate a thermodynamic data base including the exchange site concentrations associated to the montmorillonite and the selectivity coefficients of Na⁺, K⁺, Ca²⁺, Mg²⁺, and Zn²⁺ versus H⁺.

Sorption isotherms of Zn were carried out onto two different sediments in batch reactors at different pH and ionic strengths, and using NaCl and CaSO₄ as electrolytes. CEC measurements of both sediments were performed by cation displacement using CsCl solution.

Modelling of Zn retention onto sediments was carried out for the different experimental conditions, using the data base obtained previously upon montmorillonite. Assuming that clay minerals are the main ion-exchanging phases, site concentrations can be expressed in function of fractional weight content of the clayey minerals constituting of the sediments. Whatever the physico-chemical conditions tested, we observe a relatively good agreement between experimental and simulated Kd’s.

References

Isotopic record of Hadean crust in Western Australia

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Application of the ¹⁴⁷Sm-¹⁴³Nd and ¹⁴⁶Sm-¹⁴²Nd chronometers suggests that mantle depletion and related crust extraction had started during the first hundred million years of Earth history (Caro et al., 2006), but there is limited evidence for the presence of an enriched silicate reservoir before 4.0 Ga (Harrison et al., 2006). Here, we report new ¹⁴⁷Sm-¹⁴³Nd data from low-grade metamorphosed Paleoarchean volcanic and sedimentary rocks of the Warrawoona Group, Pilbara Craton, Western Australia. A Sm-Nd isochron age of 3.48 ± 0.09 Ga is in agreement with the U-Pb zircon age from intercalated volcanoclastic rocks and indicates the preservation of their Sm-Nd isotope signature since the Archean. The initial εNd value of -3.3 ± 0.5 is out of the range (+1< εNd < +3) established for the Archean cratons based on whole-rock Sm-Nd isochrons with ages agreeing with independent chronological constraints. This data is best explained by the assimilation of older continental crust, as shown by significant Ta-Nb depletion associated with LILE, Th, U and LREE enrichment (Green et al., 2000). Geochemical modeling suggests the assimilation of 10% to 20% of crustal material that may be either Archean granites, shales, or average upper continental crust (Condie, 1993). Assimilation of this crustal material with εNd values of −6 (granite), −8 (shales) and/or −10 (upper CC) by a mantle-derived melt accounts for the observed Nd isotope composition of basalts. This crustal component, with ¹⁴⁷Sm/¹⁴⁴Nd ratios of 0.99–0.12, would have been isolated from the depleted mantle at 4.0–4.4 Ga, which is consistent with the Nd model ages derived from the studied rocks. Our observations, albeit indirect, clearly show the existence of a an Hadean crustal reservoir. Its presence is confirmed by negative εNd of Archean seawater, inferred from carbonate rocks with seawater-like REE patterns. The presence of a crustal basement involved in plume magmatism indicates eruption of flood basalts onto a submerged continental platform, analogous with the Phanerozoic Kerguelen plateau (Van Kranendonk and Pirajno, 2004). This could have been an important mode of crustal production in the Archean.

References
Spatial and temporal variations in exhumation across the NW-Himalaya

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Erosional exhumation and topography in Mountain belts are temporally and spatially variable over million year time scales due to changes in both the location of deformation and climate. However, many studies are limited in the extent to which spatial variations in exhumation can be quantified due to the limited geographic extent over which samples are collected. We investigate spatial and temporal variations in exhumation and deformation across a 150x200 km region of the NW Himalaya, India. 25 new and 168 previously published apatite and zircon fission track and muscovite 40Ar/39Ar ages are integrated with a 1D model to quantify rates and timing of deformation and exhumation along strike of several major structures in the Lesser and Greater Himalaya. The model solves the advection-diffusion equation and predicts thermochronometer ages for variations in exhumation rates, thermophysical properties, and basal temperature.

The new and previously published AFT ages range from 10 to 0.6 Ma. The sample area is characterized by 0.7-5 km-high-topography, high relief (~4 km), and large (~1 to 4 m/yr) precipitation gradients. All the thermochronometer data indicate large temporal and spatial variations in exhumation. AFT ages are inversely correlated with local relief, but not with modern precipitation gradients. Results from thermokinematic modeling of all thermochronometer systems indicate: (1) Greater Himalaya exhumation rates were ~0.5-0.8 mm/yr before ~12 Ma and increased to ~2-3 mm/yr after ~10 Ma. (2) In the Lesser Himalaya exhumation rates are ~1-2 mm/yr over the last 10 Ma. The previous temporal variations in erosion in the Greater Himalaya are spatially consistent along 200 km of strike, regardless of structural variations. This implies that erosion, rather than tectons, has controlled the topographic evolution of this region over the last ~15 Ma.

Ca-Sr fractionation between margarite, anorthite, calcite, and fluid at 400-500 °C and 3.5-5 kbar

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We determined experimentally the Ca-Sr distribution between an 1 molar aqueous (Ca,Sr)Cl2-solution and (Ca,Sr) solid solutions of margarite, anorthite, calcite ± slawsonite and clinozoisite at 400-500 °C and 3.5-5 kbar using conventional cold-seal hydrothermal experiments. Solid oxide-hydroxide starting mixtures were prepared from SiO2, Al2O3, Ca(OH)2, and Sr(OH)2·8H2O (containing small amounts of carbonate impurities) weighted in stoichiometric amounts of the desired margarite composition plus ~ 3 wt% SiO2 excess to compensate for Si solubility in the fluid at run conditions. Strontium bulk compositions X Sr bulk [Sr/(Sr + Ca)] ranged from 0.07 to 0.40 with initial X Sr solid = X Sr fluid. The initial solid/fluid weight ratios were ~ 1:1. Solid run products were analyzed by REM, electron microprobe, and XRD; fluids were analyzed by inductively coupled plasma emission spectrometry.

Syntheses products are margarite, anorthite, and calcite in all runs ± clinozoisite and slawsonite in one run each at X Sr ≥ 0.15. Margarite forms idiomorphic hexagonal plates of generally less than 5 μm diameter. Anorthite and also clinozoisite are likewise idiomorphic but form significantly larger crystals with up to 100 and 150 μm lengths, respectively.

In all runs, X Sr of margarite, anorthite, and calcite is less than the corresponding X Sr bulk and X Sr fluid and ranges up to X Sr = 0.166 in margarite, 0.137 in anorthite, and 0.031 in calcite. Within these compositional ranges, electron microprobe analyses indicate continuous Ca-Sr solid solution series for all three minerals. X Sr of clinozoisite is slightly higher than X Sr of coexisting margarite, anorthite, and calcite but still less than the corresponding X Sr fluid. Contrary, slawsonite has notably higher X Sr than X Sr bulk and X Sr of coexisting fluid and other solid phases. We used our data to calculate exchange coefficients K D for the generalized reaction Ca Phase 1 + Sr Phase 2 = Sr Phase 1 + Ca Phase 2 (where K D Phase 1 - Phase 2 = (Sr/Ca) Phase 1/ (Sr/Ca) Phase 2): K D marginite-fluid ranges from 0.49 to 0.67, K D anorthite-fluid from 0.47 to 0.59, and K D calcite-fluid from 0.08 to 0.11; K D clinozoisite-fluid is 0.72 and K D slawsonite-fluid is 7.75. The data clearly show a preference of Sr over Ca for the fluid when compared to margarite, anorthite, calcite, and clinozoisite, but a preference of Ca over Sr for the fluid when compared to slawsonite. Calculated K D anorthite-calcite and K D anorthite-calcite range from 5.14 to 8.60 and 4.91 to 7.55, respectively, and indicate notably Ca-Sr fractionation. On the other hand, K D marginite-anorthite ranges from 1.01 to 1.26 and suggests only weak Ca-Sr fractionation between margarite and anorthite.
Not much gabbro in the Icelandic mantle!

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Picritic lavas from Iceland have unusual trace element signatures, including strong incompatible element depletion, that have been used to infer derivation from a source dominated by oceanic gabbros, either through deep ancient recycling [e.g. 1] or shallow recent recycling [2]. We report results of a multi-element MC-ICP-MS isotope dilution study of lavas from the Reykjanes Peninsula that include depleted lavas (‘picrites’ ± l) from 14 separate localities, with the aims of testing the recycled gabbro hypothesis and constraining the timing of incompatible element depletion.

The key features that have been attributed to a gabbroic source are positive anomalies for Sr, Ba and Eu, relatively low Ce/Pb, and negative anomalies for Zr and Hf. We would also expect Dy/YbN>1 due to melting clinopyroxene that had crystallized from liquids with flat HREE patterns. Sr/Nd, Sm/Zr and Pb/Ce increase systematically with increasing LREE depletion, consistent with reported anomalies in depleted lavas. However, Sr/Sm is essentially constant across the full spectrum of LREE enrichment, while Nd/Zr and Pb/Nd decrease systematically with LREE depletion. This suggests that the reported anomalies are substantially due to incorrect assumptions about the REE K D analogues for Sr, Zr and Pb. Eu/Eu* increases from about 1.03±0.02 in LREE-enriched lavas to ~1.08 in the most LREE-depleted lavas, an increase at least in part due to the strong concave-down curvature in depleted lava REE patterns. Most depleted lavas show Dy/YbN<1, inconsistent with large-degree melting of gabbro-dominated sources, and suggesting that their sources are simply produced by extensive melt extraction from normal Icelandic mantle sources in the garnet facies. Their more depleted isotopic compositions may largely reflect the time elapsed since this melt extraction, at most 270 Ma. Tight coupling between Lu/Hf and Sm/Nd, but not between these and Hf or Nd isotope ratios, also requires a dominant control by melt extraction on the incompatible element depletion.

Depleted lavas from the BIR1 locality, and maybe one other, show strongly elevated Sr/Sm, Nd/Zr, Ba/La and Ba/Rb; Eu/Eu*>1.1 and Dy/Yb>1 despite similar LREE depletion to many other Reykjanes lavas. So the famed Icelandic recycled gabbro signature is only clear in one ~200m location, made famous because of an international reference sample! [1] Chauvel and Hemond (2000). G¹. 1, 1525-2027

Mineralogical investigation of fly ashes of the electricity power stations of the Ptolemais - Amynteon district (Greece)

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Fly ashes were examined, those in one period of approx. 3 months of altogether six boilers from four electricity power stations (Agios Dimitrios, Kardia, Ptolemais and Amynteon, Greece), which are fired with lignite of the Ptolemais-Amynteon-basin. From each fly ash the size fractions of > 71 µm, 71 µm to 20 µm, 20 µm to 2 µm and < 2 µm are mineralogically by Roentgen-diffraclometry (RIETVELD method), as well as chemically by Roentgen fluorescence were analyzed.

It is shown that the examined fly ashes of the power stations of Agios Dimitrios, Kardia, and Ptolemais, have, essentially, the same qualitative mineralogical composition (anhydrite, lime, periclase, gehlenite, brownmillerite, Ca₃SiO₄, calcite, quartz, feldspar, muscovite/illite, hematite, amorphous phase and ± merwinite, and/or mayenite). Also their quantitative mineralogical composition is similar. Compared the ashes of the above three power stations with the fly ashes of the power station of Amynteon show only a relative little difference of the qualitative composition (anhydrite, lime, periclase, gehlenite, brownmillerite, Ca₃SiO₄, calcite, quartz, feldspar, muscovite/illite, hematite, pyroxene, hercynite and amorphous phase) but different quantitative phase composition, owing mainly to a differentiated relationship between the SiO₂ and CaO content.

The main part of the mass of the fly ashes constituted the grain size fractions > 71 µm, 71 µm to 20 µm and 20 µm to 2 µm, since the grain size fractions < 2 µm in all samples constitute less than 0.2%.

In all fly ashes by decreasing grain size was determined, on the one hand an increasing of the CaSO₄ content and on the other hand, excepting a few cases, a decreasing of content of the amorphous phase, of quartz as well as feldspar and/or the pyroxene. Beyond by the grain size fractions < 71 µm an increasing of the contents of gehlenite, brownmillerite, Ca₃SiO₄ and, in the most cases, calcite were observed.

It was shown that the contents of the amorphous phase (glass phases, unburned lignite), as well as of the not reacted silicates by burning of the lignite, decrease by the smaller grain sizes, while the crystalline, mainly calcium-rich, phases which are formed when burning, in the grain size fraction < 71 µm of the fly ashes are enriched.


The biogeochemistry of anaerobic porewaters is marked by obligate microbial syntrophy and complex ecological relationships. These in situ ecological properties are extremely difficult to probe either in vitro or in situ with specific inhibitors, since both of these treatments disrupt important microbial connections. Alternatively, stable carbon isotopic analysis of the gaseous substrates and products of methanogenesis can reveal the pathways of methane production. Carbon isotopic analyses of the methyl carbon of acetate provide us with the ability to relate laboratory derived fractionation factors between the acetate methyl and methane to natural systems in the field.

We hypothesize that isotopic estimates of methane production pathway that assume an acetate methyl isotopic composition similar to bulk organic matter can be significantly compromised during times when hydrogen concentrations are high. Such situations might occur when 1) pulses of fermentable substrates are applied or 2) methanogen activity is limited by low temperatures.

We have adapted a pyrolitic technique for the intramolecular carbon isotopic analysis of acetate in natural samples via direct injection of an aqueous solution. This method capably measures the isotopic composition of the carboxyl carbon from injections of 1 nanomole of acetate in aqueous solution. Samples with acetate concentrations less than 1mM are preconcentrated via lyophilization and reacidified to an appropriate concentration. This technique is reliable down to 30µM acetate in the original sample.

Our analyses of the carbon isotopic composition of methane, CO₂, and the intramolecular values of acetate from an acidic peatland in central Pennsylvania challenge assumptions of acetate-methyl isotopic similarity to bulk organic matter. We find the carbon isotopic composition of acetate-methyl carbon in late-winter samples are 10% depleted relative to bulk organic matter. Using a laboratory determined fractionation factor for autotrophic acetogenesis, we find that a significant percentage of the acetate in acidic peatland porewaters may derive from CO₂.
Progress in the establishment of a new Infrared calibration for the SiO2-system

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Conventionally used Infrared (IR) calibrations (Paterson, 1982; Libowitzky & Rossman, 1997) for the quantification of water in solids are established on hydrous minerals and glasses with several wt% water. These calibrations are based on a negative correlation between the IR absorption coefficient for water and the mean wavenumber of the corresponding OH pattern. The correlation reflects the dependence of the OH band position on the corresponding O-H...O distances and thereby the magnitude of the dipole momentum which is proportional to the band intensity. It has been observed that these calibrations can not be applied to nominally anhydrous minerals (NAMs) (Rossman, 2006). Up to now the ultimate cause remains entirely unclear.

To learn more about absorption coefficients in NAMs and their potential dependence on structure and chemistry we synthesized SiO2 polymorphs with specific isolated hydroxyl point defects, e.g. quartz, coesite and stishovite with B3++H+=Si4+ and/or Al3++H+=Si4+ substitutions. Experiments were performed with water in excess in piston cylinder and multi-anvil presses. Single crystal IR spectra reveal the presence of hydroxyl groups in all our samples and enable us to propose new OH incorporation models. Furthermore, IR spectra demonstrate that we successfully managed to separate generally complicated OH band patterns as e.g. observed in spectra demonstrate that we successfully managed to separate generally complicated OH band patterns as e.g. observed in conventional IR spectra. The correlation reflects the dependence of the OH band position on the corresponding O-H...O distances and thereby the magnitude of the dipole momentum which is proportional to the band intensity. It has been observed that these calibrations cannot be applied to nominally anhydrous minerals (NAMs) (Rossman, 2006). Up to now the ultimate cause remains completely unclear.

We present new material-specific correlations and resultant single calibration constants for the SiO2 polymorphs. It turns out that the magnitude of absorption coefficients within one structure type is independent of the liable OH point defect and therewith the wavenumber of the observed band position but in contrast varies with the structure itself. Similar results concerning an intra-structural constancy of the integral molar absorption coefficient have been shown before for feldspars (Johnson & Rossman, 2003).

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Thomas et al. (2006), Am. Min., 91, 467-470.

Multiple Sulfur and Carbon isotopic chemiostratigraphy of the 2.73 Ga carbonated Tumbiana formation, new insights for the Fortescue excursion

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In order to bring further insights into the environmental conditions prevailing during the δ13C negative Fortescue Excursion attributed to an increase in methanotrophic biomass, we carried out a detailed carbon (13C, 14C) and multiple sulfur (32S, 33S, 34S) isotopic study through the entire pristine core drilled from the 2.7 Ga Tumbiana Formation (Pilbara Drilling Project; Van Kranendonk et al., 2006).

Organic δ13C_CPM values vary markedly at meter scale and display a bimodal distribution with two maxima at -43 and -28‰. This isotopic record, together with palynological and other geochemical evidence, cannot be explained by secondary processes including diagenesis or metamorphism and argues for the occurrence of two distinct pools of biomass likely produced by different metabolic pathways, photosynthesis and methanotrophy. δ34S_CDT values of sedimentary pyrite vary from -5.8 to 2.7‰ (average -0.5‰). Lithologically indendent heterogeneities (at centimeter scale) in isotopic composition (>5‰), sulfur content and S/C ratio are best interpreted by coexisting microbial sulfate reduction and sulfur oxidation metabolisms. Sedimentary pyrite display Mass Independent Fractionation with ∆33S_CDT anomalies ranging between -0.24 and 1.64 ‰ (average 0.46 ‰) and correlating positively with the 12C enrichment of organic matter. This suggests that the sulfur components derived from photochemically-processed volcanic gases and delivered to the Tumbiana sediments were ultimately involved in the metabolic activity of sulfur processors.

Our results suggest that at least four different types of metabolism operating under various redox conditions were present in the Tumbiana paleo-environment and we propose that the δ13C negative Fortescue Excursion reflects methane assimilation by a consortium of organisms including Anaerobic Oxidation of Methane Archaea and Sulfate Reduction Bacteria in anoxic time of the Tumbiana basin.

Reference
**Magma chamber processes beneath Icelandic central volcanoes: Evidence from gabbros of the Austurhorn intrusive complex, SE Iceland**

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The ~6 Ma Austurhorn (15 km²) intrusive complex was emplaced at approx. 2 km depth into Neogene basalts of Southeast Iceland. The exposed gabbros, granophyres and acid-basic complexes are among the largest in Iceland and represent the exhumed roots of a late Neogene central volcano.

The 2.3 km² layered gabbro sequence at Hvalnesfjall makes up the central part of the intrusion. Our results demonstrate that the cumulate stratigraphy exceeds 800 m, making it the largest known gabbro outcrop in Iceland. The gabbro is dominated by leucocratic, plagioclase–clino-pyroxene–Fe-Ti oxide cumulates. However, seven 2-10 m thick olivine-bearing melanocratic layers define the bases of macrorhythmic units. Cumulus minerals have a limited compositional range (An85-56 in plag; Mg#84-72 in cpx) compared with closed-system layered intrusions and show no variation shows a zigzag pattern with increases in Cr₂O₃ in overall evolution from bottom to top of the sequence. Cryptic macrorhythmic units. This is interpreted to reflect crystallisation in a periodically replenished, tapped and fractionated magma chamber.

The emplacement sequence of the intrusive rocks at Austurhorn is debated. An approx. 100 m thick gabbroic body at Hvashjalli east of the Hvalnesfjall gabbro was mapped by Furman et al. (1992) as gabbro cross-cut by granophyre. Our mapping, however, demonstrates that this gabbroic body is a monster pillow that grades from lobate dolerite at the margins to gabbro at the centre. We therefore suggest that all gabbroic bodies at Austurhorn were formed by intrusion of basaltic magma into pre-existing riftotic magma chambers.

**Reference**


**Excess ¹⁷⁶Hf in early crystallised meteorites**

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The ¹⁷⁶Lu decay decay constant (λ¹⁷⁶Lu) has been determined to be 1.87 x ¹⁰⁻¹¹ yr⁻¹ using terrestrial samples of known U-Pb ages (Scherer et al. 2001, Söderlund et al. 2004), a value recently verified by an internal isochron from phosphate minerals from a 4557 m.y. old meteorite (Amelin 2005). However, previous Lu-Hf analyses from meteorites older than 4.56 Ga have ¹⁷⁶Hf excesses that are correlated with their Lu/Hf elemental ratios (Blichert-Toft et al. 2002, Bizzarro et al. 2003). To evaluate this issue, we derived an internal Lu-Hf isochron from the basaltic angrite SAH99555 yielding a Pb-Pb age of 4564.5 Ma (Amelin et al. 2007). Similar to the earlier results on pre-4.56 Ga meteorites, our Lu-Hf results show an ¹⁷⁶Hf excess corresponding to ~6% increase in the slope of the isochron. Due to the correlation with Lu, we infer this excess be generated by an accelerated decay of Lu most likely related to the formation of the ¹⁷⁶Lu⁰ isomer with a half-life of 3.7 hours. Alberède et al. (2006) proposed that ¹⁷⁶Lu was excited due to solar and/or supernova generated gamma radiation. However, the shallow penetration of gamma radiation precludes this model explaining the ¹⁷⁶Hf excess in SAH99555. We considered supernova generated neutrinos as an alternative means to excite ¹⁷⁶Lu but this process is precluded by the very small neutrino cross section. A third energy source also related to supernova shocks is cosmic rays. Cosmic rays can excite nuclei and penetrate accreted material as deep as 100-200 meters. As such, they could account for the excess ¹⁷⁶Hf in material crystallised before the supernova explosion. This model is consistent with Fe-Ni isotope data that indicate that a supernova(e) occurred after accretion of the angrite parent body (Bizzarro et al. in press).

**References**


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Geochemical characteristics of the Mashan Au-S Deposit in Tongling, Anhui Province

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The Tongguanshan copper field in Tongling, Anhui, is one of the typical skarn orefields in the middle-lower Yangtze Valley iron, copper, sulfur and gold metallogenic belt of China. The Mashan Au-S deposit located in the Tongguanshan field is related to the Tian’ebaotanshan quartz diorite. A lot of research work has been done in such aspects as mineral deposit, mineralogy, tectonics, isotope geochemistry and fluid inclusions. Based on the work done, this paper deals mainly with hydrogen, oxygen, carbon, sulfur, silicon isotopic compositions and REE geochemistry of the Mashan Au-S deposit.

The results show that chondrite-normalized REE patterns are right-inclined, and the REE distribution patterns for ores are similar to those of the Tian’ebaotanshan quartz diorite, which indicates that the hydrothermal fluids of the deposit were mainly derived from dioritic melt. The O isotopic compositions of quartzes in ore range from 6.9‰~10.7‰ with the average of 8.7‰, which are approximate to those of the pluton (9.3‰~11.1‰, with the average of 10.0‰). Together with the D isotopic compositions of quartzes in ore (-61‰~ -62‰), it shows that the metallogenic fluids were mainly derived from magmatism. The C and O isotopic compositions of calcites in ore are different from those of country rocks in the orefield. The C and O isotopic compositions range from -5.2‰~ -3.6‰ and 12.2‰~12.9‰, respectively, which are similar to the C and O isotopic compositions of magmatism. Therefore, C and O in ores might have come from magmatism. Silicon and sulfur isotopes are quite similar to those in magma or magmatic hydrothermal solutions.

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The origin and evolution of dust in the interstellar medium

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At the end of their life, stars return most of their material back to the interstellar medium. This material undergoes a complex evolution in the interstellar medium before it becomes part of the next generation of stars and planets. Small dust grains condense in the ejecta of stars as it cools because of expansion. Astronomical observations and analysis of stardust isolated from meteorites have revealed a highly diverse interstellar and circumstellar grain inventory, reflecting the varied physical and chemical conditions in their birthsites. This talk will review this dust inventory contrasting and comparing both the interstellar and circumstellar reservoirs as also the astronomical and meteoritic evidence.

Interstellar dust is highly processed during its sojourn from its birthsite (stellar outflows and explosions) to its incorporation into protoplanetary systems. Of particular importance is processing by cosmic rays in the interstellar medium and by strong shocks due to supernova explosions. The latter leads to rapid destruction due to sputtering by impacting gas ions and shattering due to grain-grain collisions. We will review theoretical calculations describing these processes and the astronomical and meteoritical evidence for their importance.
Two Late Mesozoic pulses of silicic volcanism within the North Chukotka area (NE Russia): Magma sources and geodynamic significance

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The Cretaceous Okhotsk-Chukotka volcanic belt (OCVB) is one of the largest Andean-type volcanic provinces of the Earth. Silicic magmatic rocks are the major component of the OCVB, comprising up to 90% of some segments. The lifetime of this belt is still under discussion but all existing models imply the onset of volcanism between 107 Ma and 90 Ma. However, remnants of older (Paleozoic and Mesozoic) subduction-related volcanic provinces overlap by sequences of the OCVB are known.

One such remnant has been discovered within the northern part of the volcanic belt (Tikhomirov et al., 2007). This is a 1-1.5 km thick uniform pile of welded rhyolitic tuffs intruded by related granodiorites and overlain by felsic ignimbrites of the OCVB. Zircon U-Pb ages of both tuffs and granodiorites are about 150 Ma (Late Jurassic). The continental crust is inferred to be the main magma source during both Jurassic and Cretaceous events as contemporaneous basalts are absent, and andesites take a minor part (10-15% in vol.). Sr, Nd, Pb, and Hf isotopic characteristics of the Late Jurassic assemblage are very uniform and originate from a relatively depleted source, with εHf = +4.4 to +5.0, and εNd = -0.5 to -0.1. Isotopic ratios are not correlated with rock chemistry, and therefore considerable contribution from mantle sources are considered unlikely. OCVB rhyolites display a wider range of isotopic composition (εHf = -1.6 to +3.8, and εNd = -4.1 to -2.1), and appear to result from mixing of at least 3 different endmembers within the compositional field of continental crust.

We relate the Late Jurassic magmatic assemblage to a hypothetical continental volcanic arc at the active margin of the Anyui-Angayucham oceanic basin which closed in the Early Cretaceous (Sokolov et al., 2002). Absence of apparent tectonic deformation of the volcanic sequence implies that the main Mesozoic compressional event in North Chukotka took place before the Tithonian age.

References

Melting processes by Rayleigh-Taylor instabilities beneath Continents: Evidence from Cenozoic intraplate volcanism on Zealandia, SW Pacific

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Intraplate volcanism is mainly attributed to upwelling and subsequent partial melting of hot mantle material. However, the origin of these hot mantle material is still a matter of an active debate (e.g. www.mantleplume.org). On the New Zealand micro continent Zealandia (consisting ~ 90 % of submerged continental crust) intraplate volcanism occurs widespread and nearly continuously since the initial separation activity from Gondwana about 100 Ma ago. Voluminous volcanism was associated with the Cretaceous rifting of Zealandia from Gondwana. In contrast, only scattered, low volume eruptives were produced in the Cenozoic. Two volcanic endmembers can be defined in the Cenozoic: 1) diffuse but widespread monogenetic volcanic and dike fields (e.g. Waipati Volcanic Field, Pukaki Bank, Alpine dike swarm) and 2) shield volcanoes (e.g. Banks Peninsula, Dunedin Volcano, and Chatham Islands).

The geological processes responsible for this intraplate magmatism remain enigmatic. A mantle plume origin appears unlikely as there is no age progression in the erupted lavas in direction of plate motion, although Zealandia drifted ~ 6,000 km to its present position. This combined with the absence of an anomalous hot mantle or large extensional structures requires an alternative process to trigger partial melting beneath Zealandia. It has been proposed that the gravitationally unstable lower lithosphere was subjected to multiple delamination events during the Cenozoic. Using finite element modeling, we will test two alternative mechanisms: Rayleigh-Taylor type delamination of a dense layer at the base of the lithosphere and edge driven convection. The concept of an anomalously dense lower lithosphere is supported by the geological history of Zealandia. Located at the NW margin of Gondwana it was exposed to subduction for hundreds of million of years. Influx of subducting plate derived fluids and melts may have re-fertilized and thereby densified the lower lithosphere making it gravitationally unstable with respect to the underlying asthenospheric mantle. In addition, the relatively small lateral dimensions of Zealandia might make it particularly vulnerable to erosion by edge driven convection. We will present the conditions under which these two processes are viable explanations for the intraplate volcanism in Zealandia.
The effect of water-rock interaction time on stable carbon isotope of cave drip in Qixing cave, China

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Aim
As substitute index of environment, stable carbon isotope has been used broadly in different natural records, such as tree rings, stalagmite, and so on. The aim of this work is to better understand the mechanism of palaeoclimate and palaeoenvironment reconstruction by stable carbon isotope of speleothem.

Results
The stable carbon isotope composition was measured in Qixing cave drip water in April 2002 and 2003. The results were showed as followed:

![Graph showing δ13C value vs drip height and drip speed]

Discussion and conclusion
The effect of water-rock time on stable carbon isotope of cave drip can be discussed by drip height and drip speed. According to the aboved figure, the δ13C value(PDB) of drip water changes inversely with drip height and drip speed. The reason is that the higher and faster drip indicate the thinner rocky cover, the shorter time of water-rock interaction and the less heavy carbon isotope coming from carbonate rock in common situation. The conclusion is that the water-rock time is longer, the DIC δ13C value of drip water become heavier.

Calcium and magnesium isotope systematics in rivers. Fractionation or lithological control?

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Ca and Mg are two of the most concentrated elements in continental fresh waters, and analysis of their isotope ratios by MC-ICP-MS or TIMS provides a powerful new tool for investigating the global cycles of Ca and Mg and the under constrained weathering reactions by which these elements are released from the continental crust [1,2].

Stable isotope ratios in rivers are controlled by mixtures of waters with distinct compositions, often inherited from source rock heterogeneity, but also from fractionation during a series of processes associated with weathering reactions including uptake by biomass. Ca and Mg isotope ratios in the dissolved ratios of rivers from diverse weathering environments reveal that their isotopic compositions are sometimes but not always controlled by lithology.

This is illustrated by the fact the rivers with the lowest δ26Mg drain limetone, the rock type with the lowest δ26Mg. However, the δ26Mg between the solid and dissolved phase are offest by up to 1‰. Similarly small rivers draining granite and gneiss have a δ26Mg which is distinct from the solid phases. Similar differences between the solid and dissolved phase exist for Ca isotope ratios. The difficulty in interpreting such variations is that they may arise as a result of mixtures between inherited lithological signatures or as a result of fractionation during weathering processes.

A multi-tracer approach, linking major dissolved ions, Sr isotope ratios, and Ca and Mg isotope ratios in small and large basins, and soil pore waters, allows the difficulty between inherited isotope signatures and process related signatures to be considered in more detail.

The implications are of significance for better constraining the oceanic cycles of Ca and Mg, as rivers deliver a significant proportion of Ca and Mg to the oceans.

References
Trace element sulfide geochemistry as an indicator of vent fluid pH

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Study of actively venting seafloor massive sulphide deposits allows quantitative links to be made between vent fluid and deposit compositions. Models that reproduce mineral assemblages using measured vent fluid compositions and considering transport within the deposits indicate greatest sensitivity to the large ranges in temperature, and lesser but still significant sensitivity to the ranges in pH, present within the deposits; sensitivity to variations in oxygen and sulphur fugacity, which are small except at deposit exteriors, is not as significant (Tivey, 1995). Interest in finding an indicator of past pH from seafloor vent deposits stems from the ranges in pH (~2 to ~6) exhibited in fluids venting from seafloor sulphide deposits (Von Damm, 1995), and calculated for pore fluids within vent deposit interiors (Tivey, 1995). It also stems from our understanding that the pH of the highest temperature, lowest Mg vent fluids provides information about subsurface processes (e.g., temperatures of water-rock reaction, substrate composition, interactions with organic matter and sediment, input of magmatic volatiles).

Trends observed within bulk geochemical datasets obtained from deposits within a number of different active vent fields suggest that distributions of certain trace elements can be used as indicators of pH. For example, Ag/Fe correlates well with Zn/Fe in massive sulphide deposits from vent fields where vent fluid pH is low (<3.5 at 25°C). In contrast, Ag/Fe does not correlate well with Zn/Fe in massive sulphide deposits from vent fields where vent fluid pH is considerably higher (>4 at 25°C). The latter is consistent with wurtzite or sphalerite precipitating at higher temperatures from higher pH fluids and Ag remaining in solution, partitioning at lower temperatures into other sulphide minerals (e.g., pyrite and chalcopyrite). This behaviour, reported for Main Endeavour (high pH) versus Snakepit (low pH) vent fields (Tivey et al., 1999), holds for many additional vent fields, e.g., those along the Eastern Lau Spreading Center. The consistency of these correlations to vent fluid pH suggests that detailed in situ chemical analyses may allow estimates of pH to be made within vent deposits (e.g., inside chimney walls).

References

How to cool a supersaturated solution and ‘watch’ in real-time the nucleation and growth of silica nanoparticles?

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The mechanisms and kinetics of silica nanoparticle formation in natural environments has been the subject of extensive laboratory investigations, yet, silica polymerization was usually induced by lowering the pH to near neutral values where silica solubility is at a minimum. However, in natural systems (e.g., geothermal pools or deep-sea vents) silica polymerization and silica colloid formation is a result of rapid cooling of a supersaturated near neutral fluid. So far, experimental challenges to simulate natural geothermal processes precluded the quantification of the kinetics and mechanisms of silica nanoparticles formation from cooling hot fluids.

Here we present data from X-ray and light scattering experiments that followed the nucleation and growth of silica nanoparticles in situ and in real-time with the polymerization being induced by rapid cooling of a supersaturated silica solution. A novel flow-through geothermal simulator system that was designed to work on-line with a synchrotron-based Small Angle X-ray Scattering (SAXS) or conventional Dynamic Light Scattering (DLS) cell and detector system was used. Silica solutions ([SiO₂] = 600 or 1'500ppm, and ionic strengths of 0.02 and 0.22) were equilibrated in this flow-through set-up to 230°C (all silica monomeric) and silica polymerization was initiated by continual rapid cooling of the flowing fluid to between 90°C to 20°C. This way the polymerisation of monomeric silica from a supersaturated hot spring fluid upon discharge at the Earth’s surface was simulated. SAXS, DLS (and complementary cryo-TEM) data pertaining to changes in size and polydispersity of the nucleating and growing silica nanoparticles as a function of temperature, concentration and ionic strength will be discussed.
Methane hydrological cycle on Titan

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Saturn’s largest moon Titan is covered by a dense nitrogen atmosphere mixed with a few % of methane. Titan’s atmospheric condition allows the existence of methane in gaseous, liquid and solid phase analogously to water on Earth. Detection of several types of clouds in the lower atmosphere (e.g. Brown et al., 2002), dendritic features on the surface presumably carved by flowing liquid methane (Tomasko et al., 2005) and evidence of methane drizzle at the landing site of Huygens (Tokano et al., 2006) indicate that an active hydrological cycle of methane exists on present Titan. Methane in Titan’s atmosphere may play a similar role as water in Earth’s atmosphere in that it causes greenhouse effect, clouds, precipitation and geological features. However, several important differences to the terrestrial water cycle also became clear during the Cassini/Huygens mission. Titan lacks a global ocean, but the atmosphere contains a huge amount of condensable methane corresponding to a liquid layer of 5 m depth. Titan’s methane hydrological cycle is much more affected by chemistry than the terrestrial counterpart. Atmospheric methane has a net source (surface) and a net sink (photochemistry) on geologically short timescales. Models suggest that rainfall is only possible because nitrogen and ethane can be dissolved in liquid methane, suppressing the freezing point and slowing evaporation. Availability of ethane at cloud-forming altitudes relies on the ethane production by photochemistry. This paper gives a survey of Titan’s hydrological cycle, elucidating the role of chemistry and apparent analogies and differences to the terrestrial hydrological cycle.

References

Geochemical dynamics in an active margin of East Asia: Implications from the temporal and spatial geochemical evolution of magmatism in northern Kyushu, SW Japan

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The margin of East Asia has been a locus for various tectonic events, having been affected by many arc-trench systems and back-arc basins. The upper mantle is expected to be complicated in physico-chemistry, reflecting the active tectonic environment. In order to decode the evolution of the upper mantle, clarification of the temporal and spatial geochemical variations in volcanic products is essential. Here, attention will be paid to Neogene non-subduction-related mafic volcanism in northern Kyushu, southwest Japan, ranging in age from ca 10 Ma to 0.5 Ma. The volcanism broadly has shifted eastward by ~150 km over time, and both alkali and sub-alkali lavas occur together. Their geochemical variations cannot be explained only by shallow processes such as fractional crystallization and crustal assimilation, and might reflect geochemical evolution of the upper mantle. Based on major and trace element abundances, the northern Kyushu volcanic rocks can be divided into three series: alkali basalt, sub-alkali basaltic rocks, and High Mg andesite (HMA). The alkali basalts in northern Kyushu have trace element distribution patterns similar to oceanic island basalts (OIB), suggesting asthenospheric sources within the convecting upper mantle. The sub-alkali basaltic rocks and HMA in northern Kyushu have incompatible element ratios that differ from OIB. Their compositions range from OIB-like patterns moderately depleted in HFS elements to strongly depleted patterns. These geochemical variations are best interpreted as an indication of interaction of asthenospheric-derived alkali basaltic magma with two chemically distinct lithospheric mantle sources: one is characteristically more depleted in Sr-Nd-Hf isotopic compositions and the other is isotopically enriched in these isotopic compositions. The relative contributions of these lithospheric mantle sources have changed over time and space. Contributions to the western region change from enriched to depleted character, whereas in the east, it has related its enriched character. This suggests that involvement of these lithospheric mantles in the genesis of sub-alkali basaltic rocks and HMA may be related to Tertiary lithospheric thinning caused by asthenospheric upwelling. Furthermore, isotopic compositions of alkali basalt derived from the asthenosphere change systematically over time and space, possibly associated with the opening of the Sea of Japan and rifting of the northern part of the Okinawa Trough.
Dehydration behaviour of muscovite by in situ infrared microspectroscopy

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Dehydration of hydrous minerals is one of the important elementary steps in the subduction processes. In this study, dehydration behaviour of muscovite was studied by in situ high-temperature IR microspectroscopy by using a heating stage.

Muscovite has an infrared absorption peak around 3620 cm⁻¹ due to stretching vibration of Al-OH. Changes with temperature of the OH band and its integral molar absorptivity were first investigated. The peak position of OH in muscovite showed a quasi-linear shift to lower wavenumber from 3627 cm⁻¹ at room temperature to 3618 cm⁻¹ at 500°C. Peak heights (absorbance) and areas (integral absorbance) were determined after a baseline correction on transmission spectra. Linear and integral molar absorptivities of OH in muscovite at room temperature were calculated by using a molar concentration of OH. Integral molar absorptivities of OH in muscovite decreased quasi-linearly from room temperature to 500°C (about 10% decrease).

Dehydration behavior of muscovite was then investigated at 750-875°C by using the same in situ IR microspectroscopy. Isothermal kinetic heating experiments at each temperature gave detailed decrease curves of the OH band area with time. These curves have been simulated by the 1st and 2nd order reactions or diffusion processes, and reaction rate constants, diffusion coefficients and activation energies were determined. Based on these results, dehydration mechanisms will be quantitatively discussed.

This novel in situ high-temperature IR microspectroscopic technique can be used to study dehydration behaviour of various hydrous minerals.

Hydrous aluminosilicate metasomatism in an intra-oceanic subduction zone: Implications from the Kurancali ultramafic-mafic cumulates within the Alpine Neotethys Ocean, Turkey

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The Kurancali ultramafic-mafic cumulate body, an allochthonous sliver in central Anatolia, is characterized by the presence of abundant hydrous phases as phlogopite and pargasite besides anhydrous phases as augitic diopside and plagioclase with accessory amounts of rutile, sphene, apatite, and calcite. Based on modes of the essential minerals, the olivine-orthopyroxene-free cumulates are grouped into six types as clinopyroxenite, clinopyroxenite with hydrous minerals and plagioclase, phlogopite, hornblende, layered gabbro, and diorite. Evidences from petrography and mineral chemistry suggest crystallization from a hydrous magma to form phlogopite with high Fe²⁺-Fe³⁺-Al⁶⁻-Ti, diopsidic-augite with high Ca-Al³⁻-Ti, Si-undersaturated pargasite with high Al⁴⁺-Ca-K-Na-Ti-contents and intercumulus plagioclase with a wide range of composition (an% = 40.61-98.58).

Whole-rock geochemical signatures of the cumulates including clinopyroxenite indicate that this hydrous magma is enriched in K, Rb, Ba, Sr, P, Th, U, and LREE, and depleted in HFSE (Nb, Ta, Zr, Hf, Ti), HREE, and is typical of subduction environment.

Petrographical, mineralogical and geochemical features of the cumulates show that this hydrous magma has high-K calc-alkaline affinity with slightly alkaline character, and infer a metasomatic origin. Our evidences imply that the metasomatizing component, modifying the composition of mantle wedge, is H₂O-, alkali-, carbonate-rich aluminosilicate melt which is likely to be derived from a subducted slab. We suggest that the metasomatic agents in subarc mantle lead to generation of the hydrous magma which produced the Kurancali cumulates in an intra-oceanic subduction zone during closure of the Izmir-Ankara-Erzincan branch of the Alpine Neotethys Ocean.
Trace Elements concentrations in apatites from the Sept-Îles Intrusive Suite – Implications for the genesis of nelsonites

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Cumulates of apatite and Fe-Ti oxides are formed during the later stages of crystallization in many layered intrusions. In some cases they occur as layers or lenses of nelsonite composed of about one third of apatite and two thirds of Fe-Ti oxides. Associated with nelsonite are troctolite or diorite enriched in oxides. Two different models have been proposed for the origin of these rocks. Both models suggest that a Fe-P-rich silicate liquid formed after considerable crystal fractionation of the mafic parental liquid. In the first model, Fe-Ti-oxide and apatite crystallize from this magma and accumulate on the crystal pile to form nelsonite. In the second model the silicate liquid splits into: a) an Fe-Ti-P liquid from which nelsonite forms and b) a SiO2-rich liquid.

We have investigated the whole rock and mineral compositions of nelsonites and associated rocks from the Sept-Îles Intrusive Suite, Quebec. In addition, we have determined the trace element concentrations of apatite in these rocks. Mass balance calculations show that apatite is the principle host for REE, Ca, U, Th and Sr in these rocks. To test the crystal accumulation model these trace elements were inverted to estimate the trace element composition of the magma at the time of apatite saturation. Mantle normalized trace element patterns of the estimated liquids are similar in shape to mantle normalized patterns from dykes believed to be feeders to the intrusion at this stratigraphic level. Apatite would not have been on the liquidus of magmas of the dyke compositions. A simulation (using PELE) was carried out in order to model crystallization of a magma derived from the dykes. The model mineral compositions and the trace element patterns including those of apatite match the observed compositions for Sept-Îles nelsonites and associated rocks. Thus we favour the crystal accumulation model for the formation of nelsonite and associated rocks.

Method of interpretation of in situ U-Pb zircon geochronology using data on melt and fluid inclusions

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In-situ U-Pb zircon geochronology is finding increasingly wide application and permits to define ages of separate zircon zones. Abundant evidence shows that zircons even from relatively simple in genesis rocks sometimes are zoned, and age values obtained from different zircon zones may vary in a wide range. Zircons from rocks formed in a result of different not related petrogenetic processes are much more complicated in structure, and their age values vary in more wide range. Obtained data should be interpreted in genetic terms: relations between dated zone and petrogenetic process which caused the origin of this zone should be emerged.

Mineralogical, cathodoluminescence and geochemical data are not always sufficient to obtain the reliable information on zircon genesis (1), and to locate the most perspective points for in-situ geochronology (2) as well. Cathodoluminescence data compared with optical data often provide insufficient information on zircon zoning, and substance being analyzed may be represented by mixture of several zircon zones. Cathodoluminescence images as a rule don’t reveal character of boundaries between neighbor zones: often it is not clear whether or not a margin of zone is corroded, suggesting break in zircon crystallization. Fluid and melt inclusions, areas of zircon recrystallization, zones, and fractures filled by fluid, which often distort analytical results, are not emerged on cathodoluminescence images as well. It is not quite evident that zircon core is on the surface of thin-section, or it is covered by a thin “layer” of a rim.

The most perspective features for reliable determination of zircon origin and hence for interpretation of obtained ages are direct genetic indicators – inclusions of mineral-forming environment represented by melt and fluid inclusions, which study allows distinguishing: zircons of magmatic and metamorphic origin (1); zircon of intrusive and volcanic origin (2); zircon zones, formed in result of a repeated metamorphism (3), igneous and sediment protolith origin (4). Optimal approach includes integrated study of melt and fluid inclusions from zircons and rock-forming minerals, comprehensive optical and cathodoluminescence data on zircons in a combination with their geochemical characteristics.
Helium isotope signatures in rocks, minerals, and related groundwater: Residence time of He in a sandstone – shale interlayering (Molasse Basin, N. Switzerland)

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In a rock-water system, an apparent residence time for He can be derived from the ratio of the He concentration in pore water to the He production in minerals given that 1) the rock-water system is at steady state and 2) the He flux from external sources is negligible. This second condition is crucial and needs to be assessed by the identification of the He sources in a given hydrologic environment.

In the Permo-Carboniferous shale – sandstone interlayering (PC-NCH; Molasse Basin, northern Switzerland) we investigated He and Ar isotopes and the parent element concentrations of whole rock samples and mineral separates. Shale and sandstone layers are similarly abundant in this ca. 800m thick low-permeability sequence.

In the shales, the parent elements U, Th, and Li are mainly concentrated in biotite, muscovite, clay minerals, and organic matter with ~95% of the produced He being lost from these phases. Hence, the 4He/3He ratio in the pore water can be assumed to be similar to that of the in situ production (1.3x10^7), provided that there is no external influx of He. Groundwater in the bounding aquifers has almost equal 4He/3He ratios (Pearson et al., 1991) so that such an external source can be excluded. This is also supported by the 40Ar/36Ar ratios.

Quartz, plagioclase and microcline have ratios of ~1 of measured 4He to mineral-produced 4He, and 4He/3He ratios are identical with those of the bulk rock (1.3x10^7). The low Li-content of these minerals cannot account for such ratios and they must have trapped their He from the pore water. This is supported by the higher 3He (~30x) and 4He (~4x) contents obtained for quartz and plagioclase of the sandstones compared to their production capacity. This further suggests that these minerals trapped He that was generated in the shales and migrated via the pore water into the sandstones.

Measurements of the migration of He-atoms through quartz crystals showed that equilibrium between internal (gas-fluid vesicles) and external He-concentrations is achieved during ~10 Kyr under PC-NCH temperature (70°C). By applying this new approach to constrain He isotope concentrations in pore waters across the entire PC-NCH cross section, similarly high concentrations were obtained, suggesting long He residence times in the order of tenth of millions years in the PC-NCH.

Distribution of mercury in soil near Idrija mercury mine, Slovenia

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The distribution of mercury in soil near Idrija mercury mine was investigated. Soil samples were collected from 4 locations along the Idrija River. Location 1 is upper reaches of the mine and 2 is the nearest point of the mine. Locations 3 and 4 are 5 and 10 km lower reaches of the mine, respectively. At each location, soil samples were taken by core sampler at interval of ca. 30 m from the riverside toward a hill perpendicular to the river. The individual core samples were separated with layer and used for determination.

T-Hg in soil was determined by CVAAS after wet digestion at 230°C using H2SO4-HNO3-HClO4 mixture. For MeHg determination, soil samples were treated with KOH-ethanol solution and MeHg eluted in the liquid was extracted with toluene as dithizonates and determined by GC-ECD. Chemical composition of soil samples was determined by WD-XRF.

T-Hg in surface soil ranged 0.8 to 480 mg kg⁻¹ (dry basis) and the highest value was observed in location 2. The surface T-Hg concentration tended to decrease with distance from the river toward hill, which suggests the main source of Hg in study area is the transported Hg with river from the mine. The vertical variation of T-Hg in location 4 suggests a recent dispersion of Hg, in which the surface soils at 1st and 2nd points from the river showed the lowest concentration of Hg, while at 3rd and 4th points the highest concentration was observed at the soil surface and the value decreased with depth. MeHg concentration ranged 0.8 to 16 µg kg⁻¹ (dry basis) and the lowest value was observed at location 2. The MeHg % of T-Hg in surface soil increased with the distance from the riverside toward hill. From the observations, it was suggested that the dispersed mercury from river is subject to methylation in the forest area. The dispersion of Hg was also discussed with the results of XRF determination.
A snapshot of mantle metasomatism?

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A set of fibrous diamonds from the Panda kimberlite (Canada) contain coexisting fluid (H2O-carbonate-KCl) and single-phase silicate (olivine, garnet, clinopyroxene) inclusions. These samples have preserved a snapshot of a natural mantle system at >4 GPa and >900°C. The silicate inclusions have fertile compositions (low Mg#, high CaO); however moderate to high Cr2O3 and Ni contents indicate that this apparent fertility is due to a secondary process - metasomatism by the concomitant fluid [1]. We present trace element data for the fluid (LA-ICP-MS) and mineral (SIMS) inclusions and investigate partitioning between, and the compositional evolution of, the fluid and mineral components. The trace element composition of the fluid is very similar to the Panda kimberlite, except for enrichments in Ba and Th, and a steeper REE pattern (La/Nd = 3 to 8). We will also investigate the possibility of a relationship between metasomatism and kimberlite petrogenesis.

Reference

Spatial variability in the release of terrigenic He from the sediments of Lake Van (Turkey)

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Recent analytical progress let for the first time 3H and He profiles in the pore water of lacustrine and oceanic sediments to be analyzed, which allows to determine local He fluxes. This method provides a simple and direct approach to study the He emanation on small spatial scales.

The He profiles measured in 13 sediment cores from Lake Van (Turkey) suggest that the He release from the sediments into the open water mainly occurs in the deep basin of the lake, which seems to be formed by an ancient caldera. The actual isotope signature of the terrigenic He accumulating in the open water body indicates that this He is of mantle origin (3He/4He ~ 10^-5). Furthermore, the He isotope ratios in the open water and in the sediment pore water suggest that there are at least two geochemical reservoirs, which both inject isotopically light, but different He into the lake.

The fact that the He found in the sediment samples has a heavier isotope signature than the source of the water body indicates that the sampled sediment cores do not carry that component that is relevant for the He emanation in Lake Van. Therefore we conclude that He that accumulates in the open water body has to emanate at sites where no cores were taken. Our noble gas results and the 3H measurements from the pore water of 3 additional cores show that the He emanation occurs very heterogeneously (~10 km) in the spatial domain of the tectonic active region of Lake Van.

References
Mg isotope thermometry in Earth’s mantle

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Advances in computational chemistry afford the capacity to predict quantitatively Mg isotope fractionations among high-temperature geological materials. High-precision MC-ICPMS measurements in turn provide the opportunity to test these predictions in well-characterized samples. We present new high-precision 25Mg/24Mg and 26Mg/24Mg measurements of mantle minerals and compare these ratios with predictions for temperature-dependent inter-mineral fractionations. Results show that systematic fractionations among minerals in high-temperature rocks are resolvable and are broadly consistent with theoretical predictions. Our first target was a spinel lherzolite from the San Carlos Arizona volcanic field. The crystal chemistry of the Cr-rich spinels from these mantle rocks suggests equilibration temperatures of between 800 and 820 ± 60°C (Uchida et al. 2005).

Analyte Mg was extracted from olivine (ol), spinel (sp), and clinopyroxene (cpx) mineral separates and purified using a two-column (AG50W-X12) cation exchange technique. Isotope ratios were measured using dry plasma and sample-standard bracketing to correct for instrumental mass bias.

Our initial analyses yield olivine δ25Mg and δ26Mg values of −0.079 ± 0.008 and −0.151 ± 0.011‰ (1σ), respectively, consistent with, but not identical to, previous measurements (Young and Galy 2004; Wiechert and Halliday 2007). Spinel δ25Mg and δ26Mg values are +0.333 ± 0.017 and +0.640 ± 0.025 ‰, respectively, and clinopyroxene δ25Mg and δ26Mg values are +0.117 ± 0.066 and +0.207 ± 0.011 ‰, respectively. The fractionations between sp, ol, and cpx have been estimated using density functional perturbation theory (Schauble et al., this meeting). Comparison of the measured sp-ol fractionation (A26Mgsp-ol = 0.79 ± 0.03) with these predictions yields a temperature of 835 ± 40°C, in good agreement with previous estimates. The cpx-ol fractionation yields lower T of 355 ± 20°C, suggesting disequilibrium or systematic errors involving the cpx predictions.

References


Determination of 33 elements in kimberlites from South Africa and China by ICP-MS

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In order to understand chemical characteristics of kimberlites from different areas we have determined 33 elements in 21 samples collected from South Africa and China (Shandong and Liaoning) by ICP-MS (inductively-coupled plasma mass spectrometry).

Homogenized samples (50mg) were decomposed with HNO3, HF and HClO3 in a teflon bomb. After dilution with HNO3 (2%), the elements such as Na, Mg, K, Ca, Sc, Cr, Nb, Sr, Y, Nb, Mo, Cs, Ba, REE, Ta, W, Th and U were measured by ICP-MS. For I and Br, samples (200mg) were heated in a quartz tube and evaporated I and Br were collected in a trap solution. They were measured by ICP-MS.

Concentrations of incompatible elements such as light REEs, Th, U, Ba and Hf were highly enriched in kimberlite samples compared to other ultramafic rocks, suggesting the small degree of partial melting in the formation of kimberlite magma. The Th/U ratios in the samples, with a special reference to the Chinese samples, were much higher than that in other common igneous rocks. The I/Br ratio of samples from China showed a significantly lower value than that in South African samples.

The chondrite-normalized REE patterns of the kimberlites from South Africa (11 samples), Shandong (5 samples) and Liaoning (5 samples) are shown in Fig.1, as their average values. It was found that light REEs were strongly enriched in all samples, whereas the levels of heavy REEs were very low. A marked difference was found between the concentrations of heavy REEs in two Chinese regions, i.e. the value in Shandong was much lower than that in Liaoning. The average REE patterns obtained for South Africa and Liaoning were very similar.

Figure 1: The chondrite-normalized REE patterns of the kimberlites
**Textural evolution of metal and sulphide in H-chondrites: Constraining parent-body structure**

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H-chondrites are samples of a single asteroidal parent body which show evidence for variable degrees of heating. The least "metamorphosed" members of the H-chondrite clan (H3) are mixtures of various components, clearly out of chemical and textural equilibrium. While the mineralogical and compositional effects of progressive heating have been studied in the literature, textural equilibration has received far less attention. We have therefore studied the textural characteristics of metal and sulfide in a series of H-chondrites (H4, 5, 6). These results provide constraints on the structure and thermal evolution of the parent body and have implications for the onset of processes leading to core segregation.

We have quantified: i) metal and sulfide proportions as a function of metamorphic grade; ii) the length of metal-sulfide contacts; iii) dihedral angles at silicate-silicate-metal/sulfide contacts; iv) the shape of metal/sulphide grains (circularity); v) the crystal size distribution (CSD) of metal and sulfide grain populations.

Proportions of metal and sulfide are independent of metamorphic grade, but the length of sulfide-metal contacts decreases significantly with increasing grade (metal and sulfide grains separate). Dihedral angles, grain circularity and CSD's for metal grains show little change between H4 and H5, but show significant changes between H5 and H6. These results may be rationalized in terms of textural equilibration and ripening involving diffusion. Published values for the temperature dependent diffusion coefficient of Fe in olivine have been combined with the results of thermal models describing the temperature-time paths at different depths within a parent body 180km in diameter heated internally by Al26. Comparison of the modeled length scales of Fe-diffusion relative to the average separation of metal droplets implies that the H5 samples come from a depth approximately 30km below the surface, in excellent agreement with independent estimates based upon peak metamorphic temperatures and Pb-Pb dating.

**U-Th, δ18O and paleomagnetic dating of a mid-Pleistocene lacustrine sequence: The Amora Formation, Mount Sedom, Israel**

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Dating of mid-Pleistocene carbonate sediments may be possible with the 230Th-234U and 234U-238U methods, yet, analytical uncertainties and problems of open system and presence of detrital material and initial Th hamper the dating of samples older than 200-300 kyr. Here, we present a combined approach that utilizes the U and Th isotopes with floating δ18O stratigraphy and paleomagnetic constraints, and establish a high-resolution chronology of the mid to upper Pleistocene Lake Amora in the Dead Sea basin.

The application of the δ18O record as a floating chronometer is based on the correlation found between δ18O values of synchronously deposited upper-Pleistocene and Holocene lake sediments, East Mediterranean foraminifers and Judean Mountain speleothems (Kolodny et al., 2005). The lacustrine Amora Formation consists of laminated aragonite and detritus, Ca-sulfate minerals, halite and clastic units. The sediments were deposited in the lacustrine environment of the paleo-Dead Sea basin and were later uplifted and tilted by the rising Sedom diapir, exposing ~330 m of the formation on the eastern flanks of Mt. Sedom.

δ18O values range between 6.0 and ~1.0‰, shifting periodically between glacial and interglacial sequences throughout the sedimentary section, marking corresponding shifts in the global marine records. Paleomagnetic data indicate the entire section was deposited after the 780 ka Matuyama-Brunhes magnetic transition.

Data compilation renders the age of the base of the exposed Amora Fm. to be ~750 to 700 ka BP (MIS 18 to 17), and the age of its capping sediments to be between ~200 and 130 ka BP (MIS 6 and the transition to MIS 5). Climatic-limnologic shifts throughout the sedimentation period are recorded by the lithological, chemical and isotopical properties of the sediments, and are correlated to global and regional events.

**Reference**
Ancient subduction recorded in the isotope characteristics of ~1.8 Ga Fennoscandian carbonatites

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The Svecofennian ~1.8 Ga post-collisional magmatism in the Fennoscandian Shield gave rise to a suite of high-Ba-Sr granites and shoshonitic lamprophyres interpreted to originate from a metasomatically enriched lithospheric mantle (Eklund et al., 1998, Andersson et al., 2006). In southern Finland the bimodal suite is accompanied by rare occurrences of intrusive carbonatites showing distinctively low δ13C values relative to that of average mantle carbon at around -5 ‰ (PDB). Carbonate samples from a carbonatite dike at Halpanen show δ13C values varying from -12.2 to -12.4 ‰ (n=7) while those from a carbonatite dike swarm at Panjavaara display an even stronger depletion in 13C, with values ranging from -15.3 to -16.5 ‰ (n=50).

The Halpanen carbonatite is a 10 m wide and up to 1.5 km long alvikite dike located in southeastern Finland some 200 km NE of Helsinki. The chemical composition of the dike is characterized by high contents of SrO, BaO, and REE (up to 3.63, 0.63 and 0.65 %, respectively). The Panjavaara carbonatite dike swarm is located some 180 km NE of Halpanen and comprises >50 carbonatite dikes and vein-dikes measuring 2 – 60 cm in width and from meters to tens of meters in length. The carbonatites of the Panjavaara dike swarm are also highly enriched in SrO, BaO and REE, with concentrations reaching 2.3, 3.9 and 10.0 %, respectively. Conventional U-Pb dating on monazite suggests an emplacement age of ~1.8 Ga for both the Halpanen and Panjavaara carbonatites. The Sr and Nd isotope data indicate an age of ~1.8 Ga for both the Halpanen and Panjavaara carbonatites.

The chemical characteristics of the studied ~1.8 Ga Fennoscandian carbonatites suggest a metasomatically enriched mantle source for these rocks. The depletion in 13C relative to the average mantle value could be related to subduction of organic-rich crustal material. In comparison to other carbonatites, the Halpanen and Panjavaara are notably depleted in 13C. Equally low δ13C values have been, however, reported for many eclogitic diamonds (e.g., Shirey et al., 2002).

References


Anaerobic nitrate-dependent oxidation of pyrite mediated by Thiobacillus denitrificans

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Introduction

NO3 reduction in nitrate-polluted groundwater may result from oxidation of organic matter and/or pyrite present in the aquifer rock. Although no direct laboratory proof exists that nitrate can serve as a pyrite oxidant under abiotic conditions, several field studies have provided indirect evidence for pyrite oxidation by NO3 mediated by autotrophic denitrifying bacteria. The present laboratory experiments are directed towards studying the mechanism and kinetics of water denitrification and pyrite oxidation, being mediated by Thiobacillus denitrificans.

Results and discussion

Anaerobic, nitrate-dependent dissolution of pyrite mediated by Thiobacillus denitrificans was studied by means of percolation-columns filled with pyrite powder and pyrite cubes run for 8 weeks. Input solution (thiosulfate-free specific medium for T. denitrificans growth) was supplied to the columns at a flow rate of 1 mL day-1 and the leachate was sampled once a week. Reacted samples after 1, 2, 4 and 8 weeks were examined by SEM-EDX and ex situ AFM.

Pyrite dissolution was confirmed by sulfate release to solution and nitrate reduction. Release of sulfate and iron to the solution was lower than that stoichiometrically predicted by the overall reactions:

\[ \text{NO}_3^- + 5 \text{FeS}_2 + 4 \text{H}^+ \rightarrow 7 \text{N}_2 + 10 \text{SO}_4^{2-} + 5 \text{Fe}^{2+} + 2 \text{H}_2\text{O} \]

\[ \text{NO}_3^- + 5 \text{Fe}^{2+} + 6 \text{H}^+ \rightarrow \frac{5}{2} \text{N}_2 + 5 \text{Fe}^{3+} + 3 \text{H}_2\text{O} \]

After 8 weeks precipitation of secondary minerals (ones rich in Fe(III), S and K and others rich in P and Ca) over the pyritic surfaces was detected by EDX analyses. SEM and AFM images revealed that bacteria cells were attached to surface of pyrite fragments and grains, sparsely distributed, and that the surface roughness increased throughout the experiments. Secondary minerals and organic matter coating the surface did not prevent bacterial metabolism and consequent nitrate reduction.

Although T. denitrificans is capable of catalyzing complete reduction of nitrate to nitrogen gas, over most of the entire experimental run nitrate mostly reduced to nitrite and production of gaseous compounds were not evident.
Application of the Pitzer ion interaction model to the Fe$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O System

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Ferric iron-bearing acid sulfate systems are important to a variety of industrial and surficial environments, specifically areas affected by acid mine drainage (AMD). Accurately describing the thermodynamic properties of such highly concentrated waters has been hindered mainly by the lack of experimental data for the Fe$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O system. However, with the recent availability of isopiestic measurements yielding solvent activities for [Fe$_2$(SO$_4$)$_3$-H$_2$SO$_4$] mixtures [1,2], the Pitzer ion interaction model may be applied and used as an additional tool in describing the equilibrium state of many natural systems. Hydrolysis at low pH and the importance of sulfate-bisulfate equilibria present complications in applying the Pitzer approach to the Fe$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O system. Here, we describe the application of an extended Pitzer model based upon the Clegg et al. [3] model for H$_2$SO$_4$(aq). The model fits available isopiestic data for [(1-y)Fe$_2$(SO$_4$)$_3$-yH$_2$SO$_4$] mixtures to 3.00 molal and 0.0435 \( \leq y \leq 0.9370\). A slightly less accurate representation of a more extended molality range to 5.47 molal extends over the same y values. A more limited isopiestic dataset at 323.15 K is also analyzed with the Pitzer model. Available solubility data are examined using a recent calorimetric study of ferricopiapite and rhomboclase. We also discuss some examples of model applications to geochemical problems in AMD environments. The resulting Pitzer model provides an important step toward a more detailed picture of Fe-sulfate mineral stability in AMD systems. In turn, controls on the cycling of acidity and toxic metals in AMD environments may be better predicted and identified.

References

Calculating the stability, Raman and UV spectra and acidity of As sulfides in aqueous solution

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Since the chemical and biological reactivity of As sulfides depends strongly upon their speciation, it is important to determine exactly what species are present within a given environment. Spectral probes such as Raman and UV can give partial information about speciation, but uncertainties and ambiguities generally remain. We are engaged in a program to perform state-of-the-art quantum mechanical studies of the structures, stabilities, spectra (Raman and UV) and acidity of As sulfide species in aqueous solution. We typically use very high level methods, such as CCSD with triple zeta, doubly polarized basis sets for the gas phase part of the calculation, and a lower-level polarizable continuum or nanocluster approach to simulate the effect of hydration. Anharmonic vibrational effects are calculated using 2nd order perturbation theory within a HF – DFT hybrid method. Using this approach we can accurately reproduce the Raman spectra of thioarsenious acid, As(SH)$_3$, and its conjugate bases. The Raman spectra of As(SH)$_3$ is also reproduced with errors of less than 10 cm$^{-1}$ and the As–O(H) distances with errors of only 0.02 Å. Such calculations establish that the neutral species in arsenious acid solutions is indeed As(SH)$_3$ rather than HAsO$_2$. This assignment is also supported by our calculated UV spectra. However, accurate calculation of the Raman spectra of the conjugate bases of As(SH)$_3$ requires the inclusion of both explicit waters and counterions. Trends in the acidity of As acids with changing oxidation state, ligand and degree of protonation are well reproduced, but accurate absolute values for the oxidic species are elusive. Possible reasons for the overestimation of pKas for the oxidic species are presented. We have established computationally that the conjugate bases of As(SH)$_3$ are susceptible to sulfidation by H$_2$S, while As(III) sulfides such as AsS(SH)$_2$– are susceptible to oxidation to As(V) by elemental sulfur or polysulfides. By contrast the addition of H$_2$S to AsS(SH)$_2$– to form As(SH)$_3$– is calculated to be unfavorable. We can thus generate a comprehensive picture of speciation based upon direct quantum mechanical calculation of a number of properties for possible candidate species.
Hf-W constraints on the formation and differentiation of the Moon

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Hf-W chronometry is well suited to investigate the timescales of early lunar differentiation because Hf/W ratios are variable amongst the products of the lunar magma ocean \cite{1,2}. Application of Hf-W chronometry to lunar whole-rock samples however is hampered by the production of \textsuperscript{182}W via neutron-capture of \textsuperscript{181}Ta during prolonged cosmic-ray exposure of the lunar surface \cite{3}. Almost all lunar samples contain some metals, which contain virtually no Ta and hence no cosmogenic \textsuperscript{182}W. The age of magma ocean crystallization has been derived from the W isotope composition of lunar samples \cite{4}. Almost all lunar samples contain some metals, which contain virtually no Ta and hence no cosmogenic \textsuperscript{182}W. The age of magma ocean crystallization has been derived from the W isotope composition of lunar samples \cite{4}. All lunar metals contain some metals, which contain virtually no Ta and hence no cosmogenic \textsuperscript{182}W. The age of magma ocean crystallization has been derived from the W isotope composition of lunar samples \cite{4}. Here we present new W isotope data for metals from a comprehensive set of lunar samples. Our new data are significantly more precise than most of the earlier data, mainly because we processed \approx 4 times more material than was used in earlier studies \cite{1,4,5,6}. All lunar metals separated from KREEP-rich samples, low- and high-Ti mare basalts have indistinguishable \textsuperscript{182}W/\textsuperscript{184}W ratios, which are identical to those previously reported for KREEP \cite{4}. In contrast to earlier studies \cite{4,7} we do not find systematic variations in the \textsuperscript{182}W/\textsuperscript{184}W ratios of lunar samples, despite the large variations in Hf/W ratios of the source areas. This indicates that solidification of the lunar magma ocean continued until after the effective life-time of \textsuperscript{181}Hf (i.e., \approx 60 Myr) and might have continued until \approx 200 Myr, as indicated by \textsuperscript{146}Sm-\textsuperscript{142}Nd systematics \cite{5,6}. Our new data reveal that the lunar and terrestrial mantles have indistinguishable W isotope compositions, which could indicate that the Moon mainly consists of material derived from the Earth's mantle. This however is inconsistent with constraints from dynamical simulations of the giant impact. Alternatively, W isotopes re-equilibrated during the giant impact, as has been proposed to account for the similarity in O isotope composition of the Earth and Moon \cite{8}. Whether this process can effectively equilibrate W isotopes remains to be investigated.

References


Dynamic metal speciation analysis by stripping chronopotentiometry at scanned deposition potential (SSCP)

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In the broad context of stripping voltammetric techniques, the depletive mode of stripping chronopotentiometry, SCP, has fundamental advantages for metal speciation analysis. Complete voltammetric potential-current curves are inherently rich in information content: as measurements are made from the foot of the wave to the limiting deposition current region the relevant part of the stability distribution and corresponding parts of the rate constant distribution are scanned. Conventional DC steady-state voltammetry lacks the necessary sensitivity for measurements at environmentally relevant concentrations, however analogous curves, denoted as SSCP waves, can be constructed by plotting the magnitude of the SCP stripping peak as a function of deposition potential. Analogous to the Deford-Hume expression for voltammetric waves, speciation parameters derive from the change in half-wave deposition potential that occurs on complexation, and the magnitude of the limiting plateau. The distinctive features of SSCP include (i) an effective getting around part of the Nernstian extension of the reoxidation process, leading to (ii) greater resolution than conventional stripping voltammetries, (iii) a certain insensitivity to electrochemical irreversibility, especially at a microelectrode, (iv) practically freedom from induced metal ion adsorption interferences, (v) no requirement for excess ligand during stripping, and (vi) ability to provide a certain unambiguous measure of any chemical heterogeneity in the metal speciation. In case of kinetic currents, i.e. systems with limited association/dissociation rates, invoking the Koutecky-Koryta approximation allows a rigorous expression to be obtained for the full SSCP wave. These features are illustrated by practical examples.

References

Thermal events documented in Hadean zircons by ion microprobe depth profiles

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We report the first U-Th-Pb ion microprobe depth profiles for four Hadean zircons from the Jack Hills and Mt. Narryer supracrustal belts of the Narryer Gneiss Complex (NGC), Western Australia. This ultra-high spatial resolution technique probes the age and origin of sub-micron features in individual crystals that can record episodes of zircon growth. Near-surface grain dates 2700 Ma or older are coincident with post-depositional growth/modification. Some ages may coincide with documented pre-deposition metamorphic episodes for the NGC and igneous emplacement at ca. 3700 Ma. Separate events that do not correlate in time with known geologic episodes prior to the preserved rock record are also present within pre-4000 Ma zircons. We find evidence for a ~3.9 Ga event (Fig. 1), which is coterminous within age uncertainty with one or several large basin-forming impacts (e.g. Nectaris) on the Moon and attributed to the late heavy bombardment of the inner solar system.

Figure 1. Example depth profile data for a 4.18 Ga zircon from Mt. Narryer, Western Australia.

Chemical heterogeneity in the mantle: Inferences from seismology and mineral physics

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The first claims by geophysicists of significant chemical heterogeneity in the lower 1000 km of the mantle were made about 15 years ago. I will briefly review the evolution of ideas, which were mainly based on results from classical tomography. Classical inversion methods, however, are not free of caveats which can make interpretations ambiguous. Probabilistic tomography, on the other hand, allows to infer robust probability density functions (pdfs) for long wavelength models of bulk-sound and shear wave speed, density and boundary topography in the mantle. Using appropriate depth-dependent sensitivities, these pdfs can be converted into likelihoods of variations in temperature, perovskite and iron content throughout the mantle. The sensitivities are calculated using full uncertainties in mineral physics data and, more importantly, in the thermo-chemical reference state of the mantle. We find that bulk-sound speed (density) variations are an excellent proxy for perovskite (iron) variations, and that shear-wave speed is not highly correlated to temperature as is often assumed. Compositional variations are found to be essential to explain the seismic, gravity and mineral physics data. In particular, the regions of low shear-wave velocity in the deep mantle (> 2000 km) beneath Africa and the Pacific, usually referred to as super plumes, are mainly due to an enrichment in iron, which makes them denser than the surrounding mantle. We performed comparisons with some chosen models of thermo-chemical convection. A stable and ubiquitous layer of dense material is unlikely to be present at the bottom of the mantle. Models of piles entrained upwards explain the observations significantly better.
Shock effects in quartz: compression versus shear deformation – An example from the Rochechouart impact structure, France

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The effects of the shock wave-associated stress resulting from a large meteorite impact are recorded in the microstructures of naturally shocked rocks. Quartz is especially useful to provide information on the stress conditions during shock, given the widespread occurrence of this mineral in the Earth's crust and its comprehensive experimental calibration. This study compiles effects in quartz resulting from compression due the high shock pressure, which is as a first approximation the mean stress of the shock wave-associated stress tensor, and from shear deformation due the high differential stresses during shock in target rocks and impact breccias from the Rochechouart impact structure. Microstructures that result from compression/decompression are pockets of new quartz grains surrounded by intensely shocked quartz (Fig. 1) that shows intense mosaicism, as indicated by TEM analysis. This microstructure suggests that it formed by annealing of diaplectic glass. A high density of very fine rhomboedral planar deformation features (PDFs) that can merge into a mosaicism structure in TEM is common in shocked quartz from the Rochechouart impact breccia. These features indicate high shock pressures (20-35 GPa). Shock effects in quartz that record shear deformation are mechanical Brazil twins and planar fractures. These shock effects indicate high differential stresses on the order of a few GPa. Shock effects indicating high differential stress never occur together with those indicating high shock pressure. This suggests that the differential stresses at high shock pressure (>20 GPa), i.e. at high mean stress, are ineffective to cause shear deformation. Whereas at attenuated mean stress (<20 GPa) the differential stress gets relatively more effective.

Figure 1: Pockets of newly crystallised quartz surrounded by intensely shocked quartz.

Sediment-microbe interactions in permeable sediments at hydrocarbon seeps in the Santa Barbara Channel, California

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Sediments of marine cold-seep areas exhibit high rates of hydrocarbon discharge and are unique dynamic systems with specific microbial communities connected to methane and/or oil degradation processes. Microbial activity in such systems is in general tightly coupled to advective transport mechanisms of fluids and hydrocarbons as well as to geochemical gradients in the sediment. Seeps in coastal shallow-water areas are, in contrast to deep-sea mud, characterized by sandy permeable sediments, thus enabling enhanced substrate exchange due to accelerated pore water transport processes. We investigated sandy sediments off Coal Oil Point (Santa Barbara Channel, California), one of the world’s largest hydrocarbon-seep area, to study the effect of pore water transport processes on microbial methane and sulfur turnover, biogeochemical gradients as well as microbial community structure. Our results show accelerated microbial activity of anaerobic oxidation of methane and sulfate reduction in areas where reduced fluids, rich in hydrocarbons, are seeping through highly permeable surface sediments. Vertical and horizontal biogeochemical parameters such as sulfide, oxygen, methane, and sulfate reveal gradients and small-scale distribution patterns that differ from cold-seep systems of the deeper oceans. We suggest that these gradients and the resulting microbial activity are a result of pore water transport processes, where the supply of substrates is not limited to diffusion. Our data indicate that fast substrate supply and removal of inhibitory end products is an important factor enabling efficient microbial consumption of methane in marine sediments.
Timing of protoplanetary disc dissipation and planetesimal formation in the early solar nebula

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The lifetimes of protoplanetary disks of 3-6 Ma [1] around young stars constrain the time scales of planetesimal formation. Most studies suggest that formation of asteroid-sized planetesimals in the early solar system occurred within a few Ma [e.g. 2-4], indicating that the building blocks of terrestrial planets were already present when the disk was dissipated. However, it is not yet clear, if full-sized terrestrial planets accreted within the presence of disk gas or not. While for the outer gas or ice giant planets rapid accretion and attraction of disk gas as major constituent is mandatory, the terrestrial planets obviously needed significantly longer time for complete accretion, as indicated by Hf-W ages of complete core formation of 10 Ma for Mars and 33 Ma for Earth [5]. The question if terrestrial planets accreted with the presence of gas or after disk dissipation can be answered using neon isotopes [6-10], particularly utilizing advances in high precision neon isotope measurements in recent years [11-14]. These results provide increasing evidence that Earth’s precursor planetesimals acquired solar neon as solar wind-implanted ions (“Ne-B”), similar to carbonaceous chondrite [15] or Rumuruti parent bodies. For the latter, thermochronological modelling [16-18] suggests very early brecciation and irradiation. Several irradiation scenarios are possible: 1) irradiation before disk gas dispersal, due to planetesimal orbits with high inclinations (possibly triggered by gravitational disturbances of Jupiter) 2) late accretion of fine, irradiated dust to Earth, e.g. after the moon forming impact 3) disk gas dissipation 3-4 Ma after CAIs in the inner solar system, possibly triggered by photoevaporation of the disk.

References
50Ti anomalies in primitive and differentiated meteorites

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We analyzed relative 50Ti abundances in primitive and differentiated meteorites (whole-rock carbonaceous, ordinary, enstatite chondrites, eucrites, angrites, ureilites, SNCs, NWA 2976, Itqiy and silicates of mesosiderites) and terrestrial rock standards, in order to characterise possible correlations with neutron-rich isotopes of Ni and Cr and with O isotopic systematics of early Solar System objects. Chemical purification of Ti from meteorite matrices was achieved on anion exchange resin, with chemical yields in excess of 90% and total procedural blanks < 10 ng Ti. Ti isotopic ratios were determined by MC-ICPMS using the sample-standard bracketing technique, analysing each sample 5-12 times. The accuracy and precision of our analytical protocol were estimated through replicate analyses of terrestrial standards doped with a Ti isotopic tracer, yielding a long-term reproducibility for 50Ti/47Ti of 20 ppm (2sd).

Carbonaceous chondrites are characterised by 50Ti excesses, while ordinary chondrites record deficits. Except for NWA 2976, which shows a 50Ti excess identical to that of CR chondrites, all meteorites or iginating from differentiated planetesimals record 50Ti deficits. Enstatite chondrites have a terrestrial 50Ti abundance. The range of variation in 50Ti/47Ti between all meteorites studied here spans 0.7‰. We find that 50Ti anomalies correlate with 54Cr and 62Ni variations at the planetary scale [1-2], constraining the existence of two reservoirs in the early Solar System. Further, because neutron-rich isotopes are believed to be formed in old supernova sources rarely associated with young star-forming regions, the well-preserved correlated variations may represent residual heterogeneity inherited from the molecular cloud. In addition, neutron-rich and O isotopes [3] define two mixing trends among CC and OC-D that support two distinct origins for O and Ti isotopic heterogeneities.

References


Magma genesis and differentiation at Merapi volcano, Sunda arc, Indonesia

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Merapi, a large Quaternary volcanic complex situated within the active volcanic front of the Sunda arc in Central Java, is one of the most active volcanoes in Indonesia. Its recent activity is characterized by the extrusion of high-K basaltic andesite lavas forming lava domes in the summit area and intermittent gravitational or explosive dome failures generating small-volume pyroclastic flows that are a permanent threat to life within the densely populated areas on the flanks of the volcano.

During the Holocene, Merapi erupted basalts and basaltic andesites of medium-K affinity in the earlier stages of activity and high-K compositions from ~1900 years BP to the present. This increase in K2O is accompanied by a marked increase in whole-rock 87Sr/86Sr ratios, but not by systematic variations in δ18O values, which are relatively constant and slightly elevated compared with mantle values. Whole-rock trace element and isotopic characteristics suggest that mantle source contamination played a significant role in determining the geochemical characteristics of the parental magmas of the two magmatic series. Subsequent differentiation of these magmas during ascent and storage in the arc crust involved a complex interplay of fractional crystallisation, recharge, magma mixing and assimilation of carbonates from the subvolcanic basement. Whole-rock analysis of the crystal-rich Merapi rocks can only provide a blurred picture of these processes and open-system processes, such as crustal contamination, are often masked in the whole rock isotope ratios. Therefore, a more complete picture of these processes has been assembled by combining crystal isotope stratigraphy, petrological analysis of magmatic and crustal xenoliths hosted in recent Merapi deposits and stable isotope analysis of fumarole gases. These studies indicate that magma-crust interaction and late-stage crustal contamination are volumetrically significant and have important implications for magma evolution and, potentially, the eruptive behaviour at this high-risk volcano.
Petrological characterization and tectonic implications of multi-stage garnet crystallization in eclogitic rocks from the southern Tongbai region

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We report some newly-discovered eclogitic rocks within the blueschist-greenschist unit in the southern Tongbai region, central-eastern China. This region is the NW extension of the Dabie-Hongan UHP orogenic belt. No UHP rock or true eclogite has been reported from this unit yet. The studied eclogitic rocks occur as discontinuous boudins or pods enclosed within dolomite-bearing marble. The eclogitic rocks contain mainly garnet, quartz, omphacite (Jd33-43), amphiboles, carbonates, and accessory minerals. The rock is heterogeneous in terms of mineral mode and texture.

Three textural types of garnet have been distinguished: Type I is the largest in grain size and with abundant inclusions; Type II is the medium-size and with an inclusion-free core and inclusion-rich rim; Type III is the smallest and relatively more euhedral. On the basis of chemical zoning of Type I garnet and distribution of inclusions, two stages (core and rim) of garnet crystallization have been identified. Major element compositions show that the rim part is Ca-enriched, but Fe- and Mg-depleted, relative to the core part. The core-rim chemical boundary is sharp, and in some cases, it shows an indication of resorption. Inclusions in the core of the Type I garnet imply an early greenschist-facies stage, whereas those in the rim indicate an epidote-amphibolite to eclogite-facies stage.

The eclogite-facies assemblage includes garnet + omphacite + rutile + quartz + carbonate. Glauconephane in the matrix indicates a blueschist-facies stage postdating eclogite-facies. One unique feature of the eclogitic rock is the abundant titanite rods (lamellae or needle-like) across or within garnet grains. The host rock marble shows no evidence of high-pressure metamorphism. Thus the rock association may represent a tectonic mixture. In summary, the Tongbai eclogitic rocks in the blueschist-greenschist unit record part of a subduction history that was not previously recognized.

Crystalchemical aspects and polymorphism in post-perovskite

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We synthesized post-perovskite phases of aluminous and ferrous-aluminous magnesiummetasilicate. Diffraction patterns and Raman spectra indicate marked structural deviations from the calculated CaIrO3-type structure of post-perovskite. Combined modelling of alternative post-perovskite structures based on sets of crystallite reflections spanning a reciprocal space lattice and on ab-initio calculations show our data to be consistent with postperovskite structures composed of kinked MgO- and SiO2-layers that have previously been proposed by Oganov, A.R. et al. (2005) Nature 438, 1142-1144. The transition to perovskite has been reversed in our experiments. These new phases appear to be intermittent between perovskite- and CaIrO3-type silicate. Kink density may correlate with chemical parameters and has a significant effect on the perovskite-kinked ppv phase boundary. Hence, the paragenesis of deepest mantle rock may be markedly different for depleted mantle and eventual enriched or primitive reservoirs.

Acknowledgements

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$^{87}$Sr/$^{86}$Sr of mafic microgranular enclaves in the Inagawa Granite, Ryoke belt, southwest Japan

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The Inagawa Granite is located in the eastern part of the Cretaceous Ryoke metamorphic belt, southwestern Japan. The radiometric ages of the Inagawa Granite are: 63 – 72 Ma by K-Ar biotite method [1], c. 77 Ma with an initial $^{87}$Sr/$^{86}$Sr ratio ($\text{SrI}$ = 0.7095 by Rb-Sr whole-rock isochron method [2], 71.5 ± 2.4 Ma, 63.0 ± 2.0 Ma and 67.4 ± 1.4 Ma by Rb-Sr mineral whole-rock isochron method [3], and 81.9 ± 1.4 and 82.6 ± 1.8 Ma by CHIME monazite method [4].

The Inagawa Granite in the study area (Asuke area) is divided into four intrusive units; Type I (medium-grained hornblende-biotite tonalite, granodiorite and monzogranite), II (coarse-grained porphyritic hornblende-biotite granodiorite and monzogranite), III (coarse-grained hornblende-biotite granodiorite and monzogranite) and IV (coarse-grained hornblende-bearing biotite monzogranite) [5]. Sr isotopic study of apatite revealed the initial $^{87}$Sr/$^{86}$Sr ratio heterogeneity ($\text{SrI} = 0.7093 - 0.7107$) within the pluton [3].

Type I and II granite often contains mafic microgranular enclaves (MME) of diorite. The enclaves are irregularly shaped and vary from 3 to 16 cm across. The boundary between host granite and the mafic enclaves is gradual. The enclave consists of subhedral to anhedral phenocrysts of biotite and clinopyroxene. In this study, $^{87}$Sr/$^{86}$Sr ratios of plagioclase in a matrix dominated by plagioclase, quartz, and mafic microgranular enclaves (MME) of diorite. The enclaves are irregularly shaped and vary from 3 to 16 cm across. The boundary between host granite and the mafic enclaves is gradual. The boundary between host granite and the mafic enclaves is gradual. The enclave consists of subhedral to anhedral phenocrysts of biotite and clinopyroxene.

Initial $^{87}$Sr/$^{86}$Sr ratio of the enclaves varies from 0.7086 to 0.7094. Combining initial Sr isotopic studies of MME with radiometric ages of the Inagawa Granite are: 63 – 72 Ma by K-Ar biotite method [1], c. 77 Ma with an initial $^{87}$Sr/$^{86}$Sr ratio ($\text{SrI}$ = 0.7095 by Rb-Sr whole-rock isochron method [2], 71.5 ± 2.4 Ma, 63.0 ± 2.0 Ma and 67.4 ± 1.4 Ma by Rb-Sr mineral whole-rock isochron method [3], and 81.9 ± 1.4 and 82.6 ± 1.8 Ma by CHIME monazite method [4].

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Lapland Granulite Belt: A 50 Ma cycle from burial to exhumation

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Lapland Granulite Belt consists of migmatitic metagreywackes and an arc-type norite-enderbite series. Both record granulite-facies metamorphic maximum at about 850°C and 6-8 kbar and a subsequent cooling and decompression to about 650 °C and 2-3 kbar. However, only the metagreywacke sequences demonstrate pre-maximum heating, with abundant partial melting and migmatization. The evolution began with the deposition of the metagreywackes, which probably came to end due to tectonic burial as late as 1930 Ma. The provenance of greywackes varies from Archaean to Proterozoic, just predating the burial. These ages are shown by SIMS U-Pb ages of detrital zircons. The metagreywacke sequence was intruded by the igneous series at about 1920 to 1905 Ma, shown by the TIMS and SIMS ages of magmatic zircons. The high-grade metamorphism began at about 1910 Ma by dehydration melting which is shown by the U-Pb age of monazite in leucosomes. A lot of homogeneous round shaped zircon was grown in both neo- and palaeosomes at about 1905-1890 which probably indicates the age of metamorphic maximum. Later rims, having as young ages as about 1870 are grown around cores both in metagreywackes and enderbites. These are interpreted to have formed during exhumation in the stability field of andalusite + K-feldspar. The reason for their crystallization might be fluid liberated from crystallizing neosomes.

This all would imply that the evolution cycle of the Lapland granulite belt took about fifty million years from burial to exhumation. Tectonic setting was changed from arc to continent-continent collision and further to uplift and erosion of a mountain belt during the cycle. The cycle was preceded by a relatively short deposition phase, most probably in forearc deep marine basin.

What the Nonsberg–Ultental Region tells us about subduction zones

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Since Godard et al. (1996), the Nonsberg–Ultental Region (NUR) of the Eastern Alps is thought to represent an exhumed portion of a slab subducted during the Variscan orogeny to P ≈ 2.7 GPa and T ≈ 850°C (Nimis and Morten, 2000). The mélangé is constituted mainly of migmatites enclosing minor mantle-wedge peridotites and eclogite. Locally, metasomatic contacts between migmatite and peridotite are preserved. Challenging topics concerning NUR are: i) the partial melting of the slab metasediments and ii) the metasomatism of the enclosed peridotites and the crust–mantle interaction. Isotopic Sm–Nd (grt-cpx-wr), Rh–Sr (wr) and U–Pb (zir) data define a geochronologically synchronous event at about 330 Ma (Tumiati et al., 2003; 2007). This event likely corresponds to the P–T peak, the migmatization of the metasediments and the principal metasomatic interaction between pelites and peridotites. This implies that metapelites started to melt at (U)HP (2.7 GPa?), although till now none found (U)HP-metamorphic peak. Recent works (e.g. Hermann et al., 2006) demonstrated that metasediments may melt at T > 700°C at 2.7 GPa in water-present conditions, but T < 850°C are required in water-absent conditions. Therefore, Tumiati et al. (2007) suggested a wet melting of metapelites rather than a decompressional dehydration melting. Excess fluid prompted melting in pelites and metasomatism of the peridotite bodies tectonically enclosed in the crustal slab, emphasized by the crystallization of dissakisite-(La) in amphibole-bearing peridotite (Tumiati et al., 2005). However, Scambelluri et al. (2006) suggested that peridotites could have suffered also a former metasomatism prior to the slab emplacement.

Wet partial melting of metasediments occurred at (U)HP in the NUR. This suggest a massive entrapment of crustal fluids within subduction zones down to at least 80 km.

References

Effect of rapid diagenetic calcite deposition on carbonate associated Sulfate and Calcium isotopes

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Carbonate minerals remain the primary mineral proxy used for reconstructing paleoclimate and paleoceanographic changes throughout Earth History. Recent work has expanded the use of these minerals to include the sulfur and oxygen isotopic composition of structurally bound carbonate-associated-sulfate ($\delta^{34}$S and $\delta^{18}$O$_{SO4}$ of CAS) and calcium isotopes ($\delta^{44}$Ca). While carbonate minerals are available nearly continuously over the past billion years of the rock record, they are susceptible to diagenetic alteration. Understanding and quantifying the effect that diagenesis may have on both CAS and $\delta^{44}$Ca is critical for proper interpretation of the geochemical record. In addition, the high rates of calcite precipitation in sediments where there is rapid sulfate reduction may produce effects on pore fluid calcium that shed light on calcium isotope fractionation in natural systems.

We measured both the $\delta^{18}$O$_{SO4}$ the $\delta^{34}$S of pore fluid sulfate and coexisting CAS from ODP sites 1123 (New Zealand) and 1063 (Bahamas). At both sites the $\delta^{18}$O$_{SO4}$ and the $\delta^{34}$S of CAS track the increase in the $\delta^{18}$O$_{SO4}$ and the $\delta^{34}$S of sulfate in the pore fluid. These results have implications for the fidelity of the CAS proxy. We also measured the $\delta^{44}$Ca at ODP site 1082 (West Africa). Calcium concentrations at this site decrease at the top of the core from 10mM to ~3mM, reflecting rapid calcite deposition. The $\delta^{44}$Ca, which remains at seawater values through the zone of rapid precipitation, gives a view of calcium isotope fractionation due to calcite precipitation at natural rates. We have added formulations for O, S, and Ca isotope fractionation to CRUNCH, the multicomponent reactive transport code, for the purpose of further exploring the effects of diagenesis on these proxies. We will quantify calcite recrystallization from incorporation of isotopically altered sulfate into CAS, to explore natural calcium isotope variation and fractionation, and to assess how both these proxies are affected by carbonate diagenesis.

Widespread Os isotope evidence for a magmatic pulse at the onset of Oceanic Anoxic Event 2

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The Cenomanian-Turonian Boundary Event (CTBE; ca. 93.5 Ma) is one of the best studied global Oceanic Anoxic Event (also referred to as OAE2) that punctuate the Cretaceous stratigraphic record. The CTBE is the most extensive of the Cretaceous OAEs, with global temperatures apparently the highest of the last 115 Ma (Clarke and Jenkyns, 1999; Huber et al., 2002; Wilson et al., 2002). This OAE is characterised by a positive global carbon-isotope excursion in both carbonates and organic matter. The similarity of $\delta^{13}$C curves at distant locations hint at the global nature of this event.

During this time, high amounts of organic carbon were buried in ocean basins due to an increase in primary productivity and/or enhanced preservation of organic matter owing to anoxic bottom waters. Debate, however, still surrounds the identification of the actual “trigger” mechanism of these periods of carbon sequestration.

Rhenium-osmium isotopic analyses were performed on two sample sets located in different basins during the CTBE: the Livello Bonarelli from the Furlo section in central Italy located in the western reaches of the Tethys Sea and, as Site 1260B of ODP Leg 207, located on Demerara Rise just off the ENE coast of South America, in the southern proto-North Atlantic. At Furlo, several minor C$_{org}$-rich intervals (“black levels”), generally thought to be precursor events, are interbedded with siliceous limestones beneath the Bonarelli.

Initial results from the black levels show upward increasing Os contents, peaking abruptly at the base of the Bonarelli (~10 ppb), then decreasing to 0.1-0.2 ppb: the CTBE at Site 1260B shows a similar trend, with Os contents of 25 ppb at the base of the CTBE decreasing to <0.1 ppb upwards. The initial $^{187}$Os/$^{188}$Os, calculated for individual samples and reflecting contemporaneous seawater Os isotopic values, are fairly high (0.7-1.2) in the black levels, indicating a continental weathering dominated Os system. The initial Os ratios at the base of the CTBE are, however, very low (~0.14-0.15) in both sections, and gradually increase upward to ~0.5-0.6. Such low values at the onset of the CTBE suggest a strong magmatic/hydrothermal influence (no evidence of bolide impact has been reported near this stage boundary), while the upward increase probably documents a return to a weathering-dominated source of Os in the oceans.

References
**Geochemistry of fossil bones and teeth – Reconstruction of past environments**

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Skeletal tissues such as bones and teeth are often the only remains of vertebrates that are preserved in the fossil record. They represent important archives for the reconstruction of life-history and environment because the skeletal apatite integrates chemical signals over the period of tissue formation. The isotopic composition of the food and/or drinking water ingested by the animal depends on the environmental conditions (e.g., climate, vegetation, geology). This might be incorporated into the biogenic apatite either unchanged or with fractionations during metabolism and tissue formation (vital effects).

In palaeoecology, archaeology, and palaeontology the isotopic composition of fossil bones and teeth are increasingly used for the reconstruction of diet, niche partitioning, climate, provenance, migration, metabolism and biomineralization processes (Figure 1).

However, diagenesis and recrystallisation of the microcrystalline biogenic apatite might severely bias original in vivo compositions. On the other hand chemical and mineralogical changes during diagenesis yield information about the thaphonomy. Especially postmortem-uptake of rare earth elements or uranium into the biogenic apatite enable to characterize the diagenetic milieu, detect fossil reworking or radiometrically (U/Th, Lu/Hf) date early diagenesis.

If diagenesis is carefully considered, the isotope compositions of fossil bones and teeth can yield important quantitative information about the palaeoecology and palaeoecology of fossil vertebrates and their palaeoenvironment. Results of different case studies will be discussed to demonstrate the broad application potential of isotope analysis on phosphatic vertebrate skeletal tissues.

**Bone oxygen isotope profiles (SIMS, Micromill) – Implications for archosaur growth and biomineralization**

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Accretionary, non-remodelled bone tissue can provide a multi-year proxy record of ingested meteoric water and/or body temperature. Seasonal oxygen isotope cyclicity may be used as annual time marker of osteogenesis and thus for skeletochronology of extant and extinct vertebrates such as dinosaurs (Figure 1).

Long bones of extant crocodiles (*Alligator mississippiensis*) and ostriches (*Struthio camelus*) of known individual age as well as of different sauropod dinosaurs were serially sampled to measure high-resolution oxygen isotope time series. Analyses of bone growth increments were performed with two different techniques and spatial resolutions: (1) in situ oxygen isotope measurements on polished, gold-coated bone thin sections of the same specimens with a CAMECA IMS 1270 ionprobe SIMS (20 to 30 µm resolution), (2) sampling with a Merchantek Micromill (100 µm resolution) from polished bone cross-sections and analysis of their oxygen isotope composition (δ¹⁸O<sub>CO₃</sub>) after chemical pre-treatment.

Oxygen isotope results of both techniques will be compared. Implications for skeletochronology, growth rate, and biomineralization processes of archosaurs (crocodiles, birds, and dinosaurs) will be discussed.
**Determination of PVTX data and the phase change of crustal fluids**

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Crustal fluids are the aqueous solution of salts (NaCl, KCl, CaCl2 etc.) and gases (CO₂, CH₄, N₂ etc.), most commonly a H₂O-CO₂-NaCl system. However, because of the effects of charged species, we have a little information on the phase change and the thermodynamic properties over the wide range of P and T, especially, around critical region for the ternary system. The equation of state (EOS) is the most important for understanding several geochemical processes. However, the EOS that is specified for high salinity (>25wt%) systems has not been also established yet, because experiments have not been done successfully around the critical point. In this study, we have determined the fundamental thermodynamic properties (PVTX relation and phase change) experimentally using new apparatus up to 200MPa and 600°C.

We have developed a new experimental apparatus, which is composed of a mini-piston/cylinder system set in the pressure vessel and CO₂ injector. PVT data is measured continuously and synchronously and error of measurement is within 1%. The phase change can be determined from differential V with respect to P or T. We verified the performance of our apparatus by comparing our experimental data with EOS for pure water, H₂O-CO₂ and H₂O-NaCl binary system over the P-T conditions attainable. Those results are in good agreement with preexisting EOS within accuracy of about 3%. Our experimental method serves for the determination of the thermodynamic properties on high saline crustal fluids with high CO₂ concentrations around critical region.

**Preliminary geochemical results on the CO₂ Georeactor sequestration test at the Ogachi HDR site**

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This paper reports a preliminary result of field experiments of CO₂ sequestration into the Ogachi HDR site, where a part of CO₂ will be expected to be fixed as carbonates by interaction with rocks (Georeactor; Ca extraction from rocks and carbonate fixation). The Ogachi HDR (Hot-Dry Rock) field is situated at the northeast Japan and have been studied to produce geothermal electricity.

**Experimental Procedure**

River water had been continuously injected (380 L/min, 15 MPa) into an injection well (OGC-1) and produced (40 L/min) from a production well (OGC-2) during the experiment (2 weeks). After the fluid flow rate became constant, CO₂ dissolved water (0.2 wt%) was injected with tracers (KI; 2kg/200L and uranine; 150g/18m³). The fluids from OGC-2 were geochemically monitored for their isotope and chemical compositions. The final output temperature at the OGC-2 well site is 127.5 ºC.

**Results and Discussion**

During the experiments, major chemical compositions of fluids from OGC-2 are almost constant. The tracers are first detected at 34 hours after the injection and showed the maximum concentration at 67 hours. The dilution rates of the observed to injected concentrations of KI and uranine are calculated to be 6×10⁻⁵ and 1×10⁻³, respectively. CO₂ concentrations in the fluids varied from 600 to 200 mg/L with time and showed no correlation with those of the tracers. This is due to the high dilution rate with reservoir fluids. In this field experiment, we could not discuss the fixation rate of CO₂ as carbonate.
Melting condition and origin of arc magmas beneath the Sengan region, Northeastern Japan

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Subduction zone processes play important roles in the evolution of the crust and mantle, yet are poorly constrained at present. Recent geophysical and geological studies suggest that there are periodical structures with about 50km wavelength in the mantle wedge and crust beneath Northeastern Japan (Tamura et al., 2002). In this study, we investigate 3-D thermal and compositional states of the mantle wedge and crust beneath the volcanic front of Northeastern Japan, based on the compositional variations of volcanic rocks collected from 28 Quaternary volcanoes in a volcanic region, the Sengan region (30km-30km).

Volcanoes in the Sengan region are divided into two groups. Compositional variations of the first group can be reproduced by fractional crystallization from a basaltic magma, based on thermodynamic calculation using MELTS (Ghiorso and Sack, 1995). These volcanoes are mainly distributed on the outer rim of the cluster. Magma mixing between high-MgO andesite and dacite associated with fractional crystallization is observed in the second group, based on AFC calculation and mineralogy. The second group is distributed at the central part of the volcanic cluster associated with voluminous welded tuff and granitic pluton. Major element compositions of these voluminous silicic rocks show a similar range to those reported for partial melts of amphibolite (e.g; Beard and Lofgren, 1991).

Melting conditions in the mantle wedge have been estimated to minimize the difference between the composition of partial melt calculated at a given P, T, H2O-content (Ghiorso et al., 2002) and that estimated from the observed volcanic rocks, assuming olivine maximum fractionation. The estimated mantle condition shows that the mantle beneath the central part of the cluster has a higher H2O-content than that beneath the outer rim. It is suggested that mantle-derived wet magma had supplied heat and H2O to the crust and induced crustal melting/magma mixing at the central part of the volcanic cluster. On the outer rim, basaltic magma ascended to the surface without causing crustal melting.

References

Radiocarbon analysis in tree rings of Yaku-cedar by AMS for investigating secular variation of atmospheric 14C/12C ratios

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Atmospheric radiocarbon is produced in the stratosphere by cosmic ray reaction with nitrogen (14N(n,p)14C). The produced 14C enters into the carbon cycle in the air, and it is absorbed photosynthetically by plants. Therefore, by measuring 14C/12C ratio in tree rings, it is possible to obtain information on the secular change of cosmic ray intensity.

In this study, we have used an old cedar tree (1680 year-old) from Yaku island (Kagoshima Prefecture, Japan). Samples (about 20mg) were collected from annual tree rings, and α-Cellulose, which is immovable constituent and recorded 14C/12C ratios at the time of the absorption, was extracted by treatments with acid and alkaline. The obtained α-Cellulose (about 3mg) was oxidized to CO2 and purified with a glass vacuum line. Then it was reduced to pure graphite which was used as a target (about 1mg) for the determination by Accelerator Mass Spectrometry (AMS).

Using a small sample size, as mentioned above, we could measure 14C/12C ratios with reasonable precision and accuracy by AMS at MALT. Results obtained at this time are shown in Fig.1 (for the period 524-775 A.D.) together with the IntCal04 data. The values were not on the straight-line, which is extrapolated from the year 1950 with the half-life of 14C, suggesting there were considerable variations of the 14C production. Some periods (e.g. around 660A.D.), in which Δ14C values were higher than those of IntCal04, were observed. Since IntCal04 was mainly composed from western data, our results from Yaku-cedar should be useful to understand secular variation of 14C/12C ratios in Japan.

![Figure 1](image)

Figure 1. Results together with the IntCal04 values.

Reference
Nb-Ta oxide minerals in granites and pegmatites: Tracers of magmatic to post-magmatic evolution

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Accessory Nb-Ta oxide minerals occur in some highly fractionated granites and granitic pegmatites. Their internal zoning, compositional variations and breakdown products are sensitive indicators of magmatic to post-magmatic evolution of the parental rocks.

Regular fine to coarse oscillatory zoning of columbite-tantalite and Nb-Ta-rich rutile with repeated Nb- and Ta-rich zones indicates their primary magmatic crystallization. Increasing Ta/Nb, (Nb+Ta)/Ti and Mn/Fe ratios in the Nb-Ta phases traces the degree of magmatic fractionation, whereas W, Sn, Sc, Zr, Y, U and Mg contents reflect mainly their local compositional environment. Moreover, presence of Ti,Fe³⁺-rich Nb-Ta minerals (titanian ixiolite, rutile) could serve as an indicator of higher oxygen-fugacity (fO2) conditions in comparison to the Ti-poor, Fe⁵⁺-rich ordered columbite-tantalite + ferrotapiolite assemblage. Minerals of the foordite-granite/pegmatite cooling and uplift.

Primary phases and element redistribution during Nb-Ta rutile, ixiolite); they indicate a breakdown of the Nb-Ta oxide minerals in granites and fractionated granites and granitic pegmatites. Their internal Mosaic patchy zoning of Nb-Ta-Ti phases manifest their widespread. Complex irregular convoluted zones reveal partial leaching and replacement of the primary phases; erratic Nb-Ta distribution is typical for the secondary columbite-tantalite. Mosaic patchy zoning of Nb-Ta-Ti phases manifest their recrystallization probably due to younger thermal/pressure metamorphic overprint. Subsolidus exsolution textures are typical for Fe⁵⁺,Ti,Sc,W,Sn-rich, primary Nb-Ta phases (e.g. Nb-Ta rutile, ixiolite); they indicate a breakdown of the primary phases and element redistribution during granite/pegmatite cooling and uplift.

Increasing of fluid activity and fO2 during late- to post-magmatic stage caused a breakdown of Sn²⁺-bearing foordite-thoraeulite and precipitation of secondary cassiterite + columbite-tantalite. Moreover, an influx of late-magmatic to hydrothermal Na,Ca-rich fluids facilitates replacement of columbite-tantalite, ixiolite and Nb-Ta rutile by fersmite, pyrochlore-group and other alkali-rich Nb-Ta minerals. Rarely, an activity of Sb,Ph-bearing hydrothermal fluids caused a precipitation of specific secondary Nb-Ta minerals (plumbomicrolite, stibiobetafite, stibiotantalite, Nb,Ta-rich römëite etc.).

Thermodynamic price tags for a wet mantle

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The exciting discovery of Wadsleyite as mineral host for hydrogen or as a "hydrous material" in the mantle has redox-equilibria-implications relative to other published redox models for the Earth’s mantle. Such redox models for the Earth’s mantle suggest that along the geotherm, shallow mantle conditions range from the log fO2 given by the buffer (FMQ) to levels of redox of ∆(FMQ) ≈ -2. These models have been based on studies that include: (1) xenolith studies by several methods (as reviewed by Ulmer et al., 1987) (2) stability of diamonds relative to other redox buffers (for example, Eggler and Baker, 1982 or Ulmer et al., 1978). Most redox models for the Earth’s mantle do incorporate more reduced conditions for greater depth in the mantle: the log fO2 given by the buffer (IW) at the core mantle boundary is one logical reason for this model. Deeper xenolith studies also suggest this. (Haggerty and Tompkins, 1983 or Ulmer et al., 1987). Even more reduced conditions for the mantle are implied by the abundant existence of the mantle mineral, Moissanite (SiC) whose redox stability in log fO2 can be represented by ∆(IW) ≈ -8 at pressures up to 9.0 GPa and temperatures up to 1730 K. Furthermore, the kinetics of oxidation of SiC exposed to carbonates or iron oxides from 2.0 to 15.0 GPa and temperatures as low as 1173 K has been measured in hours, not days or months! (Ulmer et al., 1998).

To have mantle phases, either with hydroxyl, or as true hydrates, that can be compatible in the redox state of the mantle seems a possibility? A companion manuscript at this meeting explores redox EOS calculations of water stability in the mantle. (cf., Woermann et al.). To our thinking, one possibility may be the influence of defects in the Wadsleyite. No direct data yet seem available for this suggestion; it is by analogy to the large range of redox values demonstrated by defect olivines that this idea should be pursued.

References
Uranium(IV) oxide surface reactivity

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The success of bioremediation of uranium-contaminated sites will depend on the long-term stability of the U(IV) oxide formed by microbially induced reduction of soluble U(VI). This contribution is part of a research project establishing the local and long-range structure and reactivity of biogenic uraninite generated under different environmental conditions in comparison to its closest abiotic analog, UO2-x (0 < x < 0.25). An abiotic uraninite solid was produced by thermal reduction of uranium peroxide with H2 yielding particles with a star-like prism shape and a size of ~700 nm. Powder XRD proved an fcc crystal lattice of cubic uraninite. Its stoichiometry was identical to that of a reference sample of UO2.0, as shown by EXAFS spectroscopy.

The dissolution kinetics of abiotic uraninite have been examined in batch and flow-through experiments as a function of pH, dissolved inorganic carbon, and dissolved oxygen. Dissolution rate constants are calculated from a mass balance approach, accounting for equilibrium solubility and the decrease of particle size as dissolution progresses. Batch dissolution experiments under anoxic conditions have shown dissolved uranium concentrations close to or even higher than predicted from published thermodynamic data. In the range of pH 6 to 9, dissolution rate constants were on the order of 1.3-3.1·10^-13 mol m^-2 s^-1, but they increased by two orders of magnitude under atmospheric conditions. Under anoxic conditions, a flow-through experiment has shown an initial U-release peak, suggesting removal of more soluble U phases from the surface. However, carbonate as a complexing agent for U(VI) did not immediately change the dissolution kinetics of abiotic uraninite, but gradually altered its surface toward higher solubility, which was a reversible reaction.

Dissolved U(VI) showed high affinity for abiotic uraninite. Further experiments will quantify the adsorption/desorption behavior, the surface reactivity and dissolution kinetics of uranium oxide as the most important factors for promoting immobilization and long-term stability in the subsurface.

Nd isotope mixing during thermal ionisation mass spectrometry: Implications for accurate 142Nd measurements

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Deviations from the exponential-law mass-bias curve are observed during some high-precision runs of the La Jolla Nd standard. The resulting measured isotope ratios (X/144) are generally higher than predicted by the exponential law (Fig. 1) and characterized by increased scatter. The onset of the deviations correlates with a distinct change in the mass-bias trajectory (from normal to reverse) of the isotope ratios.

Similar effects during Ca isotope measurements [1] were attributed to isotope mixing during mass spectrometry. For Nd isotopes, the effects of mixing during measurements are not clearly understood even though several studies have documented an apparent breakdown of the exponential mass-bias law [e.g., 2 and 3].

Figure 1: Deviations of the isotope ratios from the exponential curve during a run segment modeled as mixtures of ions from differentially fractionated sample reservoirs

This study shows that the divergence from exponential-law can be modeled as mixtures among reservoirs on the theoretical fractionation curve (Fig. 1). Such differentially fractionated reservoirs can form because of temperature gradients or heterogeneous sample distribution on the filament. Mixing of ions derived from these reservoirs can modify the composition of the ion beams significantly causing deviations from the exponential-law curve. Mixing results in an apparent reversal of mass fractionation because isotopically light ions from less fractionated reservoirs are ionized together with those from more fractionated ones.

Such mixing during mass spectrometry is a great concern when measuring the generally very small 142Nd anomalies because deviations up to 56 ppm have been observed for the 142Nd/144Nd ratios. This deviation is far greater than the variations expected for most applications. The ultimate accuracy and reproducibility of the isotope ratios is dictated by the extent of isotope fractionation and mixing in addition to instrument electronics and ion counting statistics.

Integrated air quality assessment - PM$_{0.1}$ to PM$_{10}$ magnetic particles

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Approach
In our multidisciplinary approach atmospheric air quality in the Greater Cologne Area (GCA, NW-Germany) was studied using pine needles as passive samplers. Here we report accumulation histories, particle size dependency and spatial distribution of remanent magnetic pollutants as to approximate the dust load. Environmental magnetic results are interpreted in conjunction with complementary trace element and persistent organic pollutant data.

Results
Variability between sites proofs to be significantly higher than within sites. Established accumulation rates predominantly reflect anthropogenic emissions. Minor natural processes comprise canopy effects and abrasive removal of particles. Emission specific concentrations and grain size distributions (Fig. 1) are readily detected by magnetic parameters and allow for source allocation in spatially highly resolved data sets.

Conclusions
The correlation of magnetic particles, trace elements and PAH yields a far more complete picture of air pollution in that source allocation is more readily achieved.

Sub-µm size high precision analysis of δ$^{18}$O in zircon by SIMS

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Oxygen isotopic ratios ($δ^{18}$O) of rocks provide important insights to understand igneous and metamorphic processes. Zircon is a valuable accessory mineral to study such processes because (1) it is common in igneous, metamorphic, and sedimentary rocks, (2) it provides U-Pb ages, and (3) it is retentive of primary composition. However, because zircons are small (typically 10 to 100 µm) with internal zonation, in situ microanalysis is required.

An in situ O isotopic analysis technique with ~0.5 µm$^2$ spot and an analytical uncertainty of 1.0 ‰ (1σ) has been developed using a Cameca ims 1280 SIMS. This technique was applied to a zoned zircon from a partially melted metasediment (Daniel’s Road, near Saratoga Springs, NY) in the granulite-facies Adirondack Highlands [1], which consists of a detrital igneous core (1353Ma) and a metamorphic overgrowth (1019Ma) with $δ^{18}$O values of ~ 6‰ and 12‰, respectively [2].

Five traverses with 2 µm steps, totaling 36 sub-1µm $δ^{18}$O analyses, were performed to determine the $δ^{18}$O gradient at the core/overgrowth boundary that is clearly seen by CL. The figure shows the CL image of the sample and positions of ~30 µm pits from previous SHIRIMP U-Pb analyses and ~0.8 µm dia. pits for $δ^{18}$O analyses of this study. We found a steep $δ^{18}$O gradient at the boundary that indicates O isotopic exchange between the core and the overgrowth occurred over a distance less than 2 µm. Modeled for a 50 Myr isothermal period [3], an O diffusion coefficient in zircon of ~10$^{-23}$ cm$^2$/s best fits the data. The preservation of such a steep gradient and the inferred low diffusion coefficient indicate that the zircon preserved $δ^{18}$O from crystallization through high-grade metamorphism. We envision that sub-µm stable isotope analyses will permit new investigations of materials that are rare, precious or zoned, including those of biological origin.

References
PGE geochemistry, mineralogy and Os-isotope signature in the mantle-hosted ophiolitic chromitites from the Kahramanmaraş area, SE-Turkey

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Mantle-hosted ophiolitic chromitites from the Kahramanmaraş area (SE-Turkey), have been investigated as to their chromite composition, Platinum-group elements (PGE) concentration and mineralogy, as well as Os-isotope geochemistry. Chromitites vary from Al-rich to Cr-rich, however they indifferently display enrichment in Os-Ir-Ru over Rh-Pt-Pd, with concentrations of PGE lower than 510 ppb. Consistently, the most abundant Platinum-group minerals (PGM) are Ru-Os-Ir sulfides and alloys. They occur as small grains (less than 15 µm), mainly included in fresh chromite. Base metals sulphide (BMS), Na-rich amphibole and rare phlogopite were also identified forming inclusions in chromite. Their textural position and morphology indicate that these inclusions are magmatic in origin. Based on textual relations, paragenesis and composition, it was possible to establish that PGE alloys crystallized before than PGE and BM sulfides, at temperature comprised between 1300 and 1000 degrees and under increasing sulphur fugacity. The presence of abundant hydrated primary silicates suggests that the Kahramanmaraş chromitites formed in the presence of water and volatile- and sodium-rich fluids. This observation is also supported by the Re/Os ratio relatively high, that points a mixing of mantle-derived Os with Os from a source characterized by relatively high radiogenic signature, possibly fluids originated in a supra-subduction zone (SSZ). If a SSZ setting is accepted, the concomitant presence of Al-rich and Cr-rich chromitites suggests chrome precipitation from melts varying in composition from back-arc basalts (Al-rich chromite) to boninites (Cr-rich chromite), possibly at different mantle levels (i.e. deep for the Cr-rich chromitites and close to the Moho-Transition Zone for the Al-rich ones).

Potential problems in the annealing of zircon

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Annealing experiments are often employed to study the recrystallisation behaviour and the real structure of radiation-damaged zircon. This includes dry annealing in air and hydrothermal annealing; in the latter case the reconstitution is controlled by fluid-driven reaction fronts (Geisler et al., 2003). It is well-known that the temperature-induced recovery of strongly radiation-damaged zircon involves an intermediate stage (at about 900–1100 °C) where nearly amorphous ZrSiO4 decomposes into oxides (Nasdala et al., 2002). This is explained by the preferred nucleation of tetragonal ZrO2 over ZrSiO4 (Garvie, 1965). Dry annealing of moderately radiation-damaged zircon, in contrast, does not involve this intermediate stage but rather results in a gradual reconstitution of zircon.

We have found that under certain conditions ZrO2 may also be observed in the annealing of lowly metamict zircon, and at temperatures as high as 1600 °C. For instance, we found baddeleyite on the surface, or in the entire volume, of annealed zircon crystals that were treated at 1400 °C. We attribute the high-temperature formation of baddeleyite to be an artefact, for which we see two potential causes. First, if volatile alkali elements are present in the furnace atmosphere, they may react with silica to form Na-silicate glass. Second, if annealing is done using corundum crucibles, there may be a reaction of the silica component with corundum (for instance by formation of mullite). The latter idea seems to be confirmed by recent observations that during high-temperature treatment of gem-quality ruby, baddeleyite may form at the surface of included zircon crystals (Wanthanachaisang et al., 2006). It is therefore important to consider doing annealing experiments in a controlled environment (no contaminants reaching the sample) and choosing suitable materials (e.g., Pt crucibles).

References
X-ray photoelectron spectroscopy study of coals with different rank

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Nowadays the increasing amounts of NOx and N2O converted from coal nitrogen, led to the investigation of the combustion processes and coal properties that contribute to maximise the nitrogen production and influence the variation in the emissions. Therefore it is important to determine the molecular structure of nitrogen in coal.

X-ray Photoelectron Spectroscopy (XPS) analyses were performed in vitrinite-rich coals of increasing rank to determine the nitrogen functionalities (pyridine at 398.8 eV, pyrrol around 400.2 eV, quaternary nitrogen around 401-402 eV and nitrogen-oxide around 403 eV). Nitrogen in the studied coals was found to be predominantly pyrrol. However, the coals storage procedure determined the degree of nitrogen oxidation and the other nitrogen functionalities (Fig. 1 and 2). Due to this fact, the ratios of pyridinic to pyrrolic nitrogen and pyridinic to quaternary nitrogen vary with increasing rank and also with the oxidation of the coals. The analyses of a set of non-oxidised coals with rank lower than 1.41% vitrinite reflectance permitted the observation of the decreasing of pyrrolic and quaternary nitrogen and an increase of the pyridine with increasing coal rank.

Figure 1: Representative XPS spectra of nitrogen (1s) obtained on oxidised coal.

Figure 2: Representative XPS spectra of nitrogen (1s) obtained on non-oxidised coal.

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Synthetic isotope mixtures for the calibration of ion current ratio measurements in carbon and oxygen in carbon dioxide

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Different sets of synthetic isotope mixtures for the calibration of carbon and oxygen ion current ratio measurements obtained by mass spectrometry have been prepared by mixing carbon dioxide isotopically enriched in 18O (natC18O2) and natural carbon dioxide (natCnatO2), and by mixing different natural CO2 gases with slightly different carbon and oxygen isotopic compositions [1].

These mixtures act as Primary Standards to the SI-scale for carbon and oxygen isotope amount ratio measurements in CO2. They will help to anchor existing carbon Isotope Reference Samples (i.e. NBS19, IAEA-CO-9) and therefore offer the basis for comparability of carbon (and oxygen) isotope measurement results, without any assumptive correction for the oxygen isotopes.

Via such ‘absolute’ isotope amount ratio measurements of carbon and oxygen on CO2 produced from the Primary Standard to the VPDB-scale NBS19, calibrated by means of synthetic isotope mixtures, ‘absolute’ isotope amount carbon and oxygen ratios corresponding with the zero point of the VPDB conventional scale were calculated to be $R_{13/12} = (11 137 6 ± 16) \cdot 10^{-7}$ and $R_{18/16} = (208 824 ± 48) \cdot 10^{-8}$ respectively.

References

Evidence of the earliest crust on Earth

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Understanding the earliest crust on Earth has long been considered the realm of planetary geology. Since all crust older than 4 Ga was apparently destroyed on Earth, older mafic to ultramafic rocks from Mars and the moon provided analogs. However, growing evidence from zircons is finally providing direct testimony of the first 500 myr on Earth.

Detrital and xenocrystic zircons older than 4.0 Ga, without identified parent rocks, are found in highly mature conglomerates and sandstones, and occasionally in granites, almost exclusively from the northern Pilbara of Western Australia. The oldest grains cluster at 4.35 to 4.4 Ga and are among the most intensely studied samples on Earth. Compositions and ages are variable within single grains and careful study involves imaging and in situ analysis correlated to textures [1]. Many zircons have younger overgrowths or altered domains, and bulk ages should be interpreted with caution. Some zircons are actually small “rocks”, containing a granitic suite of inclusions including: quartz, K-feldspar, and plagioclase [2]. No evidence of shocked zircon (planar fractures, detrital zircons, etc.) is seen in young ocean crust [3] or from the moon [4]. A number of tests support these results as primary including: magmatic zoning, U-Pb concordance, Th/U, type 1 REE profiles [1], and slow diffusion rates in zircon [5]. The picture emerges of an early Earth with differentiated buoyant crust, cool (perhaps cold) surface temperatures, and oceans, which was hospitable for the emergence of life by 4.2 Ga and perhaps earlier.

The composition of the earliest crust and its tectonic setting are less constrained. Nd, Hf, and Pb isotopes have long pointed to early formed protocrust. Recently, $^{176}$Hf/$^{177}$Hf ratios and low Ti in zircons were interpreted to indicate the existence of wet S-type granites, continental crust, and plate tectonics before 4.4 Ga [6], but questions remain [7].

Why are rocks older than 4.0 Ga preserved on Mars and the moon, but not Earth? Impacts and melting, commonly before 4.4 Ga [6], but questions remain [7].

References


Fractionated HSE in suboceanic mantle: Assessing the influence of refertilization processes on upper mantle peridotites

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The Totalp ultramafic massif in Eastern Switzerland consists of peridotites interlayered with pyroxenites, that have been exposed on the seafloor of the Jurassic Ligurian ocean. Petrographic observations, whole rock major element and Re-Os data in peridotites from the Totalp massif suggest refertilization of the peridotites by percolating melt parental to the associated pyroxenites. Here, we examine the behaviour of other highly siderophile elements (HSE).

Peridotites from the Totalp massif have Ir contents between 1.7 and 4.3 ppb, typical for mantle-derived lherzolites. Osmium abundances range from 2.7 to 5.2 ppb, Ru abundances range from 4.8 to 12.7 ppb, both within the range previously reported for mantle peridotites. Os/IrN and Ru/IrN are broadly chondritic to slightly suprachondritic within a range of 1.0 to 1.9 and 1.3 to 1.9, respectively. Platinum abundances range from 2 to 7 ppb; Pt/IrN varies from subchondritic to slightly suprachondritic within a range from 0.72 to 1.19. Palladium abundances range between 4 and 15 ppb, Re abundances between 0.21 and 0.76 ppb. In a few samples, Pd/IrN and Re/IrN are enriched by factors of up to 4 and 5, respectively, compared to typical upper mantle lherzolites.

Associated pyroxenites are enriched in incompatible PPGE while compatible IPGE have slightly lower abundances compared to the peridotites. Websterite layers display Pd/IrN as high as 40 and Re/IrN of up to 9; Pt/IrN and Ru/IrN are only slightly elevated, to factors of up to 3.8 and 2.1, respectively.

Single grain in situ analyses of Ni-Fe-sulfides (pentlandite, pyrite, godlevskite; alongside native copper) in pyroxenites by LA-ICP-MS yield roughly chondritic Os/Ir and chondritic to suprachondritic Ru/Ir and Pd/Ir of up to 23 and 50, respectively. Re/Ir is subchondritic to slightly suprachondritic by a factor of 2. Both HSE abundances and inter-element HSE ratios vary significantly within one sample, indicating heterogeneous distribution of HSE on grain to thin section scale.

In summary, whole rock and in situ single grain HSE data indicate that melt migration by mafic mantle derived melts produced suprachondritic Pd/Ir and Re/Ir and negligibly affected Pt and more compatible HSE.
Fluvial systems are driving landscape evolution in active tectonic settings. Examining differential denudation rates associated with specific channel and hillslope morphology contributes to understand the transient response of a landscape following uplift. Here, we explore the relationship between landscape morphology and erosion by quantifying basin-wide denudation rates of various morphological zones in the Southern Ecuadorian Andes. Cosmogenic radionuclides (\(^{10}\)Be) in quartz of river sediment were employed to constrain basin-wide denudation rates \((10^4-10^5 \text{ yr})\). Along an east-west transect across the Cordillera Real, we carefully selected small basins \((< 250 \text{ km}^2)\) to cover a wide range of morphological settings, and to be representative of specific areas of transient adjustment. Channel and slope morphology vary systematically from east to west, reflecting the transition from high-relief, strongly dissected topography in the eastern side of the Cordillera Real into relatively low-relief topography in the Inter-Andean valley. Basin-wide denudation rates range by nearly two orders of magnitude, from \(~4 \text{ mm/kyr}\) to \(~400 \text{ mm/kyr}\), and show good correlation with channel and hillslope steepness indices.

The spatial pattern of differential denudation rates across the Cordillera Real reflects the transient adjustment of the landscape to rapid river incision following tectonic uplift. Relative high denudation rates \((> 200 \text{ mm/kyr})\) are measured in the eastern part of the Cordillera Real, where slopes and channels are steep and actively adjusting to rapid incision of the trunk stream. Basin-wide denudation rates are about ten times lower in the central part of the Inter-Andean valley. The presence of smooth concave river profiles indicates that the incision signal has not yet propagated into the Inter-Andean valley.

Modern riverine chemistry and discharge is commonly used to estimate the long-term flux to the oceans of the many chemical species that have their primary source in the continental crust. Here we suggest that measurements of many modern rivers, only a few thousand years after a glacial period, are not representative of the long-term flux and we quantitatively assess the implications of such a suggestion for key marine geochemical budgets.

Blum and co-workers [e.g. 1] first developed the idea that physical grinding during glacial periods of the Quaternary was followed by rapid chemical weathering of fresh soils during the warm, wet conditions of interglacials. Recently [2], Pb isotopic records of the oceans were shown to be consistent with pulses of rapid weathering during the early stages of interglacials. The consequences for long-term Quaternary chemical weathering rates and the Sr isotopic record of seawater have been explored previously [1]. Here we focus on another important implication: that the instantaneous weathering rates implied by modern riverine cation flux are higher than the long term average. In our estimation, for regions that were glaciated 20 kyr ago but that are now ice-free, present day chemical weathering rates are a factor of 3 to 4 higher than the average rate for the past 2 to 3 Myr.

This finding has major implications for long-standing problems in ocean chemistry. For example, it remains a puzzle that the hydrothermal flux of Sr required to balance the modern riverine flux is much greater than is suggested by the extent of alteration of the oceanic crust [3]. Indeed, while there is growing convergence between ocean floor hydrothermal fluid flux estimates based on independent tracer exchanges [e.g. 4] and simple thermal calculations, estimates based upon the oceanic \(^{87}\)Sr or Mg balances that rely on the quantification of the modern riverine flux are more than an order of magnitude greater. For elements such as Sr and Mg, with long oceanic residence times, modern riverine measured fluxes do not provide appropriate estimates of the long-term inputs. The changes in weathering rates also imply dramatic variation in the supply of alkalinity and nutrients to the ocean, with consequences for atmospheric CO\(_2\).

References
Global Neodymium - Hafnium isotope systematics – Revisited

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Combined Nd and Hf isotope analyses have become widely used in solid Earth geochemistry studies, but their application for low-temperature processes is still limited. The residence time for both of these elements in the ocean is thought to be similar (500 – 2000 years) and there is a growing number of studies addressing the sources of Nd and Hf as well as internal cycling processes in the ocean. In the case of Nd, these studies have been accompanied by a number of emerging applications of Nd isotopes as a tracer for past water mass mixing and ocean circulation, since the Nd isotopic composition of various archives in the ocean has been shown to record the Nd isotopic composition of ambient seawater reliably. Due to very low concentrations of Hf in seawater and hydrothermal fluids, and associated analytical difficulties in measuring Hf isotope compositions, our overall understanding about fractionation processes and internal cycling of Hf in the ocean is not as well developed as for Nd. However, recent studies have shown that direct measurements of seawater and river waters are feasible.

The global Nd-Hf isotope systematics can be described by two linear arrays in Nd-Hf isotope space, the global silicate Earth array (“the terrestrial array”) and the global ferromanganese crust and nodule array (“the seawater array”). The offset between these two arrays provides evidence for the sources and mechanisms by which these elements are added to seawater. However, the reason for this offset is under debate, with the two preferred hypotheses being (i) incongruent release of Hf during continental weathering and (ii) hydrothermal supply of Hf to seawater.

In this paper we revisit the cause for the offset of the seawater array from the terrestrial array using simple mass balance considerations. We use these calculations for a test to what degree the seawater array can be a product of preferential weathering of “non-zircon minerals” of the upper continental crust, implying retention of zircons in the solid residue of weathering. Lutetium-Hf and Sm-Nd evolution and mixing calculations show that the global seawater array can be generated with continental sources only. On the other hand, a predominantly hydrothermal origin of Hf in the ocean is not possible because the seawater Hf isotopic composition is significantly less radiogenic than hydrothermal sources and requires a minimum contribution of 50% continental Hf. While hydrothermal sources may contribute some Hf to seawater, continental contributions are unambiguously required to balance the budget.

Reaction between ascending melt and peridotite: An experimental investigation

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Melt-rock reaction in the upper mantle is known from a variety of ultramafic rocks and is an important process in modifying melt composition on its way from the source to the surface. Evidence for depletion or enrichment by melt percolation is found in ophiolites, mantle xenoliths, and mantle sections exposed along MOR’s. It includes disequilibrium textures, changes in major-to-trace element compositions and isotopic ratios.

In this experimental study, we present a consistent set of data to evaluate the compositional and time-dependent evolution of ascending magma over a range of temperatures and pressures as a function of initial melt and peridotite compositions. In order to simulate melt-peridotite reaction processes, we perform nominally dry piston cylinder experiments with a 3-layered setup: a bottom layer composed of vitreous carbon spheres (serving as a melt trap) overlain by a peridotite layer and on top a “melt layer” corresponding to a primitive MORB composition. The peridotite layer is mixed from pure separates of orthopyroxene, clinopyroxene and spinel (Balmuccia peridotite), and San Carlos olivine. Melt from the melt layer is forced to move through the peridotite layer into the melt trap. Therefore this setup allows us to simulate reactive melt flow, as opposed to other experimental studies in which diffusion is the main driving force for reaction between a melt and a mantle rock.

Experiments have been conducted at 0.8 GPa with peridotite of variable grain sizes, in the temperature range 1200 to 1320°C. In this P-T range, representing conditions encountered in the thermal boundary layer beneath MOR’s, migrating melt is subjected to fractionation, whereas the peridotite is partially melting (solidus around 1260°C). Results show a strong dependence between phase relations in the melt layer and changes in the modal composition of the peridotite layer. Textural and compositional evidence demonstrate that reaction between percolating melt and peridotite occurs by a combination of dissolution-reprecipitation and, to a lesser degree, by solid-state diffusion. Glass compositions in our melt layers resemble those from crystallization experiments on the pure starting liquid at similar P-T conditions (Villiger et al., J. Petr., 2007), but change progressively in the peridotite layers. Silica and alkali enrichment are the most significant changes.
Unravelling the sources of silica in early-Archaean cherts with silicon isotopes
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Significant controversy exists regarding the origin of silica in early-Archaean cherts and the mechanism of their formation. Solving these questions is opportune, since recent studies have used oxygen and silicon isotopic signatures of cherts to infer high temperatures for early-Archaean oceans (Knauth and Lowe, 2003; Robert and Chaussidon, 2006). For example, do these cherts represent primary precipitates from a silica-saturated Archaean ocean or are they the products of hydrothermal emanations (Kato and Nakamura, 2003)?

We present silicon isotope data for a suite of samples from well-studied chert outcrops (3.0-3.5 Ga) in the Pilbara greenstone belt (Western Australia). Our samples cover a range of depositional environments, and include both stratiform and dike cherts. Based on mineral assemblages (sericite, Ti-oxide and zircon versus Fe-(oxy)hydroxides), major element chemistry (e.g. Al2O3 content) and Eu and Y/Ho anomalies, we distinguish chemically precipitated cherts (sericite, Ti-oxide and zircon  versus Fe-(oxy)hydroxides), major element chemistry (e.g. Al2O3 content) and Eu and Y/Ho anomalies, we distinguish chemically precipitated cherts

Genesis of intermediate to silicic igneous rocks at the end of the Sveconorwegian (grenvillian) orogeny
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The origin of voluminous granitoids at convergent plate margins and in postcollisional settings is a key question in understanding the evolution of the continental crust. In southern Norway, the end of the Sveconorwegian collision orogeny (1.13-0.9 Ga) was marked by the emplacement of abundant ferroan, metaluminous granitoids (0.96-0.95 Ga) mainly in the center of the Telemarkia terrane. These granitoids are dominated by intermediate to silicic compositions but rare mafic facies do also occur. We present here a quantitative assessment of the possible process linking these mafic facies to the dominant intermediate compositions using a combination of available major and trace elements as well as experimental data. Fractional crystallization of an ilmenite bearing noritic cumulate from the parent mafic composition produces a residual liquid with an appropriate intermediate composition after 67% crystallization. There is also a good match between the calculated and observed trace elements as well as H2O contents of the residual liquid. However, the calculated La and Ce contents are lower than the observed ones. 20% to 30% non modal batch melting of an amphibolitic source equivalent in bulk composition to the mafic facies also provides a good match between observed and calculated major and trace elements composition. Moreover, considering an H2O content of the amphibolitic source of 1.25%, the produced intermediate liquid has an H2O content ranging from 4 to 6 wt % in agreement with experimental constraints on the H2O contents of the intermediate facies (5-6 wt % H2O). This degree of partial melting is in agreement with modelled melt escape threshold which allows segregation and transfer of magma towards the upper crust. Thus both fractional crystallization and non modal batch melting satisfactorily predict the geochemical features observed in the granitoids and it is possible that both processes occurred simultaneously. Interestingly, both processes produce abundant mafic rocks, either as cumulates or residues, which must be equivalent to twice as much as the observed granitoids. As geological and geophysical evidence for large volumes of dense mafic rocks in the mid svecconorwegian crust is lacking, we suggest that these dense mafic rocks were produced in the lower crust but at a pressure lower than about 1 GPa as the low La/Yb of this magmatic suite precludes the involvement of garnet in their petrogenesis. Formation of these granitoids thus contributed to the vertical stratification of the proterozoic continental crust from a mafic lower crust to a more evolved upper crust.
Thermochronological age – elevation profiles, denudation rates and relief development

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Sampling age – elevation profiles has become a standard technique in thermochronology to determine temporal variations in denudation rates. In general, however, these analyses have considered the problem as one-dimensional, implicitly assuming that the samples record a common thermal history because the profile is vertical or denudation rates are regionally constant, and thus neglecting potential effects of topography or laterally varying denudation rates on age-elevation profiles. Although the influence of temporally steady-state topography on thermochronological age-elevation profiles is well understood, the potential effects of transient topography have not as yet been addressed in detail.

We explore the capacity of low-temperature thermochronology data, in particular thermochronological age-elevation profiles, to provide joint constraints on the denudation and relief history of mountain belts. To answer the question whether we can differentiate regional changes in exhumation rate from relief changes by analyzing thermochronological age-elevation profiles, we combine a three-dimensional thermal-kinematic model to predict thermal histories and thermochronological ages from an input denudation and relief history, with an inversion scheme based on the neighborhood algorithm. We explore both synthetic data and a new thermochronological (zircon and apatite fission-track, apatite (U-Th)/He) dataset collected along an age-elevation profile in the French western Alps, a region that has experienced modest tectonic activity but intense glaciation during the last few myr. Our results suggest that multiple thermochronometers are required along an elevation profile to discriminate between different denudation and relief history scenarios, and that relief has increased significantly in our study area over the last few myr, possibly resulting from focused glacial valley erosion during Quaternary glaciations.

Blueschist-facies rehydration of eclogites: Constraints on subduction channel fluid-rock interaction from the Tian Shan (China)

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Exhumed eclogites from orogenic belts may show a retrograde blueschist-facies overprint with still preserved eclogite-facies relics. This overprint occurs during uplift when infiltrating fluids cause the growth of hydrous minerals such as sodic amphibole, epidote and white mica. We are studying this rehydration process and its P-T-X conditions to unravel the source of the retrograde subduction fluids and the exhumation path.

In eclogites from the Tian Shan, garnet, omphacite and rutile represent the assemblage of the eclogite stage. If a blueschist-facies overprint has occurred, omphacite and garnet are partially replaced by glaucophane, white mica and epidote. This rehydration was associated with massive growth of carbonate, pointing to an infiltration of an H₂O- and CO₂-rich fluid. Whole-rock major and trace element analyses show an increase of LILE (K, Cs, Rb and Ba) and volatiles in the rehydrated blueschist, presumably incorporated in white mica. The increase of Mn, Mg, Fe and CO₂ leads to the precipitation of ankerite. Partially dissolved apatite, epidote minerals and garnet released significant amounts of REE, Pb, Sr, U and Y into the infiltrating fluid. From mass-balance calculations it is evident that up to 25 % of the REE were mobilized while the eclogite has been transformed to blueschist.

Based on geothermobarometry, the P-T evolution during rehydration under blueschist-facies conditions is characterized by contemporaneous cooling and decompression. The most likely uplift path is the so called ‘subduction channel’ which is the serpinentinized part of the mantle wedge above the downgoing slab. Fluids can infiltrate eclogites, rehydrate them and force their uplift because of reduced density and the resulting buoyancy. In addition, this process is aided by the high H₂O-content and the modified rheology of the mantle wedge. The observed data indicate that the subduction channel fluids do not only change the petrophysical properties due to metamorphic reactions, they also induce metasomatic changes in the reacting rocks.
**14C lipid biomarker ages in surface sediments off the five great Russian arctic rivers**

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Numerical climate models forecast an amplified warming in the Arctic continental region, making it reasonable to expect that substantial effects of global warming will be first observed here. This will involve effects on the huge amounts of ‘old’ organic matter stored in Siberian soils. However, existing studies are inconclusive whether there is currently a climate-warming induced release of ‘new’ old carbon from the existing studies are inconclusive whether there is currently a climate-warming induced release of ‘new’ old carbon from the existing studies are inconclusive whether there is currently a climate-warming induced release of ‘new’ old carbon from the existing studies are inconclusive whether there is currently a climate-warming induced release of ‘new’ old carbon from the...

The effect of ‘realistic’ depth-dependence of viscosity and other material properties is also assessed.

In contrast to the $F_{\text{modern}}$ bulk values, which show a decrease across the climosequence from 0.69-0.83 in the west to 0.39-0.50 in the east, CSRA of both the isolated HMW $n$-alkanes and $n$-alkanoic acids were investigated for their lipid biomarker composition and high molecular weight (HMW) $n$-alkanes and $n$-alkanoic acids were isolated and used for compound-specific radiocarbon analysis (CSRA) to obtain information on the $^{14}$C-based reservoir age of the OM currently released from the Russian-Siberian permafrost.

In contrast to the $F_{\text{modern}}$ bulk values, which show a decrease across the climosequence from 0.69-0.83 in the west to 0.39-0.50 in the east, CSRA of both the isolated HMW $n$-alkanes and $n$-alkanoic acids indicate on average the release of relative older terrestrial material organic material (OM) by the Western GRARs ($F_{\text{modern}}$ 0.24-0.34), compared to the Eastern ($F_{\text{modern}}$ 0.31-0.50).

Global warming is expected to affect the permafrost areas in the continental Siberian Arctic, causing them to shrink. This will probably lead to a deeper water penetration of the soil and, consequently, the liberation/transport of ‘older’ terrestrial material stored in these layers. The eastern GRARs CSRA results indicate that the majority of the source of this terrestrial OM transported to the estuaries in these areas are originating from the ‘top’ (relative younger) part of the soil. In contrast, the western areas are present much less influenced by permafrost, indicating that the water can penetrate deeper and consequently can liberate/transport ‘older’ OM to the estuaries. In addition, this ‘older’ OM is most likely more degraded, which agrees with the biomarker analyses.

Although this benchmark study suggests presently no major release of remobilized ‘old’ OM through the eastern GRARs, the results of the western GRARs shows how amplified warming in the Arctic might influence the stored OM; a scenario which would have major implications for the global carbon cycle and climate.

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**Effect of self-consistently generated plate tectonics on stirring by mantle convection in a 3-D spherical shell**

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The stirring of heterogeneities by mantle convection is a key process in explaining geochemical observations, but to date most studies have been performed in only two-dimensional geometry. If 3-D convection has only poloidal motion, then its stirring efficiency is similar to that of 2-D convection [Coltice and Schmalzl, 2006], but the presence of toroidal motion could make a major difference because it can lead to chaotic stirring paths even in a steady-state flow [Ferrachat and Ricard, 1998].

Toroidal flow is mainly associated with plate motions. Two previous studies have assessed the influence of steady-state present-day plate motions on mantle stirring [van Keken and Zhong, 1999; Stegman et al., 2002]. Here we instead study flows in which time-dependent plate tectonics is self-consistently generated by the rheology, similar to [Tackley, 2000] but in a spherical shell, and has a toroidal:poloidal ratio in the range observed for the Earth. Several diagnostics are used to measure the efficiency of dispersion and stretching and their spatial variation. Stirring in plate tectonics convection is compared to stirring in other convective flows that have similar convective vigor and wavelength but without plate tectonics. Three-dimensional “plate tectonic” flows are also compared to equivalent two-dimensional flows, in order to test whether the findings of [Coltice and Schmalzl, 2006] still hold when toroidal motion is also present in the 3D cases. The effect of ‘realistic’ depth-dependence of viscosity and other material properties is also assessed.

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Geochemistry of micas associated with tantalum mineralization in the Tanco pegmatite, Canada

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Tantalum is a high-tech metal which is mainly mined from rare-element pegmatites. Although the mineralogy of tantalum is well constrained, very little is known about the mineralizing processes, and in particular the role of fluids in the formation of Ta ore. In many Ta deposits, the high-grade Ta ore is associated with late micaceous alteration of central pegmatite zones. Such metasomatism was commonly interpreted as hydrothermal (i.e., due to aqueous pegmatitic fluids). However, the recent discovery of melt inclusions with extremely high concentrations of volatiles (H2O, B, F, etc...) has provided an alternate explanation. Such melts could be at the origin of the metasomatic alteration commonly encountered in granitic pegmatites.

In the Tanco pegmatite, one of the world's major tantalum deposits, micas are common accessory phases that are intimately associated with the successive stages of Ta mineralization, from the wall zone to the central zone where micaceous replacement is pervasive. The different generations of micas, both primary and secondary, associated with Ta oxides, were analyzed by electron microprobe and LA-ICP-MS in order to investigate the magmatic-metasomatic transition in the Tanco pegmatite. Their chemical composition trends permit to determine whether they crystallized from a melt or an aqueous fluid.

The primary micas range from dioctahedral muscovite to trioctahedral lepidolite and show high Li-F as well as Ta (100 to 250 ppm) contents. On the other hand, replacement micas consist of end member muscovite with high B and low Li-F and Ta (around 40 ppm) contents. The B-rich and Na-Li-Ta-poor compositions of replacement micas compared to primary micas suggest that they crystallized from a B-rich aqueous fluid. This fluid would have coexisted with a late Li-rich, Ta-saturated melt, which is consistent with an immiscibility model as advocated by Veksler and Thomas (2002).

Reference

Aluminum diffusion and Al-vacancy association in MgO

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Periclase, with end-member formula MgO, is the second most abundant mineral in Earth’s lower mantle and may play a significant role in chemical exchange across the core-mantle boundary. Aluminum and other trivalent cations diffuse very rapidly through periclase, orders of magnitude faster than divalent cations such as Mg. This is opposite to what is observed in most silicate minerals, where highly charged cations are generally among the slowest diffusing species. The culprit appears to be a highly mobile defect associate consisting of a cation vacancy electrostatically bound to a trivalent cation [1]. Lidiard [2] developed the theory for divalent cation diffusion in alkali halide crystals, and we extend it to describe the functional dependence of trivalent cation diffusivity on concentration in alkaline earth oxides. The theory is applied to Al diffusion profiles in MgO obtained from experiments over a wide range of pressures and temperatures (1 atm to 25 GPa and 1577 to 2273 K). A family of synthetic diffusion profiles was calculated numerically, for various combinations of Al-vacancy pair diffusivity and binding energy, and the best fit for each experimental profile was determined by chi-square minimization. The binding energy for all but one experiment is in the range 0.45-0.42 eV, slightly lower than theoretical values [3] of 0.65-0.71 eV, and shows no clear dependence on temperature or pressure. The activation energy for Al-vacancy pair diffusion is 2.1 eV, and the activation volume is 2.9 cm3/mol.

References
Reconciling $^{210}$Pb deficits with the physics of melt extraction

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Short-lived intermediate daughters in the uranium decay series have a broad range of half-lives suitable for timing melt production and transport processes beneath mid-ocean ridges. The discovery two decades ago of $^{226}$Ra excesses in mid-ocean ridge basalts constrained the time between Ra-Th fractionation and eruption to be on the order of 1000 years or less. The recent discovery of $^{210}$Pb deficits, correlated with $^{226}$Ra excesses in mid-ocean ridge basalts [1], indicates that the timescale must be much shorter still—less than 100 years.

A critical question is what part of the melting process the $^{210}$Pb-$^{226}$Ra disequilibrium is timing. If the fractionation can only be produced during partial melting in the mantle, then the observed disequilibrium implies melt transport rates on the order of km/yr, which would present a serious challenge to our physical understanding of melt extraction. Another possibility is that the $^{210}$Pb-$^{226}$Ra disequilibrium results from crustal processing. Numerical models have shown that shallow-level diffusive exchange with gabbroic cumulates is capable of producing $^{226}$Ra excesses (or deficits) in the melt [2,3]. We have found that the same process leads to $^{210}$Pb deficits.

A plagioclase or clinopyroxene grain interacting with its surroundings develops internal steady-state daughter concentration profiles, which represent a balance of radioactive production and decay and diffusive fluxes. Because the half-life of $^{210}$Pb is short compared to the timescale for Pb diffusion, the spatial distribution of $^{210}$Pb activity within each mineral closely follows that of $^{226}$Ra. Ra is much less compatible than Pb, and $^{210}$Pb is thus more depleted within the interior of the mineral grain than it would be if partitioning equilibrium were achieved. The result is that $^{210}$Pb is absorbed far more readily than $^{226}$Ra from any melt it comes in contact with, leaving the melt with a $^{210}$Pb deficit. This deficit develops rapidly, and reaches a steady-state value on a timescale comparable to the half-life of $^{210}$Pb, about 20 years. The magnitude of the deficit is only weakly dependent on the enrichment of the melt and on the relative diffusivities of Ra and Pb in the minerals, but is sensitive to the melt/rock ratio and to the relative mineral/melt partition coefficients of Ra and Pb. A typical value of the $^{210}$Pb/$^{226}$Ra activity ratio following gabbro exchange is ~ 0.1.

References

Carbon and iron isotopic evidence for photosynthesis in a 3.5 Ga old shallow marine depositional environment

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Different abiologic and biologic models exist for the oxidation of Fe(II)aq in the upper part of the Archean ocean; UV-induced photochemical reactions, anoxygenic photosynthetic iron oxidation, or reaction with free oxygen generated by oxygenic photosynthesis. In the O$_2$-poor, and CO$_2$-rich Archean ocean these processes would have competed with direct precipitation of Fe-carbonates. Here we discuss the origin of Fe-oxides that occur in the 3.49 Ga old Chert-Barite-Unit of the Dresser Formation at North Pole (Pilbara Drilling Project, Western Australia). This unit represents a shallow water depositional environment within a volcanic caldera, and has experienced low-grade metamorphism (<350°C). It consists from bottom to top of bedded cherts, barite-sulfide beds, and bedded Fe-rich carbonates. An underlying network of barite- and silica-feeder dikes suggests synsedimentary hydrothermal activity. Towards the top of the unit, a succession of thin alternating bands of hematite and Fe-rich carbonate occurs, that includes kerogenous laminations that resemble typical microbial mats. These laminations display a distinctly different iron isotope signature than the underlying barite-sulfide beds (-0.7 to -0.4‰), that is distinctive from the δ$^{56}$Fe of kerogen in the underlying silica dikes (-34 to -31‰). The isotopic discrepancy between these two pools of kerogen cannot be explained by metamorphism. The hematite bands display a strong positive δ$^{56}$Fe (+0.1 to +1‰), compared to the Fe-rich carbonates (-0.6 to +0.4‰) and underlying barite-sulfide beds (-0.7 to -0.4‰). These petrographic and isotopic observations exclude abiologic oxidation of Fe(II)aq by UV-induced photolysis, and suggest that oxygenic and/or anoxygenic photosynthesis were directly involved in the formation of Fe-oxides in this Early Archean shallow marine depositional environment.
Geochemical characteristics of the Quaternary volcanic rocks from Hatay region, Southern Turkey: Evidence for lithospheric mantle source

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The Hamam–Reyhanli (Hatay) region located in southern part of Turkey, consists of two distinct phases of Quaternary basaltic volcanism that display different geochemical characteristics. The first phase includes alkaline basalts and the second one tholeiitic basalts with SiO₂ contents ranging from 45.55-46.4 and 48.94-50.56 respectively. The former group contain high LILE, LREE, low HREE, Y contents, low Sr and high Nd isotopic values and display negative K, positive Nb, Ta anomalies as compared with the latter group. The geochemical data indicate that all the volcanic rocks are derived from a metasomatically enriched mantle source. The crustal contamination is not an important process in the evolution of the samples. The trace elements and isotopic characteristics of both group suggest that they were derived by partial melting of different depth of a lithospheric mantle source. The crustal contamination is not an important process in the evolution of the samples. The trace elements and isotopic characteristics of both group suggest that they were derived by partial melting of different depth of a lithospheric mantle source. The higher La/Yb, Zr/Y and La/Nb (<1) ratios reveal that the first group volcanic rocks are derived from a deeper mantle source than the second group.

The relative tempo of weathering and erosion controls supergene metal accumulation

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When the balance between weathering and erosion favors the former, chemically and mineralogically stratified weathering profiles may develop. Weathering may promote the supergene enrichment of mineralized lithologies or the formation of ore deposits from unmineralized substrates. In the first case, weathering is an ore-enrichment process; in the second, weathering is an ore-forming process. Geochronological constraints indicate that under conducive climatic and tectonic conditions, supergene enrichment of some ore deposits may occur extremely fast (less than 1 Ma; e.g., Ok Tedi). Weathering geochronology, on the other hand, indicates that supergene ore bodies in stable cratonic areas may be continuously exposed to weathering for more than 70 Ma (e.g., Carajás). Protracted exposure suggests that some supergene deposits may not reflect any one specific climatic condition, but record the combined effects of changing climates through time. Variations in precipitation, evapotranspiration, vegetation cover, and biological activity ultimately control the composition of the weathering solutions and the mechanisms affecting the dissolution, transport, and redeposition of ore elements in supergene systems. Weathering geochronology and cosmogenic isotope studies provide quantitative constraints on longevity of weathering profiles, rates of physical and chemical erosion, and rates of supergene transport and redistribution of ore elements in supergene systems. Particularly significant are contributions from 40Ar/39Ar geochronology of supergene Mn-oxides and alunite-group sulfates; (U-Th)/He dating of supergene Fe-hydroxides; and 20Al, 10Be, and ³He constraints on erosion rates. Results from these studies reveal that the most supergene ore bodies preserved on the surface of the planet are younger than ca. 70 Ma (some much younger); resulted from protracted and episodic dissolution and reprecipitation of ore minerals, with effective leaching of deleterious elements; and are preserved in areas of low to very low (less than 1 m.Myr⁻¹) erosion rates. The application of these analytical approaches on a global scale indicates that paleoclimates in the late Cretaceous-early Paleocene, the early Eocene, and the early to mid Miocene were especially conducive to weathering-driven ore forming processes.
A reassessment of prebiotic sources of carbon in the early Earth

ARON VECHT

A major reassessment of the sources of carbon is required to explain a range of anomalies associated with carbon distribution in the early earth and in the post Hadean periods.

Among these we might list:-

A. The early earth crust whether sub-continental:-acidic or granitic, or sub-oceanic:-basic or basaltic contains a very small concentration of carbon, less than 100 ppm. The sedimentary rocks which are assumed to be directly or indirectly derived from these materials contain well over 5% of carbon.

B. The earliest sources of carbon can not be assumed to have been derived from living matter and a prebiotic source of carbon must have existed in realistic quantities. Even if the micro-structural and isotopic evidence for the existence of life around 3.8Ga is assumed, which is an open question, a source of carbon must be established.

C. The large deposits of methane hydrates as well as the more recent sources of methane (Lake Kivu) cannot be explained as purely to organic sources.

To explain the above anomalies we wish to propose the concept of ‘reactive minerals’. We believe that a considerable number of reactive minerals exist well below the earths surface. Such minerals would react with water, water vapour and/or oxygen when approaching the surface. We could cite carbides and sulphides as examples, more specifically calcium and aluminium carbide. It is well known that these compounds are stable at high temperatures but react if exposed to water or oxygen. In the former case they would initially yield methane or acetylene if confined to a neutral or reducing environment, or under oxidising conditions they would yield CO2. This in turn would form carbonates and at higher temperatures result in the formation of oxides and silicates.

The existence of such reactive minerals would explain how prebiotic sources existed from which living matter could have developed. It will also show that our present figures regarding the actual carbon content of the earth are low and true values would now be in line with the carbon content of other planets and interstellar materials.
Kinetics of liquid immiscibility in the system K$_2$O-CaO-FeO-Al$_2$O$_3$-SiO$_2$

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Our previous experiments on natural ferrobasaltic liquids showed that silicate liquid immiscibility may be seriously hampered by slow kinetics, metastable crystallization of tridymite, and the formation of sub-micron immiscible emulsions. Here we present new experiments on three synthetic compositions in the system K$_2$O-CaO-FeO-Al$_2$O$_3$-SiO$_2$. Two of the selected compositions lie inside the known miscibility gaps on the joins fayalite-orthoclase-silica and fayalite-hedenbergite-orthoclase-silica. The third composition lies on the anorthite-fayalite cotectic, well outside of known regions of stable or metastable liquid immiscibility. The charges in sealed Fe containers were first kept for 24 hours at a constant super-liquidus temperature, and quenched. Then, they were rapidly re-heated to the same temperature, and subjected to in situ centrifugation for 4 hours under acceleration of 1000 g. The aim of centrifugation was to distinguish between sub-liquidus emulsions due to quench, and those that may have formed by stable, super-liquidus immiscibility. The final glasses were studied by electron microprobe and transmission electron microscopy (TEM).

High-temperature super-liquidus emulsions formed in all the three compositions. The emulsions showed a remarkable stability, and did not completely break during centrifugation. Phase separation appears to be the fastest in the Ca-free composition on the fayalite-orthoclase-silica join. Here individual droplets readily grow to sizes of dozens and hundreds of microns, and merge to continuous liquid pools. The growth, coalescence and settling of droplets are significantly slower in the Ca-bearing fayalite-hedenbergite-orthoclase-silica composition. However, the most interesting and unexpected result was the formation of very fine, sub-micron emulsion in the composition on the anorthite-fayalite cotectic, where immiscibility had never been reported. The emulsion quenched to optically transparent glass, and could be revealed only by high-temperature centrifugation, electron microprobe profiles, and TEM.

Our results imply that the kinetics of silicate liquid immiscibility strongly depends on melt composition and viscosity. In some compositions, immiscibility may not develop beyond sub-micron scale for hours or days, and can be overlooked in conventional static experiments. If actual regions of silicate immiscibility are broader than presently thought, the petrogenetic role of immiscibility should be also revisited. In nature, large, slowly cooling magma chambers appear to offer enough time, and the best conditions for a full development of silicate liquid immiscibility.

Molecular and isotopic biogeochemistry of Neoproterozoic sediments in the Rio de la Plata Craton

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The Upper Ediacaran Arroyo del Soldado group (ASG) in Uruguay and Corumbá group (CG) in SW-Brazil were deposited on the same passive continental margin of the Rio de la Plata Craton. They contain a largely unmetamorphosed sedimentary sequence of alternating siliciclastic and carbonate rocks, that have been investigated by inorganic and organic geochemical methods in order to get new insight about changes in climate and chemistry of oceans during the Neoproterozoic in SW-Gondwana.

We report isotopic data from carbonates ($\delta^{13}$C$_{carb}$ and $\delta^{18}$O) and associated organic carbon ($\delta^{13}$C$_{ker}$ and $\delta^{15}$N$_{ker}$) together with hydrocarbon distribution and concentrations of major, trace and rare earth elements (REE). The $\delta^{13}$C$_{carb}$ values display coeval excursions in the two groups (ASG, CG) and range from −5.7 to 5.7‰. Dolostones from the Bocaina Formation in CG show the lowest $\delta^{13}$C$_{carb}$ values, a typical signature of cap carbonates worldwide. The $\delta^{13}$C$_{ker}$ values vary from −26.4 to −22.8‰ in CG and from −27.4 to −12‰ in the ASG reflect variations in the primary composition of organic matter as well as in the productivity rate during deposition. The $\delta^{15}$N$_{ker}$ values in the CG samples range between −3.3 to −3.1‰, suggesting a primary contribution of cyanobacteria. More positive $\delta^{15}$N$_{ker}$ values (1.8 to 5.2‰) in the ASG samples reflect most probably a higher planktonic contribution. Positive $\delta^{13}$C and $\Delta^{13}$C–ker excursions, higher concentrations of redox sensitive elements (Mn, Fe, U and V), REE, and variations in the Ce anomaly in dark organic limestones of both groups can be explained by an increased bioproductivity and preservation of organic carbon at unusually high rates of sedimentation.

The main resolvable compounds in the gas chromatograms of the hydrocarbon saturated fraction are n-alkanes in the C$_{15}$-30 (maxima at C$_{21}$) and C$_{14}$-15 (maxima at C$_{26}$) ranges for CG and ASG samples respectively, in both cases with no odd-even predominance. Most samples have a hump of unresolved complex mixture in the C$_{17}$-30 range. The predominance of C$_{18}$ of n-alkanes in the ASG samples confirm a marine planktonic input. The biomarker distribution (extended C$_{23}$ to C$_{34}$ hopanes, steranes) in the organic limestones of the CG are diagnostic for not strictly anaerobic bacteria and a diverse community of algae.
Open tube combustion method of organic samples for stable carbon isotope analysis

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A simple and effective conversion method of organic carbon into carbon dioxide for analysis of stable carbon isotopes ($\delta^{13}C$) in samples of solid and liquid substances and sedimentary rocks is presented. The conversion of organic carbon of the samples is carried out in a quartz reactor connected to a vacuum line for CO$_2$ freezing and purification. A solid organic sample mixed with CuO is placed at the reactor bottom and the reactor is subsequently filled up with a granular CuO. One end of the CuO column is preheated up to 850°C while the other end of the column in contact with the granular CuO. The column of CuO is heated to 850°C. Volatile liquid organic samples are introduced into the reactor through a septum using a micro syringe. Complete conversion is 10 minutes for solid samples and 3 minutes for volatile liquids. Precision of $\delta^{13}C$ analysis for solid and volatile liquid organic substances is ±0.1‰ and ±0.04‰ respectively.

The method presents an alternative to the well established sealed tube methods for combustion of organic material (Buchanan and Corcoran, 1959, Sofer, 1980)

The procedure of preparing the samples for combustion is simplified owing to the use of open tubes instead of sealed ampoules. The repeated use of reactors reduces considerably the consumption of expensive materials. Simultaneous use of several reactors enhances the economical aspects of the method. The method of carbon conversion demonstrates a high accuracy of $\delta^{13}C$ analysis for solids and liquids. Validity of results is confirmed by the comparison with data obtained by the universally recognized sealed tube combustion method and analysis of international standards reference materials.

References

Sulfide mobility during melt percolation: Implications for PGE and Os isotopes from the Oman ophiolite

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This study is focused on the origin of Os isotope heterogeneity in the Oman ophiolite in the context of melt percolation and sulfide mobility. Basically, two different sulfide populations occur: (1) Residual peridotites contain pentlandite (Pn) and chalcopyrite (Cp). Cp occurs either as thin lamellae or at the margin of Pn. In subgroup 1a, the grain sizes of the rare sulfides range from 10-60 µm. They are associated with opx as spherical inclusions, or they are located at triple junctions of olivines. Sulfides of subgroup 1b occur typically as interstitial, subhedral or anhedral grains with curvilinear boundaries. The grain sizes frequently range from 100 to 400 µm and they are closely associated with spinel and/or cp, suggesting precipitation from an immiscible sulfide melt. (2) Non-residual peridotites and pyroxenitic dikes: The relative abundance of sulfides strongly increases from the residual group to the non-residual group. The primary sulfide assemblage is composed of massive pyrrhotite + Cp + Pn. Large sulfide grains (up to 700 µm) are attached to coarse grained, subhedral cpx and/or spinel. The 1a type residual peridotites have very depleted trace element abundances (e.g. Yb$_{opx}$ (cpx) ~ 1.1; Ti$_{opx}$ (cpx) ~ 0.3), (Pd/Ir)$_{opx}$ ratios of < 1 and low $^{187}$Os/$^{188}$Os ratios ($^{187}$Os/$^{188}$Os$_{opx}=90$Ma) = 0.1149 and 0.1169. The unradiogenic Os compositions yield Re depletion ages of ~ 2 Ga. Type 1b residual peridotites have chondritic to suprachondritic Os isotopic ratios ($^{187}$Os/$^{188}$Os$_{opx}=90$Ma) = 0.1234 to 0.1318 and (Pd/Ir)$_{opx}$ ~ 1 to 2.

Samples from the non-residual group have suprachondritic Os isotopic ratios ($^{187}$Os/$^{188}$Os$_{opx}=90$Ma) = 0.1367 to 0.1675. The PGE and REE abundances of pyroxenitic dikes (Os = 0.13 ng/g; Pd = 6ng/g; (Pd/Ir)$_{opx}$ = 40.4) resemble those of mantle-derived melts. The PGE and REE distribution patterns of the non-residual peridotites are similar to or transitional between those of the residual peridotites and the pyroxenites. In a $^{187}$Os/$^{188}$Os vs 1/Os diagram the radiogenic samples define a mixing line having a depleted mantle and radiogenic pyroxenitic dykes as end members. It is suggested that the initial PGE and Os isotopic composition of the Oman mantle has been locally chemically overprinted by percolating melts, dissolving and re-precipitating sulfide liquids. In regions of high melting degrees and/or high melt/rock ratios, the initial PGE budget and Os isotope composition of a mantle rock may be completely replaced by sulfides derived from an Os radiogenic source.
Estimates of particle fluxes and boundary scavenging in the seawater around the Kerguelen Plateau using $^{230}$Th$_{xs}$ and $^{231}$Pa

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The Kerguelen Ocean and Plateau compared Study (KEOPS, 19 Jan.-13 Feb. 2005) took place in the wake of Kerguelen, characterized by a recurrent bloom allocated to natural fertilisation due to iron rich shelf inputs.

Particle dynamics (settling velocities, residence times) and dissolved/particle exchanges (boundary scavenging) are essential to understand the mechanisms responsible for the fertilisation over the Plateau. This work proposes to use two oceanic radionuclides $^{230}$Th and $^{231}$Pa –both decay products of soluble and conservative U and sensitive to scavenging- as particle dynamic tracers.

The measured dissolved and particulate $^{230}$Th and $^{231}$Pa data are consistent with other published data for near shelf area and open-ocean site. Dissolved excess $^{230}$Th (noted $^{230}$Th$_{xs}$) distributions increase linearly with depth down to 700 m at most of the stations. This linear trend reaches the bottom (1550 m) for both tracers at Kerfix, located west of the Kerguelen Plateau, with dissolved concentrations ranging from 0.6 to 11 fg/kg and from 0.02 to 1.8 fg/kg for $^{230}$Th$_{xs}$ and $^{231}$Pa respectively.

A reversible scavenging model using the $^{230}$Th$_{xs}$ dataset allowed us to estimate scavenging rates ($k_1$=0.3-0.9 y$^{-1}$), re-mineralization rates ($k_{-1}$=1.5 y$^{-1}$) and partition coefficients (average K=0.15±0.06). Assessed particle settling velocities S are 800 m.y$^{-1}$ at Kerfix and surprisingly lower over the biologically productive Plateau with ca. 500 m.y$^{-1}$. These latter velocities are nevertheless consistent with the high mineralization rates characterizing this area. The deep layers of the three stations located east of the Plateau display depleted tracer distribution (ca. 50% of the Th stock is lost) interpreted as reflecting intense scavenging due to the presence of nepheloid layers.

Single column procedure for quantitative separation and recovery of cadmium (Cd) for high precision isotope analysis by MC-ICP-MS

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Cadmium isotopic analyses gain increasing interest since terrestrial Cd isotopic compositions can be measured with higher resolution and precision. However, Cd isotopic studies face analytical challenges related to potential low Cd contents, non-spectral matrix effects as well as molecular (M 40Ar+ and M160+) and elemental isobaric interferences of Sn (112, 114, 116), In (113) and Pd (106, 108, 110) (Wombacher et al., 2003). As a result, complete isolation of Cd from its sample matrix is important.

We propose a novel Cd separation procedure based on the Pb separation described in Lugmair and Galer (1992) as an interesting alternative to the current procedures of Wombacher et al. (2003) and Cloquet et al. (2005). The present chromatographic method is performed on a single stage micro column with AG1-X8 anion-exchange resin with a total processed acid volume of 7 ml.

For the 14 estuarine suspended particulate matter (SPM) samples passed through the column, total Cd recovery is better than 96%. The separation procedure removes more than 98% of the Sn present in the sample. Potential problematic elements such as Mo and Zr, inducing molecular interferences during MC-ICP-MS analyses, are not present (not detected with a Thermo Finigan element 2 HR-ICP-MS) in the Cd fraction and the recovery of Zn is less than 0.6%. No problematic presence of major elements (Na, K, Mg, Ca) was detected suggesting that a single column procedure should be sufficient for subsequent isotopic measurements on a MC-ICP-MS. Some Pb (up to 2% of the initial Pb) and Cr (up to 10%) are still present in the Cd fraction. A second processing on the same column displays a recovery of better than 96% Cd (n=3), no Sn, nor Zn and only 0.2% of Pb is recovered in the Cd fraction.

The $\delta^{114/110}$Cd value obtained on four duplicate (total chemistry) SPM samples is of 0.17±0.06(2sd)‰/amu against our in-house B-JMC Cd standard.

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**CosmoCalc: An Excel add-in for cosmogenic nuclide calculations**

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Today, we are facing a paradoxical situation: on the one hand, a better understanding of cosmogenic nuclide systematics has improved the accuracy of cosmogenic nuclide dating. But on the other hand, the increased sophistication of these methods has been an obstacle to their widespread use. CosmoCalc is an add-in to MS-Excel developed with the intention to alleviate this problem. The program as well as a spreadsheet with test data can be downloaded from the CosmoCalc website (http://cosmocalc.googlepages.com).

CosmoCalc presently implements four scaling models: Lal, Stone, Dunai and Desilets. Although the more recent models such as those by Dunai and Desilets are significantly more sophisticated than the early scaling model by Lal, they are just as easy to use in CosmoCalc. It is equally simple to compute topographic, snow and self-shielding factors. The nuclide concentrations and the product of the scaling and shielding factors are the only input required for all further calculations.

CosmoCalc uses the ingrowth equation of Granger and Smith, which is a summation of four exponentials: one for neutrons, two for slow muons and one for fast muons. Default values for the various parameters in this equation are those advocated by Granger, but alternative values can also be set.

Banana plots are sophisticated devices which depend on a large number of parameters, such as the production rates at sea level and high latitude, the scaling model, and the relative proportions of the various production mechanisms. CosmoCalc flexibility allows different kinds of Al-Be and Ne-Be plots to be generated on the fly.

CosmoCalc implements two numerical techniques to solve the non-linear systems of ingrowth equations. The default is Newton's method, which is a very fast and exact algorithm. The Metropolis algorithm is offered as a computationally more intensive, yet also more robust, alternative.

Different scaling models use different kinds of geographic input. For example, Lal's scaling model uses elevation whereas Stone uses atmospheric pressure and Dunai and Desilets atmospheric depth. Furthermore, Lal and Stone use geomagnetic latitude whereas Dunai uses geomagnetic inclination and Desilets cutoff rigidity. To facilitate the comparison of the various scaling models, CosmoCalc provides some easy-to-use conversion tools.

Regardless of the scaling model of preference, it is crucially important to use the same scaling model for the unknown sample and the calibration sites. For this reason, CosmoCalc specifies the production rates not explicitly but implicitly, by specifying the raw measurements of the calibration sites. The program comes with a set of default calibration sites, but this list can be modified by removing and adding new sites.

**The 940-864 Ma granites of the Yenisey Ridge and Taimyr foldbelts, western margin of the Siberian Craton: Geochemistry and geodynamics**

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The 940–864 Ma granites occur within Mesozoic Neoproterozoic greenschist and amphibolite facies metamorphic rocks of the ancient terranes in the Yenisey Ridge and Taimyr accretional belts of the western margin of the Siberian craton (Vernikovsky and Vernikovskaya, 2001; Pease et al., 2001; Vernikovsky et al., 2007). In all studied plutons, the granites have slightly peraluminous (rarely metaluminous) chemical compositions with widely variable Sm-Nd and Rb-Sr isotopic data, which allows referring to these rocks as S- and transitional I- to S-types granites. The S-type granites with epsilon Nd(940-864 Ma) = -7.14 – -4.48, 87Sr/86Sr = 0.71206 – 0.72163 and zircon saturation temperatures (T_z) approximately 800°C were generated on the early stage of the collisional process from crustal transitional hot-to-low-temperature melts, according to Miller et al. (2003). The granites of transitional I- to S-type were formed on the final stage of the collisional event from mantle-crustal low-temperature (T_clest < 800°C) melts with epsilon Nd(940-864 Ma) = -2.8 – -0.4 and 87Sr/86Sr = 0.7070 – 0.7192. On this stage the most evolved granitic melts are formed, having low Ca, Mg and REE contents and enrichment in Si and K.

It is likely that the 940 – 864 Ma granites were part of a microcontinent prior to the accretion and collision of its blocks (or terranes) with the Siberian continent.

**References**


The Neoproterozoic alkaline rocks of the Yenisey Ridge, western margin of the Siberian Craton: Mineralogy, geochemistry and geochronology

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The Srednetatarka alkaline massif is composed of ijolites, forming the central zone and foyaites making up the outer ring area. These medium to coarse grained rocks were intruded by pegmatite dikes. The main minerals are alkali feldspar (mainly microcline), nepheline, aegirine (or aegirine-augite), alkali amphibole (mainly arfvedsonite) ± lepidomelane, ± eudialyte, ± astrophyllite-kupletskite. Among accessory minerals there are titanite, fluorite and zircon.

Enrichment of Zr, Nb and Ce in foyaites was discovered using electron microscope investigation and x-ray spectroscopic analyses. The water enriched fluid inclusions in fluorite from ijolite have homogenization temperatures from 175 ºC to 200 ºC. The rocks of the Srednetatarka massif are highly fractionated and enriched in Rb, Th, U, Nb, Ta, Hf, Zr, Tb and Y, and depleted in Ba, Sr, P and Ti. They also have large REE contents (ΣREE = 123 - 362 ppm), LILE enrichment (La/Yb~8-16) and negative Eu anomalies (Eu/Eu* changes from 0.2 to 0.9). The Srednetatarka foyaite yielded a U-Pb titanite age of 698±2 Ma. Together with the previously-dated 696 Ma (Ar-Ar, biotite) trachydolerite of the Zakhrebetninsk complex (Postnikov, 2005), these intrusive rocks are the oldest alkaline rock of the Yenisey Ridge which could be formed in anorogenic setting.

One of the most interesting facts about these alkaline rocks is that Nb, Ta, Zr mineralization and an Al deposit associate with the Srednetatarka massif.

References

Hf and Nd isotopic composition of sediments, old and new

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We examine the Hf and Nd isotopic data for over 200 sediment samples in order to constrain Lu-Hf and Sm-Nd isotope systematics in the silicate Earth. The samples we have analyzed include sediments preserved on the continents and deposited in the ocean basins previously published [1] as well as unpublished data from >120 samples from 14 DSDP and ODP sites, chosen to represent the full range of sediment types and depositional environments. The most striking feature of the sediment data, as previously noted [1], is the strong positive correlation between Hf and Nd isotopes in these diverse terrigenous sediment samples. This sediment Hf-Nd array is coincident with the Hf-Nd mantle array as defined by MORBs and OIBs and collectively has been termed the terrestrial [1] or crust-mantle array. This array radiates from a depleted end-member with radiogenic Nd and Hf (εNd ~10; εHf ~16) toward evolved crustal values with very negative εNd and εHf values and represents mixing between components derived from the depleted mantle and components derived from continental crust.

The most prominent exceptions to this array, noted in the early Hf-Nd work on sediments [2,3], are ferromanganese crusts and nodules and metalliferous clays, which lie along a shallow slope above the terrestrial array. This anomalous array of authigenic sediments appears to represent, at least in part, the isotopic composition of seawater. This "seawater array" most likely results from the preferential dissolution of high Lu/Hf phases that are easily weathered such as apatite in old continental crust [4,5]. Regardless of the deviation from the terrestrial Hf-Nd array by metalliferous sediments and seawater, the tight coherency of the sediment Hf-Nd array indicates efficient mixing within the mantle through convection and on the Earth’s surface through diverse sedimentary processes, and also effective transfer between the two through the recycling of crustal materials via subduction zones.

References
Trace element partitioning between Mg-hastingsite and alkali basaltic melt in volcanic environment

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The occurrence of amphibole with no evidence of re-equilibration under low pressure conditions is rather rare in volcanic environment. The occurrence of a Mg-hastingsitic amphibole in trachybassic volcanic rocks of the 2001 eruption at Mt. Etna (Italy) has drawn the attention of many authors. However, the most intriguing character was found in the textures that show the original equilibrium at high P-haul between the amphibole and the surrounding glassy groundmass. This has allowed to calculate new accurate trace element partition coefficients (from LA-ICP-MS data) between Mg-hastingsite and basaltic-trachyandesite melt, well represented by the coexisting glass. Pressure and temperature conditions have been constrained on the grounds of geophysical and petrological data at 250 MPa and 980°C respectively.

<table>
<thead>
<tr>
<th>Element</th>
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<th>Element</th>
<th>Amph/melt</th>
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<tbody>
<tr>
<td>La</td>
<td>0.366</td>
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<td>Rb</td>
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<td>Ce</td>
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<td>Nb</td>
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<td>1.248</td>
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<tr>
<td>Lu</td>
<td>1.267</td>
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</table>

In detail, commonly incompatible trace elements such as Nb and Ta can be more easily incorporated in the amphibole than Th, U and LREE. This means that, if Mg-hastingsite fractionation occurs in magma reservoirs, the trace element signature of the residual melt can be strongly affected, with a significant increase in the melt of trace element ratios such as U/Nb, Th/Ta, La/Nb, La/Ta. This can have a great importance especially for those systems where amphibole is unusual, so that its role as a phase fractionated from the magma can be recognised from uncommon trace element ratios.

Lithium-bearing pegmatite resources at Fregeneda-Almendra pegmatitic field (Spain & Portugal)

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Introduction

A geological exploration is being carried out in the Fregeneda-Almendra region. This field has different types of pegmatite veins, defined according to their mineralogy, morphology and internal structure. The veins intrude a pre-Ordovician E-W metasediments belt and are located to the north of the syn-Hercynian Média-Penedono-Lumbrales complex. This complex is mainly composed of a two-mica, peraluminous leucogranite. The veins have a zoned spatial distribution: the barren pegmatites are located near to the granitic complex and the rare-element enriched bodies occur further to the north. The Li-rich pegmatites are discordant, emplaced along the regional fracture system N-S to N030° E. Metamorphism isograd decreases with the distance from the granite and parallel to its contact: from sillimanite to chlorite isograd.

Methodology

Based on a stream sediment survey, the Li content of 2529 samples was analysed. Data was statistically studied and overlapped on region geological maps. This approach lead to the recognition of petalite- and spodumene-bearing pegmatites non identified until that moment.

Petalite- and Spodumene-bearing veins

Petalite-bearing veins only occur in the Portuguese part of the field. They are emplaced in the andalusite-sillimanite zone. Pombal and Vales outcrops exhibit a maximum extension of 500m and 10m width. The bodies do not show an evident internal zonation. Mineralogy assemblage is feldspars, quartz, and petalite as major constituents; minor muscovite, montebrasite and cassiterite. Fe-Mn phosphates and apatite appear as accessory minerals. Geochemical bulk analyses allow us to say that these veins are peraluminous (A/CNK>1), have low SiO₂ content and Na₂O>K₂O. They are also impoverished in Fe(t), MgO and CaO.

Spodumene-bearing veins outcrop close to the limit of the biotite/chlorite isograd. Vau and Alberto mine have variable thicknesses of 4m to 15m. Internal zonation is not observed. Mineralogy is simple: feldspars, quartz and spodumene as major constituents; minor muscovite, montebrasite and petalite; beryl, Fe-Mn phosphates and cassiterite as accessory minerals. Further studies are required.

Final Remarks

Stream-sediment geochemistry is a powerful tool on Li-pegmatite exploration and allowed an improvement on the pegmatitic field petrogenetic understanding. It also provided the increase of mineral resources for ceramics and glass industry, which already consume material from this region.
Sm-Nd and Rb-Sr isotopic systematics of suspended sediments transported by the Solimões and Madeira River: New insights about erosion and sediment provenance in the Amazon basin

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The Amazon basin is the world’s largest Cenozoic fluvial basin with an actual drainage area of 5.8 \(10^6\) km² and a depositional area of approximately 2.5-3 \(10^6\) km². It supplies about 7% of the suspended load (Filizola and Guyot, 2004) to the world’s oceans. Filizola and Guyot (2004) give a mean annual suspended sediment flux close to 600 \(10^6\) t.yr⁻¹ at Obidos (Para state, Brazil). Ninety seven percent of this amount is contributed by Andean tributaries (62% from the Solimões River and 35% from the Madeira River).

This study reports the Sm-Nd and Rb-Sr isotopic systematics of materials being transported today by the Solimões Rio and Madeira Rio during the year 2004. Within the ORE (Environmental Research Observatory) HyBam (Hydrology of the Amazon Basin) (http://www.ore-hybam.org) monthly samples are collected from the Solimões River at Manacapuru station (A mazonas state, Brazil) and the Madeira River at Porto Velho station (Rondonia state, Brazil) (see Hybam website for more details).

The Nd isotopic composition ranges from -8.9‰ to 9.9‰ and from -10.8‰ to -12.1‰ for the Solimões and Madeira suspended sediments, respectively. The \(^{87}\text{Sr}/^{86}\text{Sr}\) ranges from 0.713 to 0.717 and from 0.728 to 0.740 for the Solimões and Madeira, respectively.

The purposes of this work are 1/ to assess possible systematic temporal variation in the Sm-Nd and Rb-Sr isotopic characteristics of the sediments, 2/ to use these potential differences of isotopic composition to constrain the geographic provenance of these sediments and the importance of bank erosion, and 3/ to estimate a global isotopic signature for sediments transported today by the Amazon River to the Atlantic ocean that can have important implications for the marine geochemistry of Nd.

Reference

Carbon and hydrogen isotopic compositions of petroleum hydrocarbons to trace alteration processes in reservoirs

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Hydrocarbons in petroleum reservoirs are subjected to viable abiotic and biotic alteration processes, such as evaporative fractionation, water washing and biodegradation. These processes cause significant changes in the molecular composition of the crude oil and therefore lead to a decrease in petroleum quality (e.g. lower API gravity, higher viscosity, higher TAN). Hence, the producibility of the respective fluids is negatively affected and the total volume of petroleum in place is reduced. Among the different alteration processes, biodegradation is responsible for the quantitative most important compositional changes in a petroleum reservoir, and therefore the ability to assess the extent of biodegradation is of particular interest for the petroleum industry.

Microbial processes favour the conversion of molecules containing lighter isotopes and therefore biodegradation leads to an enrichment of compounds with heavier isotopes (\(^{13}\text{C}, \text{D}\)) in the residual fraction. In general, hydrogen isotope fractionation tends to be at least one order of magnitude higher than carbon isotope fractionation, indicating higher sensitivity in the assessment of microbial degradation processes.

Recently it was shown that carbon isotope ratios of light hydrocarbons can be used to evaluate biodegradation processes in the Gullfaks reservoir, offshore Norway (Vieth and Wilkes 2006). However, it became clear that both source and also maturity effects have to be well constrained when using carbon isotope ratios for the assessment of biodegradation. In contrast to laboratory experiments, the hydrogen isotope ratios of light hydrocarbons in these crude oils from the Gullfaks field do not show a clear dependence on biodegradation processes. It is suggested that in petroleum reservoirs, besides differences in maturity and source, also the effects of hydrogen exchange between oil and formation water over geologic times have to be considered.

This study investigates the effects of biodegradation on carbon and hydrogen isotopes in crude oils. Here, we will present results of compound-specific isotope analysis on oil samples from different petroleum systems and demonstrate how carbon and hydrogen isotope ratios of petroleum hydrocarbons can be used to evaluate biotic as well as abiotic alteration processes in reservoirs.

References
Simulating physical weathering of basalt on Earth and Mars

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Background
Despite its importance as a surficial rock type on Earth and other planets, few studies have been made of the response of basalt to physical weathering. Heating and cooling, with or without salts and moisture, may have severe impacts on basalt clasts in many extreme environments (Leask & Wilson, 2003). We report here on an integrated programme of simulations investigating physical weathering of basalt under Earth (hot desert) and Mars conditions using a Fison’s Environmental Cabinet and a specially constructed Mars Environment Simulation Chamber.

Methods
Small blocks (9 x 2.3 x 2.5 cm) of basalt were cut, and two groups prepared: (1) thermally pre-stressed and (2) thermally pre-stressed and immersed in saturated Na₂SO₄ solution. Sample strength was assessed before and after experimental weathering using a Grindosonic, and thin sections were produced for detailed petrological examination. Ambient, block surface and internal temperatures were monitored throughout the experiments. The Earth weathering regime was set up to reflect Negev desert conditions cycling between 296K and 345K; whilst the Martian regime cycled from 190K to 277K. Cycle length was 8 hrs. in each case. Both weathering regimes also included an element of radiative heating via lamps coming on for part of the heating cycle. The Mars weathering regime was carried out in 100% CO₂ atmosphere at 9 mbar pressure.

Results and conclusions
After 36 cycles under Earth and Mars conditions, changes in strength (few %) were apparent and some microscopic cracking was observed, although no visible weathering was produced. Blocks subjected to Mars-like conditions reacted differently to those subjected to Negev desert conditions especially with regard to whether salts caused strengthening or weakening.

References
B, Li and Sr isotopes as tracers of seawater-serpentinite interaction at MAR, ODP leg 209

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The samples presented in this study are altered spinel harzburgites from ODP Leg 209 (sites 1272A and 1274A) at the Mid-Atlantic Ridge (MAR) between 14°N and 16°N. The degree of serpentinisation varies between 70 and 100% in site 1272A and from 50 to 97% in site 1274A. Despite the high degree of serpentinisation, some relics of primary phases are still preserved (olivine ≥ orthopyroxene >> clinopyroxene).

In our previous study of the light element concentration in minerals of these samples we could show that boron is enriched in these rocks by reaction with seawater, and that the same process probably leaches lithium. Here, we present the results of strontium-, lithium- and boron-isotope analysis of these samples.

δ7Li varies between -28.46 and +7.17, δ11B ranges from +29.6 to +40.52. 87Sr/86Sr ratios (average 0.708726) are close to seawater values. Using the water-rock-ratio equation of McCulloch et al (1980), we obtain a low water-rock ratio (average 38.9).

Using the fractionation factors of Liu and Tossell (2005) for boron, we can model the compositional evolution of seawater to an evolved fluid (up to δ11B +70 in solution, corresponding to δ11B + 40 in the rock) in the course of its passage through the oceanic mantle rocks.

Our results show that at ODP leg 209, B, Li and Sr isotopes can successfully be used to quantify reactions between seawater and very young oceanic mantle rocks. Low water-rock ratios lead to extremely high δ11B values. This signature could potentially be transported into subduction zones. In general, however, the B, Li and Sr isotopic composition of altered oceanic mantle should be highly variable depending on water-rock ratios and on age.

Dynamic of pedogenic carbonates in a climatic gradient: The Kabini river basin, Deccan Plateau, South India

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The chemical weathering of silicate rocks consumes atmospheric CO2. This has an impact on the long-term carbon cycle. In arid and semi-arid climatic conditions, the precipitation of pedogenic carbonates in soil, developed on silicate bedrock, is a potential carbon sink.

The West-East climatic gradient of the Deccan plateau, South Peninsular India, has induced various pedogenic carbonate occurrences, calcretes and nodules in the semi-arid zone and only nodules in the transition zone. The transition zone appears to be particularly sensitive to climatic changes and thus well designed for assessing the impact of climate change on the dynamic of pedogenic carbonates. In order to constrain the carbon sequestration in pedogenic carbonates, (1) the origin of Ca, (2) their age (U/Th dating) and (3) their current behavior (precipitation or dissolution), have to be determined.

Different types of nodules were sampled according to the structural study of the soil cover, in two representative watersheds of the transition zone. Soils, developed on a gneissic basement, show carbonate nodules either at the top of saprolite or within black soils (vertisols).

The 87Sr/86Sr isotopic ratios show that 2/3 of Sr in the carbonates originate from the parent rock and 1/3 from atmospheric inputs. This means that Ca mainly originates from the parent rock.

Preliminary U-Th ages of the well-developed nodules from the saprolite and black soils range from 15 to 23 ky while ages of soft tiny nodules from black soils would be less than 2 ky. Both populations of ages correspond to periods of weakness of the South West monsoon (drier climate). In this context, the pedogenic carbonates could be considered as paleo-climate proxies.

The current stability of the nodules was assessed by the stream chemistry of the watersheds. It indicates that the nodules are dissolving in the transition zone. The nodules dissolution significantly contributes to the output fluxes of Ca, Mg, U and REEs. However, the nodules trapped in the clayey matrix of the black soils seem to be protected from present-day chemical weathering.

References

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Seasonal dynamics of molybdenum in a permanently anoxic lake

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Mo is an essential enzyme cofactor in nitrogenase and nitrate reductase, necessary to nitrogen assimilation by phytoplankton (cyanobacteria and microalgae respectively). Mo is also considered in sediment records as a proxy of anoxic paleo-environments where sulphide builds up and precipitate molybdenum. In order to understand dissolved Mo removal mechanisms in freshwater bodies we investigated the lake Pavin water column (Puy-de-Dome, France).

Lake Pavin is meromictic and at the bottom, about 30 meters out of 91 meters remain permanently anoxic and constitutes a natural “test tube”. The anoxic bottom layer overlaps a large density gradient layer (mesolimnion) where maximum reduced sulphur species concentrations are observed, and a more homogeneous layer where reduced compounds accumulate (monimolimnion).

The Mo size fraction was studied in the meso- and monimolimnion and compared to dissolved organic carbon (DOC) behaviour. Previous studies showed clearly Mo removal within the monimolimnion and chemical association of dissolved Mo with DOC. In this work, we demonstrate that this association is effective with large reactive organic polymers (> 1kD).

Monthly sampling of rivers input, water column solutions and solid samples (sediment traps) allowed to quantify Mo and nitrogen lake annual budget. Seasonal evolution of vertical profiles for dissolved Mo, nitrate, ammonium, sulphate and sulfide are compared and related to nitrate assimilation in the epilimnion and iron sulphide formation in the mesolimnion.

Li isotopic signature of the Reunion plume inferred from Li-Pb isotope systematic of Piton de la Fournaise historic lavas

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We have investigated short-term variations of \(^7\text{Li}/\text{Li}\) at Piton de la Fournaise volcano in order to better constrain the signature of the Reunion plume source and contribution of shallow-level processes. \(^7\text{Li}\) (with reference to the IRMM-016 standard) determined in 30 lava samples erupted between 1927 and 2006 (including basalts and oceanites) ranges from +3.4‰ to +4.9‰. \(^7\text{Li}\) does not correlate with the abundance of olivine xenocrysts (whose mass fraction reaches 50% in oceanites) ruling out diffusive fractionation of Li isotopes between olivine and melt as the main cause of \(^7\text{Li}/\text{Li}\) variability. However, the heaviest compositions (\(^7\text{Li} > +4.2\%\)) are found in oceanites. Contrasting with global scale systematics, \(^7\text{Li}\) correlates negatively with \(^{206}\text{Pb}/^{204}\text{Pb}\). More precisely, three distinct arrays converge toward a unique composition, suggesting mixing between a single plume component (with \(^7\text{Li} = +3.4\%\) and \(^{206}\text{Pb}/^{204}\text{Pb} = 18.90\)) and distinct contaminants. The dominant array may reflect interaction of plume melts with altered oceanic crust having unradiogenic Pb and heavy Li signature.

The Li isotopic signature of Reunion plume, as inferred from Li-Pb isotope relationships, is lighter than that of the Hawaiian plume and plumes sampling EM2 and HIMU mantle components, and is similar to that of DM and EM1 mantle components, as sampled by depleted MORB and Pitcairn lavas, respectively (Chan et al., 2006).

In agreement with previous inferences (Vlastelic et al., 2006) Li isotopes require little, or not at all, recycling of isotopically light continental sediments or isotopically heavy altered oceanic crust into the Reunion plume source.

References
Non-skeletal carbonate precipitates: Indicators of Molybdenum isotopic seawater composition?

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Studies on black shales and oxic manganese crusts indicate that the Mo isotopic signature is a suitable proxy for the detection and interpretation of changes in past ocean redox conditions (Siebert et al., 2003; Arnold et al., 2004, Barling et al., 2001). Carbonate rocks are a reservoir not yet investigated with respect to their Mo isotopic composition. Due to their occurrence during most of Earth’s history and in a wide variety of geological settings, their Mo isotopic signature has the potential to provide a continuous record of ocean redox chemistry.

We present Mo isotopic data obtained from modern ooid sands from the Bahamas and the Persian Gulf. Their isotopic composition approximates modern seawater signature, while modern skeletal material has a significantly lighter value. Also, our data from chemically precipitated marine cements from the Carboniferous of Spain and China exhibit a heavy isotopic composition similar to today’s ocean water and a distinct offset from their surrounding isotopically lighter sediment material. This has led us to hypothesize that the Mo budget of non-skeletal marine carbonates is controlled by seawater and may serve as an archive of ocean water Mo isotopic composition. As a pilot study we analyzed a variety of geological settings, their Mo isotopic signature has the potential to provide a continuous record of ocean redox chemistry.

Colloid formation in aerated Fe(II) and As(III) containing water: Effect of phosphate, silicate and Ca on local coordination by XAFS spectroscopy

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Colloid formation due to iron oxidation and hydrolysis affects the cycling of nutrients and contaminants in environmental and technical systems. The extent of As oxidation and uptake by colloids and the composition and colloidal stability of the resulting colloids are major factors controlling the removal of As from As-rich anoxic drinking water. We investigated Fe(III)-colloid formation and concomitant As(III) oxidation and removal in synthetic carbonate-buffered groundwater (pH 7, 2-30 mg/L Fe(II), 0.5 mg/L As(III)) as influenced by phosphate (2-20 mg/L P), silicate (2-20 mg/L Si), and Ca (2.5 mM Ca- and 1.5 mM Mg-versus 8 mM Na-bicarbonate). The oxidation state of As and the local coordination of As, Fe, P, Si, and Ca in colloids collected after 4 hours of oxidation were investigated by X-ray absorption fine structure (XAFS) spectroscopy.

The removal of As from solution by uptake into settling colloids depends on a range of coupled processes such as the enhanced As(III) oxidation in presence of Fe(II), the competition of phosphate, silicate, and As for sorption sites on Fe(III)- colloids, and the effect of phosphate, silicate and Ca on molecular-scale colloid structure and colloid aggregation. While higher Fe(II) concentrations promote As(III) oxidation in solution, the associated increase of sorption sites on Fe(III)- colloids reduces anion competition, resulting in a higher fraction of colloidal As(III) (relative to total colloidal As). Increasing P/Fe ratios promote the formation of basic Fe-phosphates and increasing Si/Fe ratios the formation of ferrhydrite at the expense of lepidocrocite (which forms in the absence of P and Si). In the presence of P and Si, the P/Fe and Si/Fe ratios determine the extend to which basic Fe(III)-phosphate- and ferrhydrite-type colloids form. In the absence of Ca, colloids formed at low Fe concentration and high P/Fe ratio are colloidally stable, resulting in reduced As removal from solution. The presence of Ca promotes colloid coagulation by diminishing electrostatic colloid repulsion. Especially at high P/Fe ratios, we find that Ca is also directly incorporated into the colloid structure, suggesting the formation of mixed basic Ca-Fe(III)-phosphates. Spectroscopic data further suggest that also As(V) may be incorporated into these phosphates.

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Molecular $\delta^{13}$C values of leaf wax components from plants growing in different tropical habitats

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Long-chain leaf wax components from tropical C₃ plants were analysed for their carbon isotopic composition. Averaged $\delta^{13}$C values for alkanes (weighted mean average of the n-C₂₇ to n-C₃₅ alkanes) were $-33.5 \pm 2.8\%$ for savanna plants and $-36.9 \pm 2.5\%$ for rain forest plants. The difference of 3.4% originates mainly from (1) the different isotopic composition of the source CO₂ caused by recycling effects in the closed canopy of the rain forest, and (2) the stronger discrimination of the heavier carbon isotope due to slower assimilation of CO₂ in the shady rainforest. Similar differences (3.3 to 3.8‰) were found by Ehleringer et al. (1987) for leaf tissue material of shrubs, trees, ferns and grass from open and closed canopy habitats.

In general, tropical vegetation changes from rain forests over savannas and finally to arid grasslands due to climatic conditions. Woody C₃ plant contribution decreases with an increase of grassy C₄ plants. The $\delta^{13}$C values of the n-C₂₇ to n-C₃₅ alkanes increase in the course of this vegetation change (Fig. 1). The C₄ grasses of the savanna have the highest values due to their different metabolic pathway.

![Figure 1](image)

**Figure 1.** Averaged $\delta^{13}$C values of n-C₂₇ to n-C₃₅ alkanes (weighted mean average) from leaf wax of C₃ grasses (circle, Rommerskirchen et al., 2006, n = 24) and rain forest C₃ plants (square, n =18).

These results give a clearer look at key data for studies estimating the variation of land plant biomarker contribution to dust, soils and sediments in tropical regions. Until now such research projects often only distinguished between the molecular carbon isotopic signatures of C₃ and C₄ plants. Our study provides data about a significant difference in the molecular $\delta^{13}$C values of C₃ plants from savannas and rain forests. This has to be taken into consideration, e.g., in palaeoclimatic studies.

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Surface water freshening and high-latitude river discharge in the Eocene North Sea

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A fish-teeth derived $\delta^{18}$Op record of the early Palaeogene North Sea mirrors the global oceanic temperature evolution, except of a 2-4 Myr period across the Palaeocene-Eocene transition, when unusually light $\delta^{18}$Op values in teeth of surface dwelling sharks indicate substantial surface water freshening. The $\delta^{18}$Op decrease with a magnitude of 6.3‰ commenced during the Palaeocene-Eocene thermal maximum (PETM), and prevailed until the early Ypresian. Coeval occurring bottom dwelling sharks indicate normal marine conditions and strong water column stratification in the early Ypresian North Sea. The magnitude of the negative $\delta^{18}$Op excursion suggests a depletion of surface water $\delta^{18}$Op by 3.6‰ relative to Eocene mean ocean water. This value is lower than that of coeval freshwater lakes and indicates that large rivers sourced by strongly fractionated precipitation drained into the North Sea. The investigated odontaspid and lamnid sharks are fully marine organisms and do not live in waters with salinities lower than 20 ppt today. We consider this value as the lower salinity tolerance limit for large predators. The construction of a mixing line between marine and brackish waters and their corresponding oxygen isotopic compositions in the Eocene results in $\delta^{18}$O values of -10 to -13‰ for river waters. These values are in a good agreement with the isotopic composition of Arctic precipitation, recently estimated from hydrogen isotopes in terrestrial plant-derived n-alkanes (Pagani et al. 2006), and suggest a high-latitude source of the river discharge into the North Sea. The commencement and duration of brackish surface-water conditions in the North Sea coincide with the main phase of effusive basaltic volcanism and associated tectonic uplift in the North Atlantic region. As a result, the North Sea probably became temporarily isolated and the fluvial catchment areas extended into the high latitudes. The marginal North Sea became reconnected with the North Atlantic Ocean during the transgression at 54 Myr, when normal marine conditions returned indicated by $\delta^{18}$Op in teeth from surface and bottom dwelling sharks.

Reference

The rheological behavior of samples from Tungurahua volcano, Ecuador


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For a better understanding of eruption mechanisms it is important to investigate the rheological behaviour of the magma during its ascent in the conduit. We can reveal this information by measuring the physico-chemical properties of volcanic ejecta. Between 16th and 18th of August 2006 a large eruption occurred on Tungurahua volcano including fire fountains, ash-, rock- and pumice falls and lava flows, as well as several pyroclastic flows. Shortly after this, we collected five different rock samples from the pyroclastic flow deposit which represent the most of the mass of rocks of the pyroclastic flows produced in this eruption. The rocks of the pyroclastic flows are:

a) 5% of dome material with a low porosity of about 15%;

b) 90% of bread crust bombs which have a higher porosity of about 30-50%.

A reconnaissance study of the rheological properties of our samples obtained via glass transition temperature ($T_g$) determinations was performed. To this end we have employed an advanced dilatometric method, newly developed by Helo et al. (2006).

By detecting the dilatometric softening temperature ($T_{g,soft}$) in successive runs with the same sample at constant heating and cooling rates, we observed a shift of $T_{g,soft}$ with increasing run number, presumably due to degassing of the supercooled liquid phase. The measured $T_{g,soft}$ for the dome material were 974 °C for the first run and 1030 °C for the 10th run, and 1060 °C up to ~1100 °C for the bombs. The increase of $T_{g,soft}$ in successive runs was higher for the dome material than for the bread crust bombs.

This was unexpected as the dome material is believed to be more degassed and should therefore have a higher $T_{g,soft}$ than bombs which had less time for degassing. But the results show the opposite trend: higher $T_{g,soft}$ and a faster rise in $T_{g,soft}$ for the porous bomb material. The results of this study will be discussed in terms of the relative degassing histories and kinetics of the dome versus bomb rocks as well as their crystalline textures.

References


How fast do the Alps erode? A cosmogenic nuclide study on Central Alpine river basins

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Cosmogenic $^{10}$Be, measured in river-borne quartz now routinely provides denudation rates at the river basin spatial scale and at the temporal scale of a few kiloyears (von Blanckenburg 2005). A north-south traverse through the Swiss Central Alps reveals that denudation rates correlate with recent rock uplift rates in both magnitude and spatial distribution. As a prerequisite, we took care to investigate the potential influence of shielding from cosmic rays due to snow, glaciers, and topographic obstructions, to calculate a possible memory from LGM glaciation, and to identify a watershed size that is appropriate for systematic sampling. Mean denudation rates are 0.27± 0.14 mm*yr$^{-1}$ for the Alpine foreland, and 0.9± 0.3 mm*yr$^{-1}$ for the crystalline Central Alps. The measured cosmogenic nuclide-derived denudation rates are in good agreement with post-LGM lake infill rates and about twice as high as denudation rates from apatite fission track ages that record denudation from 9-5 Myr. Cosmogenic nuclides now provide the ability to decipher correlations between denudation rate and geomorphic parameters. For example, the rates correlate with hill slope in the Mittelland catchments, but they are independent of angle in the high Alps. We interpret this to mean that high Alpine landscapes are at threshold hillslope, where slopes cannot increase any further before failure occurs. In general, denudation rates are high in areas of high relief and high altitude. Levelling measurements show that the Central Alps are uplifting today with 0.5-1.6 mm yr$^{-1}$ (Kahle et al. 1997). The similarity in the spatial distribution and magnitude of denudation rates and those of rock uplift rates can be interpreted in several ways: (i) postglacial rebound or climate change has introduced a transient change in which both uplift and denudation follow each other with a short lag time; (ii) the amplitude of glacial to interglacial changes in both is small and is contained in the scatter of the data; (iii) both are driven by ongoing convergence where their similarity might hint at some form of long-term quasi steady state; (iv) enhanced continuous Quaternary erosion and isostatic compensation of the mass removed accounts for the distribution of present-day rock uplift.

References


A new U/Pb-spike ($^{233-235}$U/$^{202-205}$Pb) for high precision zircon dating: First results of standard zircons, precision and accuracy

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For high precision U/Pb zircon, xenotime and monazite analyses there is a new U/Pb spike ($^{233-235}$U/$^{202-205}$Pb) produced at ETH Zurich. The enrichment for the $^{205}$Pb isotope is greater than 99.95 and for the $^{206}$Pb isotope greater than 99.73. Important ratios of this new mixed double U/Pb spike are: $^{206}$Pb/$^{202}$Pb – (0.001132), $^{235}$U/$^{202}$Pb – (7.7351E-05), $^{208}$Pb/$^{202}$Pb – (10.0025) and $^{235}$U/$^{231}$U – (0.969945). The new U/Pb spike was calibrated against a highly pure metal solution based on NBS 982 and NBS 960. One of the aims to produce the new double lead and uranium spike ($^{233-235}$U/$^{202-205}$Pb was the to avoid the usage of external mass-fractionation, and to improve precision and accuracy of U-Pb measurements. In the past the instrumental mass-fractionation was estimated by repeated measurements of NBS 982 or NBS 981 material as well as of U 500 standard material.

The minimum amount of NBS Pb and U for the external fractionation correction is limited by Pb-blank, the temperature during the measurement and parameters of the ion counter system. Nevertheless, the measuring procedure needs more time for the measurement based on six Pb isotopes, three U isotopes and sometimes two additional isotope to correct interferences on the mass $^{202}$Pb.

To demonstrate the advantage of the new ($^{233-235}$U/$^{202-205}$Pb) U/Pb spike we have measured several zircons standards R33 (Black et al., 2204), 91500 (Wiedenbeck et al., 1995) and the PL zircon (Slama et al., 2006) using a “common” $^{235}$U/$^{205}$Pb and the new double U/Pb spike. First preliminary results show that the scattering of the $^{206}$Pb/$^{238}$U ages and the mean error of the $^{206}$Pb/$^{238}$U ages are much smaller compared to the use of the “conventional” $^{205}$Pb/$^{235}$U spike.

References


Identification of potential geochemical reactions in German subsurface storage sites of CO₂

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Large scale CO₂ geological storage in Germany can be realized both in deep saline aquifers and in mature natural gas reservoirs. Some of the injected CO₂ will dissolve in the already highly mineralized Na-Ca-Cl brine to form CO₂ (aq) and carbonic acid. Such a change in brine composition can lead to dissolution or precipitation of minerals within the storage formation or the cap rock. Mineral dissolution will yield an increase in porosity. Depending on where it occurs, it can either increase the storage capacity or reduce the cap rock integrity. Mineral precipitation will either result in long term mineral storage of CO₂ or - if it occurs near to the well - it can yield technical problems during CO₂ injection. Numerical simulation of reactive transport processes and associated mineral reactions are generally used for predictions of such processes. But, reaction rates of silicates are very slow and reliable thermodynamic data obtained by experimental studies of mineral precipitation or dissolution is difficult to obtain. In many cases realistic thermodynamic data does not exist for all minerals within a rock formation. Data for lacking minerals such as mixed crystals has to be estimated. If we consider high-salinity brines, which are omnipresent in the North German Basin, the Pitzer formalism has to be used. Many simulation tools do not facilitate simulation of redox reactions or alumino silicate reactions in combination with the Pitzer formalism. These limitations result in potential unrealisitic and therefore uncertain interpretations of geochemical simulation results. Another way to identify and quantify potential alteration reactions is to study natural analogues. For the case of CO₂ injection, natural analogues can be found in regions with CO₂-rich water, e.g. in active volcanic regions. Potential alteration reactions, identified by natural analogue studies can further be used as comparison and for qualitative calibration of numerical simulations. For the German storage formations Bunter Sandstone and Rotliegend sediments such natural analogue studies yield the dissolution of calcite and chlorite and precipitation of dolomite. Another slow alteration reaction is the dissolution of albite and the precipitation of kaolinite. By studying natural analogues of the Rhenish Massif, May (2005) found that the alteration of greywacke and shale rocks by CO₂-rich water led to the dissolution of chlorite and feldspar and to the precipitation of kaolinite, iron-bearing carbonates, quartz and bicarbonate water.

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Origin of UHP garnet lherzolite and serpentinised harzburgites from Pohorje, Eastern Alps, Slovenia

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The presence of former mantle rocks in continental crust sections from orogenic terrains may give important clues on the tectonic history of the region. The Slovenska Bistrica ultramafic complex (SBUC; Eastern Alps, Slovenia) occupies the south-eastern most part of the Pohorje mountains, which represent an extruded piece of continental crust subducted during the Cretaceous Eo-Alpine orogeny. The SBUC is the only known occurrence of ultramafic rocks within this nappe system apart from a few dismembered pieces in the near vicinity. The main body is composed of serpentinised harzburgites with local occurrences of garnet lherzolite, and as a whole it records a complex history of melt depletion, metasomatism, subduction and exhumation.

The harzburgites are highly depleted following melting within the spinel stability field, as exemplified by high whole-rock MgO, low Sc, LuN, and GdN/YbN, and high Cr# of Cr-spinel. Fluid-immobile trace elements (Th, Ti, Zr, Sc, V, HREE) correlate well and are consistent with a melt depletion trend. Other incompatible elements show little correlation and are probably strongly modified by the serpentinisation process. However, comparable LREE enrichment of all samples suggests that this piece of mantle was already metasomatised by melts or fluids before serpentinisation. In lherzolite CaO and Al2O3 contents were high enough to form garnet after spinel thus recording an UHP stage (4 GPa, 900°C) not visible in the harzburgites. Because of the evidence of an earlier lower pressure stage within the spinel stability field, the SBUC represents a piece of subducted mantle.

As subduction was intra-continental, the most obvious source of the SBUC is subcontinental lithosphere from the overlying continental slab, but this is in conflict with the strongly depleted nature of the rocks. Alternatively, it may have been part of the oceanic lithosphere after rifting of the N Apulia passive margin. This fits better with the geochemistry of the rocks, including negative Ce and positive Li and U anomalies - typical of weathering at the sea floor and commonly observed in abyssal peridotites. However, it is unclear how much these features are affected by serpentinization processes. A third possibility is that the SBUC represents subduction-modified depleted mantle from the hanging wall composed of S Apulia subcontinental mantle. A Re-Os isotope study is underway to obtain additional constraints on the origin of this piece of mantle.

Investigating the source of continental flood basalts: Insights from intra-lava flow osmium isotope variations

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Geochemical debates over the source of continental flood basalts usually assume that individual lava flows represent compositionally uniform and rapidly erupted products of large well-mixed magma reservoirs. This study presents an examination of intra-lava flow chemical and isotopic variations in relation to eruption sequence, which provide insights into the mechanisms of flood basalt petrogenesis.

The temporal variations implicated by the pahoehoe inflation model (Self et al. 1997) have been applied to a flow field, formed by a single flood basalt eruption, both vertically within each sheet lobe and laterally between the constituent lobes. This framework provides insight into sequential magmatic evolution during the timescale of one eruption.

We present results from a 2,660 km² flow field formed during a single eruption in the Columbia River Basalt Province, USA. Our findings show that small but statistically significant major and trace element intra-lobe variations were present at the time of emplacement e.g. MgO 3.09-4.55 wt%, Ni 17.5-25.6 ppm, indicative of fractional crystallisation. However, such data does not reveal other processes such as source variations and/or crustal contamination. In contrast, Re-Os isotopes indicate progressive crustal contamination of the magma over the timescale of a single flood basalt eruption. Initial 187Os/188Os ratios range from 0.287 (lava core) to 1.569 (lava crust) within a single 35m thick sheet lobe. These values are more radiogenic than any known enriched sources (normative mantle ~0.127, HIMU ~0.15) consistent with previous data for CRBs (Chesley and Ruiz, 1998) indicating that neither an enriched source nor the SCLM can be the cause of the radiogenic values. Preliminary data for an individual lava from the Deccan Traps indicate a similar process of contamination. These data have important implications for flood basalt genesis and the nature of their source, and indicate that uniformity of individual lavas cannot be assumed.

References
Large-scale matrix diffusion in crystalline rocks revealed by natural Cl, $\delta^{18}$O and $\delta^2$H tracers in pore water

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Matrix diffusion in crystalline rocks of low permeability has long been proposed as a retardation mechanism in radionuclide transport. However, its extent and efficiency under the conditions of underground repositories (ca. 400-700 m depth) have been difficult to define.

As part of the Swedish site investigation programme at Laxemar-Oskarshamn a continuous drillcore has been sampled, extending from a transmissive fracture zone into the low-permeability rock matrix at a depth of 112 m. Special sample-handling procedures allowed the rock to be retrieved in its saturated state and allowed its in situ water content to be measured, without modifications by drilling fluid or stress release. Pore-water chloride contents were then derived from out-diffusion experiments and the isotope composition from the diffusive isotope equilibration technique. The Cl time-series data from these experiments can be described by radial diffusion indicating that diffusion might well be important under in situ conditions. The chloride contents of the pore water are similar to that in the fracture water at the fracture-matrix interface. They describe a complex curved profile over the first 6 m of the drillcore, but then remain at background values (Figure 1) over several decametres (towards the next underlying conductive fracture). The $\delta^{18}$O and $\delta^2$H values show similar profiles. The variations in pore-water Cl, $\delta^{18}$O and $\delta^2$H reflect changes in the fracture-water composition over geological time, which can be correlated with the local hydrological history during the Holocene and Pleistocene.

Taking account of this history, the shapes of the profiles suggest diffusion-dominated transport. This indicates that in crystalline rocks, matrix diffusion occurs over decametres even under present-day conditions.

Figure 1: Changes in Cl and $\delta^{18}$O of pore water in crystalline rock as function of distance to a transmissive fracture.

Stable isotope geochemistry of amphiboles from alkaline igneous complexes

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It is now well established that the hydrogen isotope composition of amphiboles from alkaline complexes can have an extremely wide range, but also extremely low $\delta^D$ values (between ~227 and ~70‰). It has been suggested that the extreme depletion in D is controlled by internally buffered magmatic processes that may be unique to highly peralkaline magmas (Marks et al., 2004). This possibility is further explored through a complete mineralogical and geochemical characterization of selected minerals from a number of well-described alkaline complexes, including examples from Greenland, the Kola peninsula of Russia, and NW Namibia.

Amphiboles selected have compositions typical for calcic, sodic-calcic, and sodic amphiboles. The O-isotope compositions, in contrast to those for hydrogen, are quite homogeneous and are compatible with amphibole formation from mantle-derived magmas (values close to 5.5‰). In the amphiboles, the influence of Fe$^{3+}$/Fe$^{2+}$ on $\delta^D$ values is negligible ($R^2_{Fe^{3+}/Fe^{2+}} = 0.3914$; $n=17$) and the control of iron content is small ($R^2_{Fe \text{ content}} = 0.6558$; $n=23$). Our data do not support interaction with a highly reducing fluid as a cause of the low $\delta^D$ values. However, a significant correlation ($R^2_{Na+K} = 0.8196$; $n=23$) between the alkali content and $\delta^D$ value from the Ilímaussaq complex is observed. These data suggest that H-isotope compositions are controlled by a combination of Fe-content but more notably the alkali-element contents in the amphiboles, implying complex fluid-mineral equilibration in these highly alkaline magmas.

References
Revisiting the elemental composition of Enstatite chondrites
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The enstatite chondrites are a group of metal- and sulphide-rich meteorites with a highly reduced composition. They have an oxygen isotope composition that is indistinguishable from that of the Earth-Moon system [1], and partly on this basis have been cited as model precursors for the Earth [2]. However, it has proven difficult to reconcile the bulk elemental abundances of enstatite chondrites with those of the Earth. In order to explore any compositional link that enstatite meteorites may have with other planetary bodies, a good understanding of the range of their compositions is required. Previous work has used a variety of methods to determine the minor and trace element composition of these materials, with individual work often focusing upon either a restricted range of elements and/or a restricted number of meteorite samples. The highly reduced nature of the meteorites and the chemical reactivity of some of the meteorite components implies that only samples from falls should be considered for analysis. This, inevitably, makes drawing any conclusions from their bulk compositions somewhat difficult.

Here we present compositional data from a comprehensive range of EH and EL meteorite falls, using a quadrupole ICP-MS technique for trace element analysis, together with ICP-OES for the major elements. The aim is to provide an internally consistent data set for a large elemental range, such that better constraints may be placed both upon the models of enstatite chondrite formation, and their genetic relationship with other planetary bodies.

References

Experimental growth of biofilms for studies on the impact of microbes on transport processes in groundwater systems
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Introduction
The effect of biofilm growth on the physical and chemical properties of rocks and sediments, and in particular how this might influence hazardous and radioactive waste transport, is poorly understood. A review of existing work on microbial transport has shown that the impact of rapid change of pH or ionic strength and valency on established biofilms are least well understood. This work builds upon a previous project (Redox Experiment in Detailed Scale – REX), investigating rock-water and microbial interaction using diorite and groundwater from the Åspö Hard Rock Laboratory, Sweden.

Experimental test work
Initial aims were to develop methodologies for biofilm cultivation and to observe their growth. A flow-through cell was built, which was packed with crushed and milled diorite from Åspö. Artificial groundwater adjusted to pH 7.5, prepared to simulate the geochemical conditions at Åspö, was continuously circulated through the cell, and the system was inoculated with a bacterium Pseudomonas aeruginosa. After 4 days, the flow cell showed visible signs of a developed biofilm, the presence of which was confirmed by staining using Acridine orange, fluorescent stain.

Conclusions
Initial experiments have shown that it is possible to grow a biofilm within a few days on a diorite substrate over which artificial groundwater containing minimal nutrients was circulated. Future investigations will focus on physical effects of rapid changes in pH, nutrient levels, and ionic strength on established biofilms as well as the effect of phage on biofilm development. Therefore, an experimental set-up of two columns, one with and one without biofilm would seem to be the most suitable method to trace physical and chemical property changes.

References
Impact of U-mining tailings on water resources in Mailu-Suu (Kyrg)

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From 1946 till 1968, uranium ore was mined and processed in the region of Mailu-Suu (Kyrgyz Republic). The residual waste rock and tailing material (≈3 Mio. m³) has been provisionally deposited in the Mailu-Suu valley in close vicinity of rivers and instable slopes, and may be eroded and mobilized through landslides and floods.

Findings presented here are dealing with the contamination state of the local water resources, based on 55 samples including seepage, ground and surface water. Analytical methods comprise IC, ICP-OES, ICP-MS for determining the hydrogeochemistry, γ- and α-spectrometry characterizing the radiolgy of the sampled water.

Results and Discussion

Aggravated by the complex and unclear hydrogeological situation, this study reveals local infiltration and extensive contamination of river and shallow quaternary aquifer by uranium and other contaminants. Major pollution source seems to be seepage water leaking from tailings with up to 36 mg/L U and the tributary river Kulmin-Say containing 170 µg/L with a flow rate of ≈10 L/s. More than half of the samples fail the chemotoxic WHO-guideline for drinking water for U (15 µg/L). Pollutants transport downstream (N→S) is evident in both shallow aquifer and Mailu-Say river. Hydrochemical fingerprints and multivariate statistics reveal their interconnection and allow genetical clustering of groundwater samples of uncertain origin.

In sampled water, uranium is not present in radioactive equilibrium relative to the uranium-radium decay chain. The activities of uranium strongly predominate relative to their daughter nuclides indicating transport processes of dissolved uranium, likely as carbonylated species. The measured mass and activity concentrations of uranium fit well considering that 1 µg U of natural isotopic composition corresponds to 12.45 Bq of U-238. Combining all data, the radiation dose of one example well possibly used for drinking purposes is estimated to exceed the EU guideline value of 0.1 mSv/a.

Conclusions and Outlook

Radiocuclides and other contaminants from U-mining activities have affected the water resources in Mailu-Suu and may be transported down to the Fergana Basin (Uzbekistan). Beyond design of a monitoring network and awareness rising of the local population, future investigations focus on the transport pathways and behaviour of uranium, incl. the role of deep aquifers with flooded U-mines and the characterization of solid and dissolved U-species.

Isotopic constraints on picritic magmatism, Iceland

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New Sr, Nd, Pb and Hf isotope data are presented for a suite of 19 picritic samples from Iceland; Os and He isotope data for the same samples are presented by Brandon et al. (2007). The samples display compositions typical for neogene magmatism in Iceland; 87Sr/86Sr = 0.70290–0.70318, 143Nd/144Nd = 0.51230–0.51315, 206Pb/204Pb = 18.05–18.97, 207Pb/204Pb = 15.43–15.52, 208Pb/204Pb = 37.71–38.53, 176Hf/177Hf = 0.28315–0.28333. The samples span the spectrum from depleted to enriched samples (La/Sr = 0.31–1.83) and have isotopic and trace element signatures characteristic for Icelandic compositions with negative Δ207Pb (-0.3 – -3.5, excl. 1 sample), positive Δ208Pb (3.2 – 31.2, excl. 3 samples) and positive ΔNb (0.01–0.37).

Typical correlations are observed between various isotope systems (e.g. Sr-Nd, Pb-Nd, Pb-Pb etc.) and are consistent with the involvement of multiple source components. Of particular note are correlations between 3He/4He and 187Os/188Os and increasing 176Hf/177Hf, and increasing 3He/4He and 187Os/188Os with increasing 206Pb/204Pb and 208Pb/204Pb. These correlations indicate that the enriched component(s) of the Icelandic system, with radiogenic Pb isotope signatures indicative of high time-integrated U/Pb and Th/Pb, are also characterised by a non-radiogenic high 3He/4He signature. These observations are inconsistent with the high 3He/4He signature being the result of incorporation of a U-Th-poor component from the upper mantle (e.g. depleted lithosphere, olivine-rich domains) as these should also be expected to have non-radiogenic Pb isotope systematics.

In detail, two groups of data can be seen in plots of He, Pb and Hf isotopic compositions, with a subordinate group from the SW region of the western rift zone having high 3He/4He for a given 206Pb/204Pb. This provides evidence for the contribution of at least three components to magmatism in Iceland, and may suggest a spatial variation in these components beneath Iceland.

Reference

Simultaneous determination of mass-dependent isotopic fractionation and radiogenic isotope variation of Sr in geochemical samples

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In this study, we have developed a novel method of precise isotopic analyses to investigate both mass dependent isotopic fractionation and radiogenic isotopic variation of Sr using MC-ICP-MS. Isobaric interferences and matrix elements were chemically eliminated by an extraction chromatography using Sr spec. resin. We examined Sr isotopic fractionation during the separation procedure. The result of the test demonstrated that Sr isotopes were measurably fractionated on the separation process. The cumulative Sr isotopic value of the eluent indicate that no detectable isotopic fractionation of Sr was found through a few percent loss of Sr during the chromatographic separation.

In order to examine the possible isotopic fractionation of Sr in nature, we analyzed Sr isotopic compositions of GSJ igneous rock standards (Basalt, JB-1a; Andesite, JA-2; Rhyolite, JR-1), GSJ carbonate mineral standards (limestone, JLS-1; Dolomite, JD-1; Coral, JC-1; Giant clam, JCt-1) and seawater samples. No Sr isotopic variation was found among the igneous rock standards, whereas the resulting δ88Sr of carbonate mineral standards showed lighter Sr isotopic composition than that of the seawater, suggesting that lighter Sr isotopes could preferentially co-precipitate with Ca as a carbonate mineral. The resulting δ88Sr of recent carbonate samples (JCp-1, JCt-1) were identical with that of seawater samples. These results imply that simultaneous determinations of mass-dependent isotopic fractionation and radiogenic isotope variation of Sr could become a new tool for geochemical research field.

Stable isotope geochemistry of Nd in various terestrial rocks

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We have developed a precise Nd stable isotope measurement technique by the combination of TIMS and double spike method to examine the possible Nd stable isotopic variations in terrestrial and extraterrestrial materials. We will report our preliminary results of Nd stable isotope variations on 9 reagents and 8 rock samples including basalt, granite, rhyolite, calcite and dolomite. All the results are expressed as the relative deviations from the isotopic standard reagent JNd-1 in epsilon notation. The reproducibility of ε146Nd was estimated from the repeated analyses of the standard and is ± 0.3 (2SD, n=11).

Six igneous rock samples analyzed so far show no variation in Nd stable isotopic compositions instead of variations in their REE abundance pattern. The average ε146Nd is -0.2, which is slightly lower than that of JNd-1 but within the external 2SD range. Since isotope fractionation effects can be neglected in high-temperature equilibrium reactions, the average isotopic composition of the igneous rocks probably represents the bulk earth Nd isotopic composition. The GSJ reference rock sample JLS-1 (calcite) also has Nd isotopic composition indistinguishable from the igneous rocks.

The isotopic composition of the GSJ reference rock sample JD-1 (dolomite) is clearly different from the other samples ε146Nd = 2.1). Our observation confirmed the previous report using MC-ICP-MS (Ohno and Hirata, 2005). There are three possible scenarios to account for the heavy Nd isotopic enriched Nd in JD-1 dolomite. The first is that the isotope fractionation took place during the re-crystallization reaction of calcite (dolomite precursor), when most of the REEs have included into the calcite from seawater. The second is that the heavy Nd is inherited from the ancient seawater and no isotope fractionation have occurred during the REE concentration by the calcite re-crystallization reactions. The third is that Nd isotopes are fractionated during the dolomitization reaction of the precursor calcite. Since JD-1 and calcite from the same formation both have the seawater-like REE abundance pattern and similar REE concentrations indicating that the REEs of JD-1 are not affected by the dolomitization reaction (Miura et al. 2004), the third scenario is unlikely.
Late Archean molecular fossils from scientific drill cores record the antiquity of microbial diversity

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The Agouron Griqualand Drilling Project has recovered a series of cores from the Neoarchean-Paleoproterozoic sedimentary cover of the Kaapvaal Craton, South Africa. With molecular fossil (biomarker) analysis in mind, this scientific drilling effort took measures from the outset to minimize the potential for organic contamination of the core material. We present the results of organic molecular biomarker analyses of sedimentary rocks from the Transvaal Supergroup, ca. 2.67 to 2.46Ga.

Bitumens from the Agouron cores consistently show syngeneric characteristics over more than 2500m of stratigraphy, despite the very low quantities of hydrocarbon extractable from the Transvaal rocks. These characteristics include high thermal maturity, absence of biomarkers from later-evolving organisms, correspondence between more- and less-matrix-associated bitumen pools, and sharply contrasting composition of overlying strata in the same core. Furthermore, comparisons of biomarker contents in stratigraphically correlated intervals from diverse lithofacies in two boreholes separated by 24km provide strong support their syngenetic nature.

The suite of molecular fossils identified in the late Archean bitumens includes hopanes attributable to bacteria, potentially including cyanobacteria and methanotrophs, and steranes of eukaryotic origin. The presence of fossils of steroids, whose synthesis requires molecular oxygen, suggests that aerobic processes (involving the production and consumption of O2) were underway by the late Archean. This molecular fossil record provides evidence for an origin of the three principal Domains of cellular life in the Archean Eon.

The 187Os/188Os of the convecting upper mantle: An update

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What is the proportion of recycled oceanic crust that remains isolated within the mantle? Osmium isotopic data relevant to question have been accumulating for more than 40 years. Seminal papers that attempted to estimate the 187Os/188Os of the convecting upper mantle utilized data from Os alloys derived dominantly from upper mantle assemblages to conclude that the upper mantle evolved with a generally “chondritic” Re/Os. This conclusion is too vague to be used to good advantage with respect to oceanic crustal recycling and isolation, yet we have not advanced much beyond it.

Studies of abyssal peridotites, MORB and ophiolites have revealed considerable complexity in the Os isotopic evolution of the convecting upper mantle. For example, although the Os isotopic compositions of MORB and abyssal peridotites overlap, almost all MORB is more radiogenic than abyssal peridotites. Although some of the disparity may be tied to seawater-rock interactions, it is now clear that at least some MORB sources evolved with higher Re/Os ratios than are represented in most abyssal peridotites. Further, the 187Os/188Os of abyssal peridotites are quite variable. Some of these heterogeneities relate to long-term Re/Os variations in the mantle, not seawater alteration. Studies of ultramafic sections of ophiolites have provided complementary data to those from abyssal peridotites and MORB, but individual ophiolites are isotopically heterogeneous and ophiolite materials may not always record primary mantle compositions.

One of the most important recent observations regarding this topic is the documentation that even small domains within the convecting upper mantle develop and retain considerable Os isotopic heterogeneity. This is most clearly revealed in datasets for large numbers of Os-Ir-Ru alloy grains weathered from individual ophiolites, and also in suites of abyssal peridotites from discrete locations. Peridotites from the 6 Ma Taitao ophiolite (Chile) show correlations between melt depletion indicators, such as Mg# of olivines, and 187Os/188Os. This type of correlation has long been observed in samples from the subcontinental lithospheric mantle, but not directly for the convecting upper mantle. Collectively, these results suggest that some chemical heterogeneities related to melt extraction, present at the cm3 to km3 scale, were created and preserved in the upper mantle >1.5 Ga ago. This means that analysis of a limited number of samples from a given location (e.g. an ophiolite) may not yield a meaningful average composition. Based on consideration of the worldwide database for abyssal peridotites and ophiolites, the 187Os/188Os of the convecting upper mantle is ~0.125 to 0.126. This ratio, in comparison to current estimates for primitive upper mantle (>0.129) suggests that mafic slabs that are isolated from the convecting mantle may comprise 5 to 8% of its mass.
Insights into copper isotope fractionation during the oxidative phase transition of chalcocite, using time-resolved synchrotron X-Ray diffraction

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The focus of this research is to understand Cu isotope fractionation associated with the oxidative dissolution of secondary copper minerals. As previously shown, chalcocite (Cu\textsubscript{2}S) transforms to covellite (CuS) with a series of intermediate phases by the oxidation of Cu\textsuperscript{+1} to Cu\textsuperscript{+2} and the loss of Cu from the mineral structure. Mathur et al. (2005) have demonstrated that the Cu isotope composition of the solids becomes lighter during this reaction. In this study, we have combined time-resolved X-ray diffraction with Cu isotope measurements to monitor changes to Cu-S mineral structures and the concomitant isotopic fractionation of Cu.

Pure, naturally occurring chalcocite powders were placed in flow-through capillary reaction cells and exposed to various concentrations of aqueous ferric sulfate for up to 2 hrs. Real-time diffraction data were collected at intervals of 2 min at beam line X7B, National Synchrotron Light Source, using a MAR345 imaging plate. The $\delta^{65}$Cu values of the leached Cu as well as the starting and final powders were measured using a Finnigan Neptune multi-collector inductively coupled plasma mass spectrometer.

The powder diffraction data revealed that chalcocite passes through a complex series of partially oxidized intermediate phases during its transformation to covellite using $10^{-2}$ M ferric sulfate. The untreated chalcocite powder had a $\delta^{65}$Cu value of 0.46±0.12‰ and the residual covellite had a $\delta^{65}$Cu value of 0.13±0.12‰. The $\delta^{65}$Cu value of the leachate sampled after 10 min. was 2.46±0.12‰. During the reaction $\delta^{65}$Cu values of the leachate decreased over time. The final leachate sample had $\delta^{65}$Cu values of -2.55±0.12‰. The most significant decrease in $\delta^{65}$Cu values of the leachate occurred during the transition of chalcocite to anilite and corresponded to the period of highest copper yield.

References

Towards an understanding of biosilicification mechanisms: Nucleation of amorphous silica on organic surfaces

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Biochemical investigations have begun to yield information about structural and chemical properties of organic macromolecules involved in biosilicification processes. However, the mechanisms by which these molecules mediate biosilica formation remain unclear. Insights into how mineral formation occurs within living organisms can be gained by conducting experimental studies with simple model systems that emulate key features of biological systems. We employ a novel AFM-based approach to measure the dependence of amorphous silica nucleation kinetics on the chemical and structural nature of the underlying substrate.

The rate of silica nucleation was measured on COOH and mixed COOH/NH\textsubscript{3}\textsuperscript{+} surfaces, under conditions that simulate current views of the chemical environment within silica deposition vesicles of major diatom species (ambient temperature, pH = 5.0, NaCl = 0.1 mol/kg). Markedly faster rates were measured on mixed COOH/NH\textsubscript{3}\textsuperscript{+} surfaces than on either of the end-member films, suggesting that these two functional groups work in concert to promote the formation of silica at these interfaces. Differences between substrate-specific nucleation rates were determined to be controlled largely by kinetic factors rather than thermodynamic drivers. Further experiments with micro-patterned COOH and NH\textsubscript{3}\textsuperscript{-} terminated surfaces also showed that the initial stage of silica deposition occurred at the COOH/NH\textsubscript{3}\textsuperscript{+} interface. Although silica nucleation was not initially observed on purely aminated surfaces, the introduction of orthophosphate triggered the deposition of silica on these surfaces as well.

These results give insight into how silica mineralization may be controlled by organisms like diatoms. Molecules that have been identified as part of the silification mechanism either posses regions of locally concentrated positive and negative charge (silaffins), or require the presence of specific counterions such as phosphate to control silica deposition (polyamines). Phosphate anion has been previously implicated as having a probable role in controlling the self-assembly of these macromolecules into a template for silica deposition. Sites on the organic matrix that have phosphate and amine moieties in close proximity are likely to be points of initial silica deposition. These sites are also probable contact points between the constituent macromolecules in the matrix; hence, deposition of silica in these locations likely serves to cement the molecular elements of the organic matrix together.
Ascent, degassing, crystallization and eruption of H$_2$O-rich mafic arc magma: A melt inclusion perspective

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Mafic cinder cones are common in subduction-related volcanic arcs. Such cones exhibit a wide range of eruptive styles and are often violently explosive, but the mechanisms driving explosive cinder cone eruptions are still poorly understood, as is the nature of their underlying plumbing systems. Melt inclusions in phenocrysts from tephra deposits provide a record of ascent, degassing and crystallization processes beneath these cones and show evidence for temporal changes in plumbing systems that mirror changes in eruptive style and magma composition.

We have analyzed major elements and volatiles in olivine-hosted melt inclusions from 14 cinder cones in the central and western Trans-Mexican Volcanic Belt (TMVB), including the historic eruptions of Paricutin and Jorullo. Melt inclusions from each cone have highly variable H$_2$O (typically <1 wt% to maximum values of 4 to 5.5 wt%) and CO$_2$ (<50 to 5000 ppm), corresponding to crystallization pressures of <100 bars to ~5 kbars. This indicates that olivine crystallized from variably degassed melts over a range of depths extending from the mid-crust to very shallow levels. The highest CO$_2$ contents (~5000 ppm) are found in potassic minettes and basanites from the western TMVB, whereas values ≤500 ppm are typical of calc-alkaline basalts and basaltic andesites. Modeling of major element variations and comparison to phase equilibria demonstrate that olivine crystallization was driven by H$_2$O loss from melts during ascent. Olivine-melt geothermometry suggests temperatures of 1100-1200°C for these melts at depth. However, such geothermometers must be applied with caution because degassing-induced crystallization during ascent occurs increasingly below the equilibrium liquidus temperature as the melts ascend.

A puzzling feature of the inclusion data is that CO$_2$ does not decrease as rapidly with degassing as predicted by degassing models. A likely explanation involves open-system degassing in which relatively CO$_2$-rich vapor fluxes upwards through the conduit from degassing magma at greater depths. The high magmatic H$_2$O recorded by the inclusions is sufficient to drive explosive violent strombolian eruptions and produce vesicular ash and lapilli. Decreases in olivine crystallization depths over time at some cones reflect evolution of the conduit systems. During early stages, olivine crystallizes over a range of depths and is re-entrained by ascending batches of magma. In later stages, a dike-like storage region of degassed, crystallizing, and more differentiated magma forms at shallow depths beneath the cone.

Silicate weathering in anoxic marine sediments

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Two 25 m long sediment cores were taken at the continental slope of Sakhalin. Pore fluids and solids were analyzed to determine the down-core changes in dissolved cations, total alkalinity and particulate metal concentrations. The pore fluids showed consistent enrichments in dissolved Mg, Na, K and alkalinity while the particulate Mg/Ti and Na/Ti ratios decreased with sediment depths. A numerical transport-reaction model was applied to derive rates of silicate weathering from both pore water and solid phase data. The rates derived from pore water data were as high as the rates derived from the independent solid phase data. The depth-integrated rates expressed in terms of CO$_2$ consumption per area and time are close to the average rate of silicate weathering on land. These results imply that silicate weathering in anoxic marine sediments may be as high as continental weathering rates. The pore water modeling further indicates low pH values (6.2 – 6.8) and high concentrations of total dissolved inorganic carbon (100 – 200 mM) in the deeper methanogenic section of the sediment cores. UV adsorption measurements suggest an increase in dissolved humic acid concentrations with sediment depth. Silicate weathering rates were low within the upper sulfate-bearing sediment section and strongly increased below the sulfate penetration depth. It thus seems that silicate weathering may be promoted by low pH values and high concentrations of dissolved inorganic and organic carbon in the methanogenic zone. Most of the silicate minerals deposited in the slope sediments were delivered by the Amur River. The Amur River Basin is characterized by low temperatures and permafrost conditions that may suppress the rates of continental weathering in the drainage area. Our results thus suggest that silicate weathering is shifted from the continental to the marine realm if continental weathering is inhibited by unfavorable climatic conditions and if the silicate minerals are deposited in anoxic marine sediments. This would imply that the negative feedback between silicate weathering and climatic conditions may not be as strong as commonly believed since silicate weathering is not limited to continental areas. Our results further imply that the sequestration of CO$_2$ in marine sediments could be a favorable option since CO$_2$ may be rapidly neutralized in marine sediments.
Methylated arsenic-sulfur compounds in ground water

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Arsenic (As) speciation was determined by anion-exchange chromatography-inductively-coupled plasma-mass spectrometry (AEC-ICP-MS) in ground waters from a site impacted by methylated arsenic biocides. Aside from the expected four conventional As species arsenite, arsenate, monomethylarsenite (Me1As(V)), and dimethylarsenate (Me2As(V)), up to 9 additional As species were encountered. Among these, the five major species were the As(III) compound monomethylarsenite Me1As(III), and the four thio-substituted methylated As(V) compounds monomethylmonothioarsenate Me1As(V)-S1, monomethylidithioarsenate Me1As(V)-S2, dimethylmonothioarsenate Me2As(V)-S1 and dimethylidithioarseninate Me2As(V)-S2. All five compounds were identified by retention time matching to synthesized standards, and the last four identifications were additionally confirmed by electrospray-tandem mass spectrometry (ES-MS-MS) in collected AEC fractions. None of these As species have been identified in ambient waters before.

These novel As species not only occurred in most of the collected ground water samples, but usually also collectively constituted a major fraction of the total dissolved As concentration (TDAs) present. Average and maximum (in parentheses) relative concentrations measured (expressed in % of TDAs) were 5.3 (39.0) for Me1As(III), 10.2 (43.1) for Me1As(V)-S1, 2.1 (15.1) for Me1As(V)-S2, 3.1 (10.8) for Me2As(V)-S1 and 1.7 (9.0) for Me2As(V)-S2. The highest fractions of metabolites of the original biocides Me1As(V) and Me2As(V) were found in samples with intermediate TDAs concentrations, i.e. between the original emission site and the edge of the propagation plume, indicating that these novel metabolites play a role in the environmental transport and fate of the As biocides at this site. Although Me2As(V) and its metabolites were generally present at lower concentrations than Me1As(V) and its metabolites (as a result of the emission history), the fraction of dimethylated metabolites was higher on average than that of monomethylated metabolites, indicating that Me2As(V) is more reactive in the observed transformations than Me1As(V).

A preservation study of six selected samples over a period of 24 weeks showed that the novel As species were reasonably stable in unpreserved samples, but had a tendency to convert back to their original precursors, Me1As(V) or Me2As(V), respectively, over time. Cryofreezing on-site generally seemed to yield the best As speciation preservation, but unpreserved samples yielded comparable results. Acidification caused immediate and significant changes in As speciation, and must consequently be avoided for sites where these novel As species are or may be present.
How transition metals affect algal external carbonic anhydrase
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Study aims
1) Effect of transition metals on the activity of external carbonic anhydrase (CAe) of alga C. reinhardtii; 2) The ways of transition metals affecting alga CAe.

Results and discussion
Our results are shown in the table below. The data have demonstrated that the extent of transition metals influencing CAe is different and the magnitude in which these transition metals affect CAe depends on the concentration. Transition metals influence the activity of CAe by two ways: (1) directly operating on CAe at cellular surface, (2) indirectly interfering in the metabolism of CAe in algal cell.

<table>
<thead>
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<th>20µMOL/L BEFORE</th>
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<td>99.0±3</td>
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<td>Co</td>
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<tr>
<td>Zn</td>
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<tr>
<td>Cd</td>
<td>100.9±1</td>
<td>136.8±2</td>
<td>59.7±1</td>
<td>81.5±3</td>
</tr>
</tbody>
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Significant difference # between metal-excessive (20µmol/L or 100µmol/L) and normal culture condition and *between "Before" and "After" (Tukey, P<0.05). "Before" is the relative activity of CAe from C. reinhardtii that was exposed to transition metals for 24 hrs before extracting; "After" is the relative activity of CAe that was exposed to transition metals after being extracted from C. reinhardtii.

Conclusions
Effect of transition metals on CAe is species-specific. Cu and Ni affect CAe by way (1); Zn by way (2); Cd by way (1) and (2); and Mn, Fe, and Co at least by way (1).

Acknowledgements
This study was financially supported by National Natural Science Foundation of China (Grant Nos. 40603006 and 90610037) and by Chinese Academy of Sciences through the International Parership Project.

References

To harmonize the water resources system of Lake Taihu basin in China using circular economy notion
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Lake Taihu basin is located at the south end of the Changjiang River Delta in China. In recent years GDP and finance incoming of this place is almost more than 10% of the total amount of the country, accounting only 0.4% for the areas and 3% for the population. It became one of the most developing and densely populated area. However, with the rapid economic development, the water resources system of Lake Taihu basin experiences a degenerate period from 1960. The water quality standard lowered 1 level every 10 years, and this is obviously more serious in recent years. How to control the degeneration in order to use water resources more scientifically and efficiently is drawing great attention among researchers both in China and overseas.

Figure 1: Variation over past 25 years of total nitrogen (TN) in Taihu Lake in China (unit: mg/L)

It is believed that, to restore the degenerated water resources system of Lake Taihu basin, circular economy notion must be used and insisted on. It relates to all kinds of measures such as law, administration, engineering, economy, science and technology, etc. Here only two of them are emphasized as following. (1) Integrated management of water resources. (2) Insisting on “3R Principle”, saving and using water scientifically.
Earliest geological record in North China Craton: 4079 Ma
Zircon U-Pb age

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Evolution of early solid Earth is vital in the research of Precambrian geology. To date rocks older then 4.0 Ga have been only reported from Acasta gneisses in the Wopmay Orogeny of Canada, with a formation age of 4016 Ma representing the oldest crust record in North America, and detrital zircon with age from 4.1 to 4.4Ga are reported only from Jack Hill of the Yilgarn Craton (Compston and Pidgeon, 1986; Wilde et al, 2001) and South Tibet of China (Wen et al, 2006). It is worth to note, all these detrital zircons Older than 4.05 Ga are from Gondwanaland.

Here we report a zircon with LA-ICP-MS U-Pb age of 4079±5Ma, from the south margin of the North China Craton (NCC). The zircon is a fragment with size of 100×150 µm have clear core-mantle structure. It is xenocrystal zircon from a 456.4Ma andesite from Caotangou group, West Qinling belt along the south margin of NCC. Moreover, a variety of age is dated from the inherited xenocrystal zircons, including 3233Ma, 2788Ma, 2739Ma and 2714Ma (table 1). It is an age set earliest crustal record in North China Craton: 4079 Ma.

<table>
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<tr>
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<td>C1TW.13</td>
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<td>C1TW.b02</td>
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<td>2714 ± 19</td>
<td>2638 ± 9</td>
<td>2541 ± 15</td>
<td>2517 ± 17</td>
</tr>
</tbody>
</table>

Table 1 U-Pb age of xenocrystal zircon from Caotangou group (Ma)

References
Compston W and Pidgeon R T. Nature, 321, 766~770
Wen C et al. Acta Geological Sinica, 80, 1249~1251

Solar wind Mg, Cr and Fe abundances in diamond-like carbon collector from Genesis mission

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The chemical composition of the Sun provides the reference standard for a wide variety of astronomical, cosmochemical and geochemical studies. To better determine the solar composition, the Genesis spacecraft collected solar wind at the L1 point in space for 27 months from December 2001 to April 2004. Prior SIMS analyses of Genesis samples have found discrepant results for the Mg and Fe solar wind fluences from different collector materials (Burnett et al., 2007). We measured Mg, Cr and Fe abundances in a diamond-like carbon collector (sample 60062) using a CAMECA NanoSIMS 50L ion microprobe. A 4 nA -16kV O+ primary beam of about 2 µm in diameter was rastered at 25×25 µm2 on the sample surface. Positive secondary ions were extracted from the central 25% of the rastered area and measured with a double-focus multi-collector mass spectrometer. Masses 12C, 24Mg, 25Mg, 52Cr, 54Fe and 56Fe were measured simultaneously to a depth of about 500 nm from the surface. 25Mg and 54Fe implanted standards were measured before, after and in between sample analyses to quantify relative fluences. We analyzed 10 craters with one showing abnormally low 12C count rates and thus excluded. One crater showed significant surface contamination of Fe and no Fe data could be deduced. We found a Mg fluence of 4.3±0.26×1012 cm-2 and an Fe fluence of 2.39±0.15×1012 cm-2 for sample 60062. These are in good agreement with previous measurement of the same samples by ims-6f (Burnett et al., 2007). As seen before, the fluences derived from diamond-like C are higher than those from Si collectors; an explanation for this discrepancy is still lacking but the results from Si are preferred. We also collected 52Cr depth profiles. Since no Cr implant standard was available at the time of our analyses, we estimated a Cr fluence of 2.4×1013 using the relative Cr/Fe sensitivity factors in diamond of Wilson (1995). This is 4 times higher than the photosphere value (Asplund et al., 2005). However, surface contamination for this sample is apparently a contributing factor. Analyses of additional elements and collector materials will be conducted to get accurate data of the solar wind composition and to understand differences between different collectors.

References
The quarterly radiocarbon record in a coral from Daya Bay

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This study established 14C, Sr/Ca and Mg/Ca time series for a coral (Porites) from Daya Bay in the South China Sea, covering about 10 years from 1994 to 2004. About 12 samples/year were analyzed for Sr/Ca, Mg/Ca. By contrast, only 38 samples (~4 samples/year) were analyzed for Δ14C, because of larger amount of sample required. The Sr/Ca and Mg/Ca series display clear seasonal signals. There is also an abnormal segment (from 1996 to 1998) in the Sr/Ca and Mg/Ca records, probably reflecting an El Nino event. Seasonal variations of Δ14C were observed between 1999-2004 (Fig. 1). The Δ14C is higher in winter (low sea surface temperature, SST), which descends sharply in summer (high SST). Considering that summer is the upwelling season, the seasonal variations in Δ14C are probably due to the low 14C abundance in the upwelling coming from the deep marine. Consistent with Sr/Ca, Mg/Ca, the seasonal variations in Δ14C is not significant between 1996-1998, possible also due to the El Nino event.

Figure 1: The result of the Sr/Ca and Mg/Ca ratio and Δ14C record in the coral from the Daya Bay.

Mineral compositions and geochemical features of Sanhe bauxite deposit in western Guangxi province

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2Faculty of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China

The resources of accumulation-type bauxite deposits developed in Karst topography in the west of Guangxi province are abundant, and the area serves as an important bauxite base in China. The Sanhe bauxite deposit of accumulation-type is a representative one in western Guangxi province; we collected more than 20 pieces of ore samples to study the mineral compositions and geochemical features of the deposit. By slice observation, powder X-ray diffraction analysis, electron probe microanalyser (EPMA) and the major elements testing, we have determined the mineral compositions and contents: Diaspore about 68%, clay minerals (mainly kaolinite and chlorite) 14%, titania minerals (rutile or anatase) 9%, ferric oxide and ferric hydroxide minerals (mainly goethite and hematite) 6%, and gibbsite 3%. The major elements testing mainly by X-ray Fluorescence Spectrometer and the energy dispersive analysis of scanning electron microscopy show that the content of Al, Fe, Si, Ti goes down in turn; The ores mostly consist of Al2O3, Fe2O3, SiO2, TiO2 and H2O+, counting up for 98.51~99.55% of the total mass; the content of Al2O3 is 43.37~73.27% with the average of 54.75%, the value of Al2O3/SiO2 falls into 3.51~18.01, and there is a negative correlation between Al2O3 content and SiO2 content. The ores’ CIA indexes are all greater than 98%, indicating the maturity of ore’s chemical composition is relatively high. Based the counts of the elements via EPMA line analysis, using the method of moments of multifractal, the spatial changes of elements Al, Ti are analyzed; choosing weight -5 ≤ q ≤ 5, it can be seen that the width of multifractal spectrum of element Ti is 0.46, and 0.04 of Al, which shows that Ti element distribution is much more random than that of Al. The content ratios of Al2O3 ( or TiO2) to Zr, Hf, Nb and Ta in the ores are basically the same as those of the underlying limestone of Permian Maokou formation, which means the two are homologous. The gross content of ore rare-earth elements (ΣREE) varies a lot, light rare-earth elements (LREE) are enriched and the anomalous positive Ce is pronounced; all above demonstrate that the ore deposit has experienced an oxidized leaching process.
The composition and texture constrains on micro-porosities of dolomite reservoirs, Tarim Basin, NW China

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Lower Paleozoic carbonates act as high quality reservoir rocks in the Tarim Basin, NW China. As they are mostly deeply buried up to ca. 5000 m, a long and complex diagenetic history must have happened. Consequently, the primary pore spaces of such carbonates were generally disappeared due to compaction and cementation. Thus, secondary porosities mainly caused by dissolution are important for petroleum accumulation as suggested by some authors. According to this research, the vuggy porosity is mainly resulted in diverse-dissolution between calcite and dolomite during burial. And the composition and texture of the dolomite have effective constrains on this process despite of the influence of geo fluids.

Based on the observation of cores and the analysis of logging data, the dissolved micro-porosities do not show an uniform occurrence. Specifically, it is well developed in the transition interval from limestone to dolomites of Lower Ordovician Yingshan Formation, where limestone, calcareous dolomite and dolomite are inter-bedded. It is common to observe intergrowth of the calcites and dolomite minerals, and the residue of calcite dissolution is obvious but the dolomites usually remain good rhomb crystals, which indicates that the calcite is much easier to be dissolved during burial than dolomite. And the dolomites act as framework to support the pores created by the calcite dissolution. Therefore, the composition of the carbonates has important influence on the formation of the porosities, and the calcareous dolomite could be good carbonate reservoir in the basin.

However, not all the calcareous dolomite could produce high porosity and permeability, and the carbonate texture must be also taken into account. By EPMA analysis and observation, the calcite minerals show different occurrences, some of which occur in the dolomite intercrystalline pores, and the others are scattered in the dolomite crystals. Then, the dolomites can be subdivided into three groups: intercrystalline filling type (type I), intracrystalline filling type (type II) and intra-and-intercrystalline filling type (type III). The calcite of type I is much easier to be dissolved than that scattered in the dolomite. It is suggested that the fluids could not easily dissolve the dolomite crystals so as to dissolve the calcite in them. As a result, the Type I and type III dolomites could become good reservoirs in this basin.

Rodinia mantle plume: New evidence from the ~825Ma komatiitic basalts in South China

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Mantle plume or superplume activities have repeatedly been invoked as a cause for the breakup of the Neoproterozoic supercontinent Rodinia, with supportive evidence including radiating dyke swarms, globally-synchronous anorogenic igneous activities, large-scale lithospheric doming and unroofing, and geochemical signatures similar to recent plume-related magmatism. However, identification of the Precambrian mantle plumes has been difficult owing to modifications by younger geological processes, and thus the lack of more diagnostic plume-induced petrological records(high-temperature melts), such as picrites and/or komatiites has been a major argument against the Neoproterozoic South China plume model.

We present here geochronological and geochemical data from a komatiitic basalt suite of pillowed lavas in central South China. SHRIMP U-Pb dating of zircons from an evolved member of andesitic composition within this suite indicates that these lavas were erupted at 823 ± 6 Ma. All but a few highly-evolved, crust-contaminated basaltic rocks are characteristically high in MgO (10.2-17.5 %), Ni (183-661 ppm) and Cr (677-1672 ppm), low in TiO2 (0.5-0.7%), Al2O3 (10.6-12.7%) and FeO T (7.4-10.5%). By removing the effect of ~5% olivine crystallization, the Yiyang primary magma has typical komatiitic compositions with MgO ≈ 20%, FeO T ≈ 11%, SiO2 ≈ 47%, TiO2 ≈ 0.48%, Al2O3 ≈ 10%, Ni ≈ 800 ppm and Cr ≈ 1780 ppm. Such a high MgO content in the primary melts implies a melt temperature of >1500°C, suggesting that the Yiyang komatiitic basalts should have been generated by melting of an anomalously hot mantle source with potential temperature (Tp) being 260 ± 50°C higher than the ambient MORB-source mantle, similar to that of modern mantle plumes.

Our identification of the 823±6 Ma Yiyang komatiitic basalts, generated by ~825 Ma mantle plume, provides for the first solid petrological evidence to constrain the controversy of the tectonic provenance of Neoproterozoic volcanism and sedimentation within the South China Block (the combined Yangtze and Cathaysian Cratons) with direct bearing on Rodinia reconstruction models.
U-Pb zircon age of the metapelites and granitic gneisses from Nyalam High Himalayan Series and their significance to the early Palaeozoic tectonic evolution

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(yanbinw@cags.net.cn)

The Nyalam High Himalayan Crystalline Series lies in Southern Tibet (roughly 28°N, 86°E) along the China-Nepal highway. These series include pelitic schists and gneisses, augen granitic gneisses, calcareous schists, marbles and quartzites that have been intruded by tourmaline-bearing leucogranites. There are not the isotope ages of the metapelites and the granitic gneisses from Nyalam High Himalayan Series in the Southern Tibet. The study of the zircon cathodoluminescence images from the metamorphic sedimentary rock show that there are complex textures. The dating results indicate Pan-African thermal events record in the zircon. A Pan-African periods deposition age (ca. 0.50 Ga) is inferred from the age of the metapelites. Zircon SHRIMP U-Pb dating yielded an age of 478.2±4.4 (2σ) Ma for the granitic gneisses.

U-Pb ages of detrital zircons show different peak (2.4 Ga, 1.6 Ga, 0.8 Ga and 0.50 Ga), suggesting that the detrital archive records the geological event history of its source region. The 0.5 Ga zircon grains with oscillatory zoning, uniform and concordant U-Pb systems, igneous Th-U ratios, are interpreted as primary magmatic zircons.

During the Pan-African periods, the northern part of India was affected by a Pan-African event. Numerous granitic intrusions dated at around 0.5 Ga are attributed to this event. The Pan-African event is marked by an unconformity between Ordovician continental conglomerates and the underlying Cambrian marine sediments. It is tempting to correlate the early Palaeozoic thermal event with the formation of the Gondwana supercontinent.

The protolith age of the High Himalayan metamorphic rocks is generally regarded to be Precambrian to early Palaeozoic. It seems plausible that the High Himalayan metamorphic rocks represent a minimum depositional age at ~0.5 Ga. 478 Ma granitic gneisses is assigned to an important orogenic event, the early Palaeozoic thermal event indicate that early Palaeozoic tectonism has played an important role in shaping the Himalayan orogen.

Acknowledgment
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Evidences of Ghronology and Isotopic geochemistry of Bogda Rift Closure and Regional Uplift, Xinjiang

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The Bogda Mountain, with Junggar basin on the north and Turpan-Hami basin on the southwest, is a part of the East Tianshan Mountains. The Dashtou-Shepikou area belong to the northern part of the eastern section of the Bogda orogen. Rhyolite of the Dashtou group gave a Rb-Sr age of 306.7±2.3Ma, and thus is suggested to have been produced at the uplifting stage following the closure of the Bogda rift. With ɛNd (t) of +5.30~6.40, (87Sr/86Sr)i of 0.703289~0.703496, (206Pb/204Pb)i of 15.524~15.567, 207Pb/204Pb), of 15.524~15.567 and (208Pb/204Pb), of 37.198~37.810, the rhyolite is comparable in Nd, Sr and Pb isotopes to the basalt and rhyolite of the Lower and Middle Carboniferous Qijiaoqiang formation that were formed during extension and subsidence of the Bogda intra-continental rift. Minor rhyolite accompanying a large amount of basalt in the Qijiaoqiang formation are thought to have been produced by fractional crystallisation of the basaltic magma, but a large quantity of rhyolite accompanied by very minor basaltic rocks precludes their formation by fractional crystallisation of basaltic magma. These data indicate that the rhyolite is similar in Nd-Sr-Pb isotopes to the rhyolite [1,2] that was formed by fractional crystallisation of the basaltic magma. The rhyolite of the Dashtou group is likely to have been derived from an underplated basaltic body by remelting of this body in response to mantle heating. Highly positive ɛNd (t), and negative ɛSr (t) (low 87Sr/86Sr initial ratio), and low Pb isotope ratios suggested that, like the pre-collision basalt of the Qijiaoqiang formation, the mantle magma underplated at the uplifting stage following the closure of the Bogda rift.

References
Mechanisms of arsenic scavenging by iron (hydr)oxides in anoxic environments

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\textsuperscript{2}European Synchrotron Radiation Facility (ESRF)

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Iron (oxyhydr)oxides widely occur in earth’s surface environments, including soils, sediments and aquifers. Owing to their large specific area, these minerals can adsorb efficiently trace elements, as arsenic. Microorganisms are able to (trans)form iron minerals, directly by enzymatic oxidation or reduction and indirectly by complexation to organic compounds, and thus potentially play an important role in the cycling of iron and of associated trace elements. For example, bio-reduction of ferric (oxyhydr)oxides is known to be responsible for arsenic contamination of some important groundwater resources throughout the world.

We will present recent investigations of model systems relevant of arsenic behavior in anoxic soils and sediments. X-ray Absorption Spectroscopy (XAS) and transmission electron microscopy, are used to elucidate the molecular scale mechanisms of arsenic immobilization upon reduction of arsenic bearing iron oxyhydroxides. The results suggest that, in the presence of a sufficient amount of iron in the system, adsorption and co-precipitation reactions of both As(III) and As(V) with Fe(II)/(III) minerals may delay arsenic release in anoxic environments. Other processes, including the progressive leaching of iron, may thus influence arsenic mobility in these environments.

Pb-Sr-Nd Isotopic Composition of I-Type and S-Type Granites in Eastern Segment of East Tianshan Belt

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This paper reports the Pb-Sr-Nd isotopic composition of I-type and S-type granites in eastern segment of east Tianshan Belt, China. Systematical research on Pb-Pb, Rb-Sr and Sm-Nd isotopes and the crustal growth age were made on six granitic intrusions in the eastern segment of middle east Tianshan belt. Pingdingshan augen-gneissic monzonitic granite, Back hill gneissic granodiorite and Tianhudong gneissic granodiorite, with (206Pb/204Pb)\textsubscript{i} of 18.356 ~ 18.426, (207Pb/204Pb)\textsubscript{i} of 15.697 ~ 15.867 and (208Pb/204Pb)\textsubscript{i} of 38.623 ~ 38.817 ε\textsubscript{Nd (t)} of -3.7 ~ -7.8, (87Sr/86Sr)\textsubscript{i} of 0.712632 ~ 0.718410; T\textsubscript{Nd(DM)}=1.81 ~ 2.05 Ga; Shalongdong monzonite, with (206Pb/204Pb)\textsubscript{i} of 18.015 ~ 18.182, (207Pb/204Pb)\textsubscript{i} of 15.426 ~ 15.591 and (208Pb/204Pb)\textsubscript{i} of 37.67 ~ 37.824, ε\textsubscript{Nd (t)} of +2.4 ~ +2.7, (87Sr/86Sr)\textsubscript{i} of 0.703710 ~ 0.703853, T\textsubscript{Nd(DM)}=0.82 Ga; Weiya manzonitic granite(center zone) and Weiya manzonitic granite (internal zone), with (206Pb/204Pb)\textsubscript{i} of 18.181 ~ 18.293, (207Pb/204Pb)\textsubscript{i} of 15.492 ~ 15.612 and (208Pb/204Pb)\textsubscript{i} of 37.804 ~ 37.973, ε\textsubscript{Nd (t)} of -0.9 ~ -1.0, (87Sr/86Sr)\textsubscript{i} of 0.704733 ~ 0.704831; T\textsubscript{Nd(DM)}=0.3 79-0.380Ga. In combination with the geological evidence and other geochemical date, it is believed that the granites in eastern segment of middle east Tianshan belt are composed of granitoids of different ages, different genesis, and different source materials. Pingdingshan augen-gneissic monzonitic granite, Back hill gneissic granodiorite and Tianhudong gneissic granodiorite belong to S-type granites or a transformation type and are mainly autoch-paraautochthonous Syntectonic granites characterized by gneissic structure. Shalongdong monzonite belongs to I-type granites or syntactic type derived from a differentiated mantle magma assimilated and contaminated with crustal materials. Weiya manzonitic granites possibly belong to I/S-type granites or an intermediate type between I-type and S-type. The only difference in I-type and I/S-type is that the Weiya manzonitic granites have a higher crustal component to mantle component ratio than that of Shalongdong monzonite.

Reference
Nd-Sr-Pb Isotopic Geochemistry and Rb-Sr age for Late Cretaceous volcanic rocks in King George Island, Antarctica

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Introduction and Analytical Method

The samples used in this study were all collected from the Half Three Point Formation of the Fildes Peninsula, King George Island, Antarctica and were attributed to the Upper Cretaceous formation. Analysis of Nd, Sr and Pb isotope compositions were performed on an automated multi-channel mass spectrometer VG 354 at Center of Modern Analysis, Nanjing University. \(87\text{Sr}/86\text{Sr} = 0.710224 \pm 0.00062 (2\sigma)\) for NBS987 standard. \(43\text{Nd}/144\text{Nd} = 0.512465 \pm 0.00012 (2\sigma)\) for BCR-1 standard. \(206\text{Pb}/204\text{Pb}=16.939\pm0.010, 207\text{Pb}/204\text{Pb}=15.489\pm0.029\) (n=20).

Discussion of Results and Conclusion

Fitting together of Rb-Sr isochron dating of the tuffite samples measured result: \(t=71.33\pm0.3\text{Ma}, \ 87\text{Sr}/86\text{Sr} = 0.70314\pm10 (2\sigma)\). Thus, the age date is reliable, which indicate the stratigraphic age of the volcanic sedimentary rock from the Half Three Point Formation, coinciding with that of date indicated spore pollen [1]. It is further proved that the activity of the volcanic eruption in Fields Peninsula began at least in the Late Cretaceous and not in the Tertiary age. With \(\varepsilon_{\text{Nd}}(t)\) of +5.53 ± 6.15, \(\left(40\text{Sr}/86\text{Sr}\right)_{\text{i}} \approx 0.703139 \approx 0.703148, \ (206\text{Pb}/204\text{Pb})_{\text{i}} \approx 18.028 \approx 18.316, \ (207\text{Pb}/204\text{Pb})_{\text{i}} \approx 15.329 \approx 15.462\) and \(208\text{Pb}/204\text{Pb}_{\text{i}} \approx 37.091 \approx 37.612\), the tuffites are comparable in Nd, Sr and Pb isotopes to the basalt of the Lower and Middle Carboniferous Qijiaojing formation [2] and some mid oceanic ridge basalt ratio, and these matters were chiefly derived from the depleted mantle.

References


Putting diffusive Re-Equilibration to work: Determination of entrapment pressures of olivine-hosted melt inclusions

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Silicate melts entrapped in olivine phenocrysts provide snapshots of melt generation, transport and mixing processes. The range of compositional and isotopic variability they preserve far exceeds that in erupted lavas, demonstrating partial melting is near-fractional and the upper mantle is heterogeneous. However, the conditions at which these diverse melts are aggregated to produce basaltic lavas remain an open question. Here we present a new method for determining the entrapment pressures of olivine-hosted melt inclusions and, thereby, constrain the conditions at which mantle melts aggregate prior to eruption. Application of this approach to melt inclusions from the Western Reykjanes Peninsula indicates that they formed at pressures of 2-4 kbars.

Entrapment pressures are determined by first heating inclusion-bearing olivines at the estimated liquidus temperature of the host lava for several days to produce local equilibrium between the inclusion and adjacent crystal. The major element composition of structurally intact inclusions and the adjacent olivine are then determined by electron microprobe. These compositions and the furnace temperature are used to solve for pressure using a new model for the partitioning of Fe and Mg between olivine and silicate melt, calibrated using both new experiments and those from the literature.

This approach has been applied to olivine-hosted melt inclusions from a picritic lava erupted on the Western Reykjanes Peninsula of Iceland. These inclusions have \(K_{2}O/TiO_{2}\) ratios of 0.1405±0.0003 to 0.2545±0.0014, demonstrating that each represents a distinct melt, and that all are different from the host lava \((K_{2}O/TiO_{2} = 0.024)\). Our calculations indicate that these inclusions were entrapped at pressures of 2-4 kbar, so that aggregation of these diverse melts was a late-stage process that occurred at crustal conditions.
Measurement of $^{226}$Ra using a RaDeCC and its application for tracing submarine groundwater discharge

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A delayed coincidence counter (RaDeCC), which previously had been developed to determine ultra-low levels of $^{223}$Ra and $^{224}$Ra in seawater (Moore and Arnold, 1996), was used in a new way to measure $^{226}$Ra. Using a high speed Ra extraction system, Ra was pre-concentrated from a large volume of seawater (> 100 L) onto MnO$_2$-coated fibre. After the measurement of $^{223}$Ra and $^{224}$Ra with the RaDeCC, we show in this study that the $^{226}$Ra activity in the same sample can be successfully determined using the RaDeCC’s ability to record alpha decay of its daughters as total counts. In order to have enough ingrowth time of $^{222}$Rn, the column containing the MnO$_2$-fiber is hermetically sealed for a few days. The ingrown $^{222}$Rn is circulated through the RaDeCC air-loop system for ten minutes followed by shutting down of the pump and closure of the scintillation cell. Counting may be completed within a few hours for $^{226}$Ra in normal seawaters. With a standard calibration, the results from this method were in good agreement with the data obtained from another verified method using a radon-in-air monitor (RAD-7). In addition to this development, we present $^{226}$Ra data from Gamak Bay (South Sea of Korea), which has been acquired with the new RaDeCC method. A mass balance model for $^{226}$Ra in the bay reveals that the input of SGD in the shallow area (< 5 m water depth) was about 1.2-1.9 x 10$^7$ m$^3$ day$^{-1}$ in spring and summer 2006, which was two orders of magnitude higher than the total stream discharge (0.27–0.30 x 10$^5$ m$^3$ d$^{-1}$) during the study period.

References

No matrix-like rims on CR chondrules

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In the past it was widely held that chondrules are surrounded by compact matrix-like rims that formed in the solar nebula [1]; the most dramatic evidence was presented by Metzler et al. [2] for rims on CM chondrules. These thick rims are envisioned to have formed one grain at a time [3]. However, simulations and physical modelling show that the accretion of small (≤1 μm) grains produces structures with high porosities of >80%, far higher than observed (~14%) in the fine matrix of chondrites or in the purported matrix-like rims [4]. Trigo-Rodriguez et al. [5] presented evidence and arguments supporting the alternative interpretation, that CM matrix (~35 vol%) was compacted by asteroidal impacts rather than in the nebula, and that the rims surrounding most chondrules were the result of enhanced compaction near incompressible objects such as chondrules. In BSE images these compacted "rims" are darker than surrounding matrix.

A problem with studying matrix in CM chondrites is that they have experienced extensive aqueous alteration. On the other hand, in some primitive chondrites of type 3.0 or 3.1 that have experienced little aqueous alteration there is very little matrix making its chemical study and the petrographic comparison of matrix and possible rims very difficult. We have therefore focused our study on the CR chondrites, which have large amounts (~32 vol%) of matrix and large intact chondrules but have experienced much less aqueous alteration than CM chondrites. In our section of CR LAP02342 most chondrules show no textural evidence of being surrounded by rims. Potential rims are small in thickness and irregular.

Models of the formation of radially symmetric rims in the nebula require them to form one grain at a time [3] and thus be compositionally homogeneous. We have surveyed random spots in the matrix and compared them to regions near chondrules (i.e., possible rims). There is a relatively large degree of variation in matrix composition, and this carries over to the rims as well. In some cases matrix on opposite sides of a chondrule showed resolvable differences in composition, inconsistent with symmetric formation. If rim formation was not occurring at the CR-chondrite formation locations, it is unlikely that rims formed around chondrules at other locations.

References
The role of organic ligands in Fe isotope fractionation during dissolution of hornblende

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Dissolved Fe in some rivers is isotopically light by ~ 1 %o (δ56/54Fe) compared to average crustal Fe [1,2]. Fe isotopes are thus fractionated by one or more processes during weathering of crustal rocks, resulting in preferential transport of light isotopes of Fe toward the oceans and retention of heavy isotopes in weathering residues. Our ability to understand the Fe isotope budget of the crust-ocean-biosphere system, past and present, depends critically on understanding how isotope effects originate during weathering of major Fe-bearing crustal minerals.

An experimental study of hornblende dissolution by Brantley et al. [3] suggests that Fe-binding ligands play an important role not only in promoting dissolution of Fe-bearing silicate minerals, but in fractionating Fe isotopes. In those experiments, which were 4-6 days long, hornblende dissolved in the presence of acetic, oxalic, or citric acid or a siderophore molecule, desferrioxamine B. Fe-release rates correlated with Fe-binding affinity. In addition, the results suggested a relationship between Fe-binding affinity and the Fe isotope composition of the Fe released into the solvent medium. Brantley et al. hypothesized that fractionation occurs during incongruent dissolution of hornblende and that the isotope effect should decrease over time as Fe concentration in the leached layer approaches steady state.

To test this hypothesis, we have extended these experiments from 4-6 days to 70 days. We see a continuation of the relationship between Fe-release rates and Fe-binding affinity up to 22 days, beyond which precipitation of Fe (oxyhydr)oxides obscures the effect. Isotopic analyses of the solvent media up to 22 days will reveal whether the isotope effect indeed diminishes as dissolution progresses toward a steady-state leached layer. Whether this happens or not is important for constraining the mechanism of isotope fractionation. Understanding this mechanism is key to predicting how isotope effects in natural weathering environments influence the Fe isotope budget of natural waters. In addition, if siderophores leave a distinct isotopic fingerprint on weathering residues, as suggested by our preliminary work, it may be possible to detect where and when such molecules were produced in the past.

References

Non-heterogenous oxygen isotopic distribution in coral microstructures

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Massive corals have been widely used as proxies for past changes in sea surface temperature (SST) of the tropical and subtropical oceans because the oxygen isotopic and strontium/calcium (Sr/Ca) ratios of their aragonitic skeletons are believed to vary as a function of the temperature of the ambient seawater. However, recent microanalytical studies using secondary ion mass spectrometry (SIMS) have revealed large chemical heterogeneities for Sr/Ca and oxygen isotopic ratios in coral skeleton, which cannot be explained by temperature variation (e.g. Meibom et al., 2004, Rollin-Bard, et al., 2003).

We report the micro-scale image of oxygen isotopic distribution within the two basic building blocks of the coral skeleton; centres of calcification (COC) and fibers. With Hokudai isotope microscope (Cameca ims 1270 + SCAPS), obtained image for relative 83O/86O ratio in the microstructure of coral Porites ,which is the most widely used species for paleoclimatic studies, shows small variation in COC and few isotopic difference between COC and fibers at least within ~1 %. This result is inconsistent with the large oxygen isotope heterogeneities previously reported (Rollin-Bard, et al., 2003, Meibom et al., 2006), although their spot analysis could not capture full image of oxygen isotopic composition in COC. These recent works suggested that coral biomineralization processes are governed strongly by biological control (Meibom et al., 2006) or rapid environmental changes (Rollin-Bard, et al., 2003) occurred in ultra structure level. Therefore, it implied that such heterogeneities must mask significantly geochemical signal for reconstructing past temperature changes. However, our result indicates that in the case of coral Porites, such dynamic process seem not to be happened, or even happened in some degree, oxygen isotopic ratio in coral skeletons could be still robust paleoclimatic proxy for tropical SST, which play important role for understanding earth climate system. Further investigations using these microanalytical technique with ion probe can provide important informations for establishing new biomineralization model and help constrain the degree to which temperature and/or biological processes affect the composition of skeleton in corals, as well as biogenetic carbonates formed by other marine organisms.

References
The presence of mass-independently-fractionated sulfur isotopes (MIF-S) in pre-2.45 Ga sedimentary rocks, but the general absence in post-2.45 Ga rocks, have been linked to atmospheric oxygen evolution [1, 2]. However, recent studies have revealed that: (1) Archean sedimentary rocks with no MIF-S signatures are common, particularly during the mid-Archean era [3, 4]; (2) the magnitude of MIF-S may vary greatly within short (<10 m) stratigraphic intervals (e.g., 2.5 Ga Mt. McRae Fm) [5]; (3) Antarctic snow that accumulated during violent (stratospheric) volcanic eruptions trapped sedimentary rocks with MIF-S are more common in organic sulfates with small but distinct MIF-S [6]; (4) Archean sedimentary rocks with MIF-S are more common in organic carbon-rich black shales with hydrothermal alteration effects [7]; and (6) H2S that generated from the thermochemical Pyrites in a Jurassic ammonite show small but distinct MIF-S than in organic carbon-poor sandstones/carbonates [3]; (5) carbon-rich black shales with hydrothermal alteration effects [6]; Baroni M. [5] Kaufman A.J. [4] Ono S. [3] Ohmoto H. [2] Bekker A. [1] Farquhar J. and Wing B. (2003) 

References
Detrital zircon ages of metamorphic and sedimentary rocks from the Maya block (Middle America)

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The pre-Mesozoic basement of the Maya block is exposed in the Maya Mountains of Belize and in the Chiapas Massif Complex (CMC) of SE Mexico. In the CMC medium- to high-grade metasedimentary rocks occur as isolated domains in predominantly metaigneous rocks. The CMC was affected by a Late Permian tectonothermal event, culminating in partial anatexis and the intrusion of the Chiapas batholith. This strong overprint has obscured the origin of the metasedimentary precursors and hindered correlations with other basement units.

Our in-situ U-Pb dating by LA-MC-ICPMS and SHRIMP is focused on detrital zircon cores from CMC metasediments and detrital zircons from Paleozoic strata exposed in the Maya block. This allowed unraveling the provenance of the CMC, which is summarized in the Figure below. The early Paleozoic sedimentary rocks from Belize were shed mostly from a Grenville orogen and from a ~1.5 Ga old source (Rondonia, SW Amazonia). Pan-African zircons are characteristic for the Carboniferous-Permian sequence (Santa Rosa Formation) in which zircons of mid-Proterozoic ages are less abundant. This dichotomy can be observed in a similar way for the detrital zircon cores of metasediments from the CMC and, hence, both sedimentary units were involved in the late Permian orogeny of the CMC.

Formalization of copper sulfide nanoparticles in a flooded soil: Potential for colloid-facilitated transport of contaminants

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The role of colloids in facilitating the transport of strongly sorbing contaminants has been demonstrated under oxic conditions [1], but little is known about their importance in reduced environments. In microcosm experiments, we have studied in situ formation of biogenic sulfide minerals during flooding of a heavy metal contaminated soil. We especially investigated the precipitation of sulfide nanoparticles forming in the pore water upon soil reduction and evaluated their effect on the mobility of contaminants (Cu, Cd, Pb), combining electron microscopy, X-ray absorption fine structure (XAFS) spectroscopy, and wet-chemical analyses.

Results

In the bulk soil, 25% of the initially organic matter bound Cu(II) was transformed into Cu(I) sulfide minerals within just 7 days of flooding, controlling dissolved Cu to <0.4 µM. In the colloidal phase, we concomitantly observed the formation of up to 20 µM of Cu sulfide particles, comprising (i) nanoparticles with diameters <30 nm; and (ii) ~200 nm-hollow Cu sulfide structures associated with free living bacteria. Both types were apparently mobile in the reduced soil and carried substantial quantities of Cd and Pb, dominating their pore water speciation. We attribute the distinct properties of the nanoparticles compared to the hollow structures to different mechanisms of formation involving homogeneous nucleation [2, 3] and bacterially-induced biomineralization [4], respectively. Parallel to an increase in pore water ionic strength during soil reduction, both types of colloids were slowly removed from solution by deposition [5], following an apparent first-order kinetics.

Conclusion

We demonstrate that the formation of mobile Cu sulfide colloids drastically enhanced Cu, Cd, and Pb mobility in a flooded soil, albeit concomitant sequestration in immobile sulfide minerals. Our results thus point to a potentially important pathway for the translocation of class B metals from contaminated floodplain soils to adjacent surface and groundwater bodies.

References

High-pressure rocks from the Colombian Caribbean – Record of a changing convergent margin
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P-T-t evolution of Cretaceous high-pressure rocks found as fragments in a Tertiary conglomerate from the Guajira Peninsula of Colombia, record the complex multistage history of the southern-margin subduction and collision zone of the Caribbean plate and Northern South America. The metamorphic rocks include metamafites (kyanite eclogites) and metasedimentary rocks (garnet-kyanite schists, glaucophane-bearing garnet gneisses and garnet-bearing chloritoid gneisses), that represent both oceanic and continental protoliths trapped in an accretionary wedge. Early Eocene granitoids as well as gabbros and serpentinites are also common in this conglomerate.

Mineral chemistry and textural evidence show two phases of prograde syn-tectonic metamorphic growth, and peak metamorphic conditions where calculated at 770°C and minimum pressures of 17 kbars. Some of these high pressure rocks have reequilibrated completely at amphibolite-facies conditions.

The earlier prograde phases are related to the subduction-collision event in the oceanic-continental margin, and the beginning of exhumation, whereas the later amphibolite facies overprint suggests that the exhumation rates possibly diminished, probably as a consequence of shifting towards a more oblique convergent margin.

Geochemical variability in deep-sea sediments of the Eastern Equatorial Pacific: Foundation for orbital-based chronology since the Late Miocene
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Goals
The goal of this study is to provide an orbital-based chronology for sediments from the Peru Basin, eastern equatorial Pacific (EEP), that allows for the reconstruction of the deep-sea response to major oceanographic changes since the Upper Miocene. We present carbonate, opal, and XRF element data measured on samples and obtained non-destructively on 26 sediment sites. Chronology is based on magnetic polarity changes, biostratigraphy, stable oxygen isotopes, and tuning the carbonate and opal proxy records to orbital insolation. Accordingly, we obtained age models with 21-kyr control points.

Evolution since the Upper Miocene
The youngest core covers the last 1.3 Ma and the oldest core reaches back until the Upper Miocene (7.74 Ma), with sedimentation rates of 2 to 0.1 cm/kyr, respectively. A stacked carbonate record of all 26 sites minimizes local influences and provides the regional information that is necessary for large-scale climate considerations.

Accordingly, a pronounced carbonate maximum at 6.8 to 6.4 Ma is most likely associated with ‘the biogenic bloom’. Until 4.6 Ma, there is a long-term decrease with internal 400-kyr eccentricity cycles, probably amplified by pulsations of the Antarctic ice sheet and linked to the final narrowing of the Isthmus of Panama. Very low amplitudes in the 400-kyr component between 4.5 and 3.4 Ma indicate the isolation of the EEP from the Atlantic (Caribbean) due to the final closure of the Isthmus, and the time required to reorganize circulation. At 2.7 Ma, carbonate contents began to increase with a peak at 2.4 Ma. This time probably marked the first substantial glaciation of the northern hemisphere as a preservation and/or productivity spike in the EEP, followed by a gradual decrease until the Pliocene/Pleistocene boundary, a period that yields a major environmental change from oxic to suboxic conditions, indicative for a distinctive decrease in deepwater oxygen content. This change is accompanied by a 0.7-myr hiatus. During the Pleistocene, the 100-kyr amplitude of the stack started to increase at 1.3 Ma, suggesting that the response to the 100-kyr eccentricity cycle might have evolved in low latitudes and migrated to higher latitudes at 0.9-0.8 Ma. In conclusion, geochemical variability is strictly orbital controlled and traces all major oceanographic changes in the EEP.
Experimental constraints on fluorine and chlorine partitioning in the pseudosystem apatite-silicate melt-fluid(s) and applications to magmatic degassing

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Hydrothermal experiments were conducted to determine the partitioning of Cl between rhyolitic to rhyodacitic melts, apatite, and aqueous fluid(s) and the partitioning of F between apatite and these melts at 200 MPa and 900-924° C. The number of fluid phases in the experiments is unknown; a single fluid and/or vapor plus saline liquid may have been stable. The partitioning behavior of Cl between apatite and melt is non-Nernstian and is a complex function of melt composition. Values of \( D_{Cl}^{apat/melt} \) (i.e., the wt. fraction of Cl in apatite/Cl in melt) vary from 0.5 – 3.8 and are largest when the Cl concentrations of the melt are at or near the Cl-saturation value of the melt. The Cl-saturation concentrations of silicate melts are lowest in evolved, silica-rich melts, so with elevated Cl concentrations in a system and with all else equal, the maximum values of \( D_{Cl}^{apat/melt} \) occur with relatively felsic melts. In contrast, values of \( D_{F}^{apat/melt} \) range from 16-39 for these felsic melts, and they are as much as an order of magnitude greater than those applying to basaltic melts at 200 MPa and 1066-1150° C. The concentration of Cl in the fluid(s) is a simple and linear function of the Cl concentration of apatite. Values of \( (D_{Cl}^{fluid/apat}) \) for these experiments range from 15 – 44, and are nearly an order of magnitude greater than those for 200 MPa experiments involving basaltic melts at 1066-1150° C.

In order to determine the F and Cl contents and interpret volatile behavior in magmas, the experimental data have been applied to the halogen concentrations of apatite grains from chemically evolved rocks of Augustine volcano, Alaska; Krakatau volcano, Indonesia; Mt. Pinatubo, Philippines; Mt. St. Helens, Washington; Mt. Mazama, Oregon; Lascar volcano, Chile; Santorini volcano, Greece, and the Bishop Tuff, California. The F concentrations of these magmas estimated from apatite-melt equilibria range from 0.05–0.13 wt.% and are generally equivalent to the concentrations of F determined in corresponding melt inclusions. In contrast, the Cl concentrations of the magmas estimated from apatite-melt equilibria greatly exceed those determined in the melt inclusions from all of these volcanic systems except for the Bishop Tuff where the agreement is good. This discrepancy in estimated Cl concentrations of melt could result from several processes, including that apatite chemistry represents an earlier stage of magma evolution – prior to the sequestration of Cl by coexisting magmatic fluid(s).

Microbial activity associated with asphalt volcanism at the Campeche Knolls, Gulf of Mexico

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The Campeche Knolls are characterized by active oil and methane seepage, and spectacular asphalt flows covering the seafloor. We studied the biogeochemistry of this extreme environment at 3000 m water depth during METEOR cruise M67/2 with ROV QUEST.

The asphalt flows on Chapopote, one of the Campeche knolls, show a variety of surface patterns including densely populated areas hosting deep water corals, chemosynthetic bivalves and giant tubeworms, wide flat zones covered by bacterial mats and some grazers, and regions devoid of any visible life.

Here we will present the first in situ measurements of oxygen consumption, sulfate reduction and methane turnover associated with asphalt volcanism. A central question is the source of energy to the abundant life at the asphalt flows. We found indications of high methane and sulfide fluxes, as well as extremely high oxygen consumption rates associated with the asphalt flows and will discuss the proportions of microbial and chemical processes associated with these fluxes.
Evolution of a maturing arc system: The west-central Isthmus of Panama

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Geochemical data from the Cordillera de Panama documents the evolution magmatism and oceanic plate interactions over the past 90 Ma. Three geochemical associations are observed on the basis of trace element characteristics and ages: (i) Oceanic basement of the Caribbean Large Igneous Province (CLIP) displaying either flat trace element patterns or OIB signatures, CLIP rocks with an arc signature are rare. (ii) The Chagres Igneous Complex (66-45 Ma, Ar-Ar mineral ages) and (iii) a series of younger, Late Cretaceous to Early Tertiary mafic complexes with arc-tholeiitic trace element signatures (variably enriched in Cs, Ba, Rb, K, Sr). LILE/HFSE ratios display arc-type patterns, suggesting an origin from subduction below a CLIP oceanic plateau. Miocene (20-5 Ma) andesites from discrete volcanic centers across the Cordillera de Panama display a progressive enrichment from a tholeiitic to a more uniform medium-K arc character. This type of arc magmatism ceases around 5 Ma, followed by adakite volcanism (<2 Ma), which represents the youngest magmatism in Panama.

This evolution in magma sources through time can be interpreted in terms of a 2-stage process. 1. An early arc source that likely involved (i) enriched Galapagos mantle (plume or lithosphere) and (ii) typically depleted asthensphere. 2. The composition of the mantle wedge became progressively more homogeneous through time, either due to mixing of the two sources or by replenishment with undepleted mantle from the back arc. One possible cause for initiating this change in mantle sources could be tectonic re-arrangement after the break-up of the Farrallon plate around 28 Ma.

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In-situ X-ray synchrotron high-pressure measurements of magnetite

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Introduction
Magnetite is a ferrimagnetic inverse spinel where the tetrahedral positions are occupied by Fe$^{3+}$ and the octahedral sites contain equal amounts of Fe$^{2+}$ and Fe$^{3+}$. It occurs in the earth crust and the upper mantle and is also an important material in industrial applications such as data storage.

Experimental methods
For our experiments, magnetite-powder was mixed with vaseline to obtain hydrostatic pressure and sodium chloride was added to act as an internal pressure standard. This mixture was filled into a boron-resin cube. The measurements were carried out at the multi-anvil press MAX80 at the HSYLAB in Hamburg using “white” synchrotron beam. The pressure was increased stepwise up to 4.5 GPa.

The data were evaluated with the Rietveld-method using the GSAS / Expgui-software suite to obtain the cell parameters of the magnetite and the pressure standard.

Results
With increasing pressure the volume of the unit-cell decreases. At higher pressures the slope declines slowly. Further evaluation of the data will derive the bulk modulus of magnetite using the 3rd order Birch-Murnaghan equation of state.

References

Figure 1: Volume change under pressure

References
Seasonal changes in seawater pH from Boron isotope systematics in a Porites coral from the Northern South China Sea
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We report seasonal changes in seawater pH using boron isotopic variations in high and low-density bands from a Porites lutea coral from Sanya, in the northern South China Sea. Boron isotopes in coral act as a proxy for seawater pH and were investigated using the method of positive TIMS with 309Cs2BO2/308Cs2BO2 species being measured and the results expressed as δ11B relative to NBS SRM 951. The internal precision is better than 0.2 ‰ (2σ) and the external precision indicated by repeated measurement of a working coral standard is ~0.4 ‰ (2σ), which is about 2-3 times better than that by negative TIMS method, corresponding to an overall uncertainty of less than ±0.03 pH units.

The results indicate that winter seawater pH values, represented by δ11B in high-density bands, range from 7.31 to 8.15, and from 7.87 to 8.17 for summer pH values determined from the low-density bands. The pH values in winters are generally lower than in summers, which is consistent with increased uptake of CO2 in seawater during cooler seasons due to increased solubility.

There is generally an increasing trend for seawater pH values in this region from 1992 to 1995, with pH values changing from ~7.8 to ~8.17, which appears to coincide with reduced salinity caused by increased precipitation. This may indicate more alkali (higher pH) input from the runoff into the reef, in which the seawater is significantly influenced by highly modified urban inputs from the Sanya region.

Bacterial tetraether membrane lipids in soils and their application in palaeoenvironmental studies
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Branched Glycerol Dialkyl Glycerol Tetraethers (GDGTs) are membrane lipids synthesized by ostensibly anaerobic bacteria that thrive in soils and peat bogs (Weijers et al., 2006). Multiple types of branched GDGTs exist, differing in the amount of methyl branches and cyclopentanyl moieties in their carbon chains. Analysis of branched GDGTs in >150 soils indicated that soil bacteria use these differences to adapt their cell membrane to ambient temperature and soil pH conditions, which is necessary to keep the membrane in an optimal liquid crystalline state (Weijers et al., 2007a).

Upon soil erosion, branched GDGTs are transported by rivers to the marine environment. In conjunction with bulk geochemical proxies, the relative abundance of branched GDGTs in a marine sediment core located near the Congo River outflow showed that soil organic matter input varied over the last deglaciation by up to a factor 5. In addition, the degrees of methylation and cyclisation of the branched GDGTs were used to reconstruct a Congo Basin integrated soil pH and temperature record. These records reveal a gradual deglacial warming of 4°C in tropical Africa and a co-variation of soil pH with African humidity over this time interval (Weijers 2007b). This latter result might be explained by enhanced soil leaching processes with increased precipitation and vice versa.

References
The structure of the Hawaiian plume conduit from high-precision isotopic studies of Mauna Loa lavas

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The Earth’s two largest volcanoes are located adjacent to each other and astride the long-lived Hawaiian mantle plume. Mauna Loa is thought to sample the plume core; Mauna Kea, a less central part. The shield stage of Mauna Kea was well sampled (3200 m, 600 kyr) and geochemically characterized by HSDP2. Here we present results from a systematic high-precision isotopic study of a comparable portion, potentially up to 500 kyr, of Mauna Loa’s shield history.

Older Mauna Loa lavas (>60 ka), sampled along the submarine southwest rift zone, including the Mile High-Section, do not define Pb-Pb isotope lines. For the younger lavas (<60 ka), the slopes of the Pb-Pb lines increase with age. In contrast, older HSDP2 Mauna Kea basalts form Pb-Pb lines, where slopes decrease with age [1, 2]. In both volcanoes, the older lavas have higher \(^{3}He/^{4}He\) [3]. The older Mauna Loa lavas (high \(^{208}Pb* / ^{206}Pb*\), lower \(^{87}Sr / ^{86}Sr\) and \(^{143}Nd / ^{144}Nd\) and higher \(Nb/Y\)) also define separate binary isotope trends compared to the younger lavas, on the less enriched side of the trends defined by Koolau (i.e. recycled oceanic crust and sediment component). This indicates the presence of another component in the source of older Mauna Loa lavas.

Our large-scale isotopic study of Mauna Loa shield basalts confirms the apparent bilateral asymmetry of the plume conduit, originally based on distinctly higher \(^{208}Pb / ^{204}Pb\) for a given \(^{206}Pb / ^{204}Pb\) [4, 5]. The Mauna Loa source is also systematically more heterogeneous in all isotopic systems by a factor of 1.5 than the Mauna Kea source. This is maintained throughout the long magmatic history of these volcanoes. Yet older lavas from both Mauna Kea and Mauna Loa sample a more heterogeneous plume source (Loihi-like?) than younger shield lavas. Implications for the structure of the Hawaiian plume conduit, the mantle source and geophysical constraints will be discussed.

References
Low-grade zeolite facies
metamorphism in gneisses of the
Simano nappe (Arvigo, Val Calanca,
Grisons, Switzerland)

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Banded biotite gneisses intercalated with coarse light
coloured two mica gneisses and less frequently with
calcsilicate lenses are mined as building stones at Arvigo. The
rock series belongs to the upper Simano nappe of the
crystalline Penninic basement. The Arvigo quarry became
famous for a large number of Alpine fissure minerals, which
occur in extensional fractures and cavities of the granitic
gneisses. Fissures and gashes formed by semi-brittle
deformation of granitic gneisses, which were generated during
exhumation and uplift of the Alpine orogen. These fractures
and cavities were filled with fluids and new minerals
crystallized in the open space.

The Arvigo fissures contain the assemblage epidote,
prehnite and various species of zeolites. In general epidote is
overgrown by prehnite and zeolites. The specific zeolite
mineral formed in the fissures depends of the temperature
(Fig. 1). In the Arvigo fissures the following zeolites
precipitated from the fluid with decreasing temperature,
in agreement with the predicted sequence on figure 1
(300°-100°C): scolecite, laumontite, heulandite, chabazite and
stilbite.

Se isotopic variations in black shales
of the Yutangba Se deposit, China

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The Yutangba Se deposit is the only sedimentary-type Se
deposit known in the world to date. Se is present in relatively
high abundance in both host rocks and ores, with
concentrations of up to 1.3% on average in the enriched zones.
Our preliminary study showed that about 66% Se occurs as
nanograins of elemental Se (Se0) embedded in kerogen. Three
hypotheses are proposed to explain the presence of Se0: 1) sea
water Se was reduced by a high productivity of marine
plankton, which died rapidly, and were scavenged to the sea
floor to form Se-rich carbonaceous rocks; 2) larger Se crystals
are related to combustion of stone coal (Se oxidation); 3)
redox processes related to water table fluctuations, resulting in
Se oxidation-reduction reactions (Wen and Carignan, 2006).

Se isotopic measurements on Se-rich rocks provided large
variations of δ82/76SeNIST, which varied from -12.77‰ to
4.93‰ for a total range of 17.7‰. This is the largest Se
isotopic variation found so far in natural terrestrial samples.
One of the high-Se carbonaceous shale samples yielded the
most depleted composition, with a δ82/76SeNIST of -12.77‰. On
the other hand, Hagiwara (2000) reported that
bioaccumulation of Se by plankton do not lead to large
isotopic fractionation, generally about 1-2‰ between
available dissolved oxidised species and biologically reduced
Se. In addition, no significant isotopic fractionation is
observed during oxidation reactions of Se, as reported by
Johnson (2004). Obviously, the “redox model” is favoured to
explain the Se isotopic variations in the Yutangba black
shales. Above or in the close vicinity of the water table
(oxidizing conditions area), Se2 in rocks and ores is readily
oxidized to 0, +4, or +6 valences, without isotopic
fractionation. Then, Se+4 and Se+6 mobilised in oxidising
solutions may be readily reduced again to zero (or partly -2)
valence, as the water migrates and eventually encounters
lower redox potential. At the scale of the deposit, repeated
reduction reactions should induce significant Se isotopic
variations (Johnson 2004).

The extreme isotopic variation measured in the black
shales of the Yutangba Se deposit strongly supports the high
potential of Se isotopes as a powerful redox tracer.

References
Urbana-Champaign.
Distribution of mineral potassium in the Luochuan loess section, China

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Mineral potassium (K) is the dominant part of potassium in the loess and paleosols, mainly residing in feldspar and mica. We report here variation in mineral potassium contents of the Luochuan loess section during the past 130ka (Table 1).

Table 1: Mineral K content and magnetic susceptibility (MS)

<table>
<thead>
<tr>
<th>Strat. (the number of samples)</th>
<th>Mineral K (%)</th>
<th>MS (SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range  Mean</td>
<td>Range  Mean</td>
</tr>
<tr>
<td>S0(10)</td>
<td>1.42-1.67 1.55</td>
<td>67.6-155.6 102.2</td>
</tr>
<tr>
<td>L1,LL2(21)</td>
<td>1.43-1.72 1.59</td>
<td>52.2-91.2 70</td>
</tr>
<tr>
<td>L1,SS1(29)</td>
<td>1.51-1.69 1.61</td>
<td>97.5-142.5 118.2</td>
</tr>
<tr>
<td>L1,LL2(24)</td>
<td>1.46-1.65 1.55</td>
<td>49.1-117.6 72.2</td>
</tr>
<tr>
<td>S1(11)</td>
<td>1.45-1.72 1.65</td>
<td>53.6-233.3 180.3</td>
</tr>
</tbody>
</table>

Mineral potassium content varies within the range of 1.42-1.72% with the average of 1.59% in the Luochuan section during the last 130ka, and is slightly higher in the paleosol S1 than in the loess L1. In addition, the distribution curve of mineral potassium in the Malan Loess section (L1) exhibits three small fluctuations between low and high values. Mineral potassium is low in the loess L1,LL2, high in the weak pedogenic loess L1,SS1, and then low in the loess L1,LL2.

S0 and S1 were developed during the post-glacial period and the last interglacial period, respectively. L1 formed during the last glacial period, composed of three parts (L1,LL1, L1,SS1 and L1,LL2). L1,LL1 formed during the last stade of the last glacial period, L1,SS1 were developed during the interstade of the last glacial period and L1,LL2 formed during the early stade of the last glacial period. So, mineral potassium content oscillates regularly with climate change. Climate change probably resulted in leaching of diffluent elements (Ca and Na), but relatively enrichment of mineral potassium of the Luochuan loess section.

Moreover, the fluctuation of mineral potassium is similar to that of magnetic susceptibility in the Luochuan loess section during the past 130ka. Both have also a good correlation (r=0.81). MS has been considered to be a classical proxy indicator of variations in the summer monsoon strength [1]. Therefore, variation in mineral potassium contents can also reflect the East Asian summer monsoon evolution.

Biogeochemistry of the volcanic acidic waters at the Andean Volcan Copahue (Argentina)

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The naturally acidic water system near the active Volcan Copahue consists of the Copahue Crater Lake, the Upper Rio Agrio which flows into Lake Caviahue, and the Lower Rio Agrio below Lake Caviahue. The crater lake and most of the Upper Rio Agrio are extremely acidic (pH ≈0-1.6) with oxidizing conditions and poor colonization, mostly by well-known acidophilic bacteria and algae. In the lower part of the system before inflow into Lake Caviahue, microbial biomass, oxygen penetration and oxygen consumption in the sediments were similar to non-extreme aquatic habitats [1]. Lake Caviahue has a pH similar to acidic pit lakes (pH 2.2 – 2.7), but lower iron and higher phosphorus concentrations [2]. Sedimentation of algae is higher than in acidic pit lakes due to different algal communities and volcanic ash input. This results in better degradable organic carbon compounds in the sediments compared to pit lakes. Microbrial sulfate reduction proceeds in Lake Caviahue sediments at pH<3 [3], and methanogenesis occurs in deeper layers below 25 cm. Below Lake Caviahue, the Lower Rio Agrio is gradually diluted and neutralized by tributaries, thereby shifting from a chemotrophic system dominated by Fe-S-Al biogeochemistry to an organotrophic system dominated by heterotrophic processes. Epilithic biofilms are an important habitat throughout, and we assumed that respiration would increase with increasing pH. In contrast to this, we obtained a minimum curve for biomass, respiration and photosynthesis with lowest values at a site with massive mineral precipitations. This indicates that physical stress is a more important regulatory factor for the bioocoenosis than pH. We also observed considerable interannual variations in physicochemical conditions and high diurnal fluctuations of temperature and discharge in this part of the river. These fluctuations may represent a stronger stress for the biota than more acidic but stable conditions.

References


Reference

Interactions between inorganic ions, natural organic matter and iron oxides: Effects of particle size and charge distribution

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Both the humic acid (HA) and fulvic acid (FA) fraction of natural organic matter adsorb strongly to iron (hydr)oxide minerals such as goethite. The current study shows that the charge of HA in the compact part at the oxide-water interface needs to be partially separated from the electrolyte ion pairs in space. This separation can be attributed to the large size of the HA particles that limits their close access to the surface. In addition, the calculations also indicate that the positive ionic strength dependency of HA adsorption can be explained by the conformational change of HA particles with ionic strength.

Electrostatic interaction is an important mechanism by which adsorbed organic matter particles influence adsorption of inorganic ions to oxide surface. The charge distribution of both the adsorbed organic particles and inorganic ions influence their interaction. The stronger interactions between Ca and FA than between Cu and FA can be explained by the larger amount of positive charge that is located at the d-plane of goethite surface in the case of calcium. The charge distribution is thus a major factor in the proper prediction of the interactions of charged species at the metal (hydr)oxide surface.

Cenozoic extension in the Pearl River Delta region (South China): Evidence from structural geology and apatite fission track thermochronology

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The Pearl River Delta (PRD) region is located in the coastal South China Block (SCB) which was rifted in the late Mesozoic-Cenozoic time. New morphotectonic and structural studies reveal a polyphased extension in the PRD region, including one phase of extension in the NNW-SEE direction, consistent with but predating the opening of the South China Sea, and one phase in the ENE-WSW direction, which introduced NW-striking normal faults and probably a differential uplift of the basement in this area. Apatite fission track (AFT) analysis were applied for 14 samples, including granite, paleozoic rocks and Mesozoic red beds. 9 samples yield apparent ages varying from from 14Ma to 36Ma with an average confined track length of ~14µm showing a distribution of unimodal frequency, roughly contemporary to the sea floor spreading of the South China Sea, indicating a rapid exhumation of the basement as a passive margin. These ages are much younger than the published AFT ages (43–68Ma) for the western basement, indicating a differential exhumation process probably due to the polyphased extension in the coastal SCB. The very young results (<3Ma) are interpreted as neotectonic influence, since some of the samples were collected near the active fault zones in this area.

Reference
OH/F local environment in metamict titanite by $^1$H and $^{19}$F MAS NMR spectroscopy

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Titanite is a common accessory mineral in igneous and metamorphic rocks. The ideal formula is CaTi(SiO$_4$)O, but there can be extensive substitution at both cation and anion sites. Calcium may be replaced by Na, REEs, Y, U, and Th. To maintain electroneutrality there are also substitutions at the site of the (O) anion that is not bonded to Si. Thus (OH)$^-$ and F can replace O$_2^-$ in significant amounts, coupling with the cation substitutions to satisfy the overall constraint of electroneutrality. The radionuclides U and Th are responsible for alpha-decay events which mainly result in atomic displacements which cause increasing damage to the crystalline structure (metamictization; Ewing et al. 1987). The study of metamictization could help to find nuclear waste deposits since the metamicts have experienced a long-term damage by radionuclide decays.

We have examined a series of chemically and structurally well-characterized titanite samples by $^1$H and $^{19}$F MAS NMR spectroscopy to investigate the local structural environment of OH and F inside the structure as a function of the structural distortion caused by metamictization. Titanite samples with a varying degree of alpha-decay damage were selected for the experimental study. Most of the samples are from Norway and they have previously been characterized using IR spectroscopy, electron microprobe, powder X-ray diffraction, HRTEM, EXAFS-XANES spectroscopy and $^{29}$Si MAS NMR spectroscopy (Hawthorne et al. 1991).

Our preliminary results show that the amount of OH increases with the degree of alpha-decay damage. Both $^{19}$F and $^1$H MAS NMR show that the increasing amorphization results in significant NMR line broadening.

References


Spin transition in magnesiowüstite in Earth’s lower mantle

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Iron in the major lower mantle (LM) minerals undergoes a high spin (HS) to low spin (LS) transition at relevant pressures (23–135 GPa). Previous failures of standard first principles approaches to describe this phenomenon have hindered its investigation and the clarification of important consequences. Using a rotationally invariant formulation of LDA+$U$ we report a successful study of this transition in low solute concentration magnesiowüstite, Mg$_{1-x}$Fe$_x$O, ($x<0.2$), the second most abundant LM phase. We show that the HS-LS transition goes through an insulating (semiconducting) intermediate mixed spins (MS) state without discontinuous changes in properties, as seen experimentally. We show that the HS state crosses over smoothly to the LS state passing through an insulating MS state where properties change continuously. We address the change in elastic properties across this transition and its significance for the interpretation of seismic data.

Work done in collaboration with T. Tsuchiya, C. R. S. da Silva, and J. F. Justo F., and Z. Wu. Research supported by NSF/EAR 013533, 0230319, 0635990, and NSF/ITR 0428774 (VLab).
Spatio-temporal variability in diffuse hydrothermal vent fluids – Implications on biogeochemical processes

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The emission of hydrothermal fluids into the ambient seawater leads to steep physico-chemical gradients which can strongly vary over space and time. The greatly varying chemical conditions and the often very steep chemical gradients, generate a wide range of geochemical niches and potential energy sources for (micro-)organisms. An understanding of variability of vent fluids is a prerequisite for understanding the distribution and activity patterns of organisms and thus the interplay between biotic and abiotic process at hydrothermal habitats. To measure at the scale relevant for the vent organisms, high resolution in situ measurements are required to precisely characterize gradients of temperature, O$_2$, pH, sulfide and hydrogen. From these measurements microhabitat structures can be identified and they provide invaluable information on how hydrothermal habitats evolve and how vent organisms maintain their energy requirements.

Here we report on studies investigating the physico-chemical gradients of diffuse vent fluids at the Logatchev vent field (14°45’N). In situ microsensor measurements of O$_2$, H$_2$S, T and H$_2$ were used to investigate the links between the geochemical energy supply from hydrothermal fluids and hydrothermal vent communities. Microsensor time records show a highly fluctuating signal over time. At occasions where warmer fluids pour out electrode signals of H$_2$S and H$_2$ increased while O$_2$ electrodes showed a distinct reduction. This shows that beside methane also sulfide and hydrogen are available as an energy source for both free-living and symbiotic sulfur-oxidizing bacteria. Also, the maximum signal change varied spatially within the same mussel field on a distance of a few decimeters.

This work is carried out in the framework of the German DFG-Priority Program SPP1144 “From mantle to ocean”.

Major, minor and trace element analyses with XRF using synthetic standards

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X-ray fluorescence spectrometry is used extensively for geochemical analyses. Simple sample preparation, high accuracy and precision, and a good to excellent detection limits across large parts of the periodic table are the principal reasons for this choice.

Major, minor and trace element analyses are possible with respect to the task of the examination.

Accurate quantification requires accurate spectrally clean net peak intensities, accurate corrections for inter-element matrix effects and good standards either for wide range oxide major and minor concentrations as well for trace element analyses.

For major and minor concentrations a fused bead sample preparation is recommended for various reasons. Together with a set of synthetic standards (in collaboration with the British Geological Survey) 21 elements can be covered up to very high concentrations. Based on advanced FP algorithms a very good accuracy and precision can be achieved from ores, soils to technical minerals.

For accurate quantification of traces close to their detection limits a different approach is needed. Using, carefully designed, interference free, pressed powder standards, accurate background intensities are determined. Spectral line overlap factors, for both peak and backgrounds are iteratively calculated. Further corrections for tube spectral impurities are possible. Calibrated based on the corrections of mass absorption coefficients no major concentrations have to be known.

The combination of advanced algorithms with superior standards makes the analyses of traces a routine type of work.
Uranium “stable” isotope fractionation in nature: A potential paleo redox- and biotracer?

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We investigated variations of the $^{238}\text{U}/^{235}\text{U}$ isotope ratio in natural samples with MC-ICP-MS. A mixed $^{238}\text{U}/^{235}\text{U}$ isotopic tracer (double spike) was added prior to chemical separation of U from the sample matrix to correct for isotope fractionation during sample purification and instrumental mass bias [1, 2]. The uranium isotope ratios were measured relative to the international U standard U950a and are reported as $\delta^{238}\text{U}$.

The total range observed from the isotopically lightest to the heaviest sample was 1.3‰, exceeding by far the analytical precision of our method ($\approx 0.06$‰ for $^{235}\text{U}$, 2SD). The lightest U isotope compositions were observed for two Banded Iron Formations (Lake Superior and Central India) which have $\delta^{238}\text{U}$ of -0.71‰ and -0.88‰, respectively. The heaviest $\delta^{238}\text{U}$ were observed for two Unit II sediments from the Black Sea (+0.25 and +0.44‰, respectively). The U isotope composition of seawater ($\delta^{238}\text{U} = -0.41$‰) is only slightly fractionated relative to the major U source and sinks of U from the oceans (continental crust and suboxic margin sediments, $\delta^{238}\text{U} \approx -0.15$‰ to -0.40‰).

However, we observed significant isotope fractionation during (1) incorporation of U into manganese crusts and (2) U removal into black shales. In the first case we hypothesize that adsorption leads to an enrichment of light U isotopes ($\delta^{238}\text{U} = -0.52$‰ to -0.62‰), as is the case for Mo and Tl isotopes [3, 4]. In the second case reduction of soluble UVI to insoluble UIV might result in the observed heavy U isotope compositions of black shales compared to seawater. U burial in black shales also results in a correlation of U isotopes with U concentrations and TOC values. The latter might suggest that microbial reduction is involved in fractionating U-isotopes [2].

The range and direction of our observed U isotope variations agree with theoretical considerations [5] which predict U equilibrium isotope fractionation between the species $U^{VI}$ and $U^{IV}$. Our results indicate that U isotopes may be a promising tracer for paleo-redox-conditions and microbial reduction.

References
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What the evolution of soil profiles tell us about weathering rates

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A soil chronosequence developed along coastal California exhibited, with increasing time (65 to 226 kyrs), progressively deeper and more intensively weathered depth profiles. Weathering reactions involve the relative rapid, non-stoichiometric release of Na, Ca and Sr from plagioclase and the slower release of K, Rb and Ba from K-feldspar.

The spatial geometry of the weathering profiles, describing the relationship between plagioclase and K-feldspar concentrations and depth, evolves with time at Santa Cruz and is interpreted in terms of weathering mechanisms and rates. Profile linearity over the intermediate range in residual feldspar concentrations is approximated by the relationship

$$R = \left( \frac{1}{b_s} \right) \cdot \frac{m_{sat}}{S_v}$$

where R, the weathering rate, $b_s$ is the weathering gradient or slope, $S_v$ the volumetric surface area and $\omega$, the velocity at which the weathering front moves downward through the regolith. The non-linear regions of the mineral profiles, at low and high residual concentrations are described, using a spread sheet-base profile calculator, by relating R to exponential functions describing mineral surface/volume ratios and to the approach to thermodynamic saturation. A faster plagioclase weathering velocity, $\omega$, compared to K-feldspar, reflects greater thermodynamic solubility (500x). Fluid fluxes, based on weathering profiles agree closely with independent estimates using CI mass balances ($q_h = 0.07$ to 0.17 m yr$^{-1}$).

Under saturation-controlled and transported-limited weathering, the rate becomes defined as,

$$R = \left[ \frac{q_S}{b_s} \right] \cdot \frac{m_{sat}}{M_{total}} \cdot S_v$$

an expression containing no explicit kinetic term but defined by measurable terms, i.e., the ratio of fluid flux to mineral gradients in the profile and the ratio of feldspar solubility $m_{sat}$ to the protolith mass $M_{total}$. The above approaches yield plagioclase weathering rates at Santa Cruz of $R = 0.5$ to 1.4 x $10^{-11}$ moles m$^{-2}$ s$^{-1}$ that agree closely to those reported for other weathering environments of comparable climate and age.
Reading the high-grade metamorphic record
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The minerals textures and structures preserved in metamorphic rocks represent an incomplete and encoded record of their evolution during orogenesis. This record, reflecting the pressure–temperature–deformation history of the crust and a range of important crustal processes, is a primary source of information for unravelling the tectonic evolution of crustal rocks. Shortcomings in our ability to read the record preserved in rocks, in the form of their mineral assemblages and mineral textures, is a limiting factor in understanding these processes. With increasingly sophisticated methods being employed in geochronological studies, the potential for understanding the timescales of metamorphic evolution and the rates at which metamorphic processes operate may be realized. However, our success at this will depend very much on our ability to provide a sophisticated and robust metamorphic framework in which to interpret geochronological data.

Improvements in our understanding of high-grade metamorphism are ongoing, with mineral equilibria modeling emerging as a powerful approach to understanding the evolution of metamorphic rocks and metamorphic processes. Of key importance is understanding the P-T evolution of rocks via effectively reading the mineral assemblages and reaction textures, as well as being able to understand open system processes such as melt loss.

Applying mineral equilibria modeling in geologically-realistic chemical systems, as well as newly-developed methods for calculating chemical potential gradients and volumes of equilibration in rocks allow us to better understand the P-T evolution and spatial organization of minerals in rocks. Forward modeling methods such as calculated pseudosections allow observations to be interpreted within a predictive framework and likely mineral assemblage evolutions deduced. The interpretation of geochronology within this framework will allow tighter constraints to be placed on rates of metamorphic evolution.

Are ‘constant’ trace element ratios in oceanic basalts really constant?
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Pb/Ce and Nb/U ratios differ dramatically between the continental crust and the mantle. Furthermore, these ratios appear to be approximately uniform in mid-ocean ridge (MORB) and oceanic island (OIB) basalts. Nb/Ta and Zr/Hf ratios are expected to be nearly constant in both crust and mantle because of the highly similar behavior of the elements involved. This study re-examined question of how constant these ratios are using data from the GEOROC and PetDB databases as well as recent data from the literature. In particular, the study addressed the question of whether statistically significant differences existed between OIB and MORB generally, and among oceanic island chains. Data from GEOROC and PetDB were first filtered to exclude differentiated lavas, samples that were significantly weathered, and poor quality analyses. After filtering, roughly 200 MORB and 1500-2000 OIB values remained, depending on the ratio.

Overall, mean values of Pb/Ce, U/Nb, Nb/Ta, and Zr/Hf for MORB and OIB are indeed similar. Because of this, I used a statistical approach, the Student-t test, to determine if real and statistically significant differences existed. This approach reveals that MORB have statistically significant (95% confidence level) lower Zr/Hf and Nb/U ratios than OIB (39.3 vs 41.5 and 44.8 vs 48.5). Differences in Pb/Ce and Nb/Ta were not statistically significant. The Hawaiian volcanoes have mean trace element ratios close to the overall mean for OIB (partly a consequence of the Hawaiian data representing close to half of all OIB data). However, some other island chains do show statistically significant differences in ratios from Hawaii and the OIB mean. The Canaries, Cape Verdes, Easter Is. and St. Helena have the significantly low Pb/Ce (0.026 to 0.029 compared to 0.036 for Hawaii). The Canaries, Cape Verdes have high Nb/U (49 to 62, compared to the mean of 48.8 for Hawaii), while the Society Is., St. Helena, the Mascarene Is., and Tristan da Cunha have low values (46.7 to 32.32). Mean Nb/Ta of oceanic island chains range from 13.71 to 17.01 compared to 15.24 for Hawaii and 15.49 for MORB. At the extremes, the variations are statistically significant. Zr/Hf ratios vary from 38.63 to 43.6, and at the extremes these differences are significant. Variation in Pb/Ce and Nb/U thus allow for some, albeit limited recycling of continental crust into the mantle, specifically into mantle plume sources, Both Zr/Hf and Ta/Nb in oceanic basalts are systematically different from chondritic values, hence this Earth has differentiated with respect to these ratios.
Stable isotope microanalysis – A SIMS perspective

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Modern micro-sampling methods invariably reveal greater isotope heterogeneity than bulk sampling methods, a general rule being that the smaller the scale of observation, the more variation is seen. The challenge to most in situ methods is to measure accurate isotope composition variations at the highest possible precision and, preferably, with minimum sample consumption in order to preserve material for other methods. This presentation will review the state-of-the-art in secondary ion mass spectrometer (SIMS) measurement of both traditional and non-traditional stable isotopes, with particular emphasis on what can be achieved with the current generation of multicolonlector-equipped, high mass resolution instruments (e.g. Cameca IMS1270/80).

A key element in driving down analytical precision to a commonly achievable level of ca. 0.1-0.2 ‰ (RSD) is the ability to measure large (preferably >2 x 10^6 cps) secondary ion signals simultaneously using low noise Faraday detectors and amplifiers. Such large signals are readily obtained for the most abundant isotopes of major elements in specific targets and permit most analyses to be performed in only a few minutes, thus limiting sample consumption. Studies of S isotope variations in sulphides by SIMS now achieve <0.2 ‰ precision on both δ^{34}S and δ^{33}S, the latter revealing non-mass-dependent variations that, for example, have been successfully used to investigate ancient atmosphere evolution. Measurement of δ^{18}O in zircon is now a major element of many crustal evolution studies and an essential complement to in situ U-Pb geochronological and trace element studies, while δ^{18}O measurements in other silicates (e.g. garnet) are critical for evaluating metamorphic fluid evolution. The minor isotope of oxygen, δ^{17}O, while of little interest for terrestrial studies is important in cosmochemistry. At the typical signal level obtained for δ^{18}O studies using Faraday detectors, δ^{17}O is too small to measure with reasonable precision but may still be measured simultaneously using an electron multiplier, although introduction of EM’s into such measurement will be accompanied by gain drift which must be monitored and corrected, and requires substantially longer count times to achieve reasonable precision.

Recent development of in situ Fe isotope measurement by SIMS, using multiple Faraday detectors, highlights the potential of the method for such non-traditional stable isotopes, for example revealing hitherto unknown small scale heterogeneity of Fe isotopes in magnetite from banded iron formations. As with all SIMS stable isotope measurements, appropriate matrix matching of standards is critically important for accuracy and highlights the continuing need for collaboration between SIMS analysts and practitioners of other analytical techniques.

Novel functions of siderophores in Azotobacter vinelandii

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The asymbiotic N2-fixing soil bacterium Azotobacter vinelandii requires the metals Mo and Fe for diazotrophic growth. It acquires Fe by excreting small organic ligands (siderophores) that bind iron and increase its availability. But recent evidence suggests that the catechol siderophores of A. vinelandii also affect the bioavailability of other metals, and particularly of the oxoanions molybdate, vanadate, and tungstate. Here, we investigate the various functions of these catechols using a combined approach of short-term uptake-experiments and HPLC analytics.

Results

High (toxic) concentrations of tungstate induce the release of large amounts of tris(catechol) siderophore protochelin in the growth medium. The excretion of protochelin is modulated in such a way that there is just enough protochelin to bind all the WO_4^{2-} in the medium. Further, we show that the formation of W-protochelin suppresses W uptake by the cells, demonstrating that protochelin is used for W detoxification in A. vinelandii. A similar study shows that protochelin (and possibly the bis(catechol) azotochelin) are also used for vanadate detoxification.

At very low (limiting) Mo concentrations, protochelin is also present in the growth medium, and it is released preferentially to other catechol compounds. In this case, using short term uptake experiments with ^98Mo, we show that Mo-protochelin (unlike W-protochelin) is available to the bacteria, indicating that protochelin is a metallophore used not only for Fe but also for Mo acquisition in these bacteria.

Conclusion

The catechol compounds excreted by A. vinelandii, previously believed to be dedicated to iron acquisition, are multiple functional tools used for the acquisition and/or detoxification of various metals (Fe, Mo, V, W). From a broader perspective, the elucidation of the mechanisms used by N_2 fixers to acquire and detoxify metals may lead to a better understanding of the nitrogen cycle, as metals, and particularly Mo, now appear as potential controls on nitrogen fixation in terrestrial ecosystems.

References

A Holocene strontium isotope record of palaeosalinity for the Littorina Sea stage of the Baltic Sea

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The Holocene history of the Baltic Sea is characterized by a complex interplay between deglaciation dynamics and isotropic/eustatic relative sea-level changes. The resulting salinity variations experienced during the development of the Baltic Sea have been discussed extensively since the late 19th century, but are still incompletely understood. Here we present a study of Baltic palaosalinity variations based on the 87Sr/86Sr isotope record of 14C-dated sub-fossil shells of blue mussels (Mytilus edulis) found in raised-beach sediments from the Littorina Sea stage of the Baltic Sea (~8000–3000 cal BP). Scanning electron microscope images of the shells show no signs of secondary calcite overgrowths. This suggests that the sub-fossil shells are well-preserved, and that the 87Sr/86Sr ratio in the carbonate shells should reflect the isotopic composition of dissolved Sr in Baltic Sea water at the time of mussel growth. The distribution of dissolved Sr in the Baltic Sea is controlled by conservative mixing between seawater and river water, and proxy salinities are calculated using a mixing model where the concentration and isotopic composition of dissolved Sr in present-day seawater and river water are known.

The Sr isotopic composition in shell carbonate and present-day seawater was determined using a Thermo–Finnigan® Triton multiple collector mass spectrometer (TIMS). Replicate determinations of 87Sr/86Sr isotope ratios in modern shells, and comparison with measured present-day salinities indicate a relative precision and accuracy of better than ± 5 % for the proxy salinities. With this precision and accuracy, the present-day salinity differences between the major Baltic sub-basins can be detected. During the time interval 6800–3100 cal BP, the surface-water salinity in the Bothnian Bay increased from 7 to 9, while that in the Bothnian Sea increased from 7 to 13. These palaeosalinities are considerably higher than the present-day surface-water salinities in these two sub-basins of the Baltic Sea (2–3 and 5–6, respectively), and suggest that the Littorina Sea stage palaeosalinity of the Bothnian Bay was similar to that of the present-day Baltic Proper (6–8). The observed difference in palaeosalinity between the Bothnian Bay and the Bothnian Sea (7–9 vs. 7–13) suggests that deep-water-exchange between these two basins was restricted by a sill also during the Littorina Sea stage, despite the 30–90 m larger water depth at that time.

Isotopic tracers of lithospheric recycling

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Recycling between the Earth’s crustal and mantle reservoirs is a fundamental consequence of plate tectonics, and there is compelling evidence for recent recycling of oceanic crust and sediment at subduction zones from both geochemical and seismic data. The chemical and isotopic signatures of oceanic basalt provide a window into the spatial and temporal variations of the composition of the Earth’s mantle that have resulted from past recycling. Radiogenic Pb and Os isotopic compositions of ocean island basalts have long been held as evidence for significant fractions of ancient recycled oceanic crust in OIB mantle sources, and radiogenic Sr signatures have generally been attributed to recycled sediment. However, despite decades of investigations and an arsenal of radiogenic isotope systems, unambiguously identifying the nature of potential recycled components and uniquely distinguishing crustal recycling from alternative mantle enrichment processes has proven difficult. Recycled crustal materials will, after subduction and aging in the mantle, bear only limited resemblance to the original crustal “inputs” in their radiogenic isotope signatures due to changes in parent:daughter element ratios during subduction zone dewatering and variable durations of post-subduction aging.

Recent studies, though, have shown that light stable isotopes such as O and Li may have great potential as diagnostic tracers of recycled crustal material in oceanic mantle sources. Strong fractionations of light isotopes occur only in low-temperature (near-surface) conditions, with minimal fractionation at magmatic temperatures and no time dependence. Isotopic variations of O and Li in OIB outside of the relatively restricted MORB mantle range can provide strong support for a role of recycled lithospheric material in OIB mantle sources, as long as the influence of shallow magmatic processes can be ruled out. Low O isotope signatures in many OIB, including some with highly radiogenic Sr, appear to preclude a significant role of recycled sediment but are consistent with recycling of lower oceanic crust or serpentinized mantle lithosphere. Surprisingly, though, there is a growing database of heavy Li isotope signatures in OIB that, based on our current understanding of Li behavior, is not easily explained by recycled oceanic crust in OIB mantle sources. Instead, incorporation of subduction modified mantle wedge or serpentinitized lithospheric mantle could be important components of some OIB sources. The ages of such mantle can potentially be constrained based on Re-Os and Lu-Hf isotope systematics, both of which are relatively resistant to overprinting by metasomatic fluids and can serve tracers of aged melt-depleted mantle.
Quantifying the SIMS structural matrix effect

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Background
Determining absolute concentrations of trace elements by secondary ion mass spectrometry requires the use of one or more reference samples which are “matrix matched” to the material being analyzed. It is commonly posited that both the degree of crystallinity and the major element composition of a reference material influence its secondary ion yields, thereby affecting the determined relative sensitivity factors. This abstract reports on a project which quantifies the role played by sample crystallinity: the SIMS structural matrix effect.

Method
High purity disks of synthetic α-quartz and amorphous SiO₂ were purchased commercially. Special attention was given to obtaining samples with an optical polish with the surface roughness ≤10 nm. Both sample types underwent accelerator ion implantation in which the crystalline and amorphous samples were implanted during the same run, thereby assuring that both materials received identical ion fluxes (1e+14 ions/cm²). Separate Quartz-glass pairs were implanted with ¹⁰B, ²⁷Al and ⁴⁷Ti individually and the applied accelerating voltage was adjusted for each element so as to produce a maximum implant density at a depth below surface of ~200 nm.

Results
The results from single analyses on implanted pairs produced very similar depth profiles. The ratios of M⁺ to ³⁰Si⁺ at peak concentration were similar in both the crystalline and amorphous samples (see table). These results have yet to be assessed for second order issues including ion channeling during implantation, target knock-on during SIMS analysis and sample intrinsic background.

<table>
<thead>
<tr>
<th>Implant species</th>
<th>Quartz peak (M⁺/³⁰Si⁺)</th>
<th>SiO₂ glass peak (M⁺/³⁰Si⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹⁰B</td>
<td>3.6e-3</td>
<td>3.8e-3</td>
</tr>
<tr>
<td>²⁷Al</td>
<td>3.8e-2</td>
<td>3.1e-2</td>
</tr>
<tr>
<td>⁴⁷Ti</td>
<td>2.8e-2</td>
<td>2.7e-2</td>
</tr>
</tbody>
</table>

Discussion
These preliminary results demonstrate that, at least in the case of SiO₂, the structurally induced SIMS matrix effect for crystal-glass pairs with identical major element compositions is <20% for all of elements reported here. This conclusion is important because it suggests that the use of a chemically matched but amorphous reference material for SIMS mineral analyses would introduce a systematic error of only 10 to 20 percent.

How can we trace Fe isotope fractionation by weathering in soils?

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Stable Fe isotopes are fractionated during biogeochemical transformations of Fe in nature. Precise Fe isotope ratio measurements collected by several research groups using mainly MC-ICPMS have generated a substantial data set, which allows assessing natural Fe isotope variations and gaining insight into the underlying fractionation mechanisms. These studies have revealed both kinetic and equilibrium Fe isotope fractionations in laboratory systems and natural environments including soils. Hence, Fe isotopes represent a potential tool to trace past and present Fe cycling.

Iron occurs in soils in many different forms, and its transformations play an important role in weathering and soil formation. The oxidation of ferrous to ferric iron is one of the first steps in the weathering of primary silicate minerals under atmospheric conditions, which ultimately leads to the breakdown of the mineral structure. In contrast to other elements, Fe is usually not leached out of the system under oxic conditions, but precipitates immediately in the form of ferric (oxyhydr)oxide minerals. Thus, oxic weathering mainly produces in-situ re-distributions of Fe between different pools. Chemical extraction procedures are widely applied to separate specific Fe pools from soils. However, the success of these methods strongly depends on the mineralogy of the sample material, and they need to be calibrated carefully to obtain meaningful Fe pools and to avoid isotope fractionation artifacts. Therefore, we have tested whether grain size separation through physical methods might represent a suitable alternative approach to separate weathering products and residues in soils for Fe isotope analysis.

We will present Fe isotope data from an oxic Cambisol weathering horizon (Bw) on Aare granite (Switzerland). In this soil, weathering products (secondary Fe (oxyhydr)oxides) are enriched in the clay size fraction (<2 μm), whereas weathering residues (primary silicate minerals) are enriched in the sand size fraction (>63 μm). We performed and evaluated both physical and chemical separation methods in order to trace Fe isotope fractionation during weathering. The clay size fraction was found to be enriched in light Fe isotopes by more than -0.5‰ (reported as δ⁵⁷Fe) compared to the bulk digestion, whereas the sand size fraction was found to be enriched in heavy Fe isotopes by +0.2‰. An elemental and isotopic mass balance for Fe is consistent with a re-distribution of Fe within a closed system.

Our results show clear evidence for Fe isotope fractionation during weathering in soils causing enrichments of light Fe isotopes in weathering products and of heavy Fe isotopes in weathering residues. Potential fractionation mechanisms and implications for the interpretation and application of Fe isotope signatures in soils will be discussed.
The use of atomic force microscopy to study crack tips in glass

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Sub critical crack growth is the primary cause of failure in glasses, brittle ceramics and minerals when these materials are forced to sustain mechanical loads for long periods of time. Recently, a number of investigators have turned to the use of atomic force microscopy to characterize crack motion in glass. The technique has been used to study crack motion to velocities as low as $1 \times 10^{-13}$ m/s. It has also been used to characterize the roughness and fractal dimensions of fracture surfaces. By comparing opposing fracture surfaces, permanent displacements are shown to develop between fracture surfaces as a consequence of corrosion during the fracture process. In this talk we examine fracture surfaces of glass specimens that have been subjected to stresses at or below the static fatigue limit. Opposing fracture surfaces matched to an accuracy of better than 0.3 nm normal to the fracture plane and 5 nm within the fracture plane. Displacements between the upper and lower fracture surfaces that developed after a critical holding time were independent of distance from the crack tip, but increased with holding time, approaching an upper limit of about 25 nm for very long times. Despite the surface displacement, cracks tips appeared to be sharp. No evidence of plastic deformation near the crack tip was found. Results are discussed in terms of a hydronium ion - alkali ion exchange along the crack surfaces and corrosion of the glass surface near the crack tip by hydroxyl ions.

Hydrogen anomalies at seismogenic depths of the San Andreas Fault

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During drilling of the SAFOD Main Hole (San Andreas Fault Observatory at Depth), up to several percent of hydrogen were identified in drill mud gas. Hydrogen enters the well particularly in two fractured zones around the fault center, whereas apparently no hydrogen is present in the fault core in ~3100-3425 m bore hole depth.

In the fractured zone on the Pacific plate (~2700-2900 m bore hole depth), hydrogen correlates mainly with CO$_2$ and radon, whereas in the fracture zone on the North American plate (below ~3550 m bore hole depth), hydrogen concurrently appears also with hydrocarbons.

The H/D values of hydrogen in drill mud gas range from –618‰ to –708‰ SMOW. Deuterium fractionation between water and hydrogen would imply hydrogen genesis at relatively low temperatures that makes a deep hydrogen source unlikely. Moreover, we can widely rule out artificial hydrogen from drilling, hydrogen from serpenitization reaction, as well as radiolytic and organic hydrogen.

Several laboratory studies have shown in the past that freshly generated silicate mineral and quartz surfaces can catalyse the synthesis of hydrogen from water. Such reactive mineral surfaces could be generated in the rupture zone around a fault core, however, no experiments on fault zone rocks from seismogenic depths have been carried out yet. Thus, we have performed experiments on the mechno-chemical gas synthesis on SAFOD drill cuttings from seismogenic depth of the SAF, which mainly consist of clay, shale and sandstone. First results reveal an increase in gas after ball-milling the rock samples in a vaccum-tight mill. We will furthermore show results from experiments at varying conditions to verify if indeed mechno-chemical processes could account for hydrogen occurrences at the SAF.
Influences of thermal degradation on lipid composition of crop plant biomass

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Lipids are main components of fresh crop plant biomass. Only low amounts of those lipids are able to be incorporated and stabilized in soils due to e.g. the removal of biomass upon harvest or immediate remineralization. Incorporation pathways of lipids from plant biomass towards soil organic matter have been intensively studied throughout the past decades. However, it still remains unknown how the lipid composition of plant biomass is modified by thermal degradation, e.g. during burning. Within this study, we will show the effect of thermal degradation of maize and rye straw at several temperatures based on the lipid composition.

Maize and rye-straw were degraded thermally at temperatures of 300°C, 400°C and 500°C. Free lipids were extracted using ASE and thereafter separated into five fractions (aliphatic and aromatic hydrocarbons, low polar components including alcohols and ketones, acids and a high molecular weight and high polarity fraction) via a sequential chromatographic clean-up using SPE and MPLC. Deuterated molecular weight and high polarity fraction) via a sequential chromatographic clean-up using SPE and MPLC. Deuterated standards were added to the lipid fractions. Identifications and quantification were performed using a GC-MS after optional derivatisation.

The thermal degradation even at low temperatures (300-400°C) resulted in a reduction of the amounts of most lipid components, while the proportions of aromatic hydrocarbons were observed to increase. This was related to the incomplete combustion of the plant biomass forming new components at low temperatures. Especially at a temperature of 400°C large amounts of 3-6-ring PAHs including their alkylated counterparts were formed. At higher temperatures (500°C) more effective combustion resulted in lower concentrations of detectable aromatic hydrocarbons.

In contrast to predictable PAH formation, surprising results were obtained for the behaviour of carboxylic acid fractions. Similar to the other straight-chain lipids, the amounts of carboxylic acids decreased significantly with increasing temperature. But in contrast to other lipids like alkanes and alcohols, selected acids were still observable at 500°C. At 300°C preferentially straight-chain, branched, and unsaturated short-chain acids became relatively diminished in comparison to long-chain homologues. Conversially, higher relative proportions of short-chain acids were obtained upon combustion at 500°C. We postulate that these short-chain acids may have been extracted from organic components like black carbon, newly synthesised during the degradation process, which is subject of ongoing studies.

Constraining magmatic differentiation at Teide/Pico Viejo and associated rift zones, Tenerife, Canary Islands

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To unravel magma chamber processes and eruption triggers at the central volcanic complex Pico Teide/Pico Viejo (TPV) and its adjacent rift zones on Tenerife, we investigated 52 samples for their Sr isotope composition in feldspar phenocrysts. Processes such as magma mixing and contamination can be masked in whole-rock analyses, which merely represent the integrated average of all component parts involved (crystals, liquid, xenoliths). As feldspar crystals record prolonged crystallisation histories, we employ a micro-analytical approach to resolve magmatic processes. LA-MC-ICPMS represents the best means to a) yield a stratigraphy of Sr isotope ratios over core-to-rim profiles of single phenocrysts, i.e. a ‘timeline’ of the magma’s isotopic evolution and b) to carry out a large number of analyses in a relatively short time.

$^{87}$Sr/$^{86}$Sr has been analysed in plagioclase phenocrysts of the most recent eruptive products on Tenerife that built the TPV-complex and effused from the rift zones to the NW and NE over the last 35,000 yrs [1]. No correlation between $^{87}$Sr/$^{86}$Sr and An content has been detected in feldspars of these deposits, in concordance with the results from other localities such as Merapi or Krakatau [2; 3].

Crystal populations are found to be very heterogeneous amongst the sample suite and also within single samples [cf. 4]. The latter may range from no significant variation in $^{87}$Sr/$^{86}$Sr and An in some crystals to significant rises and subsequent falls of $^{87}$Sr/$^{86}$Sr independent of associated An variations in others.

A wide array of processes including FC, AFC and magma mixing is suggested to influence the evolution of TPV and rift zone lavas, demonstrating a complex interplay of differentiation processes within the TPV plumbing system.

References

No evidence of diffusive homogenisation of carbon isotopes in Yakutian diamonds

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C-N isotopes of diamonds are potentially useful in establishing the source and temporal evolution of C-bearing fluids in the mantle. Complex growth forms revealed by CL images indicate that many diamonds grew under varying conditions. However, using C-N isotopes to probe the evolutionary history recorded in successive growth bands is only of use if there is no diffusive equilibration at the µm scale. Little information is available about carbon diffusion. Harte et al. (1999) suggested that diffusion potentially homogenises C in diamonds due to their long residence in the mantle. Hauri et al. (2002) and Bulanova et al. (2002), however, argued that diffusion was insufficient to equilibrate C in Yakutian diamonds at the 50 µm scale.

Here we report SIMS data with high spatial resolution (<30 µm, spot size 20 µm) on traverses across <110> plates of Yakutian diamonds. Most diamonds, of both P- and E-type paragenesis, have δ¹³C between -8‰ and -2‰ close to that of ambient asthenospheric mantle. Variation in δ¹³C in excess of 1‰ is found between successive growth bands in 5 of the 11 stones studied to date, indicating a punctuated growth history (SIMS reproducibility ±0.2‰). Diamond 1703 from Mir records a remarkable 10‰ difference in δ¹³C between the octahedral core and rim. A traverse conducted at a 40° angle to the contact established that there is no resolvable diffusive exchange between the successive growth bands at 30 µm scale. We therefore conclude that C isotope diffusion is non-existent at the 30 µm scale and that δ¹³C variations in successive growth bands do record information about the composition of the C-bearing fluids that formed diamonds. SIMS N isotope data from the Yakutian samples is underway to characterise the coupled C-N isotope variations of these crystals.

References

Insights into enzymatic reduction of metal-oxides from single-molecule tunneling studies of multiheme cytochromes

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We have performed recent experiments that aim to elucidate the molecular mechanisms of enzymatic bacterial metal reduction by studying purified multiheme cytochromes (OmcA, MtrC) from Shewanella oneidensis MR-1 with single-molecule electron tunneling spectroscopy. Enzyme-mediated direct electron transfer (ET) between metal-reducing bacteria and mineral surfaces is a prominent environmental redox process that directly and indirectly influences subsurface geochemistry. By developing a means to chemically adsorb cytochromes to a solid surface, tunneling spectroscopy showed distinctly different conductance for OmcA and MtrC (Wigginton et al., 2007) indicative of two different surface-directed electron tunneling mechanisms for these proteins (Wigginton et al., submitted). The data suggest that one or more heme groups in MtrC participate in ET, and therefore MtrC may be tuned to a specific redox potential for biological function. In contrast, OmcA may function as a non-specific multi-pathway reductant of mineral surfaces because the tunneling spectra suggest that superexchange ET is the predominant mechanism. We are further scrutinizing this difference by using a novel configuration for biomolecule scanning tunneling microscopy (STM) to determine if MtrC and OmcA show different distant-dependent tunneling behavior. This configuration uses an insulated Au STM tip functionalized with cytochromes to systematically vary the separation distance between the cytochromes and a hematite surface. These experiments, performed as a function of solution chemistry, are also designed to provide specific information on the effects of pH, ionic strength, and electrolyte compositions on ET efficiency.

References
Biotite polytypes versus occurrence in granite body, Karkonosze, Poland

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Correlation between the polytypic compositions of biotites and their occurrence in the granite body was studied in the eastern part of the Karkonosze granite massif, SW Poland. Polytypic composition was expressed as the per cent ratio of 2M1 polytype in the mixture with the 1M (and 3T) polytypes, and was assessed based on powder diffraction patterns. The oblique texture method was used to enhance intensities of the diagnostic reflections: T14 of 2M1 and T12 of 1M.

The ratio of 2M1 decreases in the sequence: schlieren-free parts of granite, schlieren-rich parts, and schlieren themselves. Assuming that schlieren form as biotite segregations against rigid walls of country rocks during ascension of plastic magma, the magma chamber environment favours crystallization of 2M1, and the marginal parts of intrusion favour crystallization of 1M.

Biotite crystals occurring as inclusions in central parts of feldspar phenocrysts show a high ratio of 2M1 up to 43%. Biotites forming inclusions at the rims of feldspar phenocrysts have similar polytypic compositions as the main pool of biotites in the rock, and are about 25% 2M1. Assuming that the onset of crystallization of feldspar phenocrysts took place in the environment of the initial stage of magma crystallization, and that the tiny biotite crystals occurring in the central parts of feldspar phenocrysts preserved their original polytypic composition, this environment would promote the formation of the 2M1 polytype. This interpretation is in accordance with results of earlier studies (Wilamowski, 2002).

Biotites from mafic microgranular enclaves (MME) show 2M1 ratios of about only 6%, which is the lowest value recorded in the studied pool of samples. The polytypic composition of biotites from MME is either original, or established after incorporation of the enclaves. In the latter case recrystallization of biotites would occur under thermal influence of the granite magma. Indeed, the oval shapes of enclaves suggest their intensive thermal reworking. Also, the feldspar phenocrysts from granite magma often penetrate inside the MME proving the plastic state of the enclaves, which favours recrystallization processes.

Positive correlation of 2M1 with Ti content, and negative correlation with octahedral Al, are observed. Correlations between the polytypic compositions of biotites and the oxygen isotope compositions are expected. The oxygen isotope studies are in progress.

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Reference

Revisiting the oldest rocks in China

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Background

It has been known for over fifteen years that the Anshan region of the North China Craton contains the oldest rocks in China, extending back to 3811 Ma (Liu et al., 1992). Although these rocks are some of the most ancient preserved examples of continental crust on Earth, they occupy only a small portion of the craton, cropping out over an area of <20 km². We re-examined the Anshan area to determine if (i) the extent of ancient zircons is more widespread than originally defined, (ii) components older than 3.8 Ga are present, and (iii) Hf isotopic data can provide evidence of crustal evolution back to 4 Ga or beyond.

Results

Our results establish that rocks ~3.8 Ga in age are present in three areas close to Anshan City: in the Baijiafen, Dongshan and Shengoushi complexes. A mylonitized trondhjemite in the Baijiafen quarry has a SHRIMP zircon 207Pb/206Pb age of 3800±5 Ma, identical to earlier results from the area. Importantly, biotite schist from this quarry records an age of 3811±4 Ma, making this the oldest known supracrustal rock in the North China Craton. Trondhjemite collected adjacent to the site in the Dongshan complex that recorded an age of 3811±4 Ma, yielded younger zircons defining a crystallization age of 3680±19 Ma, indicating the complexity of magmatic relations in this area. A trondhjemite from the Shengoushi complex has a 207Pb/206Pb age of 3777±13 Ma, making this the third area in the district recording ages of ~3.8 Ga. The Hf data indicate that some zircons from all three complexes have depleted mantle model ages that extend back to 4.0 Ga. However, no rocks of this age have been identified and the data reveal that it is unlikely that considerably older components are present in the North China Craton.

Reference


Advection and redox processes as controls on minor elements in groundwater influenced by irrigation and surface-water exchange

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An understanding of the groundwater chemistry and transport of minor inorganic constituents must begin with the major processes of the hydrologic system. This research compares the influences of groundwater advection and redox chemistry on trace elements in a heavily irrigated agricultural hydrologic system.

Three times during 2004, samples were collected from both a groundwater transect that flows to the Merced River (California, USA) and from riverbed wells at the approximate point of flowpath discharge. Previous work (1, 2) has quantitatively described groundwater advection and denitrification in this groundwater system. Samples for this study were analyzed for a suite of dissolved elements by Inductively-Coupled Plasma Mass Spectrometry. Results are considered in the context of the U.S. Geological Survey National Water-Quality Assessment Program.

Concentrations of dissolved elements were statistically analyzed. Bromine, assumed to be a conservative tracer of advection, and manganese, an indicator of reducing conditions, were used as predictor variables. Strontium, barium, uranium, and phosphorus were relevant response variables. Principal component analyses and linear regression analyses indicate that advection dominates groundwater chemistry beneath the Merced River. Seasonal variation appears to influence whether groundwater composition is influenced by either hyporheic exchange from river surface water or groundwater supplied by the surrounding farmland. When the influence of advection is removed, redox chemistry becomes significant.

References


Stable sulfur and carbon isotopes of pore-water and solid-phase compounds in sediments of the Chapopote Asphalt Volcano, southern Gulf of Mexico

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During R/V Meteor cruise M67 2a/b (March-April 2006) to the Asphalt Volcanoes of the southern Gulf of Mexico two gravity cores were retrieved from the central depression of the Chapopote Knoll which contained viscous oil/asphalt a few meters below the sediment surface. Also several push cores were taken with the remotely operated vehicle (ROV) QUEST at sites where oil/asphalt reached closely below the sediment surface. From these cores solid-phase and pore-water samples were taken for on-board and subsequent shore-based analyses. Together with a core taken from a background site which is not influenced by asphalt/oil seepage these sediment and pore water samples are currently subject to detailed analyses of (1) the stable sulfur isotopic composition of both dissolved (sulfate and sulfide) and solid-phase (iron monosulfides, pyrite) sulfur compounds, and (2) the composition and stable carbon isotopic signatures of hydrocarbon gases.

The major aims of these investigations are to identify whether and to which extent the upward migration of oil, asphalt and gas (1) stimulates biogeochemical processes and turn-over rates, and (2) influences the stable sulfur isotopic composition of both dissolved and solid phase sulfur compounds. Furthermore, we seek to determine the potential of these – possibly unusual – stable sulfur isotopic signals of solid-phase sulfides to reconstruct hydrocarbon seepage in older geological records and to elucidate how the composition and the stable carbon isotopic composition of the hydrocarbon gases are altered by the action of typical chemosynthetic communities thriving at these sites. The values of δ34S of pore water and solid phase sulphide and furthermore of δ13C of the pore water methane give a first indication for high bacterial activity.
Sulfur speciation in quenched melts by Micro-XANES – The nature of S(IV+) in glasses

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Although Sulfur occurs only as a trace element in magmatic systems its behavior is directly related to a variety of important geological processes (e.g. formation of ore deposits, global cooling by S-rich explosive volcanism). The solubility of sulfur depends strongly on its oxidation state that may vary from S2− to S6+, and thus shows strong dependence on the oxygen fugacity in the system. XANES measurements at the S K-edge provide unique information on the sulfur species present. The fine structure at the S K-edge is dominated by localised 1s-2p transitions, which are strongly dependent on the electronic configuration of S [1]. Spectra were recorded at the ESRF ID 21 micro-focus beamline using a combination of broad and focused beams (200 µm and 0.8 µm diameter). We determined the S speciation in glasses in a variety of naturally occurring composition synthesized at 1 GPa, 1100 to 1350 °C (dry conditions) and at 200 MPa and 1050°C (5 wt% dissolved H2O). Of special interest was the detection of a S4+ species at intermediate redox conditions, i.e. the transition from S2− to S6+, as found by [2] in natural samples. The presence of such an intermediate species has important consequences on the thermodynamic treatment of sulfur equilibria in magmas. Synthetic samples were equilibrated at various oxygen fugacities and sulfur saturated conditions. In addition, disequilibrium samples were made, resulting in a continuous transition from S2− to S6+ from the rim to the center of the samples. The presence of S4+ was observed only in a few oxidized samples. However, our experiments show that the S4+ is related to beam damage induced by the electron-microprobe analysis, which preceded the XANES analysis. Furthermore, time-dependent XANES measurements indicate strongly that S4+ is also formed during the acquisition of the XANES spectra, which is particularly the case when using the focused beam. Due to this effect the S species in the disequilibrium samples were not analysed by collecting the complete XANES. Instead, scans across the samples were performed by resonant excitation at the energy position of each species. These profiles gave no indication for the presence of S4+. Finally, we have used the intensities of the respective resonances for S2− and S6+ to determine the sulfur oxidation state in the glasses as a function of the oxygen fugacity during the synthesis.

References

Controls on microbial activity and compositional alteration of crude oil during in reservoir biodegradation

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Biodegradation of crude oil and natural gas in petroleum reservoirs is of great economic relevance and plays an important role in the biogeochemical carbon cycle. Petroleum reservoirs are an outstanding habitat of the deep subterranean biosphere where hydrocarbons – the main constituents of crude oil and natural gas – are present in abundance to function as potential microbial carbon and energy sources. The effects of biodegradation on oil and gas composition are well-documented while only little is known about the underlying processes. It is, however, clear that geologic environments with significant accumulations of hydrocarbons, particularly petroleum reservoirs, are mostly anoxic. Limitations of microbial activity in petroleum reservoirs are poorly understood and are subject of ongoing investigations. Temperature is generally regarded as being very important with a threshold for biodegradation of approximately 80°C. Little is known about the availability of electron acceptors and nutrients.

This contribution will present new approaches to better assess and understand processes associated with hydrocarbon degradation in subsurface reservoirs by employing advanced analytical techniques (petroleum and stable isotope geochemistry). Model experiments with individual hydrocarbons as pure substrates or crude oil as a complex mixture of substrates provide insight into substrate specificities of numerous pure cultures of denitrifying and sulphate-reducing hydrocarbon-utilising bacteria. On this basis it can be shown that different patterns of hydrocarbon degradation in different oil fields most likely reflect differences in the respective microbial consortia. A new concept explaining observed patterns of compositional alteration will be suggested, which is based on the hypothesis that bioavailability of individual petroleum constituents is a crucial control of microbial activity. This is supported by the patterns of stable isotope fractionation associated with the oxidation of light hydrocarbons which allow the conclusion that diffusive transport of hydrocarbons exerts a main control on biodegradation rates, bioavailability of substrates and thus on microbial activity in a reservoir. Our results from various petroleum systems have strong implications with respect to the validity of the conventional perception of biodegradation as a process removing different compound classes sequentially resulting in more or less similar patterns of compositional alteration in any biodegraded oil reservoir.
Late Pleistocene and Early Holocene variability in organic matter sources in Lake El’gygytgyn, NE Siberia

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Lake El’gygytgyn is a 3.6 Ma old impact crater lake located in central Chukota, NE Siberia and has now become the major focus of multi-disciplinary drilling programs to study the climate history of the Arctic. Sediment cores recovered as pilot work from the central part of the lake in 1998 and 2003, comprise the last ~250 ka BP and thus probably represent the longest continuous terrestrial record of Arctic climate change. The results of this research will contribute to protocols for multinational teams of scientists to investigate more than 400 m of sediment expected to record climate change over the past 3.6 Ma.

Organic biomarkers representing four lipid classes (saturated hydrocarbons, ketones, alcohols and sterols, and free fatty acids) were isolated from selected depths in the core. Depths represent extreme environmental conditions (e.g. Early Holocene warmth and cold and dry conditions of the Last Glacial Maximum, LGM) determined from previous bulk sedimentary and inorganic geochemistry (Melles et al., 2007; Minyuk et al., 2007). The suite of n-alkanes recovered reflect a combination of autochthonous production and terrestrial plant input. Indices such as OEP and TAR consistently point to enhanced delivery of terrestrial OM during warm, wet conditions. In contrast, cold phases show diminished terrestrial input compared to aquatic production, likely controlled by perennial ice cover and water column stratification. Additionally, a suite of complex branched alkanes are observed within the LGM samples, yet their identification and source remain to be determined. A wide suite of sterols were also identified including cholesterol, cholestanol, stigmasterol and sigmasterol, consistent with Hanisch et al., 2004. Differences are observed between the LGM and interglacial intervals among low molecular weight alcohols, such as n-alcohols, and higher molecular weight sterols and other cyclic and acyclic isoprenoids. These preliminary results suggest complex interactions between OM sources and productivity, seasonal ice cover and regional climate.

References


Subduction erosion of lower continental crust: A mechanism to produce chemical mantle heterogeneities

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Sr-Nd-Pb-Hf-Os isotope and trace elements data suggest that the lower continental crust (LCC) may be part of the so-called enriched mantle (EM) sources (Kamenetsky 2001; Escrig, 2004; Hanan, 2004; Lustrino, 2005; Willbold, 2006). The mechanism(s) that transport LCC material into the mantle, however, remain enigmatic. Delamination and foundering of LCC during continental break-up are the mechanisms suggested most often, but may only lead to shallow-level contamination of upper mantle sources (Escrig., 2004; Hanan, 2004). Moreover, isotopic and trace element constraints on EM-type ocean island basalts require upper and lower crustal material to be mixed with ancient subduction-modified oceanic lithosphere previous to incorporation of the recycled material in OIB sources (Willbold, 2006). Subcontinental lithosphere is chemically buoyant and lower crustal signatures are generally not accompanied by the characteristic Hf and Os signatures expected for the subcontinental lithosphere. These observations provide a major obstacle for delamination processes. Erosion and subsequent subduction of overlying lower arc-crust at erosive plate margins (Clift, 2004; von Huene, 2004), on the other hand, is a suitable and straightforward physical mechanism for creating blends of the lower and upper continental crust (i.e., as sediments) and for recycling them, together with the subducted oceanic lithosphere, into the deeper mantle. Subduction erosion may thus be one of the principal mechanisms involved in generating EM sources and may also have important implications for the compositional evolution of the Earth’s mantle-crust system in general.

References

Massive H2S release to surface waters at the Precambrian-Cambrian (PC-C) boundary: Evidence from Mo isotopes

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The geological and geochemical circumstances which have caused a decline in abundance and diversity of the soft-body Ediacara fauna at the end of the Precambrian followed by the “Cambrian explosion”, is still a question of debate. Several triggers and associated kill mechanism could have been responsible for the sharp extinction at the PC-C boundary. Besides a bolide impact, flood basalt eruptions and methane release, shallow water euxinia caused by upwelling of euxinic bottom waters could provide an explanation for this biotic crisis. Further it is known that changing redox conditions like an increase in atmospheric oxygen concentrations could have played a key role for the Cambrian explosion. It was proposed that during the late Neoproterozoic period, elevated free oxygen concentrations could have triggered the evolution of eukaryotic organisms (Fike et al. 2006). Therefore it seems to be reasonable, that changing redox conditions could have also been responsible for the evolutionary changes in early Cambrian times.

To check this hypotheses we present Mo isotope signatures in black shales from two sample sets (Ara group, Oman and Yangsee Platform, China) which were deposited at and shortly after the PC-C boundary.

At the first view, the overall Mo isotopic signature of the early Cambrian black shales from Oman and China are similar to the signature found in Mesoproterozoic shales (Arnold et al. 2004). Canfield (1998) proposed that the Paleoproterozoic and Mesoproterozoic ocean was strongly chemically stratified with sulfidic deep deep waters and modestly oxygenated surface waters. Our new early Cambrian data support the idea that this stratification might have continued until the end of the Proterozoic.

On a closer inspection, a transient Mo isotopic signal following immediately after the PC-C boundary in both sample sets indicates a short but intense global non-steady state situation. Combined with the extreme Mo enrichment, found in the Chinese sulfide marker bed at the PC-C boundary, this signal can not be explained with recent Mo scavenging mechanism known from recent oceans. We put forward the working hypothesis of an upwelling of euxinic bottom water masses of an chemically stratified ocean as explanation for this Mo anomalies. This scenario not only explains the transient isotopic signal and the metal enrichment found at the PC-C boundary in several localities, it can also be responsible for the sudden extinction of the Ediacarian fauna caused by H2S poisoning.

Low-latitude calibrations of terrestrial cosmogenic nuclide production rates

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The scaling factors used for correcting production rates of terrestrial cosmogenic nuclides (TCN) for the effects of atmospheric absorption and the geomagnetic field on the cosmic ray flux, remain the largest source of uncertainty in determinations of surface exposure ages and erosion rates using the TCN technique. In the framework of the CRONUS-EU Marie Curie research training network, established to refine scaling factors and production rates, we have targeted basaltic lava flows at low latitude (where the effects of the geomagnetic field are assumed to be greatest) for natural calibration of cosmogenic 3He, 21Ne and 36Cl production rates. Sampling conducted over altitude transects permits quantification of atmospheric effects.

The first locality sampled was 6000m-high Mt. Kilimanjaro, Tanzania (03°S). Young (50 ka?) olivine- and pyroxene-bearing flows were sampled in an "elevation window" defined by the upper limit of rainforest and the lower limit of Quaternary glacial activity. Additional samples were collected from older (c. 500 ka?) cones at low elevation in nearby localities and, for relative calibrations of TCN production rates (e.g. 3He/36Cl), from glaciated surfaces at high elevations. Initial results yield cosmogenic 3He concentrations of 6.56 ± 0.21 x 107 at/g (2750 m) to 11.06 ± 0.46 x 107 at/g (3300 m), consistent with exposure ages of c. 150 ka for these contemporary flows if calculated using published production rates and scaling factors. Negligible variation in measurements of multiple samples (< 5% uncertainty) supports preservation of original flow-top features and the absence of post-eruptive erosion or burial of flows. Independent age determinations of these samples using Ar/Ar dating are on-going.

Recent investigation has moved to the Afar region of Ethiopia (12°N). Preliminary sampling has entailed collection of multiple samples over a 350 m altitude transect of a single flow on Beddi volcano in the Dabbahu rift-segment. The initial cosmogenic 3He measurements will assess our ability to perform high-sensitivity altitude calibrations.

Along with localities targeted by other teams in the CRONUS-EU network (Ascension Is. 07°N, Univ. Edinburgh and Cape Verde Is., 14°N, Univ. Glasgow) the Kilimanjaro and Ethiopia localities comprise the lowest latitude calibrations performed to date.
Fractionation of Fe and O isotopes in the mantle: Implications for the origins of eclogites and the source regions of mantle plumes

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Oxygen isotopes are widely utilised as tracers of subducted and recycled oceanic crust in the convecting mantle and in the source regions of mantle plumes. This assumes that the δ18O values reported for some ocean island basalts (OIB) and eclogites reflect the involvement of oceanic crust hydrothermally altered at low and high temperatures, respectively, in their genesis.

We have measured Fe and O isotopes in garnet and clinopyroxene mineral separates from 6 eclogite xenoliths from the Kaalvallei and Bellsbank kimberlites, South Africa. Iron isotope compositions (δ57/54FeIRMM-14) for garnet and clinopyroxene range from -0.64±0.08 (2 SD) to 0.61±0.08‰ and -0.21±0.08 to 0.57±0.06‰, respectively. Calculated bulk-rock δ57/54Fe ranges from -0.58±0.12 to 0.28±0.1‰. Garnet and clinopyroxene δ18O ranges from 3.8±0.2 (2SD) to 5.1±0.2‰ and 4.6±0.2 to 5.9±0.2‰, respectively. Calculated bulk-rock δ18O varies from 4.6±0.3 to 5.2±0.3‰. Mineral and bulk-rock δ57/54Fe values correlate positively with δ18O, implying that these isotopic signatures were produced by the same underlying mechanism.

One possibility is that the eclogites are derived from oceanic crust with a low δ18O signature produced by high-temperature alteration, which also creates the δ57/54Fe-δ18O trend. However, Fe isotopes only appear to be significantly fractionated during low temperature alteration when Fe is lost from the oceanic crust [1]. Iron isotopes are also unlikely to be fractionated by high temperature alteration as the Fe concentrations in these lithologies are unchanged from their precursors and the low Fe concentrations in hydrothermal fluids would limit isotopic exchange reactions.

It is therefore likely that the δ57/54Fe-δ18O correlations are produced in the sub-continental lithospheric mantle (SCLM) by melting and metasomatic processes. Previous studies have shown that Fe isotopes can be fractionated in the mantle by processes such as partial melting [2]. If the measured variations in δ57/54Fe and δ18O can indeed be produced in the SCLM, the implication is that the low (<5.2‰) δ18O values of some OIB and eclogites cannot necessarily be interpreted in terms of subducted oceanic crust components.

References

Interpreting soil profiles developed on loess using a GCM and a watershed weathering model

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Indicators tracking the global climate warming since the last glacial maximum in continental environments are still sparse, and display a non-uniform geographic distribution. A North-South transect in the Mississippi river valley provides a natural environment to explore the climate changes along this transect since 13 ky BP, through the interpretations of pedon scale chemical weathering as applied to a regional landscape. The studied modern soils are interpreted to have developed on loess with pedogenesis commencing between 13 – 10 14C ky BP. Mineralogical analysis of a sample subset are being compared to XRF elemental analysis to define weathering profiles across the temperature and precipitation gradient.

In order to understand the profiles we have observed and their relationship with the climatic evolution along the transect, we have used the GENESIS global climate model to predict soil temperature and moisture fluxes along the transect as a function of time. We then used these model outputs to drive the WITCH model to calculate weathering profiles. The WITCH model relies upon laboratory kinetic rate laws, rationalized within the framework of Transition State Theory (TST), to describe mineral weathering (dissolution/precipitation) in natural environments. Additionally, the model accounts for soil CO2 levels at varying depths and biogenic influences derived from the uptake or release of elements by vegetation. We compare observed soil profiles to soil profiles calculated by WITCH to learn about the effects of temperature and precipitation on weathering over the last 13 ky.
Growth of the South American convergent margin (lat. 31°-36°S) during Late Paleozoic times: A U-Pb and Hf-isotope study of detrital zircons from a fossil accretionary system

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Laser ablation ICP-MS U-Pb and Lu-Hf isotope studies of detrital zircon from different levels of the Chilean coastal accretionary system and the collisional Guarguaráz Complex W of the exotic Argentine Precordillera terrane delineate the growth pattern of southern South America during Paleozoic times: Zircons in the latter area mainly display a broad U-Pb age cluster at 0.98-1.50 Ga similar to the variation in sediments of the Argentine Precordillera, which were subducted at its western suture. By contrast, the age pattern of detrital zircons from the Late Paleozoic Chilean accretionary prism shows a mixed provenance, i.e. from the Argentine Precordillera as well as from the NW-Argentine basement to the east of it. Here, an additional age cluster of 0.39-0.58 Ga is typical for the variation of zircons grown during the Pampean and Famatinian orogenies in NW-Argentina. Minor ages of 0.60-0.98 Ga may represent the youngest zircon ages from the Precordillera and/or from the Brasiliano orogen. A second major age cluster at 1.0-1.4 Ga is consistent with a mixed signature of recycled zircons from the Precordillera and from the NW-Argentine basement. Minor age clusters between 1.50 and 3.20 Ga suggest multiple recycling of material derived from cratons in the interior of Gondwana.

Whereas metagreywackes of the coastal accretionary system at 35°S were deposited at a stable margin prior to the onset of subduction, youngest euhedral zircons (295-360 Ma) in metagreywackes at 31°S derived from a concomitant magmatic arc and were incorporated into basally accreted as well as forearc basin sediments. Initial Hf-isotope composition of around 150 representative zircons from the different age groups reveal that the respective protoliths originated from recycled sources with variable crustal residence time as well as directly from juvenile, mantle-derived melts.

Tracing terrestrial and cosmic dust with helium isotopes

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Noble gases have made significant contributions in paleoclimate studies over the past decades. Recent studies indicate that helium analyzed in key climate archives, such as marine sediments and ice, is dominated by interplanetary dust particles rich in implanted solar wind and terrigenous dust rich in radiogenic helium.

Because the helium isotopic composition of these two endmembers differs by about 4 orders of magnitude, helium isotopes, particularly their combination, are powerful proxies to monitor the flux of cosmic and continental dust.

Here, I present case studies from different sampling archives with an emphasis on Helium-4 as a novel tool for the study of eolian dust transport, dust provenance, environmental conditions of the dust source region and resulting implications for the interpretation of the paleoclimatic record.
Structure of grain boundaries in silicate materials (olivine and K-feldspar) applying focused ion beam (FIB) specimen preparation and TEM

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Our present knowledge on structure and behaviour of grain boundaries in silicates is still moderate compared to grain boundaries in metals and oxide materials. Various properties of silicates might be significantly influenced by the presence of grain boundaries and the grain boundary atomic structure. Structural grain boundary models derived from investigations on metals and oxides are frequently applied to silicates. Is such an assumption justified? There are similarities in the grain boundary structure. Melt films are observed along olivine grain- and olivine-pyroxene phase boundaries (Wirth, 1996). They are similar to amorphous films along interfaces in Si₃N₄ material (Kleebe et al., 1993).

However, there are also differences in the grain boundary structure. Based on the visibility of dislocation contrast in the TEM, the transition of low-angle to high-angle grain boundaries is suggested to be in the range of 10 – 15° of misorientation between the adjacent grains. Is this rule applicable to silicate grain boundaries? TEM grain boundary investigations on forsterite bicrystals synthesized by direct bonding question that transition range of 10 – 15°. In a recent paper by Heinemann et al. (2005) it was demonstrated that even at 21° misorientation of two adjacent forsterite grains, arrays of individual dislocations were observed. This observation suggests a different grain boundary structure from that of metals. In silicate grain boundaries charge compensation is a crucial requirement in contrast to grain boundaries in metals and therefore, a different grain boundary structure in silicates should be expected.

References


The abundances of nominally chalcophile trace elements in the main minerals of upper mantle rocks

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Knowledge about the behaviour of the nominally chalcophile trace elements As, In, Sn and Cd in the Earth’s mantle is important to understand accretion, core formation, or the Earth evolution models. The abundances of these elements in the main minerals of upper mantle rocks are unknown. We present the required data, estimate inter-crystalline partition coefficients and Earth mantle abundances for these elements and demonstrate the lithophile nature of In, Sn and Cd in the upper mantle.

The trace element abundances in the minerals were measured in situ by LA-ICP-MS on polished thin sections of 20 spinel lherzolite and clinopyroxene-bearing harzburgite xenoliths hosted in alkali basalts from worldwide intra-plate volcanic fields. The xenoliths cover a large range of equilibration temperatures (from 850 to 1250°C) and are well-equilibrated with respect to major elements and lithophile and siderophile trace elements (e.g. REE, Sc, HFSE, Co, Ni). Most of the samples are free of visible sulfides except for the xenoliths from Kilbourne Hole carrying up to 0.1 % modal Fe-Ni-Cu-sulfides.

The main host phases for the elements In, Sn and Cd are clinopyroxene (13-58 ppb In; 48-527 ppb Sn; 37-149 ppb Cd) and if present, amphibole (49-58 ppb In; 248-649 ppb Sn; 53-89 ppb Cd). The contents in the sulfides are so low (sulfide/clinopyroxene ratio < 5) that the contribution of sulfides to the bulk rock abundances of these elements is negligible. In contrast, Arsenic is to a larger extent stored in sulfide (sulfide/clinopyroxene ratio > 100). All elements show systematic partitioning trends among the main minerals as function of temperature providing evidence that inter- and intracrystalline chemical equilibrium between the coexisting phases of the peridotites is achieved. The effect of increasing temperature is to redistribute the elements from clinopyroxene into orthopyroxene and even olivine. A very good coherence in the Dcpx/opx of In, As, Se and V suggests that these elements partition into the same pyroxene site (M1) and share the same oxidation state (i.e., 3+).

The whole rocks element abundances were calculated by combining the contents in the minerals and the modal compositions of the peridotites in order to circumvent the problems of recent contaminations of the element budgets (e.g. by the transporting host basalt). The xenoliths define linear trends of bulk rock In, Cd and Sn with CaO respectively Yb. Using a primitive mantle value of 3.65 wt% CaO the correlations yield Earth mantle abundances of 18 ppb In, 35 ppb Cd and 92 ppb Sn, whose implication for the history of the Early Earth will be discussed.
Geochemical travertine records – Insights from µ-EDXRF and µ-XRD

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Natural travertines are deposited by hot springs (thermogene origin) or by low-temperature fluids (meteogene origin). Samples were chosen from a suite of travertines collected in Uganda and Tanzania along the western branch of the East African rift system. The travertine deposits are related to sites with hydrothermal activity, which are being investigated for their suitability of geothermal energy use within the BGR GEOTHERM programme. Travertines preserve a valuable record of paleo-fluid composition. Due to their inhomogeneity (thin layering) bulk analytical methods are in most cases not sufficient to unravel the small scale chemical and mineralogical changes. Hence, a combination of in situ methods with high spatial resolution (µ-EDXRF and µ-XRD) was applied. µ-EDXRF allows element mapping with a spatial resolution of 100µm by an assumed detection limit of 50 to 100µg/g for each element (>30 elements can be detected simultaneously). Locally precise measurements with a BRUKER D8-GADDS microdiffractometer allow a rapid phase analysis with a spot size down to 50µm. Such high resolution in situ analyses of mineralogical and chemical compositions are essential for reliable genetic interpretations. Due to their non-destructive and contact-less nature they are leading to a refined procedure to take sub-samples for further detailed investigations (e.g. stable isotope analysis to distinguish between meteogene and thermogene travertines).

Archetypal Archean lithosphere from West Greenland implicates shallow melting at >3.0Ga

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We present whole rock major, trace and Re-Os isotope systematics of garnet and spinel-facies peridotite xenoliths (n = 50) sampled across the North Atlantic Craton (~700km, NAC), West Greenland at c. 600 and 200 Ma. NAC whole rock peridotites have low Al/Si (0.002 to 0.06) and high Mg/Si (1.43 to 1.61), making them distinct from Kaapvaal and Siberian cratonic lithosphere. Furthermore, at a given MgO the NAC peridotites extend to distinctly lower Al₂O₃ compared with East Greenlandic lithosphere. Samples from the Kangerlussuaq and Sarfartoq regions (northern margin NAC) appear to be compositionally more heterogeneous; extending to both more fertile and more depleted Al₂O₃ and Mg# in comparison to samples from Pyramidfjeld (southern margin NAC). Low Sc and Al₂O₃ systematics of all samples can be reconciled with approximately 25-40% melt extraction at shallow garnet-facies conditions (~4GPa). V abundances in conjunction with Sc and Al₂O₃ indicate that relatively low fO₂ prevailed during the last melt extraction, although subtle differences exist in samples from the northern and southern NAC.

Whole rock Os isotope data shows considerable variation in NAC samples, with the most unradiogenic γOs (e.g. -14.2) corresponding to T_RD model ages > 3.0Ga. Harzburgites and dunites from the southern NAC indicate Mesozoic Re disturbances, possibly due to the kimberlite activity. The T_RD model age probability distribution of these samples shows relevant peaks at 1.8 Ga and 2.3 Ga possibly relating the lithosphere to orogenies and crustal formation events that affected the Archean basement of this area. Notably, preliminary olivine Os isotope systematics point to a significantly older formation of the lithosphere (~2.5Ga) and Os disturbance on the whole rock scale.

Melting conditions and distinct Mg/Si and Al/Si systematics of the Archean NAC peridotites indicate that archetypal Archean lithosphere formed in a relatively shallow, anhydrous setting. Furthermore, this data suggests that the orthopyroxene-rich Kaapvaal and Siberian lithosphere records secondary Si enrichment, thereby eliminating these continental roots as classic examples of Archean melting environments. Further lines of investigation will include resampling of the NAC, profiling of whole rock and constituent minerals for Os isotopes; lithophile and siderophile trace element systematics together with HF-Nd-Sr-Pb isotope determination measurements of pyroxenes.
Modeling cosmogenic nuclide accumulation in the upper Amazon basin

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To date, cosmogenic nuclides in detrital material have been used to determine denudation rates, but determination of cosmogenic nuclide accumulation during sediment storage in large depositional basins has received little attention. We have designed a cosmogenic nuclide-based accumulation model for depositional regimes along a river as it actively migrates across its floodplain. The feasibility of the model was tested in the Beni catchment in Bolivia, a large (~70,000 km²) Andean foreland basin draining the northern Bolivian Andes. On its way to the Amazon the river traverses through ~50,000 km² of floodplain, thereby depositing ~100 Mt of sediment per yr. The storage of sediment debouched from the source areas has been studied in great detail in terms of migration rate, sediment exchange between floodplain and channel, and therefore of sediment residence time scales11.

To resolve irradiation of sediment during transport and storage in the floodplain, the input of material from source areas was characterized cosmogenically. Samples from the High Andes, Andean foothills, and Cratonic shields give mean SLHL-scaled 10Be concentrations of 5*10^4, 1*10^5, and 4*10^5 ats/g, respectively, which correspond to mean denudation rates of 0.14, 0.5, and 0.02 mm/yr for these three areas. However, cosmogenic nuclide measurements on bedload from the active Beni channel (n=20; mean SLHL-scaled concentration of 3.7*10^4 ats/g) show neither significant accumulation nor decrease of nuclides.

Our accumulation model assumes erosion of sediment from river cut banks due to lateral migration, and an admixture of sediment conveyed directly from the previous reach. Sediment deposition is simulated by forming point bars from portions of the mixed material. Model parameters are most sensitive to initial concentration of the erosion products, channel migration velocity, channel remobilisation depth, and the relative magnitude of upstream sediment discharge to that of floodplain reworking. The model indeed predicts no significant gain in nuclide concentration from floodplain sediment remobilization for Beni river conditions. Therefore, even for a source area with erosion rates as high as the Andes, the cosmogenic erosion rate signal is preserved throughout residence in the depositional zone of the basin.

Reference

Oxygen Fugacity in the Laboratory and in Terrestrial Systems

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Several different synthetic phase assemblages – so called oxygen buffers – were devised by Eugster, 1957 in order to adjust defined oxygen fugacities in laboratories for experimental petrology at given temperatures and pressures. The “oxygen buffers” – and the corresponding acronyms – soon became popular and are now applied universally also to express fO2 levels in natural systems where, however, a correlation with the phase assemblages of the originally defined buffers is not evident. A typical example is presented by the numerous analyses of basalts with oxygen fugacities of QFM (see Ulmer et al., 2007).

From the fact that the fO2-data of the majority of basalts worldwide are arranged in a narrow belt along QFM (see Basaltic Volcanism Study Project, 1981) it is concluded that their redox state must be buffered. What may the properties and the quality of the buffers involved be? It must be realized that

- an oxygen buffer is a phase assemblage containing a certain element in different oxidation states. The entire periodic system was scanned and elements capable of coexisting in various oxidation states were marked.
- any buffer assemblage may react with any other one until one phase from buffer assemblage is quantitatively consumed and the latter buffer is thus annihilated. Eventually thus only one complete buffer assemblage can survive and will thus be dominating.

From the conditions cited above it is concluded that only the reaction: 2 H2O = 2 H2 + O2 may provide the required buffer. By thermodynamic calculations the oxygen fugacity of dissociating pure water close to QFM is confirmed for temperatures above 800 K, kinetically above the closing temperature of a reaction between basaltic magma and water, i.e. for conditions prevailing for the eruption of MORBs.

The correlation between the oxidation state of a rock and the activity of water during its formation may be extended to further systems. Thus the fact that analyses of Nakhlites were showing an oxidation state close to QFM indicates that during their formation on Mars water must have been involved – although at present neither water nor hydrous components in Mars minerals directly seem to support this conclusion.

Reference
Basaltic Volcanism Study Project, 1981
Model crustal fluids at high P and T: Implications for aluminum transport

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Fluid-rock interaction associated with metamorphism and magmatism causes mass transfer in the Earth’s crust. To understand metasomatism in model crust at high P and T, we investigated the solubilities of K-feldspar (K-fsp), muscovite (ms) and corundum (co) in H2O at 700 °C and 10 kbar. Starting materials of natural microcline, single corundum crystals, reagent KSi3O8.5 (KS3) and specpure H2O were reacted in a piston-cylinder apparatus. Fluid compositions were determined by weight loss of K-fsp and co and phase-equilibrium bracketing methods. K-feldspar and ms dissolve incongruently at the investigated pressure. With increase of 0.021 to 0.45 m KS3, Al increased from 0.012 to 0.170 m and coexisting mineral assemblage changed from co, through ms, to K-fsp. Our results locate two invariant points: I1, co + ms + fluid (0.082 m Al, 1.32 m KS3) and I2, K-fsp + ms + fluid (0.16 m Al, 2.69 m KS3). Total solubility of Al and SiO2 in the presence of dissolved K is considerably higher than in pure H2O at the same P and T, and SiO2 solubility in the presence of K-fsp is at least 0.83 mol/kg H2O, which is higher than the SiO2 in H2O in equilibrium with quartz at the same P and T (0.68 molal).

Preliminary experiments at quartz saturation at the same P and T provide the pH buffering assemblages K-fsp + ms + qtz (J1) and ky + ms + qtz (J2) and give nearly identical results. Fluid composition at J2 is 0.07 m Al and 0.098 m KS3, and at J1 is approximately 0.173 m Al and 0.264 m KS3. The results imply that the presence or absence of quartz does not effect the Al solubility for the investigated mineral assemblages. The fluids of the experiments are models of aqueous solutions equilibrated with common crustal bulk compositions such as metapelite and peraluminous and metaluminous granite. The results show that the dissolved Al content in the fluid increases as the bulk rock Al declines; i.e., a fluid in equilibrium with a model metaluminous granite has a higher Al content than one in equilibrium with a model metapelite. The high measured Al concentrations in H2O-rich fluids indicate that substantial Al transfer may occur at deep-crustal metamorphic conditions, even at low water-rock ratios. The enhanced Al solubility is a strong indication for Al-K and Al-K-Si complexing.

Influence of fO2 on the precipitation of Fe-poor sulfide minerals

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The Skaergaard Intrusion (East Greenland) differs from other layered intrusions in that it contains disseminated, stratiform Pd-Au mineralizations. In comparison with the classic disseminated sulfide-PGE horizons such as the Merensky reef in the Bushveld Complex or the J-M reef at Stillwater, the Platinoiva reef occurs at a much higher, chemically more evolved stratigraphic level in the cumulate pile in magnetite-quartz-rich cumulates. Sulfide mineralogy dominated by metal-rich Cu sulfides like bornite, and the noble metals associated with the sulfide are Pd and Au, mostly as alloys with (Cu,Fe)(Au,Pd,Pt). Typical Fe-Ni-dominated sulfides like pyrrhotite or pentlandite are absent.

Several processes have been discussed to explain Cu-enriched, Fe-depleted Pd-Au-enriched sulfide horizons: 1) fractional crystallization of (Fe,Ni)1-xS monosulfide leading to Cu enrichment in the derivative sulfide melt, 2) modification of Fe-Ni-sulfides by infiltration of Cu-enriched postmagmatic fluids, and 3) sulfide oxidation.

To simulate sulfide oxidation experimentally, we add to an (FeNiCu)1-xS monosulfide composition varying amounts of hematite and equilibrate these mixtures in welded evacuated SiO2 glass capsules at temperatures ranging from 1050 (superliquidus) to 700°C (subsolidus). Hematite reacts with the FeS component of the sulfides according to 2 FeS + 2 Fe2O3 = 6 FeO + S2, raising fS2 and sequestering FeO to the sulfide melt. In the subsolidus region, the reaction is 6 FeS + 24 Fe2O3 = 18 Fe3O4 + 3 S2, raising fS2 and stabilizing magnetite. The sequence of oxidation of sulfide species follows broadly the electromotive series, first FeS, then NiS, and finally Cu2S and CuS, eventually producing Cu-rich sulfides like bornite that coexist with metallic Cu, as observed in the Platinoiva reef. Microprobe analyses of the first experiments at 1050°C revealed a successive increase in oxygen (O2) content in the sulfur melt at the expense of S2 from < 0.5 wt.% (detection limit) to 7 ± 1 wt.% O2 in charges with > 30 wt% hematite. Iron also increases with increasing O2 content in the melt, suggesting that oxygen dissolves in the sulfide melt principally as FeO and/or FeO1.5 complexes. In the presence of sulfide melt oxidation to above the fayalite-magnetite-quartz equilibrium is difficult because the FeO component in sulfide melt tends to react with to SiO2 glass, stabilizing fayalite and constraining fO2 to near the FMQ equilibrium. In SiO2 glass, oxidation to beyond FMQ is possible only in the subsolidus temperature region.
Comparison of the ligand-promoted dissolution of kaolinite and goethite with different organic chelators at pH 6

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The cycling and environmental fate of many elements often involve the bioactivity of the microenvironment. The ability of organic acids to solubilize and complex key elements confer them a major role in the bioavailability of otherwise insoluble nutrients and toxins. The ligand-promoted dissolution of two major soil constituents, goethite and kaolinite, has been investigated in the presence of different organic ligands.

The polysaccharide alginate dissolves only little goethite until a second ligand enters the solution. The addition of oxalate and the siderophore DFO-B, respectively significantly enhances goethite dissolution. This synergistic effect on goethite dissolution in the 2-ligand systems alginate/oxalate and alginate/DFO-B can be explained by a considerable increase in the chemical affinity of the dissolution reaction in the presence of the second ligand (Wolff-Boenisch and Traina, 2007a). For oxalate, the ligand-promoted effect on goethite becomes only noticeable when the amount of goethite and/or oxalate in solution overcomes certain concentration thresholds. As to the siderophores, on an equimolar basis, far-from-equilibrium goethite dissolution rates in the presence of enterobactin are 5 times higher than analogous DFO-B-promoted rates although both chelators show low fractional adsorption <6%. Increased iron solubility and the related shift away from solution equilibrium is a more compelling explanation of the driving force behind goethite dissolution than surface complexation of these siderophores.

In separate systems, DFO-B and oxalate each caused a ligand-promoted dissolution of kaolinite and this rate increase is consistent with a mechanism involving ligand adsorption rather than chemical affinity or aluminum inhibitory effects (Wolff-Boenisch and Traina, 2007b). The concept of ligands competing for the same adsorption sites is corroborated by experiments where DFO-B and oxalate were employed to assess a potential synergistic effect on kaolinite dissolution. However, no such effect was observed. Species calculations as well as experiments indicate that DFO-B was preferentially adsorbed on the kaolinite surface. Further support for this hypothesis comes from the finding that siderophore-promoted dissolution of kaolinite showed the same relationship with aqueous ligand concentration as does the surface coverage: At low aqueous DFO-B concentrations <100 µM, increases in surface coverage and dissolution rates are more pronounced than at aqueous DFO-B concentrations >100 µM, where increase in these parameters is only marginal.

References

Experimental investigation of the CO₂ sealing efficiency of cap rocks

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Using a combination of experimental, petrophysical and mineralogical methods, transport processes of CO₂ in shales and marls, and its interactions with the mineral phase have been studied. The investigations comprised permeability, gas breakthrough and diffusion experiments under in-situ P/T conditions on cylindrical plugs of 10 - 20 mm thickness and 28.5 mm diameter.

Single phase flow tests with water were conducted to assess permeability coefficients and ensure complete water saturation of sample plugs before each gas breakthrough and diffusion experiment.

Capillary gas breakthrough tests were performed as described by Hildenbrand et al. (2002). To test for reproducibility and petrophysical changes due to the interaction of the samples with CO₂, repetitive runs were carried out on the same sample. Series of experiments with Helium and CO₂ under the same conditions have been conducted to compare the transport properties of inert and reactive gases.

CO₂ diffusion experiments were carried out according to the procedure described by Schloemer and Krooss (2004). These tests yielded unexpectedly high CO₂ storage capacities. Significant increases in (water) permeability coefficients were observed after CO₂ diffusion experiments.

Repetitive CO₂ gas breakthrough tests revealed irreversible changes of the petrophysical properties, possibly due to the interaction between the CO₂ and the sample. An increase in (water) permeability was noted after the first CO₂ gas-breakthrough test while permeability remained constant after the follow-up tests.

Mass balance calculations indicated significant CO₂ loss from the gas phase during the first breakthrough tests, whereas subsequent runs did not show any CO₂ loss. This loss of CO₂ from the gas phase is attributed to dissolution, sorption and mineral reactions.

High CO₂ storage capacities were also evidenced by manometric sorption experiments on powdered samples. In order to further clarify this issue, XRD analyses, BET tests, and Hg porosimetry measurements are presently being performed on the original and CO₂-exposed samples.

References
Surface charge and potential at carbonate mineral surfaces

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The surface chemistry of divalent metal carbonate minerals has received ample attention. The macroscopic properties of carbonate mineral surfaces were initially studied using electrokinetic measurements and potentiometric titrations. Since the 1990’s, the application of sophisticated surface imaging and spectroscopic methods plus the development of molecular models for (hydrated) carbonate mineral surfaces have significantly advanced our comprehension of the microscopic structure and reactivity of carbonate–aqueous solution interfaces. Surface complexation models for carbonate mineral–solution interfaces reproduce the macro-scale surface charging behaviour taking into account surface coordination sites derived from spectroscopic information [1,2]. Charge Distribution MULTIsite Ion Complexation (CD–MUSIC, [3]) modelling allows one to also include micro- and nano-scale information such as the presence of crystallographically distinct surface coordination sites, structural information of surface complexes, and possibly surface morphology. The CD–MUSIC model for carbonate mineral surfaces will be presented and tested against independent surface titration and potential measurements.

References


Barium isotope compositions of chondrites revisited

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The decay of the short-lived nuclide $^{135}$Cs to $^{135}$Ba with a half-life of 2 Ma offers potential for the study of volatile loss. However, the application of Cs-Ba cosmochronometry is only feasible if sufficient live $^{135}$Cs was present in the early solar system and if nucleosynthetic isotope anomalies are absent to allow for the unambiguous identification of radiogenic effects. The initial $^{135}$Cs/$^{133}$Cs = $4.8 \times 10^{-4}$ reported in [1] should result in well resolvable $^{135}$Ba variations in chondrites. However, two studies reported nucleosynthetic Ba isotope anomalies [2, 3] in bulk chondrites. For example, Ranan and Jacobson [3] observed enrichments of $^{137}$Ba/$^{136}$Ba and $^{138}$Ba/$^{136}$Ba up to 25 and 60 ppm, respectively for carbonaceous and ordinary chondrites.

Here, we readdress the issue of nucleosynthetic and radiogenic Ba isotope anomalies in bulk chondrite samples. To this end, four chondrites (Murchison CM2, Allende CV3, Saint-Séverin LL6, Pillistfer EL6) and one terrestrial sample were analyzed using a ThermoFinnigan Triton thermal ionization mass spectrometer.

After normalization to $^{136}$Ba/$^{136}$Ba, the $^{135}$Ba/$^{136}$Ba isotope ratios for all samples agreed to within 20 ppm with the terrestrial Ba standard, and no radiogenic $^{135}$Ba isotope anomaly was resolvable within uncertainty (2 se). Also, the $^{137}$Ba/$^{136}$Ba and $^{138}$Ba/$^{136}$Ba ratios deviated by no more than 17 ppm which is within the measurement uncertainty (13 to 37 ppm, 2 se) and were not resolvable, except for Pillistfer which differed from the Ba standard value by 47±22 ppm and 53±33 ppm (2 se) for $^{137}$Ba/$^{136}$Ba and $^{138}$Ba/$^{136}$Ba, respectively.

Our first results suggest that i) live $^{135}$Cs was not abundant enough to provide a useful cosmochronometer in bulk chondrite samples and ii) nucleosynthetic anomalies in chondrite samples [2, 3] may be nonexistent and thus, the solar nebula was probably very homogeneous. In that regard, however, we need to further evaluate whether the $^{137}$Ba/$^{136}$Ba and $^{138}$Ba/$^{136}$Ba anomalies observed in Pillistfer are real.

References

A Late Jurassic A-type granitoid, named Baijuhuajian granite in western Zhejiang Province, SE China, emplaced along the Jiangshan-Shaoxing fault zone and intruded an Early Jurassic anticline volcanic basin bounded by Sinian sedimentary strata composed of sandstone and siltstone. The granite exhibits a porphyritic texture and is composed of alkaline feldspar phenocrysts, and groundmass of K-feldspar, plagioclase, quartz and biotite. The granite is peraluminous (A/CNK > 1.1) and shows A-type geochemical signatures. The granite is characterized by high contents of SiO₂ (>75%), total alkalis (Na₂O + K₂O ≥ 6.3%), total REE (223 – 438ppm), HFSE as well as high FeOt/MgO ratios (15 – 25). It is also characterized by low contents of CaO (0.57 – 1.02 %) and extremely low contents of P₂O₅ (<0.01%), TiO₂ (0.06 – 0.14%) and Sr (7.23 – 38.81ppm). The fine-grained groundmass with perthite indicates shallow-depth emplacement of a relatively high temperature dry magma. The granite falls into within-plate field in various discrimination diagrams and can be classified as A 2-type granites, which is indicative of emplacement in a post-collisional setting. These features are similar to the A-type granites from the Lachlan Fold Belt, Southeastern Australia.

U-Pb zircon dating constrains the age of this granite to be 141Ma. Slightly negative ε Nd(T) (-2.46) and negative to positive zircon ε Hf(T) (-0.3 to 4.56) suggest binary mixing of possibly mantle-derived magma and crustal materials.

The tectonic regime was compressional in the Mesozoic prior to the emplacement of the Baijuhuajian granite, resulted from the subduction of Paleo-Pacific plate underneath the SE South China Block. Our results suggest that the tectonic regime in SE South China changed at ~141 Ma, from collisional to extensional settings, leading to upwelling of the asthenosphere and mantle-derived magma interacted with crustal materials before the emplacement along the Jiangshan-Shaoxing fault zone in SE South China.

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Fe-FeS-silicate partitioning of chalcophile and siderophile elements: Implications for core formation

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The concentrations of weakly siderophile and chalcophile elements in the primitive mantle provide important constraints on the conditions of accretion and terrestrial core formation, in particular the possible role of late sulphide addition and of late volatile loss.

In order to explore the possible impacts of these processes, we have determined the partitioning of V, Cr, Cu, Zn, Ga, Nb, Ag, Tl and Pb between Fe-FeS liquids and a range of liquid silicate compositions at 1.5-14 GPa and temperatures of 1280-2300 °C.

Many of the observed variations in partition coefficient are consistent with the known properties of Fe-alloys. For pure Fe metal coexisting at 1700 °C with a silicate melt of mantle FeO content, the metal/silicate partition coefficients are as follows: V(0.12), Cr(0.3), Cu(36), Zn(0.9), Ga(6), Nb(0.015), Ag(20), Tl(1.1) Pb(3.5). Adding C (at graphite saturation) to the metal increases Metal/silicate partition coefficients of Nb by an order of magnitude, those of V and Cr by a factor of 3, has small negative effects on Cu and Zn and larger negative effects on Ag and Pb partitioning. On going from Fe to FeS liquid the sulphide/silicate partition coefficients change approximately to: V(0.6), Cr(0.9), Cu(100), Zn(2), Ga(3), Nb(0.4), Ag(100), Tl(40), Pb(35).

Using these and literature data, a protracted period of accretion under reducing conditions appears to be required to satisfy the observed V and Cr contents of the mantle. This type of accretion path leads to around 30% of earth’s Nb residing in the core. Application of these constraints to the other elements indicates that late sulphide addition to the core can explain the Pb and Tl contents of the mantle and their isotopic signatures, but the amount required (1.5-2%) seems precluded by the strongly chalcophile nature of Cu.
Storage of crustal forming events in lamprophyres: Examples from the Fennoscandian Shield

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Lamprophyres are volatile-rich, peralkaline to alkaline, mafic to ultramafic igneous rocks, which typically occur as dyke swarms. Lamprophyres often contain mineral assemblages that were formed during the early stages of magmatic evolution, making it notoriously difficult to date their intrusive event (Rock, 1990).

The Fennoscandian Shield is composed of Archaean continental blocks in the northeast and the accretionary arc complexes of the Svecofennian Orogen (1.93-1.76 Ga) in the southwest. The magmatic end of the Svecofennian Orogen is represented by several low-volume bimodal shoshonitic granitoid intrusions as well as shoshonitic lamprophyres and carbonatites.

For this study, samples of shoshonitic lamprophyres intruded into both the Archaean and Proterozoic domains of the Fennoscandian Shield were examined. By analysing different isotope systems (e.g. U-Pb; Rb-Sr; Sm-Nd) as well as utilising the high spatial resolution capabilities of secondary ionisation mass spectrometry (SIMS), we aim to acquire geochronological data from the lamprophyres as well as the crust in which they have intruded.

Zircon grains were separated for SIMS analysis from three samples from the Lake Syväri region of eastern Finland and five samples from the western Lake Ladoga region of Russian Karelia. Zircon rims consistently yield ages between 1.78-1.77 Ga. These parallel the results of Eklund & Shebanov (2005) for the Áva ring intrusion in southwest Finland, and are similarly interpreted as the age of the lamprophyre intrusions. Cores yield a variable array of ages, which correspond to several well-established crustal formation events within the Fennoscandian Shield.

Preliminary Sm-Nd isochron ages from two Lake Ladoga samples are 1.67 Ga, while a Rb-Sr isochron from a Lake Syväri sample was 1.68 Ga. These are in agreement with K-Ar ages given by Haudenschild (1988) from the country rocks in eastern Finland, reflecting cooling and thus exhumation rates. εNd(1800) was found to be near zero for all three samples, indicative of shield scale mantle metasomatism at approximately 1.9 Ga. Partial melting of this subductively enriched mantle wedge generated the lamprophyric magma.

Our results show that by utilising several isotope systems coupled with high spatial resolution techniques, age data from diverse crustal forming events may be obtained from lamprophyres.

References

Ferric iron in clinopyroxene from the garnet peridotite facies: Systematics and partitioning behaviour

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Ferric iron is an important minor element in the Earth's mantle. Its presence in individual minerals is influenced not only by crystal chemistry and bulk rock composition, but also by the prevailing oxygen fugacity, which is known to vary laterally as well as with depth (e.g. Woodland & Koch 2003). Aside from garnet, pyroxene can be a significant carrier of Fe3+ in the garnet peridotite facies of the upper mantle. Fe3+ contents of clinopyroxene (cpx) measured by Mössbauer spectroscopy are reported for 32 garnet peridotite xenoliths from South Africa and Lesotho. Together with literature data, this enlarged data set allows a more robust analysis of the systematics of Fe3+ incorporation in cpx and partitioning behaviour of Fe3+ between cpx and garnet than that previously attempted (Canil & O'Neill 1995).

Measured Fe3+/Fe tot in cpx ranges from 0.10-0.38 and exhibits a general decrease with increasing equilibration temperature (the Fe3+ -insensitive BKN two-px thermometer). Such an anti-correlation is not found for Fe3+ cpfu in cpx. The reason for this is that the Fe3+ content of cpx also changes with temperature in the presence of garnet (i.e. Ellis & Green 1979). Fe3+ contents correlate with Na, underlining the importance of the aegerine component in these cpxs. Such a relationship is not observed in spinel peridotites (Woodland et al. 2006; Canil & O'Neill 1995), indicating a change in substitution mechanism for Fe3+ in cpx going from the spinel to the garnet peridotite facies.

Partitioning of Fe3+ between cpx and garnet is T-dependent. This has the effect of transferring Fe3+ into garnet with increasing T along a geotherm, which can influence how the fO2 will vary with depth.

References
Characterization of elemental release during interaction of bacteria with basalt and granite

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We used batch reactors to characterize the rates and mechanisms of elemental release during the interaction of a single bacterial species (\textit{Burkholderia fungorum}) with basalt and granite at $T = 28^\circ\text{C}$ for 36 days. We supplied glucose as a C source, either NH\textsubscript{4}\textsuperscript{+} or NO\textsubscript{3}\textsuperscript{-} as N sources, and trace apatite in the rocks as a P source. We measured the release of Al, Ca, F, Na, Mg, P, Si, and Sr under several biotic and abiotic conditions with the aim of evaluating how actively metabolizing bacteria might influence basalt and granite weathering on the continents. Over the entire experimental period, reactors containing viable bacteria yielded the highest elemental release rates. Large pH decreases occurred when using NH\textsubscript{4}\textsuperscript{+}. No pH changes occurred when using NO\textsubscript{3}\textsuperscript{-}. We attribute pH lowering to either organic acid production or H\textsuperscript{+} extrusion during NH\textsubscript{4}\textsuperscript{+} uptake. Protons may be produced and consumed simultaneously during NO\textsubscript{3}\textsuperscript{-} uptake, resulting in a net zero pH change. Elemental release rates inversely correlate with pH, suggesting that proton-promoted dissolution was the dominant reaction mechanism. In the granite reactors, formation of Al-F and Fe-F complexes may have enhanced mineral solubility by lowering Al and F activities. Within the context of this study, bacteria appear to elevate the rate of long-term atmospheric CO\textsubscript{2} consumption by Ca-Mg silicate weathering between factors of 2 and 5 over corresponding inorganic rates. The effect is greater for basalt than granite. With respect to the granite experiments, we propose that microbially enhanced Ca release from apatite and fluorite may contribute to elevated Ca/Na ratios commonly observed in granitic watersheds.

Ab initio molecular dynamics study of Li speciation in aqueous fluid at high pressure

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Fluids play an important role in almost all geochemical processes, such as dissolution and precipitation of minerals, isotopic fractionation or mass transport in hydrothermal systems. A key parameter for a quantitative understanding of fluid properties and geochemical processes involving aqueous fluids is the complexation of the dissolved ions and molecules. Since the speciation does not only depend on the chemical composition, but also on pressure and temperature, any direct approach for studying the molecular structure and transport in fluids at conditions of the Earth’s interior requires in situ experimental techniques (e.g. x-ray diffraction, x-ray absorption, Raman and infrared spectroscopy). However, most of these methods are insensitive to low concentrations of light elements, such as Li. Recently, due to the massively increased computing power, ab initio molecular dynamics (AIMD) simulations have become a powerful technique for molecular modeling of fluids with a complex chemistry that are not well described by classical models.

Here, the hydration of a Li ion in aqueous fluid is studied as a function of pressure by AIMD simulation at constant temperature ($T=1000$ K) and constant volume. The pressure is derived from an equation of state of pure H\textsubscript{2}O fluid. The calculations show that structural changes of the H\textsubscript{2}O fluid in the studied pressure range from $P=3$ kbar to $P=60$ kbar also affect the hydration of the Li ion. Since the number of H\textsubscript{2}O molecules in the first hydration shell of the Li ion is subject to rapid dynamic change, a distribution of coordination numbers can be calculated for each pressure. With increasing pressure, the average coordination number increases with considerable decrease of 3- and 4-fold and respective increase of 5- and 6-fold coordinated Li. The ionic coordination changes in aqueous fluids as a function of pressure could affect the isotopic fractionation between minerals and fluids and consequently could have implications for models of the geochemical element cycles. As a test of the possible P-dependence of the Li-isotope fractionation, experimental studies on the model system spodumene - fluid are currently being performed and will be discussed.
Chemically altered basalt at high-latitudes on Mars: TES, OMEGA, and GRS integrated data sets

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TES, OMEGA, and GRS provide unique and complementary insights into martian compositions. TES and OMEGA measure the compositions of the upper hundred to tens of microns while GRS measures the upper few tens of centimeters. TES oxide abundances (wt. %) for the Surface Type 1 (ST1) and 2 (ST2) global spectral endmembers are calculated by combining compositions of mineral-phase endmembers in proportion to their relative modeled abundances (vol. %). TES chemical trends reveal higher abundances of FeO for ST1 (ST1 15.2 % vs. ST2 12.4 %) and higher abundances of SiO2 for ST2 (ST2 57.9 % vs. ST1 53.9 %). Results from OMEGA are in agreement with TES oxides. OMEGA pyroxene maps are closely correlated with the equatorial-distribution of ST1 (High FeO) while high-latitude ST2 materials lack evidence of mafic absorption bands and are consistent with an enrichment of high-silica phases.

Recent GRS studies report chemical trends (wt. %) for 'regions' dominated by TES ST1 (RT1) and ST2 (RT2) materials. GRS RT2 chemistries have higher abundances of FeO (RT2 20.1 % vs. RT1 17.6 %), K, and Th compared to RT1. Abundances of SiO2 (RT1 44.7 % and RT2 45.8 %) and K/Th ratio do not show significant spatial variations.

The constant K/Th ratio across RT1 and RT2 is not consistent with subaqueous or deep subaerial aqueous weathering of basalt as K would fractionate from Th. Fractional crystallization and subduction zone magmatism could enrich K and Th, however GRS does not detect an enrichment of Si as would be expected. The lack of any enrichment in SiO2 between GRS RT1 and RT2 indicates that evolved volcanics (andesites) are not present in high-abundances at regional-global scales. The favored model from the GRS team is thus initial bulk differentiation processes on Mars producing compositionally distinct magma source regions in the mantle. RT1 and RT2 basaltic provinces with distinct trace element compositions could then be produced. Differences in SiO2 between TES ST1 and ST2, however, must also be taken into consideration. Thin coatings or rinds of high-silica phases (tens of microns) affect the shape and position of absorptions in emission spectra of basalt. Such coatings on Mars may form from near-surface ice and/or surface-atmosphere interactions with little to no water penetrating or cycling into the surface. Limited degrees of alteration in only the upper few tens of microns of the surface would affect TES derived chemistries and may be undetectable to GRS due to a deep sampling depth. TES, OMEGA, and GRS data sets support: 1) Distinct magma source regions and basaltic compositions for ST1-RT1 and ST2-RT2 and 2) Secondary coatings or rinds of amorphous high-silica phases at high-latitudes on ST2-RT2 basalt.

New experimental constraints on the Na-in-cordierite thermometer and its application to high-grade rocks

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The mineral cordierite is a common and important rock-forming mineral in medium- and high-grade aluminous rocks of the amphibolite- and granulite-facies. Large cations such as Na and K in cordierite can also be considered for thermobarometry. Experimental investigations with synthetic starting materials have shown that the Na content decreases not only with increasing T (Mirwald, 1986; Thompson et al., 2002) but also strongly depends on aH2O (Thompson et al., 2002).

To investigate the systematic variation of Na-in cordierite with T in metapelites we performed experiments using a natural quartzphyllite sample (Grt + Bt + Mus + Chl + Ab + Qtz). The experiments were done in a hydrothermal apparatus at 0.3 GPa and at six different temperatures (T = 580°C, 630°C, 650°C, 680°C, 730°C, 780°C) with varying amounts of H2O present (dry, H2O-undersaturated, H2O-saturated). In addition, experiments which contain significant amounts of H2O were also buffered with respect to fO2 (HM-buffer). The experimental investigations yielded the assemblage cordierite + biotite + muscovite + quartz at 580°C. Above 650°C and 680°C, K-feldspar + plagioclase + melt were also observed. T conditions, calculated by using the coexisting feldspars, yielded T of 640°C and 682°C in excellent agreement with the experimental conditions, indicating a high degree of equilibration within the experiments. In all experiments cordierite is present and the Na content in cordierite shows a systematic variation which strongly decreases with increasing T ranging from 0.154 Na apfu at 580°C to 0.059 Na apfu at 780°C. Preliminary results indicates the variation of Na-in-cordierite can be described with a linear function such as: T(°C) = (Na [apfu] - 0.43002)/(-0.000474).

Application of this thermometer to contact metamorphic rocks from the island Kos (Kalt, 1998) and to migmatites from the Bayerische Wald (Variscan Belt, Germany, Kalt et al., 1999; Tropper et al., 2006) yields contrasting results. Whereas the agreement above 700°C is very good, below this T, our calibration yields T which is too high, compared to conventional thermometry. One of the reasons of the discrepancy could be the presence of Na-bearing muscovite in our experiments, which might perturb Na partitioning into cordierite at these T.

References
High resolution ion microprobe analysis of sulphur isotopes in speleothem carbonate

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Sulphur emitted into the atmosphere from the combustion of fossil fuels is regarded as a key mechanism in climate forcing at both the local and regional scale. Trace amounts of sulphate in speleothem carbonate at some cave sites show an increase in concentration towards the present day, reflecting the increase in SO2 emissions since the onset of the industrial era and the early 1980’s. This suggests speleothems may record local aspects of atmospheric sulphate content. However, speleothem sulphur concentrations are low and manual techniques for sulphur isotope analysis allow only low resolution sampling. Microanalytical techniques are thus required to build a comprehensive palaeoclimate record.

Ion microprobe analysis has been used to extract sulphur isotopes from speleothem carbonate at high resolution. Two stalagmites from the Italian and Austrian Alps have been used to pioneer this technique. Growth rates are less than 100 µm/yr and concentrations of sulphate range between pre-industrial levels of 10 ppm to modern day values of 70 ppm. Analysis at annual resolution encompassing the past 100 years demonstrates an excursion in sulphur isotopic composition from values close to the carbonate bedrock end-member value in the pre-industrial era, to values isotopically depleted in 34S, reflecting the increase in SO2 emissions with industrial activity.

Counting statistic errors for the low sulphur concentrations (~10 ppm) are ±4 % while for the higher concentrations (~ 70 ppm), these errors approach ±1.5 %. New, low sulphur standard material is being investigated so that instrumental conditions can be optimized to provide higher precisions at low (10-50 ppm) sulphur concentrations.

EMP Study of Early Cambrian Barite Deposits in East Guizhou, China

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Geological Setting

The Lower Cambrian black shale sequence of the Niutitang Formation in southeast Guizhou China hosts a barite layer. The ore-bearing rock series is composed of black silicalite, carbonaceous shale interbedded with phosphorite, barite and carbonate shale in ascending sequence. The stratified main ore bodies, partially in lenticular form, are dominantly embodied in the silicalite and black shale of the lower section of the Niutitang Fm. of the early Cambrian.

Discussion of Results

Systematical samplings for the election microprobe (EMP) were taken in the Dahebian barite deposit in Tianzhu County of Guizhou Province China. Samples of barite ore were analyzed using JEOL JXA8100 in the Key Laboratory for Nuclear Rersources and Environmental Research of Ministry of Education, East China Institute of Technology.

Based on the election microprobe (EMP) study, the hyalophane K,Ba[Al2Si2O8] was reported for the first time in the barite deposits which is a typical low-temperature mineral(Table 1), and we analysed the origin of hyalophane based on studying about its chemistry composition, optical character and their correlation, more, researched the genesis of Dahebian and Xinhuan barite deposits. The study provides mineral evidence for the submarine hydrothermal exhalative genesis of Dahebian and Xinhuan barite deposits

Table 1. The electron microprobe analyses of the hyalophane in Dahebian and Xinhuan barite deposits (w%M)

<table>
<thead>
<tr>
<th>Sample No</th>
<th>mineral</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>FeO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>MnO</th>
<th>SrO</th>
</tr>
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<tr>
<td>Ys-8</td>
<td>hyalophane</td>
<td>47.47</td>
<td>24.79</td>
<td>0.04</td>
<td>0.02</td>
<td>0.25</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>DHB-11</td>
<td>hyalophane</td>
<td>54.55</td>
<td>23.66</td>
<td>0.08</td>
<td>0.02</td>
<td>0.25</td>
<td>0.06</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Xinhuan</td>
<td>hyalophane</td>
<td>52.32</td>
<td>23.68</td>
<td>0.14</td>
<td>0.02</td>
<td>0.26</td>
<td>0.06</td>
<td>0.04</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Acknowledgements

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Affinity of the Trans-North China Orogen: Constraints from detrital zircon U-Pb and Hf isotope compositions from the Fuping Complex, North China Craton

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There is a broad consensus that the North China Craton was assembled by the collision between the Eastern and Western Block along the Trans-North China Orogen at ~1.85 Ga [1]. However, controversy exists on the affinity of the Trans-North China Orogen. The Fuping Complex is located in the central segment of the Trans-North China Orogen and is considered to be the most promising area to investigate the evolution history of the North China Craton. In this study, we investigate the U-Pb and Hf isotopes of about 200 detrital zircon grains from the Wanzi Supracrustals, which are the major lithologies of the Fuping Complex, and the results provide important insights into the problem. The analytical results on metamorphic zircon rims give ages of 1825-1843 Ma, corresponding to the tectonothermal event that led to collision between the Eastern and Western Blocks. Other analytical data on igneous zircon cores mainly yield two age populations at ~2.1 and ~2.5 Ga, with some inherited ages scattering between 2.6 Ga and 2.8 Ga. These two groups of age are equivalent to those of the ~2.1 Ga Nanying granitic gneiss and the ~2.5 Ga Fuping TTG gneiss, respectively [2]. All zircons with ~2.5 Ga age from different samples possess positive initial $\varepsilon_{Hf}$ values, ranging from +1.4 to +10.9, with a peak at about +5. The depleted mantle Hf model ages of these zircons show a peak at about 2.8 Ga, identical to the main crustal formation age of the Eastern Block [3] and distinct from that of the Western Block [4]. These data suggested that the Fuping complex was emplaced in a continental margin arc system at the western margin of the Eastern Block, thus have affinity to the Eastern Block. The zircons of 2.1 Ga population have initial $\varepsilon_{Hf}$ values of -4.9 to +6.0 and a younger depleted mantle Hf model age peak at 2.61-2.67 Ga, interpret as a re-melting of the above 2.5 Ga rocks with minor juvenile material contribution. This study was supported by the Hong Kong RGC Grants (7048/03P, 7063/06P, 7058/04P and 7055/05P) and a NSFC grant (40429001).

References

Geochemical characteristics and isotope dating of moyite at the southeastern margin of the Kuruktag block, Xinjiang, China

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The plutons from the southeastern margin of the Kuruktag block, Xinjiang, which belong to Proterozoic or Carboniferous according to previous studies, are mainly the moyites. Geochemically, these rocks are metaluminous, alkaline I-type granites. The rocks are also characterized by enrichment of LREE and the REE-Chorinite patterns are similar to those of the he crustal granite. With respect to the trace element, the spider diagrams of the rocks are consistent with the volcanic arc granites. The zircon U-Pb dating yielded an age of the 430±1.0Ma (Fig 1), representing the emplacement age of these plutons. This study indicate that the existing of late Caledonia tectonic-magmas in the study area at the first time. The volcanic arc granites suggest the southeastern margin of Kuruktag block was a part of the east Tianshan early Paleozoic magmatism arc.

Keywords: Zircon U-Pb dating, moyite, the southeastern margin of the Kuruktag block

Figure 1. U-Pb dating result diagram of zircon from moyite

References
Li and B isotope characteristics of ultrahigh-pressure metamorphic rocks from Sulu, China

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We analyzed the Li and B isotopic composition of metamorphic rocks from Sulu recovered by the Chinese Continental Drilling Program to constrain the behavior of Li and B and their isotopes through dehydration of subducted crust up to conditions of ultrahigh-pressure (UHP) metamorphism and to rehydration during exhumation of UHP rocks. The analyzed samples show large variations in both Li content and δ7Li, ranging from 4 to 29 ppm and -12.4 to 0.5‰ for fresh eclogite, 8 to 22 ppm and -3.6 to +3.6‰ for retrogressed eclogite, and 1.2 to 11.6 ppm and 1 to 3.1‰ for ultramafic rocks, respectively. Most samples are characterised by very low B contents (<1ppm), with δ11B values varying from -14 to 0‰ for fresh eclogite, -10 to -1‰ for retrogressed eclogite, and -3 to +12‰ for ultramafic rocks. The Li and B isotope data indicate that isotopically heavy continental basaltic rocks have been transformed during subduction into isotopically light eclogites. Fluids released from the subducted rocks may (i) induce local melting and eventually be “stored” in local melt pockets and veins within restitic rocks or (ii) metasomatize mantle rocks. In both cases, mobilization of Li and B through the fluids results in large heterogeneities in the concentrations of Li and B, δ7Li and δ11B on centimeter to decimeter scale. For instance, higher B content and heavier δ11B value in garnet peridotite relative to neighboring eclogite (subducted crustal rocks) indicate that mantle-derived rocks were metasomatized by fluids released from the subducted slab. Similar small-scale isotopic heterogeneity is also found between fresh and amphibolized eclogite, illustrating the addition of isotopically heavier Li and B during retrogression. Because of the superposition of the effects of dehydration and retrogression and the mineralogical control on the partitioning and isotopic fractionation of Li and B, Li and B and their isotopes may or may not behave coherently in the same system during slab subduction and subsequent exhumation of UHP rocks.
Geochemical characteristics of the Early-Cretaceous mafic rocks from eastern China

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Sr-Nd-Pb isotopic compositions of the Early Cretaceous mafic rocks from different tectonic units of the eastern China, including western Shandong province in North China, Dabie orogenic belt and northeast margin of the lower Yangtze region are studied to deduce the characteristics of the Early Cretaceous subcontinental lithospheric mantle (SCLM) of eastern China.

The results suggest that the sources of these mafic rocks from different units have significant different Sr-Nd-Pb characteristics. The mafic intrusions from Jinan and Zouping, west Shandong province, have lower initial Sr compositions of 0.7041 ~ 0.7055, $\varepsilon_{Nd}(t) = -6 ~ -18.7$, and $^{206}Pb/^{204}Pb(t) = 16.55 ~ 17.00$, $^{207}Pb/^{204}Pb(t) = 15.22 ~ 15.35$, $^{208}Pb/^{204}Pb(t) = 36.29 ~ 36.95$. Those from North Dabie have $^{87}Sr/^{86}Sr(t) = 0.7067 ~ 0.7085$, $\varepsilon_{Nd}(t) = -6.5 ~ -19.1$, $^{206}Pb/^{204}Pb(t) = 16.37 ~ 17.40$, $^{207}Pb/^{204}Pb(t) = 15.31 ~ 15.45$, $^{208}Pb/^{204}Pb(t) = 37.11 ~ 37.98$. Compared with the mafic rocks from North China craton, those from Dabie have higher $\mu$ data and Th/U ratios, much closer to EM I in the $^{206}Pb/^{204}Pb$-$^{207}Pb/^{204}Pb$ diagram. However, the basaltic rocks from Luzhong, east Yangtze block have $^{87}Sr/^{86}Sr(t) = 0.7057 ~ 0.7065$, higher $\varepsilon_{Nd}(t)$ data (-3.9 ~ -6.2), and also higher Pb isotopic ratios: $^{206}Pb/^{204}Pb(t) = 17.88 ~ 18.08$, $^{207}Pb/^{204}Pb(t) = 15.50 ~ 15.55$ and $^{208}Pb/^{204}Pb(t) = 37.93 ~ 38.18$, close to EM II. In $^{143}Nd/^{144}Nd(t)$ and Pb evolution diagrams, the samples from each unit are well coupled with the area of lower crust , respectively.

The enriched isotopic characteristics of the mafic rocks from all units suggest the contribution of the lower crustal materials into the mantle source. Based on geochemical, isotopic and geochronological data, crustal contamination during magma ascending can be eliminated. Thus, it can be concluded that the involvement of different lower crustal material is one of the main processes which resulted in different isotopic characteristics in the mantle sources of different tectonic units in Eastern China at the Late Mesozoic by source mixing. The lithosphere delamination may be a possible dynamic model for explaining the incorporation of the lower crustal materials into the mantle source, but metasomatism model cannot be ruled out.

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Why carbonatites in the Lesser Qinling have high HREE compositions?

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Carbonatites are typically characterized by very high concentrations of LREE. They have very high LREE/HREE ratios. However, the carbonatite dykes in the Lesser Qinling, China, shows flat to weakly LREE-enriched chondrite-normalized patterns (La/Yb=1.0-5.5), which is in marked contrast with all other published carbonatite data. The calcite crystals analyzed by LA-ICPMS also show similar geochemical feature to their whole rocks. Xu et al. (2006) suggested that the carbonatites represent calcite-rich cumulate that had crystallized from a carbonatite melt. However, it cannot explain that why they contain higher HREE (e.g. Yb>30 ppm) than all other published carbonatite data. Calcite-rich cumulate is common in carbonatites (Woolley and Church, 2005). But the process cannot produce that other carbonatites have high HREE. Xu et al. (2006) considered that strong enrichment of HREE in the carbonatites may require their derivation by small degree of melting from a garnet-poor source. The explanation is not ideal, because other carbonatites may also derive from a garnet-poor source, and do not show high HREE contents. In addition, these carbonatite dykes is rarely intergrowth with pegmatitic quartz vein. Field observation indicates that their ages are close. Thus the high HREE abundances in the carbonatites may indicate that they underwent complex genesis processes. Regrettably, we cannot get unambiguous answer.

References
The age and reworking of Cathaysia crustal basement

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U-Pb dating and Hf isotope analysis of detrital zircons have been used to analyse the crustal evolution of the eastern and western parts of the Cathaysia Block in SE China. Zircons from the Oujiang River in eastern Cathaysia indicate that the basement is dominantly Paleoproterozoic (1850-1870 Ma, 2100-2400 Ma) in age with minor Archean components; it was extensively reworked in Jurassic-Cretaceous time (100-155 Ma) to produce the widespread Yanshanian magmatic suite. Both the 1850-1870 Ma event and the Yanshanian magmatism show wide ranges in Hf-isotope composition, consistent with mixing between crustal and juvenile magmas. Marked downstream changes in the relative proportions of zircon age populations emphasize the care required in using detrital zircon data to estimate continental growth rates. Zircons from the North River indicate that the crust of western Cathaysia was generated mainly during Neoproterozoic time, although it contains some Archean (2500-3500 Ma) to Mesoproterozoic components. This crust was strongly reworked during Caledonian (ca 450 Ma), Indosinian (ca 240 Ma) and Early Yanshanian (ca 160 Ma) thermal events; there is little evidence for juvenile crustal growth in any of these events. The distinct patterns of crustal evolution suggest that eastern and western Cathaysia may represent separate microcontinents, accreted to the older Yangtze craton, and transposed by extensive strike-slip faulting along major sutures.

Geochemistry of dissolved rare earth elements in the Xijiang River, China

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Flowing in the south of China, the Xijiang River is the largest tropical and subtropical rivers in Asia. It originates in the Maxiong Mountain on the Yunnan-Guizhou Plateau, drains a large area of typical karst landform especially in its upper-middle reaches in Yunnan, Guizhou and Guangxi Provinces, where is the center of the Southeast Asian Karst Region. This work focuses on the geochemical characteristics of dissolved rare earth elements (REEs) in the rivers draining the karst regions.

Concentrations of dissolved REEs of the mainstream and its tributaries were measured by using a method involving solvent extraction and back-extraction and subsequent measurements on ICP-MS. The rivers have very low dissolved REEs concentrations, range from 24 to 689 ppt, with a mean value of 125 ppt. The pH value, major cation and DOC (dissolved organic carbon) concentrations of the river waters are the most important factor controlling the concentrations of dissolved REEs in the river water. Negative corrections are observed between dissolved REEs concentrations and pH and major cation concentrations, and a positive correction is also observed between dissolved REE concentrations and DOC concentrations.

Most of river samples have heavy REE enriched patterns relative to PAAS (Post Archean Australian Shales), with (La/Yb)N=0.26–0.94, mean value=0.68. The obvious negative correction are observed between (La/Yb)N ratios and pH value, HCO₃⁻ and DOC concentrations. Usually, fractionation of REEs occurs during weathering and transport processes. LREE (light rare earth element) were preferentially absorbed the particle, and HREE (heavy rare earth element) preferentially dissolved to solution from rock during weathering process. Moreover, The HREE forms stronger complexes than the LREE with inorganic ions, such as CO₃²⁻ and OH⁻. So the enrichments in heavyREE for the Xijiang river waters, which drains a large area of karst landform, are most easily explained by the formation of carbonate and hydroxide complexation in solution. Most of river samples show negative Ce anomalies, and the most pronounced negative Ce anomalies occur in rivers of high pH. So the negative Ce anomaly is strongly pH-dependent in alkaline rivers.

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Dependence of the external and surface morphologies of matrix olivine particles on growth condition

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We have synthesized olivine particles from silicate vapor to study the growth mechanism of the matrix olivine in meteorites like Allende chondrite.

These matrix olivine particles in primitive meteorites were found to exhibit various morphologies and surface microtopographs [Nozawa et al., 2007 this conference]. Since morphologies involve a lot of information about the growth conditions, we have experimentally tried to reproduce the morphologies and surface microtopographs to compare these morphologies with the natural one.

Forsterite melt droplets were prepared in a graphite cell (45×20×30 mm) in a vacuum chamber (Ar, 100 Pa). A 100W of CO₂ laser was employed to heat a forsterite polycrystalline spherule for melting in <100 sec. There is a temperature and gas concentration gradient along the graphite plate. The former and the latter were measured respectively by a thin (φ=0.1mm) thermocouple and by measuring the thickness increase interferometry during the experiment. The forsterite crystals were characterized by TEM, FE-SEM, AFM and DICM. The latter two have been employed to observe the surface microtopographs.

As the temperature T, decreased and thus the supersaturation, σ of the vapor increased, the forsterite morphology changed from a bulky type (T=1000-1450°C, δ<9) to a platy type (T=700-1000°C, δ=9-17 (Fig.1)), then to a columnar needle shape (T=500-820°C, δ=13-25), and finally to a droplet type (T<500°C, δ>25). Various 2-dimensional islands with the step height of 0.3 mm-few mm were observed: rectangular growth islands with a smooth-edge step (T=1200-1500°C, δ<2), islands with a rough-edge step (T=900-1200°C, δ=3-10), and a droplet type (T<800°C, δ>16). These external and surface morphologies have been compared with natural matrix olivines.

In conclusion, these external and surface morphologies are comparable to those of matrix olivine observed in the matrix of Allende meteorite. Therefore, these olivine are concluded to be formed at 2000°C followed by rapid cooling in ~10 s. down to 700°C.

Particle fluxes and scavenging of radionuclides in the western Northwest Pacific Ocean

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Introduction

²³⁰Th, ²¹⁰Pb and Pu are particle-reactive radionuclides and are therefore removed from the water column by a scavenging process. Because of substantial input of terrigenous materials from riverine input and atmospheric input of continental dust, and the relatively high primary productivity, the western Northwest Pacific margins may be important for removal of reactive radionuclides by scavenging (Yamada and Aono, 2006). The objectives of this study are to measure the activities of ²¹⁰Pb, ²³⁰Th and ²³⁹,²⁴⁰Pu in settling particles in the western Northwest Pacific margin and to discuss the removal of reactive radionuclides by scavenging and particle transport processes on the margins of the western Northwest Pacific Ocean.

Materials and methods

A mooring of three conical time-series sediment traps was deployed at two sites in the western Northwest Pacific Ocean for nine months. The analytical procedure for ²¹⁰Pb, ²³⁰Th and ²³⁹,²⁴⁰Pu was essentially the same as that described by Anderson and Fleer (1982). A double-focusing sector-field ICP-MS instrument was used for the determination of the Th and Pu isotopes in settling particle samples (Zheng and Yamada, 2006).

Results and discussion

Total mass fluxes, ²¹⁰Pb fluxes, ²³⁰Th fluxes and ²³⁹,²⁴⁰Pu fluxes showed large seasonal variations and their weighted mean fluxes tended to increase with depth, with an especially large increase near-bottom. The ratios of the observed ²¹⁰Pb fluxes to the ²¹⁰Pb deficiency fluxes in the near-bottom traps ranged between 1.22 and 2.63. The mean total ²³⁰Th fluxes at the near-bottom traps were 4.2–6.7 times higher than that expected from production in the overlying water column. The high fluxes of particulate ²¹⁰Pb, ²³⁰Th and ²³⁹,²⁴⁰Pu collected by the near-bottom traps reflect a combination of enhanced scavenging of dissolved ²¹⁰Pb, ²³⁰Th and ²³⁹,²⁴⁰Pu by the high fluxes of particles in the region, as well as the lateral redistribution of particulate matter itself by downslope gravitational settling and by alongshore transport by currents.

References

Coupled C-S-Fe isotope variations in Archean-Paleoproterozoic shales trace microbial metabolisms and redox state in the early Earth

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Systematic variations among $\text{C}_{\text{org}}$, $\text{S}$, and Fe isotope and elemental compositions in 89 low-metamorphic grade drillcore samples of fine-grained Archean-Paleoproterozoic sedimentary rocks (Kaapvaal and Pilbara cratons) constrain microbial metabolisms and redox state between ~3.3 and ~2.2 Ga. Mineralogical and chemical compositions vary greatly: Fe (1~35 wt.% as total Fe), S (0~4 wt.%), and $\text{C}_{\text{org}}$ (0~12 wt.%). $\text{C}_{\text{org}}$-rich rocks have strongly negative and variable $\delta^{56}\text{Fe}$ values (-2.3 to +0.6‰), where the most negative $\delta^{56}\text{Fe}$ values are restricted to samples where $\delta^{13}\text{C}_{\text{org}} < -35$, down to -50‰, suggesting that Fe$^{3+}$ reduction may have been driven by methanogens in these samples. $\delta^{34}\text{S}$ and $\delta^{56}\text{Fe}$ values for these samples are negatively correlated, where $\delta^{34}\text{S}$ values as high as +15‰ suggest bacterial sulfate reduction under sulfate-limited conditions, consistent with an important role for methanogenesis. The negative $\delta^{56}\text{Fe}$ values, however, indicate that reactive Fe$^{3+}$ was not limited. These relations provide powerful evidence that low-$\delta^{56}\text{Fe}$ Archean sedimentary rocks do not owe their origin to a low-$\delta^{56}\text{Fe}$ Archean ocean via extensive precipitation of oxides, as has been proposed, but instead reflect major biogeochemical cycling processes.

In contrast, S- and $\text{C}_{\text{org}}$-poor samples have restricted $\delta^{56}\text{Fe}$ values (-0.6 to +0.2‰), higher $\delta^{13}\text{C}_{\text{org}}$ values (35 to -25‰), and modestly positive $\delta^{34}\text{S}$ values (0 to +5‰). The Fe budget in these samples is dominated by detrital components, and $\text{C}_{\text{org}}$ and $\text{S}$ isotope compositions record a component of photosynthesis and bacterial sulfate reduction, respectively. Some of these rocks have high Fe$^{3+}$/Fe$^{2+}$ ratios, suggesting significant oxidation at ~3 Ga.

Collectively, these results provide evidence for a diverse biosphere in the Archean that involved a consortium of microbial communities that included cyanobacteria, sulfate-reducing bacteria, and methanogens/methanotrophs; bacterial Fe$^{3+}$ reduction may have been driven by dissimilatory iron reducing bacteria, sulfate-reducing bacteria, methanogens/methanotrophs, or a combination of these. The significant inventory of Archean sedimentary rocks that have highly variable $\text{C}_{\text{org}}$, S, and Fe isotope compositions indicates that extensive microbially-mediated redox cycling of Fe, S, and $\text{C}_{\text{org}}$ occurred in the Archean-Paleoproterozoic oceans. The Archean oceans could have been at least temporally, locally, and slightly oxygenated in order to form and retain sulfate and reactive Fe$^{3+}$. Therefore the oceans between ~3.3 and 2.2 Ga must have been, to some degree, stratified in redox state.

In situ isotope analysis of Fe in pyrite using laser ablation-ICPMS

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Introduction

Iron isotope provides us various key information about how the oxidative-reductive circumstance of the very dawn time was. Pyrite (FeS$_2$) is the most important mineral in sediments because of several unique features such as chemical robustness through mechanical transmutation or secondary metamorphic events. In order to derive precise and reliable Fe isotopic data from pyrite, recently developed laser ablation-ICP-mass spectrometry (LA-ICPMS) has been widely employed (Horn et al., 2006). However, in-situ isotopic analysis of Fe from pyrite using the LA-ICPMS technique has been retarded mainly because of poor analytical sensitivity and repeatability of the isotopic ratio measurements. It is widely recognised that the deterioration in analytical sensitivity and precision can be attributed to redeposition of sample around the laser ablation pit, and the measured isotope ratios (e.g., $^{56}\text{Fe}/^{54}\text{Fe}$) changed through ablation time (Jackson and Guenther, 2006, Hirata et al., 2005). In order to improve the reliability and precision of the Fe isotopic ratio measurements, resulting precision and accuracy of the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio data obtained by the LA-ICPMS technique were rigorously tested.

Method

The graph below illustrates the changes in measured $^{56}\text{Fe}/^{54}\text{Fe}$ ratio against ablation time obtained by laser ablation of pyrite sample, demonstrating the isotopic fractionation (ca. 1‰ level) through laser ablation.

Series of experiments revealed that mass bias factor on $^{56}\text{Fe}/^{54}\text{Fe}$ ratio measurement was seriously dependent upon the amount of sample re-deposition around the ablation pit. In this paper, we will describe the new approach to minimize the isotopic fractionation using a femto-second laser ablation system.

References


Sulfur system in anoxic confined aquifers in the northeastern Osaka Basin, Japan

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We used δ34S values and chemical compositions of groundwater to investigate the influence of sulfate reduction and sulfide oxidation processes in a confined aquifer system in the northeastern Osaka Basin (NEOB), central Japan. Shallow confined groundwater (<100 m) in the basin is recharged mainly from mountainous areas to the north, and flows south and southwest through the aquifer system. Anion composition of the groundwater is dominated by HCO3– throughout the basin. However, concentrations of redox-sensitive species such as dissolved oxygen, NO3–, Fe2+, and Mn2+ show that groundwater conditions become increasingly anoxic along the flowpaths. Moreover, SO4/(SO4 + 2HCO3) molar ratios decrease with increasing δ34S along the flowpaths, which demonstrates that sulfate is reduced in the NEOB aquifer system. Groundwater with both high total dissolved solids and high SO4 content was observed mainly in areas down-flow from faults. Because of the high SO4 content, the anion composition of this groundwater cannot be adequately explained by a simple sulfate reduction process. A Rayleigh distillation model with ε = –20‰, which allows for sulfide oxidation within marine sediments in proximity to faults, explains the chemistry of all groundwater samples, including those with high SO4 content. The model demonstrates that 76% of initial sulfate is reduced at maximum, and that reduced SO42– content is up to 48.5 mg/L after sulfide oxidation in the NEOB aquifer system.

Adsorption and coprecipitation behaviors of platinum(II) complex ions on and with manganese(IV) dioxide and manganese(II) hydroxide: Model reactions for the concentration mechanism of platinum into oceanic manganese nodule

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In oceanic manganese nodule and crust, platinum (Pt) is more concentrated than sea water and earth’s crust. However, the concentration mechanisms of Pt and its chemical state have not been clarified because of its extremely low concentration. From thermodynamic investigation, Pt is considered to be present as Pt(II) complex ion ([PtCl4–n(OH)n]2-) in deep ocean water. Therefore, we investigated the adsorption behavior of Pt complex ions ([PtCl4–n(OH)n]2-) on manganese(IV) dioxide (δ-MnO2) and the coprecipitation behavior of Pt complex ions with manganese(II) hydroxide (Mn(OH)2) as model reactions for the concentration mechanisms of Pt into manganese nodules and crusts. δ-MnO2 and Mn(OH)2 that is finally oxidized to manganese(IV) dioxide by dissolved oxygen are regarded as model compounds of manganese nodule and crust. Pt(II) complex ions were vigorously adsorbed on δ-MnO2. The XPS and XANES spectra for Pt showed that the Pt(II) complex ions adsorbed on δ-MnO2 were oxidized to Pt(IV). Based on the analytical result of EXAFS spectrum, the Pt(IV) was present as PtO4 species, suggesting that the adsorbed Pt(II) may be oxidized and substituted with Mn(IV) in δ-MnO2. Pt(II) complex ions were also coprecipitated effectively with Mn(OH)2. The Pt(II) may be oxidized to Pt(IV) after the oxidation of Mn(OH)2 to MnO2.

In conclusion, the concentration mechanism of Pt into manganese nodule and crust can be deduced as oxidative substitution by the redox reaction between Pt(II) in [PtCl4–n(OH)n]2- and Mn(IV) in manganese(IV) dioxide.
Transition from MORB through intermediate type to IAT magmatism in the northern Oman ophiolite

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Wadi Rajmi area in the northern Oman ophiolite had been recognized as an “anomalous” crustal section in the Oman ophiolite, including the dike swarms crosscutting sheeted dike complex and large occurrence of gabbro-norite (e.g. MacLeod & Rothery, 1992). In this area, the crustal section shows over 7km thick sequence of layered gabbro, layered wehrlite, heterogeneous gabbro-norite, isotropic diorite-tonalite, foliated gabbro, isotropic and pegmatitic gabbro, sheeted dike complex and pillow lava, from bottom to top. Besides three boninitic dike swarms are found from this area, and they are intruding into lower crust to pillow lava. Layered wehrlite, heterogeneous gabbro-norite and isotropic diorite-tonalite are regarded as the late intrusive complex intruding into layered gabbro and foliated gabbro. Layered gabbro blocks rarely appear in heterogeneous gabbro-norite. The boninitic dike swarms crosscut all earlier plutonic rocks including the late intrusive complex and dikes.

Based on mineral and bulk chemistry, we could distinguish three types of magma products (MORB, IAT and intermediate type) in the crustal sequence of Wadi Rajmi area. Trace element and REE contents of the boninitic dike swarms indicate a very low-Ti (TiO$_2$= 0.14-0.61 wt.%) and a depleted chondrite-normalized REE pattern (La$_{chondr}$/Sm$_{chondr}$= 0.63-1.67). These characteristics indicate that the boninitic dike swarms have IAT affinities and some of these have high-Ca boninite affinities. Clinopyroxenes from the boninitic dike swarms are a very low TiO$_2$ (<0.33 wt.%) in consistent with the bulk rock characteristics. Clinopyroxenes from gabbro-norite indicate slightly lower TiO$_2$ content (0.05-0.74 wt.%) than those of layered gabbro and foliated gabbro (TiO$_2$=0.18–0.91 wt.%; corresponding to MOR gabbro). Clinopyroxenes from layered wehrlite have a very low TiO$_2$ content (0-0.15 wt.%) and REE patterns with are comparable with those of boninite dike swarms. These mineral chemistry of the late intrusive complex indicate that these rocks crystallized from intermediate type magma between MORB and IAT.

The occurrence of three types of magma suggests that the tectonic setting of the Oman ophiolite was changed from accretion stage of MORB oceanic crust at mid-ocean ridge through reconstruction stage of oceanic crust by intrusion of intermediate type magma to IAT magmatism stage (subduction related magmatism).

Reference

2.7 Ga Re-Os age for C-rich slate of the Joy Lake sequence, western Wawa subprovince, Minnesota

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Re-Os dating of carbonaceous rocks using H$_2$SO$_4$-CrO$_3$ dissolution [1] provides a powerful new geochronologic tool for application in Archean terranes. Using this method, we determined ages of ~2.7 Ga for C-rich slates in the Joy Lake sequence, the oldest Re-Os ages yet reported for C-rich sedimentary rocks. The Joy Lake supracrustal sequence (western Wawa subprovince, Superior province, north-central Minnesota) consists of volcanic and sedimentary strata with intercalated mafic tuffs, intruded by layered peridotite-pyroxenite-gabbro sills of the Deer Lake complex. Poor exposure and lack of geochronologic data for this sequence hinder construction of a geologic framework for the Wawa supracrustal rocks, compromising correlation with other sedimentary sections in the Superior province.

Carbonaceous slates of the Joy Lake sequence have well-developed cleavage subparallel to bedding and contain nodules, disseminations, and bedding-parallel stringers of pyrite [2]. Samples from two drill holes (DH26503 and DH26506) yield isochron ages of 2695±14 Ma and 2684±16 Ma and initial $^{187}$Os/$^{188}$Os (Os$_i$) of 0.15±0.16 and -0.29±0.20, respectively. The ages, identical within uncertainty, are consistent with ages for Timiskaming-type sequences in the Wawa (~2688 to 2695 Ma) and Abitibi subprovinces (~2677 to 2680 Ma) [3,4], that represent late-orogenic deposits and likely postdate the Joy Lake sequence.

A chondritic Os$_i$ (0.109 at 2.69 Ga) is expected in Archean shales [5], but the negative Os$_i$ for DH26506 requires explanation. Re may have been released from intercalated high Re/Os mafic tuffs during recent exposure and local oxidation. The C-rich rocks are a ready sink for mobile Re. This could shift isochron data points to higher $^{187}$Re/$^{188}$Os with minimal slope change, increasing scatter and uncertainty for the Os$_i$. This would shift the isochron to the right, producing a spuriously low or negative Os$_i$ intercept. If the Re addition is recent, the age is not affected. Notably, the shales in DH26506 are in direct contact with pyroxenite [2].

References
Geochemistry and origin of black shale hosted Ni-Mo-PGE-Au mineralization in south China

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Most of the world’s PGE mineralizations are mainly associated with mafic intrusions. There is, however, increasing evidence that economic levels of PGEs can be found in other environments. In this regard, the black shale-hosted PGE deposit has recently become a promising important source of PGE and many other metals in the world.

In the Yangtze Platform of South China occurs a thick sequence of metal-rich black shales of Neoproterozoic to early Cambrian age. An extreme multi-metal enriched sulfide ore bed has been identified in the lowermost strata of the Niutitang Formation in Lower Cambrian. Compared to average upper continental crust value, this multi-metal rich ore layer contains >10,000 times enrichment in Re and Os, and >1,000 times enrichment in Pt, Pd, Ag, and Au. In recent years, we have conducted a detailed geochemical and isotopic investigation in an attempt to decipher the depositional environments, to trace the source of metals, and to establish an ore genetic model for this special type of mineralization. Our Re-Os and Pb-Pb isotope dating of the black shales and sulfide ores suggested an age of ~530 Ma for deposition of the black shales and Ni-Mo-PGE-Au mineralization. A detailed trace element study shows that both the sulfide ores and their host black shales share similar element distribution patterns with pronounced depletion in Th, Nb, Hf, Zr, Ti, and extreme enrichment in U, Ni, Mo, and V compared to average upper crust. The high field strength elements such as Zr, Hf, Nb, Ta, Sc, Th, rare earth elements, Rb and Ga show significant interelement correlations and may have been derived mainly from terrigenous sources. The redox sensitive elements such as V, Ni, Mo, U, and Mn; base metals such as Cu, Zn, Pb; Sr and Ba may have been derived from mixing of seawater and venting hydrothermal sources. The chondrite-normalized REE patterns, positive Eu and Y anomalies, and high Y/Ho ratios for the Ni-Mo-PGE-Au sulfide ores are suggestive for a submarine hydrothermal-exhalative origin. Hence, we suggest that this type of mineralization is different from the magmatic-hydrothermal or epithermal origins as proposed for some black shale hosted PGE-Au mineralization elsewhere. A modern analogue of such type deposit could be organic-rich sediments of the Bering Sea, which are known to have high PGE concentrations.

Using isotope geochemistry to trace the origin of ore forming materials in the Jiaodong gold province, China

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The Jiaodong gold province is the most important gold concentration area in China and the largest hydrothermal vein gold producing area in the world. For tracing the origin of oreforming materials in this region, we integrated and analyzed the composition of sulfur, lead and strontium isotope in the major gold ore deposits and the host late Archean Jiaodong Group, Mesozoic Linglong biotitegranite and Guojialing porphyritic granodiorite.

The value of δ34S in the Jaiodong Group is 4.7‰ in average and ranges from 3‰ to10‰. This in the Mesozoic granites is 7.4‰ and 6‰-10‰, respectively. The δ34S of gold ore ranges from 4.0‰ to 11.8‰, and shows a tower distribution. The value of 206Pb/204Pb in the Jiaodong Group, Linglong biotite granite and Guojialing porphyritic Granodiorite ranges from 16.111 to18.025, 17.143 to 17.288 and 16.408 to 17.851, respectively. The value of 207Pb/204Pb in the three geologic bodies varies from 15.043 to 15.762, 15.413 to 15.456 and 15.342 to 15.581, respectively. The value of 208Pb/204Pb in the three geologic bodies is 36.752-38.824, 37.625-37.855 and 36.645-38.394, respectively. The initial ratio of Sr in the Mesozoic granite, gold ore, altered rocks or minerals and fluid inclusions ranges from 0.706 to 0.716, 0.709 to 0.712, 0.703 to 0.713 and 0.710 to 0.716, respectively.

Similarity exists in isotope components among gold deposits and host rocks. This indicates that the oreforming material is the mixture between crustal and mantle. The gold deposits may be formed in the relative close environment, where had no large scale intrusions entering in continental crust.
Noble gas isotopic ratios of volcanics and xenoliths from northern Taiwan-Luzon Arc

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The Taiwan-Luzon Arc, which was generated in response to the subduction of the South China Sea Plate, is currently colliding with the eastern margin of the Eurasian continental plate at the arc’s southern and northern ends. Systematic temporal and spatial variations in the geochemistry of the magmas erupted along the arc are ascribed to the involvement of the subducted continent-derived sediments or crustal slivers close to the collision zones.

Three 3He/4He ratios of hornblende, biotite and pyroxene separated from the arc volcanics near the collision zone were obtained. The ratios of Hsiaolanyu lava from northern arc are less than 2.3 and 1.3 times atmospheric ratios (Ra). The other is 3.0 Ra of Mt. Arayat lava from southern part of the Taiwan-Luzon arc. This implies that the crustal component played an important role in the petrogenesis of the arc magmatism, at least near the collision zone, to lower the 3He/4He ratios of the lavas.

The helium isotopic ratios of olivines from xenoliths of Lanyu, Batan and Diogo island fall in a range from 8.1 to 10.1 Ra. They are close to the value of the average MORB ratio. However, the co-existing amphibole from the same nodule of Batan Island (8.4 Ra of olivine) shows a much lower ratio of 4.7 Ra, which are similar with the ratios of the arc lavas. In addition, pyroxenes and amphiboles from gabbroic xenoliths of the arc lavas exhibit a wide range from 2.3–7.6 Ra. It infers that they cumulates in origin at different stages of fractionation in former magma chamber.

Combined with the Sr-Nd-Pb and helium isotopic data, we can conclude that at least two components, i.e., crustal component (Ra<1) and MORB component (Ra ~8), are necessary for the generation of Taiwan-Luzon arc magmatism.

Tracing water exchange between mantle and continental crust with the δD values of NAMs in granulate

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Introduction

A poorly defined parameter of the inner Earth water budget is the possible flux through the mantle and continental crust boundary. Therefore, in the aim to obtain new constraints on Mantle-Crust exchange, we undertook to determine the D/H ratio of granulates from North China Craton.

Results

3 set of granulates were analyzed: Archean-early proterozoic granulate xenoliths from Nushan, granulate from Hannuoba archean terrain, and phanerozoic granulate xenoliths from Hannuoba, for which the water contents have been previously determined by FTIR spectrometry (Xia et al, 2006 and Yang et al, submitted), with value ranging from 150 ppm up to 2300 ppm. The CRPG IMS 1270 ion microprobe were used for D/H ratio in situ measurements of Cpx, Opx and Plag. Measurements where performed with a 0–10 µm diameter primary beam, and calibrated against already known NAMs and hydrous minerals. The δDSMOW values obtained for Plag of the 3 samples set range from –80 to –150, for Opx from –150 to –100 for Nushan, -150 to –50 for Hannuoba Terrains and –100 and – 20 for Hannuoba xenoliths and all the measurements on Cpx range from –60 to +20.

Discussion and conclusion

The high δD values observed for Cpx suggest that Cpx were affected by a diffusion hydrogen loss, as well as some Opx from Hannuoba. The preferential loss of hydrogen from Opx and then Opx may be associated to their high initial water and iron content, both supporting H loss. Therefore the initial granulate δD values should be the one preserved in Plag and part of the Opx, and is similar in the 3 localities, mostly ranging in between –100 and –150. This low δD value may reflect either a lower continental crust or a deep mantle plume signature, but significantly differ from the expected composition of the upper mantle (~60 to ~80). This suggests that not any water flux affected the granulate H isotopic composition, even for the Proterozoic granulate from Nushan that were transported to the surface during Cenozoic volcanism.

References

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Study on fluid inclusions of volcanic rocks in Songliao basin: The significance for natural gases

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Introduction

The Songliao basin is the largest sedimentary basin in China with most significance in producing oil and natural gases. In recent years, Chinese geologists found and explored the natural gases genetically linked to Mesozoic volcanic rocks in this basin (Qin et al., 2001). Three types of volcanic rocks have been identified in the basin, which are basaltic igneous flows, andesite and rhyolite. All those volcanic rocks are richness in fluid inclusions (Fig.1). The widely spreading Mesozoic-Cenozoic volcanic rocks along Tan-Lu fault belt in east China and the gas-liquid compositions from fluid inclusions are drawn great attention to geochemists. This study focus on the compositions of fluid inclusions bearing in these different volcanic rocks series.

Experiment and Results

The chemical compositions of fluid inclusions are determined with RM-1000 laser Raman spectroscopy produced by Renishaw Company at Institute of Geology & Mineral Resources, Xi’an. The results show that most of the fluid inclusions are mainly composed of CO\textsubscript{2}, CH\textsubscript{4}, CO, H\textsubscript{2}, N\textsubscript{2}, H\textsubscript{2}S and SO\textsubscript{2}. The relative high concentrations of CO\textsubscript{2} in fluid inclusions are correspondent to funding of CO\textsubscript{2} reservoir with inorganic genesis widely distributed in different sub-sags of the basin in the past decade. In contrast, the other components in fluid inclusions among the combustible CH\textsubscript{4}, CO and H\textsubscript{2} consist of main components of the natural gases explored in the basin. The compositions of fluid inclusions of volcanic rocks are also good proxies to trace the mantle degassing since Mesozoic in east China.

Acknowledgment

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Different accumulation of Pb, Zn, and Cd in river sediments and in lake sediments originated from ancient zinc smelting activities in northwestern Guizhou, southwestern China

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Zinc smelting in northwestern Guizhou, southwestern China resulted in significant heavy metal accumulation in sediments. In this study, river sediments were collected in a river in the smelting region, and lake sediments were collected in a lake ca. 10km downwind from zinc smelters. Concentrations of Pb, Zn, and Cd in the river sediments varied greatly in the range of 4,375-21,850, 7,275-30,425, and 42.0-95.0 mg kg\textsuperscript{-1}, averaging in 14,022, 24,441, and 72.9 mg kg\textsuperscript{-1}, respectively. Ratios of Pb/Cd and Zn/Cd in river sediments were in the range of 104-266 and 173-390, respectively. However, Concentrations of Pb, Zn, and Cd in lake sediments were in the range of 66.0-160, 130-1200, and 2.60-71.0 mg kg\textsuperscript{-1}, averaging in 99.7, 536, and 26.0 mg kg\textsuperscript{-1}, respectively. Ratios of Pb/Cd and Zn/Cd in lake sediments varied narrowly in 2.14-25.4 and 16.9-50.0, respectively. Normally, Pb, Zn and Cd accumulated vertically in the lake sediments in the depth of 0-15cm, and then their concentrations dramatically decreased to sediment baselines. In river sediments, Pb was mainly in carbonate bound fraction (35-51%) and iron and manganese bound fraction (26-47%); Zn was in carbonate bound fraction (32-39%) and iron and manganese bound fraction (38-48%); whereas Cd in residue fraction (16-50%) and carbonate bound fraction (15-45%).However, in surface lake sediments, organic bound fraction was the dominating chemical forms of Pb (34-82%), Zn (3.8-46%), and Cd (31-84%); while residue bound fraction accounted for 14-39% for Pb, 17-69% for Zn, and 4.0-55% for Cd, respectively. High organic matter content (14-45%) may reasonably explain high concentrations of organic bound metals in lake sediments. In river sediments, Pb\textsuperscript{206}Pb/\textsuperscript{207}Pb, Zn\textsuperscript{206}Pb/\textsuperscript{208}Pb ratios varied in 1.182-1.185, 0.399-0.403, respectively; however, in lake sediments, these ratios were in the range of 1.178-1.220, 0.477-0.486, respectively. These results suggested that Pb, Zn, and Cd in river sediments were from release of zinc smelting slags, however, in lake sediments, they were originated from dust deposition of zinc smelting emits. Elemental fractionation during smelting may cause big differences in Pb/Cd and Zn/Cd between river sediments and lake sediments.

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References

Some anaerobic microbial communities in peat bogs and the influence on the biogas formation

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Microorganisms play important roles in the transformation of peaty organic matter. The interplay between organic matter transformation and microbial activities is complex in the peat environment and the underlying mechanisms or pathways for carbon cycling may vary from case to case. The goal of this study was to investigate distribution of anaerobic microbial communities under varying geological or chemical conditions in different peat environments, and search for patterns of microbial organic carbon transformation under varying organic matter types conditions by simulate experiment. Samples were collected from mangrove bog (modern to 10,000 years) in Hainan province and from burial peat (Holocene) in Yunnan province of China. Content of total organic matter ranged from 27.6% to 55.7%.

There are four kinds of main advantage germ clusters in the peat bogs including fermentation bacteria, anaerobic cellulose-degrading bacteria, sulfate-reducing bacteria and methane-producing bacteria. Fermentative bacteria ($10^4$ to $10^6$ cells/g) based on MPN were significantly higher than sulfate-reducing bacteria or acetogens (< $10^3$ cells/g) in all peat samples. The distribution or number of fermentative bacteria to some extent correlated positively with the organic matter content (e.g., humic acids) in some but not all samples, suggesting that organic matter content may not be the only factor controlling the population of fermentative bacteria. We focused on fermentative bacteria because they play a critical role in transforming cellulose organic matter to smaller organic molecules bio-available to other dissimilatory microorganisms such as sulfate-reducing bacteria or methanogens.

On the other hand, fermentative bacteria create anaerobic environment, which removes oxygen and enriches hydrogen in the organic matrix. By concentrating and purifying the advantaged species of the fermentation bacteria, we culture the advantaged germ in different matrix. Highly nutritious peat environment could be simulated and then the bacterial-degradation experiments of plant may be controlled well. The experiment has already carried on for 6 months, The degrader of Fermentation bacteria causes that organic matter from the plant lost a great deal of oxygen, and cause the matrix enrich more hydrogen. we can also know that the production rate of bacteria-degrading biogas is 5-10 times larger than the production rate of hydrolysis gas without bacteria. Thus fermentative process may help enhance the quality of organic carbon preserved as fossil fuel in geological formation.

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Extreme fractionation of low salinity magmatic fluids

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Most crustal magmatic fluids are predominantly chloride solutions, but in certain situations, notably in some granite pegmatites, water-rich fluids occur which have low salt contents (<seawater salinity). The consequences of low salinity include higher gas solubilities, resulting in potentially higher bicarbonate levels, and low concentrations of Ca, permitting higher concentrations of additional ligands such as fluoride and phosphate. LA-ICP-MS analysis provides a means of determining many of the significant pegmatite components in single inclusions, and has been carried out in Leeds using a Geolas Q laser ablation system (193nm ArF Excimer laser) coupled to an Agilent 7500c ICP-MS. Calibration is with glass SRMs and with solutions loaded in capillaries.

Fluid inclusions from the quartz core of the Muiane Li-pegmatite, Mozambique (sampled by O. Von Knorring), are 3 phase at room temperature, with CO₂ liquid and vapor. Large inclusions (25-60 µm) are common. LA-ICP-MS analysis of individual inclusions reveals significant variations within texturally similar settings, and in particular Na/K (wt) ranges from <1 to >15. Extreme enrichment in Cs (to >2000 ppm) and Li (to c.3000 ppm) is associated with high Na/K ratios and possibly arose as K-feldspar and micas were precipitated. Such fluids are also enriched in B (to c.3000ppm). Not surprisingly, spodumene is a major mineral in the deposit and pollucite has been reported. Some high Na/K fluids are very rich in As (>25000ppm), while others contain only a few thousand ppm As. A solid As daughter phase has been observed in a few very large inclusions.

The results are taken to indicate that in the final stages of magmatic fluid evolution, extreme fractionation effects can be produced, reflecting the growth of new solid phases. However vapour-liquid separation may play an important role in the development of the decoupled As-enrichment.
The influence of minor elements on melting of eclogite in the mantle

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An important role for recycled mafic crust in upper mantle magma-genesis is frequently postulated. Models vary between those in which siliceous to basaltic melts from minor mafic heterogeneities in peridotitic upper mantle are extracted directly from their upper mantle source regions without significant interaction with peridotite wall-rock before eruption, to those which postulate reaction and resorption into enclosing peridotite of siliceous partial melts from eclogite or pyroxenite, resulting in refertilisation of the peridotite and formation of new, opx-enriched lithologies. Melting of these refertilised peridotites provides the erupted magmas.

Critical to testing these opposing models is detailed knowledge of the partial melt products of mafic lithologies at high pressure. We report experimental investigations of high pressure melting of volatile-free eclogite and carbonate-bearing eclogite, focussing on the importance of some minor elements in controlling subsolidus mineralogy, low degree melting relations and partial melt compositions.

We determined the phase relations and partial melt compositions of a nominally anhydrous altered MORB composition (GA2) with 49.7 wt% SiO2, 0.37 wt% K2O, 3.34 wt% Na2O, 0.23 wt% P2O5 and 1.82 wt% TiO2 from 3-5 GPa and 1200-1600°C. We identify two distinctive melting regimes. Low degree melting (≤20%) is eutectic-like and is dominated by contributions from accessory phases (K-feldspar, rutile, quartz/coesite and possibly apatite), with additional components from garnet and clinopyroxene. At 3 GPa K-fd, rt and qz are residual phases up to about 40°C above the solidus, but at higher pressures K-fd and rt melt out close to the solidus. At higher degrees of melting, once accessory phases are melted out, melt compositions are controlled by melting along ga-cpx cotectics. Low degree melts are dacitic and trend towards andesitic and basaltic andesitic with increasing temperature. At 3 GPa Na, Ti and K are incompatible, but at 4 and 5 GPa Na becomes compatible, yielding increasingly fractionated Na/Ti and Na/K in melts.

Similar dual melting behaviour is observed in partial melting of Ca-Mg-carbonate-bearing eclogite, where low degree partial melts are sodic calcio-dolomitic to dolomitic and are controlled by eutectic melting relations on the calcite-magnesite join, with minor contributions from ga + cpx. Increasing degrees of melting, or melting of residues after carbonate melt extraction, result in progressively more siliceous partial melt compositions. Interactions between these carbonated melts and peridotitic wall rock could generate a spectrum of enriched source lithologies suitable for some magmas.

Heavy metal concentrations in soils and tea plants in Sürmene and Çayeli area (NE -Turkey)

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The study area covers two geologically different regions which have intensively been carpeted by tea plants in the Eastern Black Sea. The rocks exposed in the region contain considerable amount oftrace metals due to Upper Cretaceous massive sulfide formations and Tertiary epithermal mineralizations. Tea plants grow over the soils derived from such mineralized rocks indicate different concentration in Cu, Pb, Zn, Fe, Cd, P, Al, Na, K, S. Most of the analyzed elements except Al shows higher content ratios in basaltic and sedimentary rocks. Al content is found to be high only in tea plants growing on the dacritic rocks.

The highest average Cu values (26.17 ppm) occur in tea plants in Çayeli area. Pb reaches the highest value in Çayeli (1.94 ppm) in tea plants. The highest Cu, Pb, Zn concentrations were recorded in soils at Sürmene area whereas the highest Al (7.56 %) concentration was observed in Çayeli. The soils in Sürmene area sampled during the first sprout period of tea plants contain relatively high amount of Cu.

In order to better understand the element distribution processes in tea plants, some experimental studies were undertaken. Young tea plants were planted in small boxes and were applied with Cu, Zn, Cd and Mn element complexes and fertilizers. The effect of fertilizers in element mobility was undertaken. Young tea plants were planted in small boxes and were applied with Cu, Zn, Cd and Mn element complexes and fertilizers. The effect of fertilizers in element mobility was found to be significant. Especially Ammonium sulfate fertilizer increased element uptake of tea plants by lovery pH. Bioavailability coefficients of the applied elements are as follows, Cu: 0.14, Zn: 0.18, Cd: 2.45 and Mn: 0.15. The differences in the amount of irrigation played an important role in bioavailability and uptake of elements both in soil and tea plants. Cu, Zn, and Mn are relatively easily uptaken by the tea plants from the soils often watered. The amount of water has no effect on Cd uptake.

The Pb concentration sharply decrease from road side (1.08 ppm) to 100 m in land (0.37 ppm).
Geochemistry of biotites in Ali-Abad and Darreh-Zereshk porphyry copper deposits, Yazd, Central Iran

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Darreh-Zereshk and Ali-Abad are two relatively small porphyry copper deposits in Central Iran. The biotite compositions used to interpret nature, physicochemical conditions of magma source and petrogenesis of these granitoid rocks. Biotites from granitoids of the Aliabad-Darreh Zereshk areas are green and brown types. On the basis of IMA classification, these biotites can be classified mainly as phlogopite on the basis of ratios of 100 (Mg/ (Mg + Fe)) which vary between 17 and 22. Also, plotting of 100Fe2+/(Fe2+ + Mg ) ratio of the studied biotites on a stability diagram correspond to temperature about 600 to 750°C and confirming magmatic origin for these biotites. In addition, biotite composition used for discrimination of the granitoid magma. The chemical composition of studied biotites show that the granitoids of the Aliabad-Darreh Zereshk areas are calc-alkaline I-type.

The main substance constitutes and chemical composition characters of the dust in the urban district of Beijing

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With the development of urbanization, industrialization, population growth, and traffic growth, the environmental pollution has been more serious in the city. The statistic shows that one third of the population live in the city. The study of heavy metals’ characters and migration in the city is of highly important and practical because of its toxicity and accumulation in organism. The dust in the urban area tend to form a repeated cycle of rising and sinking under the action of external forces and develop into particles that are likely to be breathed by human bodies, thus causing great harm to human health and environment.

Dust has been collected and studied as the medium carrying heavy metal pollutants. The dust samples are collected within the 4th Ring Road and the composition, chemicals and granularity was tested. The dust in the urban area is mainly composed of quartz, plagioclase, dolomite, calcite, and hornblende, which account for 80 to 90 per cent of all the minerals. Besides, there is a small quantity of mica, microcline, sericited feldspar, carbonaceous granule, glass, etc. The content of K2O and Na2O is higher in the coarse grains than in the fine grains. The averages of content of 16 elements are all higher in the fine grain than in the coarse grain. The sequence of the heavy metals from most seriously contaminates to the slightly contaminates in the dust are cadmium, mercury, zinc, copper and arsenic.

References
The mantle neon from the Jinchuan sulfide deposit, NW China

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The noble gas isotopic compositions in the clinopyroxene, olivine, orthopyroxene and chalcopyrite from the second diggings of the Jinchuan sulfide deposits, NW China, have been determined. Stepwise heating method had been taken in order to get the noble gas isotopic compositions from the different micro-sections in a sample. The ranges of the neon contents and isotopic compositions in the samples studied were shown in the following table.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>20Ne/22Ne range (average)</th>
<th>21Ne/22Ne range (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>8.75—12.22 (10.58)</td>
<td>0.02594—0.04100 (0.03125)</td>
</tr>
<tr>
<td>700</td>
<td>9.39—11.705 (10.39)</td>
<td>0.02669—0.06380 (0.03636)</td>
</tr>
<tr>
<td>1000</td>
<td>7.77—11.77 (9.64)</td>
<td>0.02649—0.06430 (0.03795)</td>
</tr>
<tr>
<td>1300</td>
<td>7.81—11.97 (9.62)</td>
<td>0.02292—0.04530 (0.03275)</td>
</tr>
<tr>
<td>1600</td>
<td>8.04—11.30 (9.22)</td>
<td>0.02536—0.04070 (0.03289)</td>
</tr>
<tr>
<td>Total</td>
<td>9.00—11.368 (10.02)</td>
<td>0.02697—0.04400 (0.03361)</td>
</tr>
</tbody>
</table>

Apparently, the neon isotopic compositions of the samples were different from atmospheric. Higher 20Ne/22Ne values were found at 400ºC and 700ºC with an average of 10.58 and 10.39, respectively. In the three isotopes diagram of neon, the data points are dispersive, which shows a characteristic mixed on multi-member fluid. However, the data points are concentrated or show a correlation between 20Ne/22Ne and 21Ne/22Ne at every temperature step. It is noticeable that the line at 400ºC closed to Loihi line, the line at 700ºC trends to MORB line, and the lines at 1000ºC, 1300ºC and 1600ºC shown an addition of radiogenic neon. The fluids released at lower temperature were mainly come from fluid inclusion, so it is surmisable that the mineral captured mantle fluid during crystallization.

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A molecular model for microbial Se(VI) reduction

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Background

The redox cycling and mineralization of selenium is largely controlled by microbial processes. Phylogenetically diverse species of Bacteria and Archaea are able to reduce soluble selenate oxyanions [Se(VI), SeO₄²⁻] to insoluble elemental selenium [Se(0)]. Although Se-reducing bacteria are known to govern the redox transformation of selenium in a broad range of terrestrial and aquatic environments, the mechanisms of microbial selenate reduction remain poorly understood. In this study, we apply molecular techniques to identify the genes involved in selenate reduction pathway.

Methods

Transposon mutagenesis and direct cloning techniques were used to identify genetic regions in the Se-reducing bacterium Enterobacter cloacae SLD1a-1 associated with selenate reductase activity. The mini-Tn5 transposon system was used to produce mutants that have lost the ability to reduce selenate. E. cloacae mutants and genomic library clones heterologously expressed in E. coli S17-1 were screened for activity on LB agar supplemented with sodium selenate. The rate of selenate reduction by the clones was measured in liquid minimal media, and the Se(0) minerals formed by the clones were examined using XANES and SEM.

Results and Discussion

Essential genes required for microbial selenate reduction were identified. The experiments showed that mutation of the Fumurate Nitrate Reduction regulator gene, menaquinone biosynthesis operon, and twin-arginine translocation operon produces derivative strains that are deficient in selenate reductase activity. Complementation by the wild-type sequences restores the ability of mutant strains to reduce Se(VI). These results demonstrate that: 1) oxygen sensing molecules regulate the expression of selenate reductase genes; 2) selenate reduction activity is dependent on the secretion of the reductase enzyme to the periplasmic space; and 3) anaerobic electron carriers are involved in the shuttling of electrons to the terminal selenate reductase protein. We propose a molecular model to describe microbial Se(VI) reduction.
Metamorphic evolution and tectonic implications of the Qianlishan-Zhaozhishan complex, westernmost part of the Paleoproterozoic Khondalite Belt in the Western Block of the North China Craton

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A major advance has been made in understanding the Paleoproterozoic amalgamation of the North China Craton at ~1.85 Ga following recognition of two Paleoproterozoic continent-continent collisional belts, named the Trans-North China Orogen and Khondalite Belt[1-2]. In the last few years, extensive work has been done on the Trans-North China Orogen[3-5], but few investigations have been carried on the Khondalite Belt in the Western Block, which has hindered the further understanding of the tectonic amalgamation of the Yinshan and Ordos Terranes and the formation of the Western Block. In this study, we present metamorphic data for the khondalites in the Qianlishan-Zhaozhishan Complex in the westernmost part of the Paleoproterozoic Khondalite Belt, which places rigorous constraints on the evolution of the belt and amalgamation of the Western Block. The Qianlishan-Zhaozhishan Complex is composed predominantly of S-type granites and supracrustal rocks, including Al-rich gneisses, quartzites, marbles and calc-silicate rocks, collectively called khondalite series in the Chinese literature. Petrographic studies show that the Al-rich gneisses from the Qianlishan-Zhaozhishan Complex underwent four distinct metamorphic stages. M1 is represented by quartz + plagioclase + muscovite + biotite + garnet core, forming at 550-650°C and 6-7 kbar. The M2 stage formed sillimanite, garnet, cordierite, K-feldspar, plagioclase and quartz at the T-P conditions of 750-800°C and 6-7 kbar. It was then followed by the M3 stage that represents the formation of cordierite coronas surrounding garnet, indicating a nearly isothermal decompression. Finally, the rock experienced a retrogressive stage (M4) represented by the appearance of andalusite and late muscovite. These mineral assemblages and their approximate P-T estimates define a clockwise P-T path involving nearly isothermal decompression for the Qianlishan-Zhaozhishan Complex, supporting the recently proposed model that the Western Block formed by the collision between the Yinshan and Ordos Terranes along the Paleoproterozoic Khondalite Belt.

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References


The source and distribution of volatile elements on Hadean Earth

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The Earth’s atmosphere is an integrated product of planetary evolution processes that reflects the chemistry of the contributing materials (precursors) and the energy supplied. According to astrophysical models, potential precursors that could have delivered significant quantity of water or hydrogen to the primitive Earth include the solar nebula, comets and carbonaceous chondrite-like materials of different sizes (planetary embryos, micrometeorites and IDPs). The comparative study of H, N and C isotopic compositions between those potential precursors and the Earth suggests that a major source of highly volatile elements is carbonaceous chondrite-like material (e.g. Marty and Yokochi, 2006). As such components cannot be the major building blocks of the Earth, however, the mode and timing of their supply as well as the possible events having affected the water and other volatile elements need to be constrained in order to understand the evolution of the primitive Earth’s surface environment. In this context, noble gases are advantageous tracers of physical processes and their time scales given that they are chemically inert and that several radiogenic isotopes of appropriate production rates exist.

Xenon isotopes indeed provide an exceptional set of chronological tracers: ¹²⁹Xe was produced by the now extinct β-decay of ¹²⁹I (T₁/₂= 15.7 Myr), and ¹³¹-¹³⁶Xe were produced by the spontaneous fission of ²³⁸U (T₁/₂= 4.45 Gyr) and now extinct ²⁴⁴Pu (T₁/₂= 82 Myr). As the respective proportions of ²⁴⁴Pu and ²³⁸U fissions to ¹³¹-¹³⁶Xe isotopes are poorly constrained due to the similar relative yields, we determined the proportions of ²⁴⁴Pu and ²³⁸U fission derived ¹³⁶Xe according to the relative abundances of ⁴He-²¹Ne-¹³⁶Xe, for a set of new noble gas data obtained for Kola plume (Russia) samples (Yokochi and Marty, 2005). The ²⁴⁴Pu contribution of mantle plume-related component is estimated to be 33-60 % of total fission ¹³⁶Xe. This value is significantly lower than what is expected for a chondritic reservoir (96 %), and is similar to the previously proposed best estimate for the MORB mantle (32 ± 10 %). This result implies that the whole mantle was subject to degassing after the decay of ²⁴⁴Pu, over the entire Hadean. In line with this result, a model age of the atmosphere based on the ratio of radiogenic ¹²⁹Xe/³⁶Ar suggests that the atmosphere was subject to hydrodynamic loss over 150 Myr after solar system formation, much longer than previous model estimates using xenon isotopes alone.

References

More on Os isotope anomalies in chondrites: Possible carriers

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Recent, highly-precise isotopic analyses of various bulk meteorites and acid residues have revealed that some primitive chondrites contain isotopically anomalous presolar grains which record diverse stellar nucleosynthesis. Another essential but still unsolved issue is whether or not the chondrite precursors, including presolar grains, were homogeneously distributed in the early solar nebula at the time of planetesimal formation. We have previously demonstrated that bulk samples of carbonaceous, enstatite and ordinary chondrites have uniform 186O/188Os, 188Os/186Os and 190Os/188Os ratios when decomposed by an alkaline fusion total digestion method, although acid residues of some carbonaceous chondrites were enriched in Os isotopes produced by s-process nucleosynthesis [1]. These results suggest that chondrite precursors were thoroughly mixed in the early solar nebula, and we speculated that the main carrier of the anomalous s-process Os was presolar SiC grains. Reisberg et al. [2], similarly carried out sequential acid leaching of the bulk Murchison meteorite, and found that an s-process-enriched Os-rich component was accessible with mild leaches (e.g. hot HCl treatment). They proposed that the main carrier of the s-process Os may not be presolar SiC grains but rather more easily digestible presolar phases such as graphite or metal alloy.

To investigate this issue further, we have carried out a hot HCl leaching experiment for the Murchison acid residue prepared by a relatively mild CsF/HF technique. The bulk sample of this residue was strongly enriched in s-process Os (ε186Os = +11.0). The hot HCl leaching recovered ~10% of the Os in the residue, which was also enriched in s-process isotopes (ε186Os = +8.0) but not as high as the bulk residue. This indicates that the HCl insoluble phase in the residue is more enriched in s-process Os, corroborating the existence of acid resistant SiC grains as an s-process Os carrier. The leachate is known to have a 54Cr anomaly, an isotope that can be produced by r-process nucleosynthesis [3]. Therefore, the leachate may contain an HCl digestible, r-process Os carrier, the existence of which may be masked by the HCl digestible s-process Os carrier. The likely hosts of the s- and r-process Os remain unclear. We will conduct further leaching tests (e.g. HNO3, HClO4) on the Murchison residue as well as other chondrite acid residues to better identify the carrier of isotopically anomalous Os in the chondrites.

References

REE geochemical study on the formation environment of the Hishikari epithermal gold deposit, Japan

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In order to investigate the formation environment, especially redox environment, during the mineralization at the Hishikari epithermal gold deposit, Kagoshima prefecture, Japan, the concentration of rare earth elements (REE) and Y in the Hosen No.1 auriferous quartz vein were determined by ICP-MS after acid dissolution and selective separation. The Hosen No.1 vein shows well symmetric banded structure and it was classified into four main bands (band I - IV). This vein was consisted of quartz, adularia and smectite associated with electrum and metal sulphides (e.g. pyrite, sphalerite and galena). Adularia could be commonly observed in each band, especially it is abundant in the earliest precipitation stage of each band. Electrum and other metal sulphides occurred with adularia and/or smectite. The quartz vein samples were collected from each band at -20 and +62.5 meter levels. The samples collected in the band II were analyzed separately by specific minerals due to the existence of electrum and sulphide-rich band called “ginguro” band.

The total concentration of REE including Y was varied from 9.72 to 0.45 and from 5.11 to 0.66 ppm at -20 and +62.5 meter levels, respectively. The highest concentration at each level was obtained in the samples obtained from the band II containing “ginguro”. The chondlomite normalized REE patterns of all the samples at both -20 and +62.5 meter levels showed a strong positive Ce anomaly. These results suggest that the Hosen No.1 quartz vein was precipitated and formed by mixing with oxidizing fluid (groundwater or meteoric water) and hydrothermal fluids after loss of H2S and CO2 gasses, and increase in pH due to boiling.

In order to investigate this issue further, we have carried out a hot HCl leaching experiment for the Murchison acid residue prepared by a relatively mild CsF/HF technique. The bulk sample of this residue was strongly enriched in s-process Os (ε186Os = +11.0). The hot HCl leaching recovered ~10% of the Os in the residue, which was also enriched in s-process isotopes (ε186Os = +8.0) but not as high as the bulk residue. This indicates that the HCl insoluble phase in the residue is more enriched in s-process Os, corroborating the existence of acid resistant SiC grains as an s-process Os carrier. The leachate is known to have a 54Cr anomaly, an isotope that can be produced by r-process nucleosynthesis [3]. Therefore, the leachate may contain an HCl digestible, r-process Os carrier, the existence of which may be masked by the HCl digestible s-process Os carrier. The likely hosts of the s- and r-process Os remain unclear. We will conduct further leaching tests (e.g. HNO3, HClO4) on the Murchison residue as well as other chondrite acid residues to better identify the carrier of isotopically anomalous Os in the chondrites.

References
Mantle heterogeneity as evidenced by Raobazhai peridotite, North Dabieshan, China

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The peridotite bodies occurred near Raobazhai, in north Dabieshan trends northwestwards extending more than 10Km. The peridotite body consists mainly of harzbergite and dunite, with a few lherzulite mostly amphibolized due to amphibolite facies metamorphism. All of them are highly serpentinized. Major mineral paragenesis of the peridotites are Ol+Opx+Spl and Ol+Spl. The peridotite bodies are highly deformed and are mylonitized. REE distribution pattern and trace element geochemistry evidenced the chemical heterogeneity of these mantle-derived rocks.

There are a number of garnet pyroxenite enclaves scattered within the peridotite body as small pods, decimeters in size, enclosed in the serpentinized peridotites. Major mineral components of the garnet pyroxenite are: garnet (Prp25—35), sodium augite(Jd 10—25 ) with a small amount of ilmenite. There are two stages of retro- metamorphism: the retrogressive granulite facies superimposed by amphibolite facies. On the basis of garnet–clinopyroxene geothermometry Kd=4.06–5.28; T=793–919℃, P=1.5 Gpa are estimated for the garnet pyroxenite.

It is inferred that the peridotites are mantle rocks about 60Km in depth. During the exhumation of the orogenic belt it was tectonically emplaced into the lower crust in solid state and then uplifted to shallow depth. The REE distribution pattern and the Ni-Co-Sc diagram reveal that they are chemically equivalent respectively to the basaltic melt and ultramafic residua. Incompletely removing of mantle melting products from source area could be a possible mechanism for the mantle heterogeneity.

Si and Mg isotopic constraints on the astrophysics of CAI formation in the early solar system

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Silicon and magnesium isotope ratios can be used to constrain the pressure ($P_{H2}$) and duration of melting of calcium-aluminum-rich inclusions (CAIs) in the early solar system. Recent results (Shahar and Young 2007) show that these primitive protoplanetary objects most likely melted for integrated timescales of tens of days at $P_{H2} < 10^{-6}$ bar. Here we show that the isotopic compositions of CAIs further require that they formed not only at lower pressures than the more abundant chondrules with which they are found, but also at orders of magnitude lower number densities, constituting an important constraint on the astrophysical setting of CAI formation.

The substantial Si and Mg isotope fractionation in CAIs suggests that their number densities were too low to permit an overall elevation in background partial pressure of Mg and SiO that would have prevented fractionation. We quantify this effect by estimating the pressure of gas molecules or atoms produced by a population of evaporating CAIs:

$$ P_{i,vac} = \frac{3J_i r_t^2 N_{CAI}}{(D_{gas} T)^{3/2}} kT $$

where $N_{CAI}$ is the number of CAIs within a sphere defined by a radius equal to the characteristic length scale for diffusion in the gas $(D_{gas})^{1/2}$ and $J_i$ is the flux of an element $i$ (e.g., Mg or SiO) from a single CAI. Modification of $J_i$ by $(1+P_i/P_{i,eq})$ to account for deviations from vacuum and approaches to equilibrium vapor pressures results in the expression

$$ \frac{P_i}{P_{i,eq}} = \frac{P_{i,vac} / P_{i,eq}}{1+P_{i,vac} / P_{i,eq}} $$

For typical conditions indicated by Si and Mg isotope fractionation, including $T = 1673$ to 1873 K, $P_{H2} = 10^{-9}$ to $10^{-4}$ bar, equations (1) and (2) yield a maximum number density of CAIs during their melting of $1x10^{-3}$ to $2.0$ m$^{-3}$, or a linear spacing of $> 0.8$ to $8$ meters. This number density is four orders of magnitude lower than that for chondrules (Young and Galy 2004; Cuzzi and Alexander 2006).

References
Cenozoic volcanism of kamafugite and carbonatite in Western Qinling, China: Evidence of DUPAL-like asthenospheric mantle flow

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Dispersed Cenozoic potassic volcanism appeared over much of Tibet plateau and adjacent area during late stages of India-Eurasia plate collision and post-collision. Although widespread this volcanic activity appears to be distinct from that producing Large Igneous Provinces being characterized by greater compositional diversity and a lack of evidence for deep-mantle plumes. However, an additional feature is the dominance of DUPAL-like Pb isotopic compositions and εNd in asthenosphere-derived melts, attributed variously to the influx of Indian Ocean mantle, endogenous mantle plumes or delaminated cratonic substrate. “Dispersed” volcanism may therefore pose fundamental questions concerning the dynamic behavior of sub-continental mantle in relation to continental plate collision. Is the asthenosphere mobilized during such plate collision? and to what extent and by which mechanisms may plate kinematics coupled to mantle flow? May be, the studies of Cenozoic Carbonatite and kamafugite in Western Qinling, China can answer the questions.

The kamafugite and carbonatite in Western Qinling, China located to the northeastern boundary of Tibet plateau. The volcanic rocks have the characteristics rich in LILE, LREE and HFSE (such as Nb, Zr, Th and U et al.) especially. The distribution patterns of REE chondrite-normalized is very like to OIB. Initial 87Sr/86Sr are lower (in the range of 0.70381-0.7094 for kamafugites, of 0.70529-0.71332 for carbonatites), initial 144Nd/143Nd (in the range of 0.512924-0.512404 for kamafugites, of 0.512928-0.512221 for carbonatites) are higher but homogeneous comparing to Sr isotopes of the volcanic rocks. A lot of volcanic rocks have the εNd (in ppm) and εNd (vs. 87Sr/86Sr).

All of these mentioned above show that WQL Cenozoic kamafugites and carbonatites are a ultra-potassic volcanism related to mantle plumes and contained EM1 and EM11 end members in their mantle sources. Despite the apparent lack of plumes in the Western Qinling, the studies of Western Qinling Cenozoic volanic rocks of kamafugite and carbonatite, and seismic tomography suggests the Cenozoic volcanism in Western Qinling is matched by swell-like low-velocity anomalies in the upper mantle or shallow-level perturbations of the asthenosphere. Spatial and temporal associations of the volcanism further suggest that discrete asthenosphere, i.e. so-called “crust-mantle transitional belt” were generated during late stages of the Idia- Eurasia continental collision.

Study of Lu-Hf geochronology - A case study of eclogite from Dabie UHP Belt

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We developed Lu-Hf isotope geochronology with isotope dilution multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Chemical separation of Lu and Hf from bulk rock is set up while the Lu cut of the chromatography contains Yb and 176Lu/176Yb is always larger than 30. The correction of Lu and Yb interference on Hf adopted in this work is based upon an exponential law although Lu and Yb concentration in the Hf cut is very low (176Lu/176Hf and 176Yb/176Hf are less than 2×10^-6 and 2×10^-7, respectively). Internal precision of 176Hf/177Hf measurements for natural samples is better than 0.0015% while the external precision is better than 0.0010%.

Fig 1 176Lu/177Hf-176Hf/177Hf isochron of eclogite sample SH02. The middle two points are isotopic compositions of the mixture of garnet and bulk rock. The mixing proportion of garnet with whole rock and omphacite are 0.5 and 0.3 respectively.

We obtained a garnet-whole rock isochron age of 254 ± 16 Ma (2σ) for a Shanghe eclogite from the Dabie ultrahigh pressure metamorphic belt (see fig 1). The relative larger error is due to the low Lu concentration in garnet (1.1 µg/g) and close 176Lu/177Hf ratios in both garnet and bulk rocks (0.05 vs 0.01).

The result of Lu-Hf isochron represents the garnet formation age during continental subduction and late peak- and post- ultrahigh pressure(UHP) metamorphism didn’t disturb the Lu-Hf isotopic system in garnet.

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Zircon and apatite fission track study on the mineralization of Nanliang gold deposit, eastern Hebei, China

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Xiayingfang gold ore district, Hebei province, China, occurs in Xinglong-Kuancheng arcuate fold area of Yanshan platform fold belt in eastern Yinshan-Yanshan EW tectonic belt. A granite-porphyry intrusion, the principal part of magma activity in this area, is close related to the gold mineralizing process. This paper aims at studying the hydrothermal metallogenetic epoch and thermal history of Xiayingfang gold deposit, based on zircon and apatite fission track analyses for different alteration zones.

The zircon and apatite ages of six samples from ore and altered rocks range from 154 Ma to 120 Ma and from 114 Ma to 103 Ma respectively, indicating a about 22-50 Ma metallogenic duration, and the metallogenic time falls into early Yanshan epoch. The age data and quantitative AFT modelling show that there are two stages of gold mineralization, in which the first stage is of higher temperature and rapidier cooling rate than the second stage and the time and temperature of the turning point between them is about 120 Ma and 100°C. The first stage of mineralization resulted from intrusion of a granite-porphyry body and took place in about 150 Ma, and second stage of the mineralization was related to both rhyolite-porphyry and magma cryptoexplosive breccia and occurred in about 135 Ma. Combined with the minerogenetic temperature of 370-290°C, 230-170°C and 150-80°C in vanward-, main- and late-mineralization period respectively, the ZFT and AFT ages correspond to the main- and late-mineralization period separately. Since the samples from different places are heated in different degree by the metallogenetic hydrothermal solution, the less the distance from the thermal source and the long the heating time is, the lower the measured fission track age. It is demonstrated that the quartz-sericitization alteration is earlier and lasts longer than the potassic alteration. Therefore, we consider fission track analysis of the minerals is useful to researching the metallogenetic epoch and thermal evolution history of hydrothermal deposits.

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Mass transfer during volatile exsolution in magmatic systems:
Insights from the analyses of silicate melt and magmatic fluid inclusions

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We analyzed silicate melt and primary magmatic fluid inclusions in numerous granitic systems and in the basaltic andesites of the Villarrica volcano to quantify the distribution of several elements between silicate melts and magmatic volatiles.

LA-ICPMS analyses of co-existing silicate melt and fluid inclusions, entrapped in mairalitic quartz crystals, allowed direct quantitative determination of fluid/melt partition coefficients. Investigations of various granitic systems (peralkaline to peraluminous in composition, log fO2=NNO-1.7 to NNO+4.5) exsolving fluids with various cholorinities (1 to 13 mol/kg) allowed us to assess the effect of these variables on the fluid melt partition coefficients (D). Partition coefficients for Pb, Zn, Ag and Fe show a nearly linear increase with the chlorinity of the fluid (D Pb~6*MCl, DZn~8*MCl, DAG~4*MCl, DE~1.5*MCl, where MCl is the molarity of Cl). This suggests that these metals are primarily dissolved as Cl-complexes and neither oxygen fugacity nor the composition of the melt affects significantly their fluid/melt partitioning. Partition coefficients of Mo, As, Sb and Bi are highest into low salinity (1-2 mol/kg Cl) fluids with maximum values of DA~20, DAs~10, DSB~8, DW~15 indicating dissolution as non-chloride (e.g., hydroxy) complexes. Fluid/melt partition coefficients of copper are highly variable, but highest between vapor like fluids and silicate melt (D Cu~2700), indicating important role of ligands other than Cl. Fluid/melt partition coefficients of Sn and W show a weak positive correlation with the chlorinity of the fluid (D Sn~0.3-42, DW~0.8-60), but likely decrease with decreasing oxygen fugacity or melt peraluminosity.

In situ quantitative determination of fluid/melt partition coefficients in mafic systems with the use of natural samples is limited due to the lack of well preserved fluid inclusions. However, very high excess concentrations of Cu and Ag have been analyzed in plagioclase-hosted silicate melt inclusions in basaltic andesites compared to those in co-genetic pyroxene and olivine (up to 4800 ppm Cu vs. 40-200 ppm Cu in plagioclase vs. pyroxene and olivine hosted melt inclusions). The excess Cu is due to heterogeneous entrainment of a high temperature (~1000 °C) vapor phase rich in Cu, Ag and S. This suggests that high-temperature magmatic vapors may play an essential role in the transport of Cu, Ag and S from mafic to felsic magmas in complex magmatic reservoirs.

Geochemical fractionation and anthropogenic metal pollution in sediments of Nakagawa River in Tokyo, Japan

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Nakagawa River sediments were collected from the whole river and analysed for heavy metals in the less than 63 µm grain size fraction. The geochemical fractionation of heavy metals was examined with a sequential extraction scheme and the concentration of iron, manganese, lithium, cobalt, cadmium, chromium, copper, nickel, lead and zinc were measured in the liquid extracts by flame atomic absorption and inductively coupled plasma mass spectrometry. A certified reference stream sediment sample (JSd-2) provided by the Geological Survey of Japan was also analysed using the same procedure as a check. The association of Cr and Pb with oxides and Zn with carbonatic and oxides were comparatively higher. Nakagawa River sediment was considered to be polluted on the basis of unpolluted sediments and geochemical background values with respect to Cr, Pb and Zn, which were several times higher than the limiting concentration where toxicological effects are expected. The geoaccumulation index for most of the sampling points also lies above zero indicating contamination in Nakagawa sediment for the aforesaid metals. The pollution could be linked to anthropogenic activities such as industrialization, urbanization, deposition of industrial wastes and others. A final evaluation of the Nakagawa River sediments heavy metal pollution will be made from the study results.
The evolution of \( m_u \) and the isotopic composition of lead in the early solar system and young Earth

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A loss of volatile elements during the condensation of the solar nebula is the main fractionating process of CM, CO, CV and ordinary chondrites. These building blocks (constituting 85% of meteorite falls), from which the terrestrial planets accrete over the next 10-40 Ma, retain CI refractory element relative abundances but display deficiencies in their volatile elements correlating with condensation temperatures. As a consequence, these earliest condensates from the cooling solar nebula display, on average, an order of magnitude increase in \( m_u \) (\( m = 238\text{U}/204\text{Pb} \)) from \( \sim 0.1 \) to \( \sim 1 \). Additional volatile element loss and further increase in \( m_u \) continues to occur from impact melting on various scales throughout the accretion process. Differentiation of planetesimal bodies, such as metal-silicate separation, also produces chemical heterogeneity that may affect \( m_u \). Our best value for the bulk Earth \( m_u \) comes from analyses of terrestrial Pb, which has evolved uniformly in isotopic composition over geologic time and provides an integrated \( m_u \) value of \( \sim 9 \) for the crust and upper mantle. However, the possibility of other reservoirs in the core and lower mantle has hampered efforts to precisely determine the total bulk Earth \( m_u \) value.

New and published meteorite data are presented to examine the effects of volatile element loss on U-Pb isotope systematics in the early solar system. Recent studies using the extinct Hf-W chronometer have shortened older estimates of the time between the origin of the solar system and the separation of the Earth’s core. Accordingly, some proposed solutions to the Pb paradox—the positioning of both the Earth’s crust and mantle to the right of the Geochron on Pb-Pb diagrams—that were based on a \( >50 \) Ma time span for Earth’s accretion and core formation, are invalid. Allowing only 10-20 Ma for production and loss of radiogenic Pb before being retained by the Earth causes but minor rotation of a Geochron anchored to Canon Diablo initial Pb. Scenarios for the evolution of \( m_u \) in the early solar system and young Earth, and comparisons with Mars, the Moon and other meteorite parent bodies will be given. It is concluded that the Pb paradox as well as the \( \kappa \) conundrum are due predominantly to long-term storage of radiogenic Pb in, and decoupled U, Th, and Pb transport among terrestrial reservoirs. In contrast, \( m_u \) values are established at the time of planetary formation by the accretion of material that has suffered earlier and concurrent loss of volatile Pb, and can differ significantly among the terrestrial planets.

Relative and absolute timescales in metamorphism - Observations, calculations, estimations

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Presently there are several ways to record metamorphic processes through time. (i) In first order, metamorphic petrology is needed to set constraints on the relative record of metamorphic processes, and to provide information about the prograde and retrograde P-T evolution, and the metamorphic peak. Presently, detailed P-T paths can be reconstructed by comparison of information obtained from thin section observations (assemblage sequences, mineral zonations, mineral growth and resorption textures) and such gained by thermodynamic calculations, e.g. by using quantitative phase diagrams. (ii) Second, detailed petrographic observations are necessary to relate the evolution of rock forming minerals - used for P-T path reconstructions- to the evolution of accessory minerals commonly used for geochronology. In this context, trace element (TE) zonation patterns of rock-forming and accessory minerals can be useful. However, their application as thermometers and as “correlators” must be considered with caution, because their incorporation in accessory and rock forming minerals, as well as their distribution among minerals on a thin section scale is far from well understood. These problems can strongly influence the interpretation of P-T-t paths as well as dating results (e.g. Lu-Hf dating of metamorphic garnet). (iii) Dating of accessory and rock-forming minerals will provide evidence about the absolute timing of metamorphic processes, and the duration of orogenies. In addition it allows to discriminate between mono- and polymetamorphic evolutions, which cannot be distinguished unambiguously on the basis of structural and petrological data. Furthermore, the combined use of different dating techniques may allow to estimate cooling rates of metamorphic rocks, and our growing understanding between the evolution of accessory and rock-forming minerals to estimate the timing of prograde P-T paths. (iv) The use of T-t dependent processes, like mineral growth rates and diffusion rates, can set additional constraints on the timing of metamorphic processes. E.g. the knowledge of mineral growth rates may help to clarify the timing of prograde P-T histories, whereas diffusion rates can be used to model cooling rates of orogenic processes.

Finally, I should emphasize that only the combination of different techniques will lead us to a true understanding of the crustal evolution through time.
Zircon formation versus zircon alteration – New insights from combined U-Pb and Lu-Hf in situ LA-ICP-MS analyses, and consequences for the interpretation of Archean zircon from the Limpopo Belt

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We demonstrate that the combination of U-Pb and Lu-Hf isotope data obtained by LA-ICP-MS provides a powerful tool, which allows distinguishing zircon domains grown during several metamorphic-magmatic events from altered domains affected by complete single and/or multiple Pb-loss. This discrimination is possible, because the U-Pb and Lu-Hf isotope systems are decoupled during zircon alteration. We show that the initial \(^{176}\text{Hf}/^{177}\text{Hf}\) ratio once "incorporated" into the zircon lattice remains nearly unaffected during later alteration processes which cause Pb loss. Newly formed zircon overgrowths always have higher initial \(^{176}\text{Hf}/^{177}\text{Hf}\) than previously grown domains, due to the incorporation of additional radiogenic \(^{176}\text{Hf}\) formed by \(^{176}\text{Lu}\) decay in the rock’s matrix between the different zircon growth events. Such \(^{176}\text{Hf}\) is not incorporated into zircon domains affected by post-growth alteration. By applying the U-Pb and Lu-Hf systems, in combination with cathodoluminescence (CL) imaging, we can show that zircon grains in the Sand River gneiss of the Limpopo Belt grew during three events; during magma crystallization at 3.28 Ga, a first anatexis at 2.64 Ga, and a second anatexis at 2.02 Ga. Our data also show that abundant zircon domains underwent multiple Pb loss, and that many of the 2.02 Ga old zircon domains result from complete Pb-loss of zircon domains already formed at 2.64 Ga. In contrast, all domains of complex zoned zircon grains from the Zanzibar granodiorite gneiss were formed during a single magmatic event at 2.61 Ga, but most of them suffered single and/or multiple Pb loss.

Recent bimodal eruptions from the Torfajökull-Veidivötn volcanic system, south-central Iceland: Insights into magmatic processes and their rates

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Historical bimodal composition eruptions spanning Torfajökull central volcano and neighbouring Veidivötn fissure swarm in southeastern Iceland were studied to examine the nature and timing of basalt and rhyolite petrogenesis at an active divergent plate boundary. Post-glacial eruptions in the area have sampled both tholeiitic and transitional alkaline basalts as well as co-eruptive high-K rhyolites. Physical mixtures of these magmas were erupted at the boundary between these volcanoes, although this study focuses instead on lavas and tephras that most closely approach the mafic and felsic endmember magma compositions that fed the most recent eruptions in 871AD and 1477. Major and trace element data demonstrate that the samples sit near the ends of previously defined regional mixing trends. Whole rock and mineral U-Th-Ra-Sr isotopic compositions are consistent with both limited compositional variation in magma sources and relatively rapid petrogenetic timescales. Rhyolites display the greatest \(^{230}\text{Th}\) excesses of up to 17%, yet have only slightly lower \(^{230}\text{Th}/^{232}\text{Th}\) activity ratios than co-eruptive Veidivötn basalts. Both magma types display small but significant \(^{226}\text{Ra}\) excesses, up to \(~ 10\%\) in the rhyolites and \(~ 60\%\) in the basalts. Trace element and isotopic data are consistent with crustal melting of a mafic source protolith of Holocene age to generate the 871 and 1477 rhyolites. The requirement for a young rhyolite protolith is inconsistent with previously suggested models involving old silicic segregation lenses or isotatically subsided source rocks to make Icelandic rhyolites. Mineral separates yield zero-age U-Th isochrons, and Ra-Th isochrons of a few kyrs, indicating that the crystals formed shortly prior to eruption, consistent with petrographic and mineral chemistry indicators that they are phenocrysts. We propose a model to explain the compositional similarity of west Torfajökull rhyolites with historically erupted rhyolites in which the former are produced by partial melting of transitional alkaline basalts, while the latter are sourced from mafic protoliths that are chemically similar to the Veidivötn tholeiites but have suffered extensive K-metasomatism prior to melting.
Geochemical effects of deep subduction on the continental crustal materials

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Subduction of continental crustal materials to depths >100 km is well documented worldwide. However, how subduction affects the geochemistry of subducted continental materials is poorly understood. Deeply subducted (>100 km) sedimentary and granitic rocks from the Chinese Continental Scientific Drilling (CCSD) project are used to address such a critical question. Geochemical data on fresh pelitic, psammitic, and granitic rocks from 2800-3000 m and 4300-5000 m of CCSD main borehole show that (1) at similar SiO$_2$, Al$_2$O$_3$ and CaO, leucogranitic gneisses have the highest magnitude of variations in Rb/Sr and Rb/Cs ratios; (2) degrees of variation in Rb/Sr and Rb/Cs ratios appears to depend on K$_2$O; and (3) strong fractionation of Cs from Rb, and U from Th, resulting in highly elevated Rb/Cs (up to 400), and Th/U (up to 32) (Fig.). This can be explained by hydration induced K-feldspar to phengite transformation [1] which preferential retain Rb over Sr and Cs that preferentially partition into a fluid. Pre-HP dehydration or HP-UHP hydration of continental materials also fractionates Th over U, which greatly increased the Th/U ratio of the hydrated continental materials, leaving lower Th/U ratios in the residue fluids. Zircons grown from such a fluid could have lower Th/U ratios, which is common in UHP metamorphic zircons [2].

References

Environmental vanadium distribution in soil in a V-Ti-Fe magnetite ore area, Panzhihua, south-west of China

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Vanadium (V) is a widely distributed trace element in the earth’s crust. It had been confirmed that vanadium is an essential element for human and animals by the end of 1970’s (Cantly, 1978) and has high or middle poisonous to animals when its bioaccumulation reaches to a certain degree. The transfer ability and bioaccumulation of V in surface environment depends on its concentration, as well as its speciation.

Panzhihua, located at the upstream of Yangtze River, P. R. China, has a world famous V-Ti-Fe magnetite ore. It is the biggest V-Ti-Fe ore in China, which occupies 64% of the total vanadium in China. The investigated soil is of Xigeda type.

In this paper, the distribution of total vanadium and its speciation in soil got from different depths (4 layers, 0-5 cm, 15-25 cm, 30-50 cm and 50-75 cm) in this famous V-Ti-Fe magnetite ore area has been studied. The contents of total vanadium and vanadium speciation were determined by sensitive catalytic oscillopolarography.

The result show that the average content of vanadium in soil is 102 µg·g$^{-1}$, which is much higher than the average value 86 µg·g$^{-1}$ in China; the vanadium contents in soil samples came from mining area and smelting area are obviously higher than that from agricultural area and non-mining area. At the same sampling site, the content of vanadium is decreased by the increasing of sampling depth.

The sequential extraction analysis procedure of Tessier et al (1979) for heavy metals was used for the vanadium speciation separation. Although the main existing form of vanadium is residual form, the biological effect of vanadium in this area can be ignored. The summation content of exchangeable V and carbonate bound V, which can be directly bioaccumulated in natural conditions, is over 2 µg·g$^{-1}$, while in most other research area is usually less than 1 µg·g$^{-1}$. So the vanadium in this area has high transfer ability and high biological effect.

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The solubility of gold in H₂S vapor

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Although there is extensive evidence that magmatic vapors are capable of transporting high concentrations of some ore metals, modeling of the processes responsible for ore deposition is severely limited by the paucity of data on the solubility and speciation of metals in the vapour phase. As complexes with HS⁻ and H₂S are the principal forms of dissolved gold in aqueous liquids and H₂S partitions strongly into the vapor phase of hydrothermal systems, it is likely that gaseous H₂S is important in promoting the volatile transport of gold. In this paper, we report the results of the first of a series of experimental studies designed to investigate the solubility of gold in H₂S-bearing water vapor.

This first study examines the solubility of gold wire in H₂S gas. The experiments were conducted in titanium alloy autoclaves at 300 to 400°C and pressures up to 230 bars. The total pressure was assumed to be equal to the pressure of H₂S gas and was calculated from the PVT properties of this gas. The redox potential was controlled by the S/H₂S pair. At the end of an experiment, the autoclaves were quenched and Au condensed on the walls of the vessel was dissolved in aqua regia. The solubility of Au in H₂S gas was calculated from its concentration in this acid. The results of our experiments indicate that the solubility of Au in H₂S increases with both temperature and fH₂S, reaching a concentration of 95 ppb at 400°C. Based on the fH₂S dependency, we propose that the species controlling the solubility of Au in H₂S gas has the form AuS·(H₂S)n or AuHS·(H₂S)n with a solvation number between 1 and 2 at 300-400°C. The equilibrium constants for the reactions controlling formation of these two species are log K = -11.1 ± 0.2 at 300°C (both species), -10.7 ± 0.3 and -10.5 ± 0.3 at 350°C, and -10.6 ± 0.2 and -10.4 ± 0.2 at 400°C, respectively.

Results of this study and preliminary experiments in the Au-H₂S-H₂O system, which yielded even higher Au solubilities, provide evidence that H₂S may play a major role in dissolving Au in hydrothermal vapor, something which may be key to understanding the genesis of porphyry and epithermal gold deposits.

Influence of ‘A’ cation ionic-radius on the structure and bulk modulus of ABO₃ perovskite and postperovskite

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Recently, high-pressure experiments and theoretical calculations demonstrate that (Mg,Fe)SiO₃ postperovskite is the predominant mineral in the lowermost mantle called the D° layer, and phase transition from perovskite (Pv) to postperovskite (PPv) has significant geophysical implications for the nature of the D° layer (Hirose 2006). The available experimental data of bulk modulus and 0 K transition pressure from Pv to PPv were investigated for ABO₃ perovskite and postperovskite, it was found that a linear relationships between the radius of ‘A’ cation and bulk modulus exists in ABO₃ Pv and PPv. The bulk modulus decreased linearly with increasing the radius of ‘A’ cation. On the other hand, there is also a positive linear relation between the ‘A’ cation ionic radius and the 0 K transition pressure for germinates perovskite, which indicates the transition pressure increasing linearly with the increasing the radius of ‘A’ cation, so the transformation into postperovskite phase becomes more difficult with the large ionic radii of ‘A’ cation in ABO₃ perovskite (see Fig.). As the phase transitions from Pv to PPv is due to the distortion of BO₆ octahedra in Pv, our results suggest that the ionic radius of ‘A’ cation probably play an very important role on the structure and the phase transformation of ABO₃ compounds.

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Environmental geochemistry in relation to agriculture and human health in Hainan Island, China

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As the biggest island in tropical China, Hainan Island possesses advantageous hydrothermal conditions, high biodiversity and soil diversity.

The environmental geochemistry of this area is determined mainly by the special geological background and pedo-geochemical processes, which are characterized by the diversified lithology and tropical soil formation processes.

One major problem is the high Al toxicity of soils of the island. Total and exchangeable aluminum of soils in different weathering stages are high as compared to that of parent materials. About a half of the studied soils contain exchangeable aluminum higher than the threshold value of causing hazard to plant. Soils developed from basalt in the north part of the Island have the highest aluminum content while that from marine deposit lowest.

Agricultural production, including tropical cash crop cultivation, is affected soil acidity and acidification. Rubber cultivation has an accelerated acidification. Rice and upland crops also changed the acidity of soils of the Island.

Calcium is severely deficient in soils, surface water and plant. One nutritional problem is the intake of Ca of local people from their daily diet is much lower than that of nation-average as well as that of subtropical region.

It is suggested that based on the understanding of the environmental geochemistry problems, we are able to adjust agricultural structure in the way of interfering the cycling of some important plant nutrients for improving agricultural production and human health in this tropical Island.

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Dynamic reactivity of metals in soils – Relevance to uptake by plants

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To predict the availability of metals to biota, it is necessary to understand both solution and solid phase supply processes in the environment. The kinetics of metal release from particles and complexes can limit the rate of uptake of metals. Complex dissociation rates in solution can be measured by several approaches. The rate of release of metal ions from particles in soils and sediments has been difficult to assess directly. The technique of DGT (diffusive gradients in thin-films) had been used to measure dissociation kinetics in solution and release from solid phase in soils. DGT perturbs the equilibrium system by lowering the local concentration of metals and measuring their supply. By modelling the dynamics of the DGT-soil system, kinetic information, such as the rate constant of supply from the solid phase and the labile pool size of metals, can be obtained.

Measurements have been performed in several metal soil systems. The results show that the rates of Zn and Cd supply are generally faster than those of Ni for the same soil. Relative slow rates of supply for Ni are consistent with general understanding of its kinetics of release from complexes. In clay soils the rate of release of Zn and Cd are generally too fast to measure, but measurable rates can be observed in some sandy soils. The rate of supply of Zn in freshly spiked soils is generally too high to measure, but measurable rates can be observed in some sandy soils. The rate of As release from solid phase to solution in the rhizosphere was much slower than that in the bulk soil. These kinetic findings are relevant to the uptake of metals by plants because DGT emulates the prime effect of the plant on soil, namely removal of metals.

To assess the metal dynamics in soils in relation to uptake by plants, we have used the measured Michaelis-Menten parameters of plants to predict the fluxes of metal that they remove from a given soil. The fluxes were comparable to the fluxes measured by DGT, showing that plants and DGT perturb the metal chemistry of the soil to similar extents. The soil kinetic parameters measured by DGT which influence the metal uptake by the device, will therefore also exert a control on the metal uptake by plants.

References
Structural and geochronological studies of the Fuping Complex: New constraints on the tectonic evolution of the Trans-North China Orogen

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The Trans-North China Orogen (TNCO) is interpreted as the site where two discrete continental blocks, called the Eastern and Western Blocks, amalgamated to form the coherent basement of the North China Craton in the late Paleoproterozoic[1-2], but its deformatonal history and timing have not been well constrained. In this study, we present structural and SHRIMP zircon data for the Fuping Complex, one of the largest complexes in the TNCO. Detailed mapping and structural investigations reveal that the Fuping Complex experienced four distinct deformatonal episodes (D1 to D4). The D1 is characterized by isoclinal tight fold (F1), penetrative F1 fold axial planar foliation (S1) and mineral lineation (L1). Earliest L1 displays a preferred NW-SE orientation with a shallow plunging angle, indicating the earliest direction of collision. The D2 is the major deformatonal episode in the complex, represented by ubiquitous E to SE-verging isoclinal, overturned -to- recumbent folds (F2) of varying scales, F2 fold axial planar foliation (S2) and crenulation lineation (L2). Both D1 and D2 deformations corresponded for the prograde metamorphism (M1). The extensional D3 generated regional-scale NW (W)-SE (E) trending upright open folds (F3) that warped the whole complex into dome and basin patterns. The last D4 is characterized by brittle fabrics and low-angle detachments, which are related to the complete exhumation of the complex. Both D1 and D4 corresponded for the decompression (M2) and retrograde (M3) metamorphism, respectively.

SHRIMP U-Th-Pb zircon ages from leucocratic dykes reveal that pre-D1 leucocratic dykes were emplaced at 2484±13 Ma, whereas zircons from syn-D2 folded leucocratic dykes yield SHRIMP zircon ages of 1843±12 Ma and 1844±18 Ma, respectively. Zircons from post-D2 leucocratic dykes give SHRIMP zircon age of 1817±14 Ma, older than published zircon ages of 1790±8 Ma and 1799±9 Ma for post-tectonic undeformed granitic pegmatite dykes. Structural and SHRIMP U-Th-Pb zircon data indicate that the Fuping Complex, together with adjacent Wutai and Hengshan Complexes, underwent uniform deformatonal histories incorporated into an eastwards subduction during final assembly of the North China Craton at ~1.85 Ga.

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References

FTIR features of coals from the Ordos Basin (NW China): Implications on hydrocarbons from coal

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The Ordos Basin, located in NW China, is typical of accumulation of multi energy resources including oil, gas and coal. We have performed the study on some coal samples with variable maturation from brown coal to anthracite by Fourier Transform Infrared (FTIR) Spectroscopy analyses. The goal is to have a deeper understanding of the evolution of hydrocarbons from coal. The method of curve-fitting analysis was used in order to more precisely quantify peak areas of different coal structure. Despite of the fact that the studied samples are not along a natural series due to different bioprecursors, they may also imply the ability and evolution of hydrocarbon generation of coals. Analytical results indicate that variation of IR spectra corresponds to the stage of hydrocarbon generation relatively well.

Firstly, when vitrinite reflectivity (Ro) of the samples is below 0.6%, IR spectra area around 1705 cm⁻¹ which represents stretching vibration of oxygenous groups in coal descends fastly with the maturation increasing. This implies that a lot of hydroxyl group and methoxyl group break off from coal and become carbon dioxide to migrate. IR spectra area of 2950 cm⁻¹ and 2920 cm⁻¹ represents asymmetric stretching vibration of methyl and methylene, respectively. However, we did not observe a clear change of these two function groups. In this stage, only a few amounts of oil and gas were generated based on thermal simulation experiment of brown coal.

Secondly, when Ro of the samples reaches 1.3%, FTIR spectra area around 1705 cm⁻¹ decreases to zero. Meanwhile, IR spectra area of 2950 cm⁻¹ and 2920 cm⁻¹ diminish continuously, which means plenty of aliphatic group and aliphatic ring break off to becoming oil and gas. The ratio of methyl (CH₃) to methylene (CH₂) representing the length of aliphatic chains of coal and a branching index increases. This may be ascribed to the break of long aliphatic chains and the conversion of hydroaromatic methylene structures to aromatic rings during hydrocarbon generation. A large amount of oil and gas have been generated through the thermal simulation experiment, and the coal almost reaches the hydrocarbon generation peak in this stage.

Thirdly, when Ro exceeds 1.3%, IR spectra area of 2950 cm⁻¹ and 2920 cm⁻¹ disappear, and the process of hydrocarbon generation from coal stopped. The CH₃/CH₂ ratio does not represent the length of aliphatic chains here. In summary, abundance of hydrogen and oxygen in coal decreases and carbon concentrates along with the coal rank increasing and hydrocarbon generative maturation.

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A general kinetic model of plagioclase dissolution

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Feldspar dissolution is of great geochemical interest and has been intensively studied in the laboratory. The plagioclase solid-solution series provides a unique candidate for fundamental investigations of feldspar dissolution. Factors that affect dissolution kinetics of a particular plagioclase composition include saturation state, pH, ionic strength, organic ligands and temperature. Feldspars consist of a tectosilicate framework where variation in the distribution of Al and Si generate order/disorder phenomena. In the entire plagioclase feldspar solid solution series, the Al content increases from endmembers albite (Na[AlSi3O8]) to anorthite (Ca[Al2Si2O8]). These factors have significant influence on the dissolution kinetics and are potential indicators of dissolution mechanism.

We use a stochastic model to study plagioclase dissolution. The model incorporates bond-breaking, bond-forming, surface diffusion, detachment and attachment of various Si- and Al- ions and complexes to and from solution. The resulting dissolution is the outcome of the stochastic treatment designed to explore the kinetic behavior of a many-body process. The model involves the full crystal structure, highlighting the essential correlation of dynamics of neighboring sites on the surface.

We examined eight different plagioclase compositions, representing the entire solid solution series. Our results indicate that “unlimited deepening” into the bulk structure by leaching of Al yields a consistent log-linear dependence of dissolution rate on anorthite content. Only when the dissolution process is confined to the top several surface layers, the transitional point (about An70) can be successfully generated. At this point rates accelerate rapidly, and log(rate) departs positively from its linear relationship with An. In the case of (Al, Si) disorder, unlimited leaching of Al results in a 5-fold increase in dissolution rate from low albite to totally disordered high albite. In contrast, (Al, Si) disorder had no discernible effect on reaction mechanism involving the top layers. Subsequent modeling results on ∆G dependence, aluminum inhibition and surface chemistry are all comparable with previous experimental data in the framework of top-layer reaction mechanism. This confirms (1) feldspar dissolution under acidic conditions is a surface-controlled process, (2) surface processes modify the uppermost unit cells by leaching of Al, and (3) a thick layer of precipitates is generated on top of the leached interface.

Partial melting during the exhumation of the UHP rocks in Dabieshan Massif

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The partial melting associated with or induced by decompression during the exhumation of the UHP rocks is one of the most important physicochemical processes postdating the collision event in an orogen. The strongly deformed foliated granite (orthogneiss) and associated felsic or pegmatitic granite pods and veinlets are widespread in the UHP and HP units in Dabieshan massif, which can be interpreted as the result of decompositional partial melting of the UHP rocks in the mid-lower crust under amphibolite conditions. The granitic and felsic pods or veinlets are clearly intrusive, as they contain deformed enclaves of eclogite, retrograded eclogite and country rock gneiss, and the contact in some cases is cross-cutting. In some localities where larger UHP eclogite bodies occur, there is a gradual transition, from eclogite → amphibolized eclogite → eclogitic amphibolite → amphibolite (frequently with symplectites of plagioclase + amphibole) → (garnet bearing-) biotite hornblende plagioclase gneiss (so called UHP rocks) → (garnet bearing-) foliated granite. The REE distribution patterns of the UHP rocks suggest a common type of protolith. The foliated granite has the geochemical characteristics of A-type granite and formed in the post-COLG environment. The geochemical features and Pb-Sr-Nd isotope tracing indicate that its magma source is related to the UHP rocks.

Most of the partial melting phenomena are concentrated in the fractures within the eclogite, retrograded eclogite and their country rocks, which supports that the partial melting must be happened during the decompressive retrogression of the eclogite to amphibolite facies and the uplift of eclogite to lower-middle crustal level. The large-scale migmatites (metatexites) and the foliated granite (anatexite) of the UHP/HP terrane in the Dabie massif are important geologic records of partial melting and the transfer of the thermal state in the crust. It is also an important physicochemical process in decreasing the competence, enhancing the deformability of the rocks and stimulating the transformation from the compressional regime to the extensional regime.

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Dissolution morphology as an indicator of respiration mechanism in *S. oneidensis*

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The mechanisms and kinetics of dissimilatory iron respiration by bacteria are important to a variety of globally significant environmental processes. As a tool to examine iron respiration, the dissolution of iron (oxy)(hydr)oxide particulate coated glass slides under a variety of conditions was observed with atomic force microscopy (AFM). It was found that the dissolution morphology of the particulates in the presence of wild-type *S. oneidensis* MR-1 is heterogeneous (Figure 1), whereas an abiological chemical reductant, 9,10-anthrahydroquinone-2,6-disulfonate (AH2DS, oxidized form of AQDS), dissolves the coatings homogeneously. The behaviour of a gspD deletion mutant (deficient in solid-iron mineral respiration) respiring via an exogenous electron shuttle, AQDS, was also examined. The resulting dissolution morphology was homogeneous, similar to the abiotic experiments using AH2DS. These results suggest that the kinetics of respiration of wild-type *S. oneidensis* MR-1 may be in part controlled by transport, whereas, the action of chemical reductants are primarily limited by surface processes. It is likely that wild-type organisms respire on iron (oxy)(hydr)oxides using a different reduction pathway(s) or kinetic regime(s) from AH2DS and may explain the difficulty in comparing the kinetics of bacterial respiration to a chemical reductant.

Figure 1: Heterogeneous dissolution of iron oxyhydroxide particulates exposed to wild type *S. oneidensis* MR-1 for one day. Image size is 85 µm and Z-scale is 436.32 nm.

Zircon U-Pb age and Hf isotope evidence for growth and reworking of the Yangtze continental nucleus

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To understand the connection between continental cratonization and global tectono-thermal event is essential for recognizing the formation and evolution of continental crust. For this purpose, a combined study of zircon U-Pb and Hf-O isotopes was conducted on migmatite, gneiss and metapelite from the Kongling complex (the only Archean microcontinent outcropped in South China) and the Liantuo sandstone in Yichang. The results show great significance for growth and reworking of Yangtze continental nucleus. A detrital zircon as old as 3.8 Ga was revealed by SHRIMP U-Pb dating for the Liantuo sandstone of middle Neoproterozoic age, implying the existence of crustal materials with this age in the Yangtze Block. Its Hf isotopes suggest growth of juvenile crust at 4.0 Ga. Zircon U-Pb ages for the migmatite and gneiss from the Kongling complex suggest two episodes of magmatism at 3.2-3.3 Ga and 2.9-3.0 Ga, probably marking formation of Yangtze continental nucleus at Mesoarchean. Their Hf isotopes suggest extraction of mafic protolith from the depleted mantle no later than 3.5 Ga ago.

U-Pb ages of 1.97±0.03 Ga were obtained with low Th/U ratios of 0.01 to 0.14 for metasediments and amphibolite from the Kongling complex, indicating that the ages are a record of Paleoproterozoic metamorphic event. εHf(t) values of about −6.5 and model Hf ages of about 3.0 Ga were acquired for zircons from the metapelites, suggesting an Archean source. Thus a response to the Paleoproterozoic global tectono-thermal event in South China is reworking of Archean continental nucleus. A survey of Paleoproterozoic ages throughout the Yangtze Block suggests that metamorphic event and subsequent magmatic activity occurred in the north, but only magmatic activity in the south. Both metamorphic and magmatic activities are associated with formation of a unified basement responsible for cratonization of the Yangtze Block. This provides a geodynamic connection between the formation of this craton and the global tectonomagmatism in the Paleoproterozoic, marking continental accretion by arc-continent collision orogeny during assembly of the supercontinent Columbia.

A number of Neoproterozoic U-Pb ages were also dated in detrital and metamorphic zircons, consistent with those widely occurring in the periphery of the Yangtze Block. This period of tectono-thermal events is associated with contemporaneous rift magmatism in response to the Rodinia breakup. It results in not only remelting of Archean and Paleoproterozoic arc-derived crust but also prompt reworking of Neoproterozoic juvenile crust. Therefore, the growth of continental crust in the Yangtze Block started since the early Archean, but a stable craton through reworking did not occur until the Paleoproterozoic.
Controlling mechanism of thermochemical sulfate reduction
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Thermochemical sulfate reduction (TSR) is the reaction to form H₂S, which not only can critically affect the economic value of hydrocarbon gas, but is highly toxic and corrosive for production equipment. However, the exact nature and reaction mechanisms which influence the TSR are not known. In present study elemental sulfur and different sulfates are applied to investigate hydrocarbon reduction in different aqueous. Our result suggests that the nature of the aqueous is critical for TSR reactions and products. Aqueous with elemental sulfur can trigger the reaction quickly and complete the reaction within short time, but gas products dominated by H₂S and CO₂ with minor amount of hydrocarbon gas (<5%) clearly contradict those natural gases from most TSR areas. Acid salt aqueous phase formed by strong acid and weak base (Ca, Mg) seems facilitate TSR, and produces gases dominated by hydrocarbons with well situated amount of H₂S (0~25%). However, aqueous with alkali metal (Na, K) sulfate is hard to trigger TSR reaction because of the neutral pH of salt aqueous phase by strong acid and strong base. Therefore, slightly acidic medium with abundance SO₄²⁻ should be the prerequisite for initiating TSR at carbonate reservoirs. Therefore, the likelihood and intensity of TSR can be predicted on the base of concentrations of four type of anions (Cl⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻) and two type of cations (alkali metal ions such as Na⁺, K⁺ and alkaline earth metal ions such Ca²⁺, Mg²⁺) in formation water. This result is compatible with our case study in the Sichuan Basin where the aqueous within TSR occurrence area contains high concentration of SO₄²⁻ ion and alkaline earth metal ions (Ca²⁺, Mg²⁺) with low concentration of CO₃²⁻ and HCO₃⁻ ions.

References

Mantle metasomatism in the peridotite xenolith from Panshishan,
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Panshishan alkaline basalt is located in the joint area of Jiangsu and Anhui Provinces. It is a Cenozoic volcanic cluster (N13) of Luhe-Yizheng in the SE seaboard of China. The alkaline basalt contains a lot of spinel lherzolite xenoliths. Detailed electron-microprobe study revealed that substantial mantle metasomatism taken place, and many metasomatic mineral phases related to mantel melt/fluid occur in the intergranular spaces of primary ones. Detailed observation revealed that the course-grained metasomatic Cr-diopsides develop between the primary olivine grains, and a primary Cr-spinel is found in it. A lot of fine-grained Cr-spinels develop in the Cr-diopside, which exsolved from the Cr-diopside. At the joint position of the Cr-spinel and Cr-diopside a kind of silicate glasses develops, rich in Si, Al and K and poor in Fe and Mg, which are believed to be derivatives of the metasomatic process of melt fluid. And between the Cr-diopside and the primary olivine a spong-rim develop, which consists of feldspar + silicate glasses (Fe-,Mg-rich, Si-,Al-,K-poor and volatile-rich) + olivine + apatite + Cr-spinel. It is suggested that the upper mantle rock could have been at least undergone two periods of mantle metasomatism in the area. First period of metasomatism formed the mineral assemble of feldspar + olivine + apatite + Cr-spinel + Cr-diopside, which could be related to a melt/liquid with higher viscosity; And the second period of metasomatism formed the silicate glasses rich in Fe and Mg and depleted in Si and Al, which might indicate a melt/liquid with lower viscosity. The Metasomatic phenomeon can account well for that the mantle source of the alkaline basalt had been undergone enrichment process during Neocene.

Acknowledgments
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Lithogenic inputs over the Kerguelen Plateau (Southern Ocean) traced by the dissolved REE concentrations and Nd isotopic composition

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The Southern Ocean is regarded as a key region in understanding the role of biogeochemical cycling on the variation of global climate (Marinov et al. 2006). Although this Ocean is characterized by HNLC conditions, areas of high biomass do occur including the Kerguelen plateau. These bloom occurrences are attributed to natural fertilization due to iron inputs from the Kerguelen archipelago and plateau (Blain, Treguer et al. 2001). The major goal of the KEOPS project was to study the result of this natural iron fertilization, and in particular to identify its sources.

REE are an extremely coherent group in terms of chemical behavior (Elderfield and Greaves 1982). Seawater Nd isotopic composition is a tracer of water mass pathways and of their interactions with continental material. Although the oceanic cycles and sinks of dissolved Fe and REE are different, the dissolution of lithogenic material constitutes the main source for both dissolved Fe and REE in the ocean. Therefore, we propose to use REE concentrations and Nd isotopic compositions in the Kerguelen Plateau waters to 1) trace the origin of the observed iron enrichment and 2) quantify the fluxes of the lithogenic inputs.

We will present dissolved seawater REE concentrations and Nd isotopic compositions from 9 stations upstream from and above the Kerguelen plateau. The REE patterns display positive Eu anomalies in the water masses above the plateau, which are similar to those of the Kerguelen basalts, suggesting that the high dissolved REE contents observed in the waters above the plateau result from the dissolution of lithogenic material, such as from Kerguelen or Heard Islands. Lithogenic fluxes were estimated larger than 110 ± 21 ton Nd y⁻¹ and 37000 ton Fe y⁻¹, for dissolved Nd and Fe, respectively. The under processing Nd isotopic composition analyses will allow a better understanding of the dissolved/particulate exchange occurs at Kerguelen Plateau/water masses boundaries and also allow to quantify this exchange.

Spherical diffusion couple, closure of core composition, and geospeedometry

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In dealing with diffusion in minerals, a spherical diffusion couple is often encountered. Examples include diffusion between the core and mantle (or two concentric layers) of garnet, or spinel, or zircon. This problem does not seem to have been solved analytically before. I present an analytical solution for a spherical diffusion couple. The concentration evolution is shown in Figure 1 and differs from the one-dimensional diffusion couple in a couple of ways. One is that the mid-concentration position (or interface) moves to the shell with smaller radius as a function of time. Nonetheless, a spherical diffusion couple may be fit well by an error function: diffusivity obtained from such a fit is only slightly different from the actual diffusivity, but the interface position is noticeably away from the original interface. Therefore, the original boundary between two layers is not at the position of mid-concentration. The solution is applied to derive the closure conditions for the center of the core, which is compared with the numerical solution for the specific case of oxygen diffusion in zircon (Watson and Cherniak, 1997). Furthermore, given a measured concentration profile, if it can be shown that it is due to diffusion (not growth), the mean diffusion distance may be obtained, from which the cooling rate may be inferred.
Preliminary studies on Sr/Ca and Mg/Ca ratios in aragonitic marine bivalve shells by ICP-OES, ICP-MS and LA-ICP-MS

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The trace element composition of marine biogenic carbonates is gaining increased attention as a proxy for past climates and environments. We have employed ICP-OES, ICP-MS, and LA-ICP-MS to determine the trace element ratios of the shells of Arctica islandica. We evaluated the applicability of these three instruments and explored the characteristics of Mg:Ca and Sr:Ca ratios.

The sample material was life-collected from different localities around Iceland. Each shell was sampled in youth, mature and gerontic life stages (umbo, middle part, tip). The results are as follows: 1) Sr:Ca ratios: ICP-OES data are similar to the ICP-MS results; LA-ICP-MS data for middle portions are same as ICP-OES values; 2) Mg:Ca ratios: LA-ICP-MS results of umbonal and middle shell portions are lower than corresponding ICP-OES results, but the data from tip parts are slightly higher; And ICP-OES results are higher than corresponding the ICP-MS results, this findings coincides with previous findings by Andreasen et al (2006);

For a better interpretation of the results, we used EMPA to analyze the spatial distribution of Sr and Mg in cross-sections of the specimens. According to these element distribution maps, Mg is less homogeneously than Sr. In many portions of the annual increment, the Mg concentration is very low and Sr high. These data suggest that Mg and Sr ions behave totally different in aragonitic shells than in calcitic skeletons. The Mg content may be related to the organic matrix, while Sr may be more related to the carbonate matrix. This may be the reason for the difference in the three analyses.

Reference

He and Ar isotopic composition of pyrite and its significance in XZ uranium ore-field, South China

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XZ uranium ore-field was one of the most important granite-type uranium deposits in China. Many arguments such as mefeworic, magma ann mantle derived fluid on the original of the ore-forming fluid. Isotopic composition of He and Ar in pyrite, one of the most important paragenetic minerals with pitchblende in XZ uranium ore-field been applied to reveal the origin of the ore-forming fluid in this paper. Pyrite paragenetic with pitchblende was sampled from the mine galley. He and Ar isotope was analyzed by the MI-1201G inert gases mass spectrometer. Calculated results shown in table 1 and the results discussed below:

<table>
<thead>
<tr>
<th>No</th>
<th>3He/4He (×10⁻⁷)</th>
<th>⁴He(×10⁻⁶) cm³/STP/g</th>
<th>⁴He*(×10⁻⁶) (m³/STP/g)</th>
<th>Re/Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.66±0.80</td>
<td>10.15</td>
<td>0.22</td>
<td>0.79</td>
</tr>
<tr>
<td>2</td>
<td>2.08±0.17</td>
<td>62.65</td>
<td>0.22</td>
<td>0.15</td>
</tr>
<tr>
<td>3</td>
<td>0.76±0.15</td>
<td>62.87</td>
<td>0.22</td>
<td>0.055</td>
</tr>
<tr>
<td>4</td>
<td>1.36±0.30</td>
<td>59.15</td>
<td>0.22</td>
<td>0.098</td>
</tr>
</tbody>
</table>

Table 1. He and Ar isotope composition of Pyrite

NB: Ra=1.39×10⁻⁶; radiogenic origin ⁴He* correct formula

³He/⁴He value varied in 0.79–0.06Ra, higher than 0.01–0.05Ra, the crust ³He/⁴He value, but lower than 6–7Ra, the continental mantle ³He/⁴He value. All samples distributed between the crust original and the mantle original in ³He/⁴He diagram, which suggests that it had the crust and mantled mixed original of the ore-forming fluid. ⁴⁰Ar/³⁶Ar value varied between 282–319, all samples distributed between the crust original and the mantle original range in Re/Ra vs.⁴⁰Ar⁴He diagram, which also suggest the characteristic of mixed Ar original. The isotopic composition of He and Ar in pyrite might suggest that ore-forming fluid of XZ uranium ore-field might be the mixed product of crust and mantle fluid.

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References
Geochemical constraints on the petrogenesis of Devonian arc picrites and associated lavas from the North Junggar terrane, NW China

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The Junggar terrane in Xinjiang Province, sits adjacent to the Siberian and Kazakhstan plates. Recently, we recognized a near 100-m-thick picritic lava flow in a Devonian arc in Jungguar terrain. The picritic lavas, which occur in the lower part of the Middle Devonian strata, are overlain by basalts and andesites. The picrites are highly porphyritic. Olivine, clinopyroxene and rare chrome spinel with Cr# (Cr/Cr+Al) values (0.63–0.86) are phenocrysts, embedded in a matrix of groundmass plagioclase, clinopyroxene, and Ti-magnetite. Glass does not appear to be preserved, but minor metal sulfides are present. All lavas are characterized by negative Nb, Ta and Ti anomalies with similar abundances of HFSE with MORB, exhibiting typical for island arc volcanic rocks. The Zr/Nb ratios (23–66) of the picrites and basalts resemble the MORBs (10–66), suggesting the MORB-like sources. However, the Ti/V (23–35) and Zr/Sm (18–23) ratios of basalts are higher than those of picrites (14–17 and 14–15 respectively), and the basalts display flat-type REE-chondrite patterns whereas the picrites are characterized by lower total REE concentrations and slight enrichment of light REE. In contrast, the andesites have much higher total REE abundances and LREE/HREE. All suggest that they are not cogenetic related. However, they have similar ($^{87}$Sr/$^{86}$Sr)t (0.70328–0.70433) and εNd(t) values (6.4–7.3), overlapping with modern island arc field. Consequently, primary magmas were most likely generated in N-MORB-type mantle, which was modified by the addition of a fluid component derived from subducted basaltic crust. However, the basalts were generated by partial melting of amphibole-bearing spinel peridotite, and the picrites resulted from low degrees of partial melting of garnet peridotite with residual garnet, and the andesites may have been generated by partial melting of eclogites.

Continental paleotemperature reconstructions: Distribution of GDGTs in a variety of lakes

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In spite of the rising tide of using the TEX86 index in the reconstruction of marine sea surface temperature, applications to lake environments are still limited, with only a few large lakes surveyed. Calibrations of modern environmental conditions with surface sediment Tex86 temperatures in smaller lakes are lacking or not apparent in many settings. We have collected surface sediments from a variety of lakes extending from the Arctic, to southern Patagonia and northern Chile. These include Norwegian cirque lakes, a maar lake in Patagonia, Argentina, a meteorite impact crater lake in Siberia, and a glaciated valley lake in England. In each case, we collected a suite of measurements of the physical parameters of the lake, such as temperature, salinity, pH, etc, in order to determine how the modern distribution of GDGTs correspond to the current environmental conditions across a large range of limnologic conditions. Preliminary results indicate the temperatures calculated from the TEX86 index are consistent with the measured annually averaged surface water temperature, although complications related to soil-derived sources are apparent in some cases. A complete set of data and selected downcore reconstructions of late Holocene conditions will be reported at the conference.
Molecular level simulations of the H$_2$O, CO$_2$ and CO$_2$-H$_2$O systems up to high temperatures and pressures

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H$_2$O, CO$_2$ and CO$_2$–H$_2$O are the most frequently encountered fluid systems in and around the Earth, widely existent in various geospheres, as revealed from direct measurements or from the study of fluid inclusions in various rocks and ore deposits. In this study, we have carried out a series of molecular dynamics and Monte Carlo simulations to predict the properties of these systems up to high temperatures and pressures, which are difficult or even impossible to attain with experimental measurements.

For pure water, we selected a potential model (SPCE) established at normal temperature and pressure and found remarkable reproducibility of molecular dynamics simulations over wide temperature and pressure ranges. Compared with the most recent published high-pressure experimental data up to 5.0 GPa, the simulation results show very good agreement with errors less than 1.0% and reveal a trend to be more accurate as the increase of pressures.

For carbon dioxide, we have proposed an optimized potential model utilizing the established techniques of molecular dynamics and histogram reweighting grand canonical Monte Carlo simulations. This model is demonstrated to show excellent predictability for thermodynamic, transport, and liquid structural properties in a wide temperature-pressure range with remarkable accuracies.

Thereafter, through comprehensive isothermal-isobaric molecular dynamics simulations, the pressure-volume-temperature-component (PVTx) data of CO$_2$–H$_2$O have been extended beyond experimental range (below 1673.15 K, 1.94 GPa) to about 2573.15 K and 10 GPa.

Finally, an equation of state (EOS) was laboriously developed for the H$_2$O, CO$_2$ and CO$_2$–H$_2$O systems. This EOS reproduces all the experimental and simulated data covering a wide temperature and pressure range from 673.15 to 2573.15 K and from 0 to 10.0 GPa within experimental or simulation uncertainty.

References

Diagenetic environment of Qingbulake basic complex, Xinjiang, NW China

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The Qingbulake basic complex is located 120km southeast to the Tekesi County, Xinjiang, NW China. As the Sm-Nd age is similar to the Karatunk complex in the south margin of Altay orogenic belt and Huangshandong complex in eastern Tianshan, these intrusions were considered to be formed in the similar post-collisional environment.

In this study, the high precise SHRIMP zircon U-Pb age of 434±6.2 Ma for diorite from the complex reveal that the major mafic magmatic events took place in the early to middle Silurian. According to recent research on the regional tectonic evolution (e.g., Li et al., 2006, Gao et al., 2006), at least in early Silurian, the southern Tianshan oceanic crust began the subduction to central Tianshan plate and ended in early Carboniferous. Geochemical studies of the Qingbulake basic complex show that it is characterized by low content of Ti, depletion of Nb and Ta and enrichment of large lithosphile elements and slight enrichment of LREE. The magma also displays some features of inland arc magma (Zhang et al., 2006).

So the Qingbulake mafic complex may be closely related to the subduction of southern Tianshan ocean crust to Yili-Central Tianshan plate.

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References
The Trans-North China Orogen –
A long-lived arc:
Evidence from SHRIMP U-Pb zircon ages of granitoid gneisses in the
Lüliang Complex

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The Lüliang Complex is situated in the central segment of the Trans-North China Orogen (TNCO), a continent-continent collisional belt along which the discrete Eastern and Western Blocks amalgamated to form the basement of the North China Craton [1-5]. The complex consists of supracrustal and granitoid gneisses, of which the latter can be subdivided into the Yunzhongshan TTG gneisses, Guojiazhuang granitic gneisses and Chjianlan-Guanlishan granitoid gneisses. These granitoid gneisses are mostly calc-alkaline and considered to have formed in a magmatic arc environment. SHRIMP U–Pb analyses reveal that the Yunzhongshan TTG gneisses were emplaced at ~2499 ± 9 Ma, representing the earliest arc-related magmatic event in the Lüliang Complex. This was followed by the intrusion of the Guojiazhuang granitic gneisses at 2375 ± 10 Ma. The most widespread arc-related magmatic event in the region was the emplacement of the Chjianlan-Guanlishan granitoid gneisses at 2199-2173 Ma, respectively. Metamorphic zircon overgrowth rims from a tonalitic gneiss yielded a weighted mean 207Pb/206Pb age of 1872 ± 7 Ma, consistent with the metamorphic age range of 1880-1820 Ma defined by metamorphic zircons from various high-grade rocks in the TNCO. Thus, the evolution of the Lüliang Complex involved emplacement of the Yunzhongshan TTG suite at ~2499 Ma, the Guojiazhuang granites at ~2375 Ma and the Chjianlan-Guanlishan granitoid gneisses at 2199-2173 Ma, with the final collision between the Eastern and Western Blocks in this area occurring at 1872 ± 7 Ma, the whole series of magmatic events lasting nearly 650 Ma. This suggests that the Trans-North China Orogen represents a long-lived magmatic arc. This study was financially supported by the Hong Kong CERG grants (7055/05P, 7058/04P, and 7063/06P) and a Chinese NSFC Grant (40429001).

References

Crustal architecture of the Dabie orogen: Constraints from U-Pb age,
Hf and O isotopes in zircon from UHP granitic gneiss

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Zircon U-Pb dating, Hf and O isotope analyses were carried out for granitic gneiss from North Dabie, the largest lithotectonic unit of ultrahigh-pressure (UHP) metamorphic rocks in the Dabie orogen, east-central China. The results are used to provide not only insight into its protolith origin and metamorphic history with respect to continental subduction, but also constraints on crustal architecture prior to and after collision. Zircon U-Pb dating gives consistent ages of 751 ± 7 Ma for protolith crystallization, and two group ages of 213 ± 4 to 245 ± 17 Ma and 126 ± 4 to 131 ± 36 Ma for metamorphism. Most of zircon Hf isotope analyses show negative εHf(0) values of –5.1 to –2.9 with crust Hf model ages of 1.84 to 1.99 Ga, suggesting that their protolith was originally derived from reworking of Paleo-proterozoic crust. The remaining analyses from one sample exhibit strongly positive εHf(0) values of 10.6 ± 0.8; some of them have the highest values of 12.4 to 14.5, corresponding to the youngest Hf model ages of 743 to 827 Ma relative to the depleted mantle. Thus, gneiss protolith was derived from reworking of the Paleoproterozoic crust due to rift magmatism in response to the Rodinia breakup at about 750 Ma. This differs from bimodal protolith of the classic Central Dabie UHP metamorphic zone, which has zircon Hf isotope features indicating prompt reworking of Neo-proterozoic juvenile crust. Oxygen isotope analysis yields zircon δ18O values of ~3.26 to 2.79‰, which are considerably lower than those of the normal mantle. This suggests differential involvement of meteoric water in protolith magma by remelting of hydrothermally altered low δ18O rocks. It appears that North Dabie shares the same ages of Neoproterozoic low δ18O protolith and Triassic UHP metamorphism with Central Dabie, but it was significantly reworked at Early Cretaceous. The Rodinia breakup at about 750 Ma would lead to not only growth of juvenile crust in an active rift zone for bimodal protolith of Central Dabie, but also reworking of Paleoproterozoic crust in an arc-continent collision zone for the North Dabie protolith. The difference in the occurrence of Cretaceous ages between North Dabie and Central Dabie suggests that the two UHP metamorphic units were not located on the same level during the Cretaceous magma emplacement, but a lower level for North Dabie. This also provides a constraint on the source depth of Cretaceous granitoids, which was probably deeper than the North Dabie gneiss.
Artificial radionuclides recorded in lacustrine sediments in Bosten and Qinghai Lakes, NW China

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Establishing accurate historical records of the distribution, inventory and source of artificial radionuclides in the environment is important for environmental monitoring and radiological health protection due to their high toxicity, and useful for identification and risk assessment of possible future environmental inputs of radionuclides from nuclear weapons testing and from accidental release from the nuclear fuel reprocessing plants. Historically, variation of studies, such as the reconstruction of pollution history of accurate dating of lake sediments, is important for many characteristic for various Pu sources. On the other hand, a useful tool for next researchers to study the history of anthropogenic pollutants in the environment.

We applied a sector-field ICP-MS to study the recent sedimentation in ca. 10 lakes in China via measurements of both Pu and U isotopes, besides the conventional radiometric determination of 239Pu. In this work, we report the results of Lake Bosten and Qinghai in the Northwestern China. The Pu activity profile obtained with SF-ICP-MS was in agreement with a γ spectrometric 137Cs profile, indicating that the 137Cs and Pu activities convey essentially the same information about sedimentation processes in the investigated lakes. Based on the isotopic compositions of Pu and U isotopes, the sources of artificial radionuclides and the potential application of Pu isotopes for sediment dating will be discussed.

References


The Re-Os systematics of the Bixiling eclogites, Dabieshan, central China

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The Bixiling ultrahigh pressure (UHP) mafic massif, located in the North Dabie high-T/UHP granulite-facies zone, Dabieshan, central China, is one of the largest and most extensively studied outcrops of eclogite-facies rocks in the world [1]. This massif is involved in Triassic subduction and subsequent exhumation of the Yangtze craton beneath the North China craton, as is well recorded by garnet-omphacite Sm-Nd isochrones [2]. However, the ages of possible older metamorphic events and of protolith formation are still debated, which adds uncertainty to the geodynamic models of the Dabie-Sulu orogenic belt.

Here we present preliminary Re-Os results of 15 eclogites and 2 granite gneisses collected near the eastern edge of the Bixiling massif (N:30º43', E:116º17'). Os and Re were extracted using Carius tube digestion + bromine extraction + micro-distillation/anion exchange techniques and analyzed by NTIMS (Os) or by ICPMS (Re). Non-radiogenic Os concentrations are extremely low (<1 pg/g) in all eclogites except DB42 (386 pg/g). This is consistent with the formation of the massif by fractional crystallization of a roughly cogenetic magma in a crustal intrusion. DB42 is thought to represent a basal norite cumulate, which stripped Os from the overlying magma as it formed. Re concentrations vary from 51 pg/g to 2835 pg/g. With the exception of a ratio of 0.1565 for DB42, 187Os/188Os ratios vary from 8 to 390. These high ratios are mainly due to the very low non-radiogenic Os concentrations. Except for one sample (BXL-3, with 2835 pg/g Re), all Re-Os data yield unreasonably old TMA ages, implying significant Re loss, most likely during subduction-exhumation.

If a 750 Ma protolith age is assumed, 20%-60% Re loss is calculated, which is similar to that inferred for subduction of oceanic crust [3,4]. On the other hand, Sm-Nd results from garnets suggest that the Bixiling protolith formed less than 300 Ma before subduction [2]. Our Re-Os results are consistent with only the oldest limit of this estimate; younger ages would require a protolith with an unreasonably high Re concentration. Analysis of mineral separates prepared from BXL-3 indicates that garnet and omphacite host only a small fraction of the total Re in this sample. An additional phase (sulfide?) is required to explain the missing Re.
Relationship between Hg and sulfur in coal from Huaibei coalfield, China

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Many authors have reported that Hg in coal can exist in solid solution within pyrite. Correlations between sulfur and Hg are often attributed to this mode of occurrence and are most common in coals that are extremely enriched in Hg.

The result of this study shows that coal samples from the Huaibei coalfield have relatively low sulfur values (average 0.59%). The correlation coefficient between ash and sulfur is -0.08, indicating that sulfur in the Huaibei coals has an intermediate (organic and inorganic) affinity. In a study of 29 coal samples from the Huaibei coalfield, We observed that organic sulfur is the dominant sulfur form when the total sulfur is near 0.5%. Some literatures report that organic sulfur compounds can capture Hg and result in the enrichment of Hg in coals.

The conclusion shows the relationship between Hg and sulfur in all 29 coal samples that we examined; note that the correlation coefficient is only 0.17 (n=29). Interestingly, and it shows a significant positive correlation between Hg and sulfur (n=21, R=0.64, p<0.05) is obtained by excluding the eight samples from the No. 5 and 7 coal seams, which were influenced by a magmatic intrusion. This suggests that the magmatic intrusion not only increased the concentration of Hg in seams 5 and 7, but also changed the mode of Hg occurrence in these seams. The significant, positive correlation between Hg and sulfur in coals from the No. 3, 4, and 10 seams suggests that Hg in these coal seams is bound to both organic sulfur moieties and within sulfide minerals.

Rb-Sr isochron age of gold-rich quartz veins in the Lingqueshan gold deposit, Shandong Province in China

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Mineralogenetic matter, mineralogenetic liquid, and mineralogenetic age are three core problems in mineral deposit Research. Among them mineralogenetic age is a important aspect in mineral deposit research. To ascertain the mineralogenetic age of a mineral deposit has significance in ascertain the relation between the mineralogenetic function, regional tectonics function, metamorphic function and magma function, and has significance in research of mineralogenetic matter, mineralogenetic liquid, and mineralogenetic cause of formation. Now direct determination to the mineralogenetic age method mainly are K-Ar method, Ar-Ar method, fluid inclusion Rb-Sr isochrone method, Sm-Nd method, Pb-Pb method, and so on. Since in 80th in 20 century the method of fluid inclusion Rb-Sr isochrone was used in mineralogenetic age research, many domestic and overseas scholars did attempts in this aspect, and some scholar put forward some oppugn with the lack and dependability of this method. The paper has determined the Rb-Sr isochron age of Gold-rich quartz veins in the Lingqueshan gold deposit, and discusse the mineralogenetic age.

The Zhao-Ping fracture zone is the master gold metallogenic zone in China, but the study on the gold deposit lays in the hanging wall of the Zhao-Ping fracture zone is very rudimental. The Lingqueshan gold deposite lays in the hanging wall. In order to know the timing of the gold deposition, so the Rb-Sr isochron dating methods have been adopted to date deposite, the result indicates that the age of the Lingqueshan gold deposite is 118±9.4Ma. It is consistency with the age of Jiaodong gold deposits concentration zone (120±10Ma). That is to say, the large-scale metallogeny of the Zhao-Ping fault zone hanging wall took place in early cretaceous occurred in north western Jiaodong Peninsula.
Zircon U-Pb age, Hf and O isotope insight into origin of Neoproterozoic granitoids in South China

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The genetic links between rift magmatism, crustal growth and reworking, and granitoid petrogenesis are an important issue with respect to supercontinent breakup. A combined study of U-Pb age, Hf and O isotopes in zircons from Neoproterozoic granitoids in South China, including the Jiangnan orogen between the Yangtze and Cathaysia Cratons, the Kangdian rift along the western margin of the Yangtze Craton, and the Dabie-Sulu orogen along the northern margin of the Yangtze Craton. Two generations of magma crystallization are discerned for the granitoids, with double-bimodal features in their zircon Hf and O isotope compositions. Despite consistently high δ18O values of 8.1 to 10.4% for zircons, ~825 Ma S-type granitoids in the Jiangnan orogen show not only positive εHf(t) values of 3.4 to 5.4 with young Hf model ages of 1.17 to 1.25 Ga, but also negative εHf(t) values of ~3.4 to ~1.6 with old model Hf ages of 1.81 to 1.92 Ga. In contrast, 760~750 Ma bimodal I-type intrusives in the Kangdian rift are characterized by positive εHf(t) values of 3.5 to 9.9 with young model Hf ages of 0.94 to 1.18 Ga, and by both low and high δ18O values of 4.2 to 6.2‰ relative to 5.3±0.3‰ for normal mantle zircons. Bimodal protoliths of 780~750 Ma ages for metagneous rocks in the Dabie-Sulu orogen have consistently low δ18O values of ~4.3 to 4.4‰ for igneous zircons, but their Hf isotopes are subdivided into two groups: one has positive εHf(t) values of 5.9 to 12.9 and young Hf model ages of 0.82 to 1.24 Ga, and the other has neutral εHf(t) values of ~2.7 to 2.3 and old Hf model ages of 1.68 to 1.92 Ga.

The zircon Hf-O isotope systematics provides a link of granitoid petrogenesis to orogenic collapse, rift magmatism, water-rock interaction, and the Rodinia collision. Growth and reworking of juvenile and ancient crusts are dated by means of zircon εHf(t) values and model Hf ages in combination with U-Pb ages. While a change in magma source from arc-derived crust to asthenospheric mantle keeps pace with the tectonic advance from supercontinental rifting to breakup, reworking of pre-existing arc-continent collision orogen in either successful or failed rifts plays a basic role on their composition. As a result, the granitoids have principally inherited their source features in element and isotope geochemistry, with additional changes due to partial melting, fractional crystallization or crustal contamination. A plate-rift model is thus proposed to resolve paradoxical interpretations concerning trace element and isotope patterns of both arc-like and rift-like sources in given suites. It also provides a resolution to the controversy between arc-derived and plume-related magmatism for the Neoproterozoic igneous rocks in South China.

Re-Os systematics of lithospheric peridotites from Nushan, east China: Implications for multiple modifications of SCLM

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The Nushan Quaternary volcanic cone in northeast Anhui province, carries abundant mantle xenoliths which including spinel and garnet phase peridotites with or without volatile-bearing minerals such as amphibole, phlogopite and apatite. 12 representative xenoliths were selected for determination of Re and Os concentrations and Os isotope compositions.

Os and Re abundances range from 0.876 to 2.417 ppb and from 0.019 to 0.306 ppb respectively, while 187Os/188Os and 187Re/188Os ratios vary from 0.1149 to 0.3130 and from 0.037 to 0.805 respectively in this sample set. 4 of 12 samples have Os concentrations of <1.0ppb. Such low Os concentrations have usually been attributed to S-undersaturated melt percolation that remove Os-bearing sulfides. 2 of 3 fertile garnet lherzolites have high equilibration temperatures (~1100°C) and the highest 187Os/188Os ratios, similar to the present value of PUM (~0.1296). All spinel lherzolites from fertile to refractory in major chemical compositions, with or without amphibole and/or phlogopite have unradiogenic 187Os/188Os ratios. 6 of 12 samples have 187Re/188Os ratios higher than the PUM ratio of 0.435 that indicating recent Re addition. Nushan mantle xenoliths define a well-correlated linear trend between 187Os/188Os and both Al2O3 and Yb, through the PUM composition and give the model age of primitive melt extraction event (~2.0 Ga).

Previous data indicate that 143Nd/144Nd and 87Sr/86Sr isotope ratios of clinopyroxenes separated from the sample set fall on the mantle array in the depleted quadrant. It is interesting that 187Os/188Os and 143Nd/144Nd ratios have a linear positive correlation for the sample set. The sample with the most depleted 187Os/188Os ratio has the richest 143Nd/144Nd ratio and 2 garnet lherzolites with the highest 187Os/188Os ratio have rather depleted 143Nd/144Nd ratios. The decoupling of Os and Nd isotope compositions of the Nushan mantle xenoliths indicate that SCLM experienced complex multiple modification via modal and/or cryptical mantle metasomatism after primitive melt extraction.

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Fluid phase separation from residual intercumulus aluminosilicate liquid of the Merensky Reef

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Fluid inclusions in both symplectitic and miarolitic quartz of the Merensky Reef of the Bushveld Complex (South Africa) have been studied using cryometry, microthermometry, Raman-spectroscopy, LA ICP-MS, scanning electronic microscopy, gas-chromatography and isotopic methods. This allowed us to obtain principally new information about an order of fluid phase separation from the Merensky Reef crystallizing intercumulus liquid.

We attempted to document at least three generations of fluid separated from boiling residual aluminosilicate intercumulus liquid in the following sequence.

The earliest fluid phase composed of homogenous high dense gas mixture (from CH₄-98.48 and N₂-1.52 to CH₄-73.21, CO₂-24.42 and N₂-2.37 mol.%) was identified in primary gas and co-existing anomalous (combined) fluid inclusions from miarolitic quartz.

The next generation was hetero phase fluid, composed of brines or water-salt solution, containing a free low dense gas phase (CO₂>N₂). This fluid was observed in primary multiphase and coexisting gas-rich inclusions from interior zones of miarolitic quartz.

The latest generation was also heterophase fluid (low salinity water-salt solution and free low dense gas phase) that was found in primary water-salt and syngenetic CH₄-rich gas inclusions from peripheral zones of miarolitic quartz crystals.

The results give us a possibility to suggest that magmatogene fluids that successively separated from aluminosilicate liquid changed from homogenous high dense gas phase to immiscible heterophase oxidized mixture during the crystallization evolution of the Merensky Reef.

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Different forms of sulphur in the Lower Cambrian Ni-Mo mineralized black shale in Zunyi, Guizhou Province, southwest China

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A great and famous Ni-Mo polymetallic deposits are developed in the Lower Cambrian Niutitang Formation in South China. As these mineral deposits are all sulfide, we measured different forms of sulfur in the outcrop Zhuliushui section, Zunyi (SW China) and have a preliminary analyses on their distribution.

Analytical results indicate that along the section, in wallrocks around deposits, the sulfur-content is less than 1%; whereas at the deposit seam (ca. 20-cm-thick) the content exceeds 1%, even high up to 23.807%. This implies that the formation of mineral deposits is closely related to sulfur. In order to know what roles do different kinds of sulfur play, three forms of sulfur including sulphate, pyrite sulfur and organic sulfur were further investigated. It is showed that the content of sulphate is mostly lower than 1.0%, while the other two forms ranging from 0.0441-6.233 (pyrite sulfur) and 0.0192-16.822 (organic sulfur), respectively. This likely implies that the sulfur in the mineralization comes relatively low from sulphate and great from pyrite. Futhermore, under microscopic observation, most of the pyrites occur in the formation of crystal granule, which may be ascribed to slow and successive sedimentation during the early diagenesis.

Otherwise, there is not a good relation between the organic and pyrite sulfurs, as the variation of the former was greater than the latter. Thus, it is suggested that the organic sulfur was also not the key factor in the process of pyrite’s formation. In a word, based on the above analyses, we tentatively suggested that both hydrothermal fluid and sulfur produced by biodegradation were responsible for the mineralization here.

Lastly and interestingly, besides the high sulfur content in the presently known Ni-Mo mineralized deposits, we also found another sulfur-peak in the upper 10-cm-thick seam, which located about 5 m on the above. Whether this is an indicative of another mineral deposit needs a more comprehensive investigation in the future.

Reference
Climatic and environmental glaciochemical records from a climatic interaction region, East Antarctica over the past 780 years (1215-1996 AD)

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An 82.5-meter ice core was retrieved from marginal area of Dome A, East Antarctica by Chinese Antarctic Scientific Research Expedition in 1998/1999. Previous research shows that the area belongs to a continental-oceanic climatic interaction region.

Based on the ion chromatography analysis, we present the glaciochemical characteristics of the ice core in Antarctica over the past 780 years (1215-1996 AD). Our results show that the climatic and environmental variability during 780 years in this area can be divided into three stages as follows:

Stage I is from 1215 to 1460 AD, with a gradual decrease of the local annual snow accumulation rate and concentrations of most major ions.

Stage II is from 1460 to 1800 AD, reaching the lowest accumulation rate and representing strong cooling. Concentrations of the major cations of Na⁺, Mg²⁺ and the anion of Cl⁻ in sea salt reduce distinctly, with the maximum drop in NO₃⁻ and MSA, indicating the possibility to trace environmental changes by chemical ions. This period coincides with the Little Ice Age in the Northern Hemisphere.

Since 1800, Stage III is characterized by a rapid increase of the annual accumulation and concentrations of the major cations and anions, implying the increase of local temperature, which is consistent with the global warming after the Industrial Revolution.

It seems that in Antarctica, the global climatic and environmental variability is recorded in the climatic interaction region rather better than in the other regions.

References

Mantle fluids involved in metallogenesis of the gold deposits in the hanging wall of Zhao-ping fault: Evidence of H-O isotopes

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The Jiaodong region is located on the eastern margin of the North China Craton and the western Circum-Pacific tectonic belt. It is bounded by the Wulian-Rongcheng fault and the Dabie-Sulu ultrahigh-pressure metamorphic belt in the southeast and the Tanlu fault in the west.

The Jiaodong region is the lage cluster of gold mineralization in China. Zhao-Ye gold zone is one of the major gold mineralization zones in Jiaodong. There is many large and medium-sized gold deposits, such as Linglong gold deposit, Dayingezhuang gold deposit and Xiadian gold deposit. But most of this gold deposits are located under Zhao-Ye gold zone. The gold deposits are located in the hanging wall of the Zhao-Ye gold zone have little people to study except Sun Zhongshi (Jilin University). At present, Lingqueshan gold deposit located in the hanging wall of the Zhao-Ye gold zone have put into production, it is advantage for studying on the material sources.

Fluids are distillation of ore-forming, which origin, movement and matter uninstall reflect the whole process of ore forming. The composing of ore-forming fluids is an important parameter to demonstrating geochemistry character of ore-forming. The paper study on the geochemistry character of H-O isotopic of gold deposit located in the hanging wall of Zhao-Ye gold zone, in order to discussing the origin of fluids of ore forming.

Zhao-Ye gold zon is one of the major gold mineralization zones in Jiaodong. The gold deposits located in the wall of the Zhao-Ye gold zone have little people to study, which occurs mainly in the Jiaodong rock group. The ores are mainly of the auriferous quartz vein type hosted in NE trending fractures and faults. Wall-rock alterations are most potassic alteration, siliconization, quartz-sericitization, pyritization and carbonatization. According to research of geological characteristics of deposit and analysis of fluid inclusion of quartz. The δ¹⁸O value of the the quartz vein ranges from 4.78% to 10.12%, and the average value is 6.22%. The δD of H₂O values of fluid inclusion vary from –73.13% to –100.15%, and the average value is –86.63%. The research shows that this area mineralogenetic heat fruit is mainly curtain fountain, and participated in a certain degree of magma water and atmosphere water, has the same mineralogenetic hear fruit system with the other Zhao-ye gold deposit.
Effects of cave environmental condition on drip-water hydrogeochemical characteristics

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Speleothems contain large amount information of earth paleoenvironment change. Multi-proxies, supported by a series of hypothesis, have been used to interpret paleoenvironment change of karst. However, the records of speleothems are seldom coincident within the same cave and contradictory results have been reported. To clarify high resolution, short time scale information urged to reduce noise. Understanding hydrogeochemical processes happening in cave roof can contribute to interpret paleoenvironment change. Cave systems were monitored in Jiangjun Cave in Anshun county of Guizhou province, China, lasted for a year. NaCl was adopted to trace sources of cave drip water, time scales of drip water responding to precipitation, and processes of water dynamics in the cave. 4 drip points were monitored. The result shows that time scale of drip-water responding to rainfall was very quick (0~9 days). Drip water chemical components were directly originated from soil and greatly affected by the soil thickness. The thinner soil was; the less substances water dissolved. Water passed more quickly, which decreased the possibility of dilution happening in drip water, simultaneously, increased the contribution of rock to drip compositions. Different sources of water affected drip water dynamic process, which led to piston flow for JJD-1#, and increased drip ratio and water head pressure for JJD-2#. As well while water was of much quantity. The process of rock dissolution and calcite precipitation mainly controlled elements variations of 4 drip waters while water transported in the route and acted with soil and rock. Consequently, as an important karst environmental factor, soil decides and controls drip compositions of cave drip waters, which means more attentions must be paid to soil in future study.

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Tracing natural CO₂ geological sequestration processes with noble gases

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Isotopic and elemental fractionation of noble gases can be used, together with other gases, to identify and quantify the origin, migration and sequestration processes of natural CO₂ gas deposits. The Jackson Dome CO₂ reservoir lies north east of the Jackson Dome intrusive in Mississippi, USA. The reservoir occurs between 4270m and 5180m depth and is assumed to have formed by thermal decarbonation reactions associated with the Jackson dome intrusive contact with related carbonate formations. 10 gas samples were collected and analysed for both noble gases and major gas composition. CO₂ ranges from 98.75% to 99.38%. Trace amounts of CH₄ and N₂ are correlated, and both correlate negatively to CO₂, suggesting that CH₄ and N₂ have a different source to that of the CO₂. The highest concentrations of N₂ and CH₄ are found on the crest of the trapping structure.

³He/⁴He ratios range between 4.27Rₐ and 5.01Rₐ (where Rₐ is the atmospheric value of 1.4×10⁹), indicating a strong mantle signature. CO₂/³He ratios vary between 1.07×10⁹ and 4.62×10⁹ and are in the range of the values found in pure magmatic samples (1-7×10⁹). The source of the CO₂ is not due to thermal decomposition of carbonates, but is dominated by magmatic gas.

The relationship among major gases (CO₂ and N₂), ⁴₀Ar, ⁴He and Ne isotopes shows that the gases in Jackson Dome reservoir are a mixture of a fractionated air component, a magmatic end member and a radiogenic/crustal component. ²⁰Ne can be crudely used as a groundwater proxy. Anti-correlation of ²⁰Ne with CO₂/³He shows that groundwater plays a role in CO₂ sequestration and may be responsible for more than 70% of CO₂ loss. This is a common feature seen in other magmatic CO₂ rich natural gas fields (Gillifan et al., 2007)

²⁰Ne/³⁶Ar in the gas phase is higher than the groundwater ratio of ~0.16 with values of 0.798 to 1.35. CO₂/³He ratios correlate with both ²⁰Ne/³⁶Ar and ³¹C (CO₃⁺) values. We explore a variety of models to explain this data including: oil-groundwater partitioning; gas-groundwater partitioning; excess air dissolution and noble gas re-dissolution. A solubility controlled Rayleigh fractionation of groundwater modified by oil interaction appears to account for all correlations.

Reference

Redefining feldspar-water interfaces

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Currently prevailing theory or hypothesis on kinetics is that feldspar dissolution is controlled by surface reactions. However, recent atomic scale electron microscopy studies of naturally weathered K-feldspars in the Navajo sandstone, Arizona (Zhu et al., 2006), labdorite dissolved in pH 1 solutions in the laboratory at room temperature (Hellmann et al., 2003), and alkali-feldspars dissolved at 200 °C and 300 bars (our unpublished) show that there is an amorphous layer on the dissolving feldspar surfaces. Furthermore, K-feldspars from the Navajo sandstone show tightly adhered coating of kaolinite and a 3-5 micron thick smectite (Zhu et al., 2006). We believe the amorphous layer and secondary coating layers are important characteristics that bear significances on the feldspar dissolution kinetics. We advance two hypotheses for explaining the field-lab discrepancy. First, the secondary minerals rinding on feldspars are not at local equilibrium with groundwater, as traditionally assumed, but their slower precipitation rates can raise the groundwater saturation state with respect to feldspars to very close to equilibrium, and thus retard the feldspar dissolution rates. Feldspar dissolution reaction in aquifers is within a complex web of reactions, in which secondary clay precipitation plays a key role. Second, a thin (~ 10 nm) amorphous layer, possibly leached in origin, is found on feldspars that we examined. The presence of the amorphous layer on naturally weathered feldspars requires reconsideration of the details of surface reaction controlled mechanism.

Stable sufer isotopic composition of H2S and it’s TSR origin in Sichuan basin, China

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The natural gas has widely some H2S in Sichuan basin; the contents are from minium to 18.6 percents. The high H2S-bearing natural gas lies in the Feixianguan Formation, Leikoupo Formation and Jialingjiang Formation of Triassic; the Sinian, Carboniferous and Permian reservoir have lower contents H2S, Xujiahe Formation of Triassic and Jurassic have micro or free sulfur in natural gas reservoir. The research shows that the gypsiferous rock of Feixianguan Formation, Leikoupo Formation and Jialingjiang Formation of Triassic, Sinian and Carboniferous reservoirs provide the physical matter for TSR; the Permian lower H2S-bearing natural gas is mainly from the pyrolysis of organic sulfur source rock. The stable isotopic composition of sulfur show that the sulfur isolate of H2S-bearing gas has a short at 7~11‰ of the reservoirs sulfate, and that the sulfur isoltes of lower H2S-bearing have widely distributing and about 15‰ short of most data. The stable isotopes of sulfur have a wide distribution extent and step change in the gypsyiferous rock of Triassic, which are similar to the H2S in the distributed law(Fig.1), the data indicate that the sulfur comes from the sulfate in the H2S and TSR occurs in the respective reservoirs. Otherwise, the temperature conditions are similar as the TSR occurs, which means that the H2S generates in the similar temperature condition and the fractional process of sulfur isotopes have no concern with the sulfur isotopes of sulfate, the temperature and extent of reaction are the key factors in the TSR process.

Fig 1. δ13S of H2S and gypsum of Sichuan basin

References

Investigation on the origin of Se-rich soils and selenosis in Yutangba, China

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Yutangba was known as a typical high-selenium (Se) area in China where a sudden incidence of human Se poisoning occurred in 1963. The surface exposed Se-rich carbonaceous cherts and carbonaceous shales (locally known as stone coal) of the Permian Maokou and Wujiaping formations at north part of Yutangba were generally considered as the major source of Se that was enriched soils in Yutangba and other places in Enshi Prefecture. However, little study has been conducted to confirm the source of Se in soils of Yutangba, and the causes of the sudden incidence of human Se poisoning was still in debate so far (Zhu et al. 2004).

161 soil samples were collected from the entire Yutangba area. Abnormal Se content was observed in 11 soil samples with Se concentrations ranging from 346 to 2018 mg/kg with an average of 899±548 mg/kg. Selenium fractionation was investigated in 3 of them based on the sequential extraction protocol described by Kulp et al. (2004), which showed that elemental Se extracted by 1mol/L Na\(_2\)SO\(_3\) was the predominant fraction (>90%) while other fractions are a few percent. These abnormal soil samples were further studied using SEM with EDX for elemental Se. Native Se crystals were discovered and they were surprisingly well preserved mainly as cubic-prismatic in form and more than 20µm in size (ground soil powder). These morphological characteristics are very similar to that of reported native Se crystals derived from natural burning of stone coal on the subsurface of abandoned stone coal spoils, but significantly different from the elemental Se formed by bacterial. This result indicated that the source of Se in cropland soils was different from that of soils which was not cultivated or disturbed by human activities. It provided the strong evidence that local people ever baked soil on the Se-rich stone coal fires and then they dispersed these baked soils containing much more higher dissoluble Se and insoluble native Se over the cropland to fertilize soil. This cultivated practice, ever used by villagers lived in Yutangba and other high-Se areas in Enshi, introduced abruptly a large amount of Se into their cropland, which is further accumulated in local people’s food chain. The occurrence of native Se crystals in Yutangba cropland soils explains the source of Se in soils and the reason for the sudden incidence of human Se poisoning in 1963.

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Sn/W-bearing A-type granites in Nanling Range, South China

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There exists an early Yanshanian (J\(_1\)-J\(_2\)) Sn/W-mineralized A-type granite belt in Nanling Range, South China. It extends from Huashan, Guposhan, through Juuyishan, Qitianling, Qianlishan up to Xitian in a NE direction for some 400 km. The total granite exposure area is over 3000 km\(^2\).

These granitic bodies are accompanied with the contemporary dioritic and monzonitic stocks and rhyolitic volcanics. The mafic microgranular enclaves with magma mixing features are very common. In general, the granitic bodies can mostly be divided into two intrusive phases: the coarse-grained major phase (mainly 163~156 Ma) and the fine-grained later stage additional phase (mainly 143~151 Ma).

The granite rocks are very acidic in composition, (SiO\(_2\)=67.89~77.11%), rich in K\(_2\)O (3.99~6.29%) and alkalies (K\(_2\)O+Na\(_2\)O=7.38~9.62 %), slightly meta-aluminous to weakly peraluminous (ACNK=0.92~1.10).

In trace elements, all the major phase granites and the contemporary intermediate stocks and mafic enclaves are enriched in Rb, Cs, U, Th, LREE, Y, Nb, Ta, Zr, Hf, Ga etc LILEs and HFSEs, as well as Sn/W. They belong to aluminous A-type granites. Compared with the major phase granites, the later stage granites are more acidic (SiO\(_2\)>76%), more alumina-saturated (ACNK=1.00~1.21), and more enriched in Rb, Cs, U, Th, Y, Sn, W etc. trace elements, but relatively depleted in LREE, Zr etc. HFSEs. These later stage granites are often Sn/W-mineralized with large even giant tonnage. Chemically these rocks are very close to S-type granites.

The J\(_1\)-J\(_2\) time in Nanling Range region was a post-orogenic extensional geotectonic setting. Upwelling of the asthenospheric mantle along the NE-trending deep faults resulted in melting of lower crust. The mantle fluid/melt may bring in Sn/W etc. ore-forming elements and mobilize them from the basemental rocks. The higher back-ground Sn/W concentration in melted protoliths and well evolved fractionation of granitic melts are also necessary prerequisites for formation of industrial Sn/W deposits.
Fe isotope variations in North Pacific deep water over last 80Ma
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Fe-Mn crust has proved to provide excellent records of isotope composition of dissolved Fe in deep seawater. Investigating the variability of Fe isotope composition of Fe-Mn crusts is an important approach to trace Fe cycling in marine environments.

A crust named CLD01 (160°44’24’’E, 21°45’N, water depth = 2210 m) from the central North Pacific has been selected for Fe isotope study. This crust has been subjected to detailed investigation in terms of radiogenic isotopes, and its age has been constrained using multiple approaches extending to ca. 80Ma (Ling et al., 2005). The sub-samples were obtained by micro-milling, and Fe isotope measurements were performed using a Nu Plasma HR MC-ICPMS at high-resolution mode after chemical purification. The results are expressed in ε units which are deviations in parts per 10^4 from the same isotope ratios of the reference material IRMM-14. The overall variations in ε57Fe units are from -8.8 to 0.9, within the range of Fe isotope composition of Fe-Mn crust reported before. In more detail, the Fe isotope compositions of the crust start with -3.6 ε57Fe units at the surface, broadly increase to maxima of 0.9 at ca. 50Ma, then decrease sharply to -8.8 at ca. Ma. Furthermore, the ε57Fe values obtained from the crust are negatively correlated with 206Pb/204Pb and 208Pb/204Pb ratios.

These results illustrate for the first time that the evolution of Fe isotope composition in North Pacific seawater back to latest Cretaceous, and confirms that the average Fe isotope composition in seawater is light relative to the bulk silicate Earth. In general, the main Fe sources for open oceans are terrestrial aerosols and MOR hydrothermal plumes. The crust studied is far away from MOR, and there is no evidence of MOR hydrothermal contribution in terms of Pb- and Nd-isotopes. While the exact reason why the overall Fe isotope composition in seawater as recorded in Fe-Mn crust is lighter than bulk silicate Earth remain to be investigated, it is interesting to note that the Fe isotope compositions of precipitates resulting from Fe(III) hydrolysis are significantly lighter than those of residual solutions. The main turning point in the trend of Fe isotope variation occurs at ca. 50Ma, which is broadly coincident with the switchover of terrestrial inputs from North America to Asia (Ling et al., 2005). The strong linkage between Fe- and Pb-isotope compositions strongly suggests that Fe isotope variation in North Pacific deep water is related with global climate change through source inputs.

Reference

He isotope data evidence of crust contamination for mantle melts resulting to the PGE mineralized layered basic intrusions
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He isotopic composition of magmatic fluids from various PGE mineralized layered basic intrusions have been studied for understanding the role of mantle-crust interaction in formation of large Pt-Cu-Ni deposits. 3He/4He ratio have been obtained for Noril’sk, Talnakh, and Chineisky PGE mineralized layered basic intrusions (Russia), as well as for the Bushveld Complex (South Africa). All our results have been compared with He isotopic data of Hawaiian and Icelandic basalts and others no mineralized small basic intrusions of the Noril’sk Region (Basu et al., 1995).

3He/4He ratio is a sensitive indicator of crust substance contamination for mantle melts in processes of magmatic ores formation. 3He/4He value >8-10*10^-6 corresponds to mantle He, while <1*10^-6 value is connected with crust source. These ratio values up to 1-8*10^-6 are typical for mixture of mantle and crust He in fluids.

It is important to note, that only basalts and very small basic intrusions with pure ore mineralization contain mantle He, whereas crust He is predominant in all the large Pt-Cu-Ni deposits from layered basic intrusions. This result correlates well with S and C isotopic data (Riabov et al., 2001).

The results obtained give us a possibility to suggest that crust contamination of mantle melts is one of the important factor in formation of large and unique Pt-Cu-Ni deposits for layered basic intrusions.

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References
Geochemical and mineralogical pattern recognition and modelling with Bayesian approach at the hydrothermal gold deposits

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The Bayesian approach is an effective method of identifying the certain probability mineralogical and geochemical type mineralization on trace element in galen, pyrite and other distribution or e mineralization. Monomineral samples have been identified using computer upon Bayes method and exploration geochemical techniques of gold deposits for MGT. In order to realize the method, we have used a data bank consisting the results of analysing more than 12000 monomineral samples collected from main hydrothermal gold deposits on territory of CIS. Bayes approach applied to geochemical data such as posteriiori probabilities and discriminate analysis provide a numerical and graphical means through which the relationships of the trace elements and samples can be studied. There methods were used here beside GIS to find MGT that can be used as geochemical indicators of regions with gold mineralization.

The results of analyzing100 monomineral samples of pyrite from Au-Ag Shkolnoe deposit (Tajikistan) reveals multiformalation anomaly of superposition which is a combination of three MGT as:

1. Gold - silver type (85 % and more)
2. Gold- sulfide - polymetalic type (46 %).
3. Gold - sulfide type (40 %).

Mineralogical and geochemical maps (MGM) are results of generalization and analysis of MGT and GIS of different objects. There arises the possibility of quantitative modeling using spatial links of objects and multivariate models helps significantly in making optimal managerial decisions that give maximum economic effect.

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Instrumental mass fractionation overcome by total evaporation

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A select suite of isotopes, including Li, Cu, V, Lu, and Re, along with isotopic mixtures of unknown isotopic composition, require special analytical techniques to overcome instrumental mass fractionation (IMF). Generally, measurements subject to IMF are corrected using a known ratio either intrinsic to the system or externally added to the sample and measured simultaneously with the sample. For many systems, e.g. Os, and for many types of measurements, e.g. ICP-MS, internal ratios or doping works well. For other cases, e.g. NTIMS Re measurements, neither approach readily works. Therefore, following the work of Suzuki et al [1], an updated total evaporation (TE) technique is employed. In theory, if the entire sample is evaporated until exhaustion and all the ions collected, mass fractionation is overcome, thereby improving accuracy and precision, with less dependence on the analyst.

An experiment was designed to test TE against single-collector peak jumping and multi-collector static measurements using a variety of ¹⁸⁵Re/¹⁸⁷Re ratios (~0.6 standard; ~4 sample; ~37 spike) with the expectation of documenting differences in measured ratios due to variability caused by IMF. Preliminary results demonstrate, within statistical uncertainty, that TE provides equally accurate, equally precise data that is marginally less dependent on the analyst.

While the initial results did not indicate a drastic improvement in accuracy or precision, further optimization of the analytical procedure may result in better data. NBS peak jumping, and to a lesser extent Triton static collection, have undergone multiple filament warm-up, focusing, and centering optimizations during thousands of Re measurements. On the other hand, TE measurements are currently utilizing default parameters. Optimization of procedures and parameters including filament heating; ideal initial, final, and maximum intensities; heatslope (mA/cycle); integration time; and mathematical constants is on-going. Fine-tuning these parameters and procedures should result in higher quality data, surpassing other data collection techniques.

Total evaporation may be extended to other isotopic systems including Li, B, Cu, Ir, V, Br, and Lu. Additionally, total evaporation may provide improved accuracy and precision for artificial isotopic mixtures such as double spikes (e.g. Os, Mo, and Pb). In summary, TE provides an alternate method of data collection for samples subject to, but not internally or externally correctable for, IMF.

References

Formation of 4.5 Ga continental crust

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Geochemical models of crustal growth on early Earth have tended to favor mafic over felsic compositions for a variety of reasons including: lack of a mechanism to produce stable continental-type crust from a magma ocean (high P of feldspar w.r.t. hydrous melt, low feldspar growth rate w.r.t. convective vigor), problems reconciling Sm-Nd systematics, apparent inconsistency with Nb/Th/U ratios, and the absence of >4 Ga crust. However, Morse (1987) proposed a model that transcends most of these objections. He invoked a sinking, undercooled, two-phase plume that, upon reaching the base of a magma ocean, rapidly crystallizes olivine. The light, evolved liquid produced (assuming that the fluid in equilibrium with olivine is silica-rich at high P) ascends to shallow depths. Nucleation from sparse centers in the highly polymerized melt results in rapid crystallization of tonalitic rockbergs that coalesce into regions of stable, felsic crust. Recent Lu-Hf results on Hadean zircons tend to support the case for an early continental-type crust. Thus we have re-evaluated this proposal for the case of a ~250 km deep magma ocean using recent experimental data in conjunction with the MELTS program. Melting experiments in the CMAS system at 6.5 GPa and 1850°C (Asahara & Ohtani, 2001) yield liquid compositions characterized by 45-52% SiO₂. We modified the liquid composition by adding Fe to achieve MgO/(MgO+FeO)=0.8 and partitioning pyrolite levels of incompatible elements (e.g. K, Na) into the melt. Upon ascent to 0.2 GPa, the hygroscopic liquid containing 2% H₂O rapidly evolves during cooling to produce a dioritic (57% SiO₂) composition at 950°C. Thus an early felsic crust appears feasible even without the disequilibrium effects of the Morse model. He emphasized that a network-rich liquid would be characterized by a relatively high viscosity enabling the ‘pop-up’ crust to maintain sufficient mechanical integrity to resist remixing with the ultramafic magma ocean until rapid crystallization occurred. At the surface, proto-crust would tend to migrate to down-welling loci and be stabilized by the locally cooler conditions. As the base of the crust heats up in response to shutdown of the descending cell, felsic liquid produced would tend to ascend diapirically to shallow levels creating a feedback that sustains the presence of continental-type crust. Most of the arguments against an early continental-type crust described above lack rigor or have been transcended by recent evidence. Morse’s (1987) model provides a plausible mechanism to produce felsic crust in the earliest stages of Earth evolution. Subsequent re-working and eventual recycling of this proto-continental crust into the mantle provides an explanation for the isotopic characteristics of Hadean zircons and the apparent absence of pre-4 Ga continental crust.
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