Neogloboquadrina pachyderma (N. pachyderma (sin); Darling et al, 2006), is reported in many studies as a reliable indicator for cold, high-latitude environments as it dominates the polar planktic foraminiferal assemblages. However, N. pachyderma is also found in the cool and nutrient-rich waters of upwelling systems of the subtropical and tropical oceans. We have determined the vertical and spatial distribution of N. pachyderma towards the end of the south west (SW) monsoon in the north western and central Arabian Sea and combined it with hydrographic data, genetic analyses and species concentration (>100 µm) in plankton tows (0-700 m) taken on Meteor cruise M74-1b in late September 2007. A west-east transect off the Oman Margin displays the highest concentration (7 specimens /m3) in depth of 700-500 m at a transitional station between the Oman upwelling area and the open-East Arabian Sea. However, the depth of maximum concentration of N. pachyderma shoals to 300-200 m towards the east, approximately 540 km distance from coast and considerably outside of upwelling region off Oman. In the central Arabian Sea, N. pachyderma occupies the whole upper water column, exhibiting relatively high frequencies down to 700m, at temperatures as high as 28° C and as low as 10° C. The depth habitat of living N. pachyderma in the Arabian Sea has remained largely uncertain, but microscopic observation during the cruise and successful genetic amplification of specimens from 700m, reveal that N. pachyderma was indeed living at great depth within the water column. However, it is as yet unclear whether it was actively growing and reproducing at these depths. Genotyping confirms the presence of a new and potentially isolated N. pachyderma genotype in the Central Arabian Sea which is the only one found to date in this region. It is highly likely that N. pachyderma lives throughout the year at very low concentrations and flux, as recorded by a sediment trap time series in the Central Arabian Sea. Our new ecological observations and the presence of live specimens suggest that the new N. pachyderma genotype of the Arabian Sea can tolerate warm water temperatures of up to 28°C and salinity between 35.5 and 36.2 psu. On the other hand, from the relatively large number of living specimens in the deeper waters of the oxygen minimum zone (OMZ), we speculate that this new genotype inhabits the cold, low oxygen conditions of the OMZ during a part of its life cycle. However, further investigation will be required to determine whether the new N. pachyderma genotype is adapted to live and reproduce within the extremes of the Arabian Sea OMZ.

Geogenic pollution of groundwater by arsenic within the NW Thuringian basin

Michael Abratis¹, Lothar Viereck² & Juraj Majzlan³

Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Burgweg 11, 07749 Jena, Germany

¹michael.abratis@uni-jena.de
²lothar.viereck@uni-jena.de
³juraj.majzlan@uni-jena.de

The aquifer system of the Lower Triassic Buntsandstein Formation, an important source of drinking water in north-western Thuringia, is affected by elevated arsenic concentrations. Data from most of the water wells in this area show arsenic concentrations around 30 μg/L, which is well above the limit value for drinking water (10 μg/L). The regional distribution of arsenic in the groundwater and the lack of anthropogenic sources of arsenic within this area point out to a geogenic induced pollution.

The average concentration of the toxic, carcinogenic trace element arsenic in rocks of the upper continental crust is about 4.8 μg/g (Rudnick & Gao, 2003). However, it can be several times enriched in certain sedimentary lithologies such as pelites and coal beds.

In our present study we investigate all sequences of the Buntsandstein Formation with their different lithologies in order to identify the relevant carriers of arsenic. Geochemical analyses on samples from selected drill cores and outcrops show that arsenic has accumulated in some of the rocks. We found high concentrations for arsenic of >50 μg/g in the pelitic sequences, especially in primarily gray-green clay stones. Enrichment of the trace element thus depends on the mineralogy and on the redox states of the lithologies. It seems likely that elevated arsenic concentrations are related to specific lithofacies of the aquifers that contain more sediments of lacustrine origin.

Aim of the current study is now to identify the appropriate mineral phases that adsorb or incorporate arsenic and immobilize it and to identify the processes and conditions under which arsenic is mobilized from these phases and transferred into the groundwater.

Reference:

Facies patterns and event sedimentation during the Holocene along the Belize coast, Central America

Friederike Adomat, Eberhard Gischler

1 adomat@em.uni-frankfurt.de
2 gischler@em.uni-frankfurt.de

Vibracores from five localities along the inner carbonate platform offshore Belize allow reconstruction of the coastal development and paleo-hurricane landfalls during the Late Holocene transgression period. 26 vibracores were collected in transects across four coastal lagoon environments and a swamp and marsh area along the central coast of Belize. The study area is located ~20 km from the offshore Belize Barrier Reef and is situated to the west of the central shelf lagoon. Sediment composition and texture analyses, radiocarbon dating and shell identification were used to describe and correlate sedimentary facies. The two localities Manatee Lagoon and Colson Point Lagoon show successions with shell beds and peaty sequences, with indications of retrogradation of facies, reflecting Holocene sea-level rise. Shell beds with bivalves and gastropods are possibly expressions of fluctuating salinities, possibly caused by precipitation and/or storm events, dated to 2.2 kYBP and 5.9-4.8 kYBP. Additional ages of shell beds are currently being measured. Sediments at Commerce Bight Lagoon contain event beds with shells of marine organisms such as corals (Porites, Cladocora) that are interpreted as overwash deposits (and/or possible indications for migration of the barrier spit). Event beds were dated to ~1.5 kYBP and 5 kYBP. At Mullins River Beach, the two seaward cores show distinct sand layers (~7.9 kYBP) as well as alternations of mud and silt layers, which could also be the results of event deposition. Cores from Sapodilla Lagoon indicate constant and uniform mud-rich lagoon sedimentation since >6 kYBP. Cores from Manatee Lagoon and Colson Point Lagoon show sediment deformation structures at the bases, which were probably seismically generated during the late Pleistocene. Comparisons with other paleo-storm records in the region suggest that overwash deposits have developed and were preserved only close to storm tracks proper and in lagoons that are separated from the sea by relatively narrow barriers.
Diagenesis and pore space evolution in Permosilesian and Mesozoic aquifer sandstones in the Thuringian Basin, Central Germany


¹Michaela.Aehnelt@uni-jena.de

The Thuringian Basin in Central Germany is a structural trough with Buntsandstein and Zechstein outcropping at the margins and Keuper sedimentary fill in the center. Major aquifer units are Permosilesian, Buntsandstein and Keuper clastics. This study compares aquifer features and aquifer evolution of Permosilesian, Buntsandstein and Keuper fluvial sediments. The case study intends to characterize the chemical, textural, compositional, and diagenetic influences on aquifer properties with special consideration of pore space attributes (volume, connectivity, geometry, reactive surface area, surface roughness) in order to better understand fluid migration in sedimentary basins in the present and past.

The Permosilesian sediments occur in present depths of about 1500-2500 m. Buntsandstein is encountered in depths between approx. 400-900 m. Keuper clastics crop out in the center of the Thuringian Basin and extend to present depth of a few hundred of meters. Maximum palaeoburial depths were in the range of up to 5000 m and more for the Permosilesian, of 2800 m for the Buntsandstein and of approximately 1300 m for the Keuper.

The Permosilesian fluvial sandstones are moderately to well sorted sublitharenites and litharenites. Major diagenetic features are early ferrous clay coatings and matrix, and some authigenic quartz cement, feldspar as well as lithoclast alteration (including leaching, illitization), minor blocky carbonate cements and intense kaolin or illite formation (tangential illites, meshwork illites). The Buntsandstein sandstones are poorly to well sorted arkoses to subarkoses. Diagenetic features are early ferrous clay coatings, authigenic quartz overgrowth, feldspar alteration (including leaching, illitization), blocky sulfate and carbonate cementation and late cement dissolution, formation of illite (early tangential illites, radial illite rims, late meshwork illites) and locally kaolinite. The Keuper sandstones are moderately to well sorted lithic subarkoses and feldspatic litharenites. Diagenetic features include early hematite coatings, authigenic quartz overgrowth, in part blocky carbonate cementation linked with feldspar and lithoclasts displacement, cement dissolution and illite formation.

Differences in initial composition, diagenetic evolution and resulting cement and clay mineral content are reflected in geochemical characteristics, petrophysical data and in data of the specific surface area (BET, image analyzes). Comparison of petrophysical characteristics reveals low porosity and permeabilities in the Permosilesian sediments ($\Phi = \text{up to } 10\%, K = 0.01 - 1\text{ mD}$), and higher ones in the Buntsandstein samples ($\Phi = \text{up to } 24\%, K = 0.01 - >100\text{ mD}$). Keuper sandstones exhibit porosities of 14 - 21 %. Data of specific surface area seem to be linked to petrophysical and compositional data.

Generally, differences in aquifer quality are attributed to differences in the initial composition (provenance and depositional conditions), in the burial history and diagenetic evolution with special impact of recent telodiagenetic influences.
Sediment cores are one of the most important records of the historical changes in the water level of inland water ecosystems. Understanding changes in inland water ecosystems is substantial due to their impact on the global carbon biogeochemical cycle. To study past fluctuations of the lake water level, a 35.7 cm sediment core was extracted in 1999 from the center of Lake Agung in East Java Indonesia and then characterized for its magnetic and geochemical properties as well as microscopic components using polarization microscopy. Results show that sediment has high of both magnetic susceptibility and organic contents. In addition the microscopic components are primarily characterized by biogenic components. We identified a turbidite layer at a depth of 22.8-29.3 cm, indicating past fluctuations in the lake water level. The reduction of the water level could have changed the redox condition of the littoral sediment and resulted in release of the greenhouse gasses.

Key words: turbidite, geochemistry, magnetic susceptibility, sediment records, lake water level

Affiliations: Institute for Earth Sciences University of Jena
Deciphering condensed sequences: A case study from the Oxfordian (Upper Jurassic) Dhosa Oolite member of the Kachchh Basin, western India

Matthias Alberti¹, Franz T. Fürsich², Dhirendra K. Pandey³

¹alberti@gpi.uni-kiel.de
²franz.fuersich@gzn.uni-erlangen.de
³dhirendrap@hotmail.com

In large parts of the Kachchh Basin, a Mesozoic rift basin situated in western India, the Oxfordian succession is characterized by strong condensation and several depositional gaps. The top layer of the Early to Middle Oxfordian Dhosa Oolite member, for which the term ‘Dhosa Conglomerate Bed’ has been introduced, is an excellent marker horizon. Despite being mostly less than 1 m thick, this unit can be followed for more than 100 km – almost throughout the basin. A detailed sedimentological analysis has led to a complex model for its formation. Signs of subaerial weathering, including palaeokarst features, suggest at least two phases of emersion of the area. Metre-sized concretionary slabs floating in a fine-grained matrix, together with signs of synsedimentary tectonics, point to a highly active fault system causing recurrent earthquakes in the basin. The model considerably refines the current understanding of the basin history during the Late Jurassic. Large fault systems separated the basin into several sub-basins. The main reason for condensation in the Oxfordian succession is an inversion that affected large parts of the basin by cutting them off from the sediment supply. The Dhosa Conglomerate Bed is an excellent example, demonstrating the potential of condensed units in reconstructing depositional environments and events that took place during phases of non-deposition. Although condensed sequences occur frequently throughout the sedimentary record, they are particularly common around the Callovian to Oxfordian transition. A series of models has been proposed to explain these almost worldwide occurrences, ranging from eustatic sea-level highstands to glacial phases connected with regressions. The succession of the Kachchh Basin shows almost stable conditions across this boundary with only a slight fall in relative sea-level, reaching its minimum not before the late Early Oxfordian.

Matthias Alberti
Christian-Albrechts-Universität zu Kiel, Institut für Geowissenschaften, Ludewig-Meyn-Straße 10, 24118 Kiel, Germany.

Franz T. Fürsich
Friedrich-Alexander Universität Erlangen-Nürnberg, GeoZentrum Nordbayern, Fachgruppe PaläoUmwelt, Loewenichstraße 28, 91054 Erlangen, Germany.

Dhirendra K. Pandey
University of Rajasthan, Department of Geology, Jaipur 302004, India.
Fluid inclusions and compositional zoning in epidote from veins in UHP eclogites (Dabieshan, E’ China)

Nina Albrecht¹, Gerhard Wörner², Yilin Xiao³, Alfons M. van den Kerkhof⁴

¹nalbrec@gwdg.de
²gwoerne@gwdg.de
³yxiao@gwdg.de
⁴akerkho@gwdg.de

Fluids linked to deep burial form and evolve under (ultra-)high pressure (UHP) conditions and are characterized by enhanced element solubilities [1], resulting in transport and fractionation of both fluid-mobile and nominally immobile elements [2]. Consequently, reconstructing fluid evolution related to UHP metamorphism is essential for a better understanding of element mobility and element redistribution among Earth's reservoirs.

Representing fossil pathways of fluid flow, we sampled mineral veins in UHP eclogites from the Triassic Dabieshan continental collision zone. These veins provide indirect access to the fluids circulating during deep continental subduction. Primary fluid inclusions entrapped during vein mineral growth are assumed to preserve remnants of pristine liquids. Three vein generations are distinguished based on mineralogy and field evidence. (1⁴) Early, small-scaled quartz + rutile veins consistently within the UHP eclogitic foliation are assigned to peak metamorphic conditions. (2⁵) Later, coarse-grained phengite + epidote/clinozoisite + barroisite + apatite + quartz + rutile ± kyanite ± omphacite ± paragonite ± zoisite veins, irregularly crosscutting the eclogitic foliation, are assigned to near-peak HP conditions. (3⁶) Late, large-scaled and irregular albite + phengite + epidote/clinozoisite + quartz (+ secondary chlorite) veins formed during the retrograde stage.

Petrography, microthermometry and Raman spectroscopy reveal primary high-density nitrogen inclusions (0.31 – 0.56 g/cm³) in eclogitic quartz as well as three assemblages of aqueous inclusions in both vein and eclogitic quartz: (i) primarily trapped CaCl₂ + NaCl ± MgCl₂ brines (30 – 35 wt% NaClₗ with eutectic temperatures Tₑ down to -75°C), (ii) primary to pseudosecondary CaCl₂ + NaCl solutions (17 – 27 wt% NaClₗ with Tₑ clustering mainly around -52°C) and (iii) secondary NaCl-bearing fluids (0 – 12 wt% NaClₗ with Tₑ between -35 and -10°C). The occurrence of type (i) and type (ii) inclusions is restricted to eclogitic quartz as well as to 1⁴ and 2⁵ generation vein quartz, while type (iii) inclusions are observed in all samples. Homogenization temperatures among the aqueous groups are bimodally distributed and scatter around 200°C and 400°C. They exhibit a clear correlation of high salinities with high Tₑ and low salinities with low Tₑ, mirroring a decrease in element load of the fluid from the metamorphic peak towards the retrograde stage.

Supporting a depletion trend over time, epidote group minerals from 2⁵ and 3⁶ generation veins show a compositional 3-step zoning from LREE- and LILE-rich allanitic cores, slightly resorbed, depleted clinozoisite mantles and trace element-poor epidote rims.

The results reflect an evolution from highly saline, trace element-enriched (L-/MREE, LILE) Ca-Na-(Mg)-brines near the metamorphic peak towards low salinity, trace element-poor Na-solutions along the retrograde path. The earliest fluids are interpreted to originate from prograde mineral decomposition and dehydration and their initially high solute content is ‘consumed’ by precipitation of vein minerals (Ca, REE, LILE → epidote group minerals, apatite; Mg → amphibole; Na → albite, paragonite) and diluted by a late introduction of meteoric waters. The nitrogen is suspected to be inherited from metasedimentary lithologies in which the sampled eclogite bodies are embedded.


Petrological and geochemical investigations on the pseudotachylytes of the Alpine Fault, New Zealand

Altenberger, U.¹, Oberhänsli, R.¹, Timmermann, M.¹, Günther, C.¹, Toy, V.²

¹ uwe@geo.uni-potsdam.de, roob@geo.uni-potsdam.de, timmer@geo.uni-potsdam.de, Christina.Guenther@geo.uni-potsdam.de
² virginia.toy@otago.ac.nz

Pseudotachylytes of the Alpine Fault Zone, New Zealand represent fossil frictional melts of upper crustal origin. They are formed during seismic pulses in different protoliths. Toy (2008) and others presented detailed investigations on structural and PT-evolution. However, based on the current knowledge we start to examine the fluid-friction-melt interaction and the disequilibrium melting processes on surface samples and the ICDP drill core DFDP-1B. Petrological, microstructural and geochemical analyses show, that the central veins, at which dislocation and frictional melt have initiated as well as the injection veins show a significant and complex compositional layering. In addition to chilled margins different vein parallel layers are formed. In some cases pseudotachylytes reworked older generations, i.e. seismic slip reactivate older slip planes. Some samples show pseudotachylytes crosscutting as liquids. The different layers, as proven by electron microscopy and electron-microprobe indicate chemical differences. Some of these results are used as a tool of the sequence of non-equilibrium melting of the different phases as well as changes in the rheological parameters, such as viscosity and density. A remarkable phenomenon of the pseudotachylytes of the Alpine Fault is the frequency of vesicles, open or filled representing gas or fluid bubbles. The calculation of the cavities reveals the influence of the high water content of the protolithes and in some cases additional external water.
Mineral transformations and bacterial diversity in As-rich waste dumps

F. Y. AMOAKO1*, J. MAJZLAN1, E. KOTHE2

1Friedrich-Schiller-University, Institute of Earth Science, Jena, Germany
(→ Felix-Yebo.Amoako@uni-jena.de) (Juraj.Majzlan@uni-jena.de)
2Friedrich-Schiller-University, Institute of Microbiology-Microbial Phytopathology, Jena, Germany (→ Erika.Kothe@uni-jena.de)

Weathering and mineral transformation of sulphidic waste genenerate Fe-rich secondary phases which often retain metals and metalloids in metastable, nano-crystalline, or amorphous phases. The fate and chemical stability of the pollutants are important factors for their impact on the environment, especially ground water pollution and acid mine drainage (AMD). This research addresses the secondary mineral phases and the microbial impact of highly weathered waste materials from the Medieval arsenic dumps in the Kaňk deposit, Kutná Hora (Czech Republic), Rotgülden-Salzburger Land (Austria) and a historical mine from Chyžné (Slovakia).

The olive-green and yellow powdery secondary mineral phases occur in large amounts, and form either aggregates of varied dimensions in the waste dumps or as precipitates of dripping water from wall rock underground. The minerals were identified using mineralogical methods [1], such as, powder X-ray diffraction and electron microscopy, and confirm the presence of kaňkite (FeAsO₄·3.5H₂O), (para)scorodite (FeAsO₄·2H₂O) bukovskýite [Fe₂(AsO₄)(SO₄)(OH)·9H₂O], and zýkaite [Fe₄(AsO₄)₃(SO₄)(OH)·15H₂O], as described by [1] and [2]. The microenvironment of the minerals shows their formation in a clay-rich matrix which acts as a seal for the weathering eluate solution in the dumps. The elements identified in the primary sulphides and weathered products can be categorised as mobile or immobile, in order to better understand their partitioning into minerals and aqueous phases.

The bacterial diversity was assessed by cultivation in order to study the role of microorganisms in the weathering processes and their influence on the mineral transformation, thereby leading to the release of the pollutants. So far, 25 bacterial and 9 fungal isolates have been obtained from the Medieval deposits in Kutná Hora. The material shows low colony forming units and hence low microbiological prevalence. The bacteria are mainly coccioid with slow growth rates on arsenate containing media; two aerobic, nine anaerobic, ten facultatively anaerobic and four neutral strains have been found. Nineteen bacterial strains are gram positive, and six strains are gram negative and; eighteen bacterial strains are able to excrete siderophores. Nineteen bacterial strains are resistant to 5, 10 and 20 mM arsenate concentrations, with 5 strains resistant to 1 M arsenate. The fungi identified to be ascomycetes, basidiomycetes, yeasts or zygomycetes are producing high amount of spores.

Literature


Fluid-controlled mineralogy of hyperaluminous rocks, Arkaroola, South Australia deduced from chemographic analysis

Tom Andersen¹, Marlina Elburg², Paul Bons³

¹tom.andersen@geo.uio.no
²elburg@ukzn.ac.za
³paul.bons@uni-tuebingen.de

The relative stability of critical mineral assemblages in hyperaluminous rocks from Arkaroola, Australia in isothermal-isobaric log activity (or chemical potential) space can be deduced by semiquantitative chemographic analysis based on observed equilibrium mineral assemblages. The idealized compositions of phlogopite (phl: K\textsubscript{0.5}M\textsubscript{g}Al\textsubscript{3}Si\textsubscript{3}O\textsubscript{10}(OH)\textsubscript{2}), muscovite (mus: K\textsubscript{0.5}Al\textsubscript{2}Al\textsubscript{3}Si\textsubscript{3}O\textsubscript{10}(OH)\textsubscript{2}), K-feldspar (ksp: KAl\textsubscript{3}Si\textsubscript{3}O\textsubscript{8}), sillimanite / andalusite (als: Al\textsubscript{2}SiO\textsubscript{4}), cordierite (crd: Mg\textsubscript{2}Al\textsubscript{4}Si\textsubscript{5}O\textsubscript{18}), sapphirine (spr: Mg\textsubscript{2}Al\textsubscript{4}SiO\textsubscript{10}), corundum (crn: Al\textsubscript{2}O\textsubscript{3}) and spinel (spl: Al\textsubscript{2}MgO\textsubscript{4}) can be described in the five-component system KO\textsubscript{0.5}-MgO-AlO\textsubscript{0.5}-SiO\textsubscript{2}-HO\textsubscript{0.5}. This is also the case for aqueous fluid (H\textsubscript{2}O) and the dissolved species SiO\textsubscript{2}, K\textsubscript{2}O and MgO. According to the phase rule, five phases coexisting in equilibrium make up an isothermal-isobaric invariant assemblage in this five-component system. Assuming water saturation (a\textsubscript{H\textsubscript{2}O}=1), which is reasonable given the geological setting, assemblages with four mineral phases define invariant points in a 3D petrogenetic grid in $\log a_{\text{MgO}} - \log a_{\text{SiO}_2}$ or $\mu_{\text{MgO}} - \mu_{\text{SiO}_2}$ space. The geometry of the grid is constrained by observed low-variance mineral assemblages. In the absence of thermodynamic data, in particular for dissolved aqueous species, the grid remains semiquantitative in the sense that the relative positions of stability volumes for individual phase and the spatial orientation of divariant planes (two solid phases) and univariant lines (three solid phases) are given, but not their absolute sizes or coordinates. The main importance of this type of petrogenetic grid is to illustrate differences in stability conditions between contrasting assemblages / rocks, or trends of change in composition-dependent parameters with time.

Stability volumes for K-feldspar, muscovite, phlogopite, cordierite, sillimanite / andalusite, sapphirine, corundum and spinel need to be considered. The grid geometry is constrained by twelve critical low-variance assemblages that correspond to observed mineral assemblages in hyperaluminous rocks from the area. The phase assemblages correspond to points on the phlogopite saturation plane, spreading out from silica oversaturated conditions with quartz to conditions deeply within the silica undersaturated domain represented by phlogopite + spinel. The main variation along this trend is due to coupled increasing $a_{\text{MgO}}$ and decreasing $a_{\text{SiO}_2}$. A likely interpretation of this trend of evolution is that an initially silica oversaturated system (i.e. a biotite granite) has gone through a progressive desilification process. The system has remained saturated in phlogopite throughout, and the sequence of phase assemblages corresponds to successive steps of silica loss. In either case it is necessary to invoke a source of fluid that is: Large and / or long-lived, (ii): Highly silica undersaturated (i.e. not previously equilibrated with granitoids of the continental crust), (iii): Having sufficiently high Mg concentration to remain in equilibrium with phlogopite throughout the process.
Seismic interpretation of the deep subsurface in the northwestern German North Sea sector (Entenschnabel)

Jashar Arfai 1, Fabian Jähne 2, Rüdiger Lutz 3, Christoph Gaedicke 4, Jonas Kley 5

1Jashar.Arfai@bgr.de
2Fabian.Jähne@bgr.de
3Rüdiger.Lutz@bgr.de
4Christoph.Gaedicke@bgr.de
5jkley@gwdg.de

We present results of a detailed seismic mapping project focused on the northwestern part of the German North Sea sector. The mapping study in the so called Entenschnabel area has been carried out within the framework of the project Geo-scientific Potentials of the German North Sea (GPDN). Based on 3D and 2D seismic surveys, stratigraphic and geophysical measurements, geological profiles were constructed to illustrate the main structural elements in the study area. Additionally, thickness and depth maps of prominent groups and formations provide an overview of the interaction of structural elements and sedimentation as well as erosion.

The northwestern part of the German North Sea underwent a multiphase tectonic evolution leading to complex rift dominated structures, with the Central Graben as the main structure. The structural evolution from the Late Paleozoic to the Cenozoic influences the accommodation space and distribution of formations, their internal geometry and thicknesses.

Results of seismic interpretation in the northwestern German North Sea indicate several phases of uplift and subsidence. There is evidence for major tectonic events in the study area from the Middle to Late Triassic, in the Late Jurassic to Lower Cretaceous and in the Late Cretaceous. Several pre-existing structural elements were reactivated by following tectonic events. Furthermore, the halotectonic movement of the Zechstein salt dominated the structural evolution of the overlying Mesozoic and Cenozoic rocks, especially inside the German Central Graben. Typical structural elements in salt basins like diapirs and their rim-synclines as well as turtle-structures are also mapped in the Entenschnabel area.
The crucial role of impact-induced heat and hydrothermal circulation on the generation of hydrocarbons and ore deposits is well known from a number of impact craters world-wide. A prime example is the ‘Siljan Ring’ in central Sweden. The ring structure was formed around the central uplift of a Late Devonian meteorite crater, which represents the largest known impact structure in Europe. This study focuses on the Stumsnäs 1 core, drilled in 2011 in the southern part of the ‘Siljan Ring’ by a private Swedish company (AB Igrene), for exploration of natural gas and geothermal energy reservoirs. The Stumsnäs 1 core represents a structurally complex section and records evidence for hydrothermal activity along the impact-induced fracture networks. The core section reveals that about 90 m of Palaeozoic (Lower to Upper Ordovician) sedimentary rocks are sandwiched between Proterozoic igneous basement rocks. The sedimentary contact to the underlying Proterozoic basement (more than 260 m recovered by the drilling) is a prominent unconformity. The contact to the overlying ca. 190 m thick slab of Proterozoic basement is a few meters wide complex fault zone, comprising alternating thin slices of sedimentary and granitic rocks together with fault breccia and gouge. The tectonic emplacement of the basement rocks over the sedimentary succession is apparently impact-related and caused folding and faulting of the underlying sediments, which were partly cut out, repeated and inverted. Minor fault zones occur throughout the Stumsnäs 1 core and have large damage zones with intense fracture networks along which alteration and mineralisation took place, likely also impact-related. Hematitisation and chlorite-epidote alteration are common along the fractures. Veins and small cavities are mostly filled with calcite, quartz and epidote-chlorite. Pyrite mineralisations also occur along the fracture zones. Although they are not of economic importance, they clearly record evidence for hydrothermal activity. Economically exploited ores are known, for instance, in the Ordovician limestones near Boda town in the eastern part and on the island of Sollerön in Lake Siljan in the southwestern part of the ring structure. In Siljan, oil and shale-gas migrate freely along naturally fractured rocks and at some locations reach to the surface, for example, oil seeps in the Upper Ordovician limestones at Solberga quarry to the northeast of Stumsnäs. The Stumsnäs 1 core shows also oil stain along a fracture in the limestone unit (Kullsberg Limestone). Stylolites are present in the sedimentary section and may also allow, or in some cases prevent, fluid flow depending on the percentage of sealing with insoluble minerals. Therefore, small scale faults and fractures are critical for fluid migration and hence for ongoing exploration for natural gas and geothermal energy reservoirs in the Siljan impact structure.
Evidence of metasomatism of metapelite and talc schist of the Eclogite Zone of the Tauern Window (Austria)

Donjá Aßbichler¹,², Alexander Proyer¹,³

¹Department of Earth Sciences, University of Graz, Austria
²now at: Department of Earth- and Environmental Sciences, LMU Munich, Germany, d.assbichler@lmu.de
³now at: Department of Geology, University of Botswana, Private Bag UB 00704, Gaborone, Botswana, alexander.proyer@mopipi.ub.bw

Metamorphism implies mineral transitions and/or reactions assuming a closed chemical system. In most cases fluids are required to enable these metamorphic reactions. This aspect includes that metamorphic systems have to be open with respect to fluids. Although they are often regarded as closed to the transport of other materials (elements), e.g. for geochemical evaluations or pseudosection calculations, it remains uncertain to what extent the composition of the original rock is actually changed during metamorphism, particularly at lithological contacts which imply sudden changes in composition and thus chemical potential gradients.

The Eclogite Zone (Austria) is characterized by alternating layers of eclogite, metapelites and minor marbles and metapsammites. This study documents the first observation of talc schist in this area. According to geothermobarometry, PT-conditions of at least 26 kbar and approximately 580°C were attained.

To evaluate the importance of metasomatism, the contact zone between eclogite and a metapelitic rock and a talc schist with ultrabasic composition and of uncertain origin were investigated along two profiles. In each case, eclogite in contact to the host rock shows almost no change in volume. The eclogites display slight composition changes which reflect the the composition of the adjacent rock: A minor gain of (the oxides of) Si, Ca and Na and loss of Mg occurs at the contact to the metapelite, whereas minor enrichment in Mg and depletion in Na was determined at the contact to the talc schist. Both schists, however, have experienced considerable volume loss of up to 30%: The composition of the metapelite changes strongly towards the contact. It is mainly depleted in Si and Ca, coupled with enrichment of K, Mg, Fe and Na. The talc schist shows a depletion of Mg, Fe, Si, Na and Ti and no major element enrichment. Trace element changes are less spectacular but mirror changes in the major elements (Sr goes with Ca, Ba with K, etc.).

These changes in bulk composition are expressed in mineralogical, textural and mineral chemical changes of considerable complexity. Rare garnets and epidotes with oscillatory zoning patterns near the contact indicate the effect of locally abundant fluids.

There is clear evidence that theses features are not caused by retrograde interactions. The compositional changes are too systematic and complex to be explained as primary (volcano-) sedimentary layering or mixing of clays and ashes. As the lithological boundaries are planar over distances of tens of metres at least, the volume losses are not induced by folding but rather by (pure or general) shear. Some composition changes cannot be explained by local material exchange between the two lithologies (bimetasomatism) alone. A common effect is an increase of the Na concentration from both sides towards the contact, which cannot be explained by diffusion processes between the adjacent layers. Remarkable is a thin quartz vein parallel to the contact of eclogite and metapelite, suggesting potential mobilisation and transport of Si and other elements parallel to the contact and advection as an additional factor to diffusion in a stagnant pore fluid.
Computed tomography on porosity of xenoliths in volcanic rocks – a software comparison

C.J. Auer¹, K.U. Hess², S. Wiesmaier³, D.B. Dingwell⁴ V.R. Troll⁵

¹christof.auer@uni-muenchen.de
²hess@lmu.de
³sebastian.wiesmaier@uni-muenchen.de
⁴dingwell@lmu.de
⁵Valentin.Troll@geo.uu.se

¹²³⁴Dept. of Earth and Environmental Sciences, LMU, Munich, Germany
⁵Dept. of Earth Sciences, CEMPEG, Uppsala University, Sweden

In volcanic systems, fragments of host rock may be incorporated into magma and potentially disintegrate. When the system erupts before the host rock got completely digested, fragments of host rock may be preserved in the volcanic products as xenoliths.

We chose interesting granitic-xenolith-bearing samples from the Wudalianchi intra-plate volcano in NE-China and the Tatara-St. Pedro continental arc volcano in Chile and made x-ray computed tomography measurements with a GE phoenix® v/tome/x s micro-CT scanner.

At the example of xenolith porosity characterization, we aim to compare the results from two different software tools with different segmentation approaches; on one hand the MATLAB-based tool Tomoview, developed by our research group and on the other hand the freely available software BLOB3D developed at the University of Texas (Ketcham 2005). The porosity was evaluated by volume distribution and the vesicle population density function. A methodic comparison of the results from the different software approaches has been carried out and was additionally compared with microscopy slices of the same samples.
In highly evolved magmas Fluorine (F) is, after water, one of the most abundant volatiles and phonolitic magmas can contain up to 1.3 wt% F. Combined data for the influence of F on rheology and structure has only been available for the haplogranitic system (K₂O-Na₂O-Al₂O₃-SiO₂) and simpler compositions up to now. The aim of this study was to investigate the relation between rheology and structure in peraluminous and peralkaline Na₂O-CaO-Al₂O₃-SiO₂ melts and glasses with 1-18 mol% F as a model for phonolitic magmas.

We measured the viscosity of the glasses with the micropenetration method and investigated the structure of our glasses using ¹⁹F nuclear magnetic resonance (NMR) spectroscopy. Our results show that F decreases viscosity in peraluminous melts more strongly than in peralkaline melts. The different effects of F on viscosity seem to be related to different incorporation mechanisms of F in the melt/glass structure. ¹⁹F NMR spectra show that in peralkaline glasses F exists in at least 5 different environments: salt-like F-Na and F-Ca environments as well as F-Al and F-Si environments. In peraluminous melts the salt-like F-Na and F-Ca environments are missing and F only exists in F-Al and F-Si environments.

The observation that the salt-like F-Na and F-Ca environments only exist in the peralkaline melts suggests that these sites can only be formed in the presence of network-modifying Na and Ca cations. The formation of salt-like F-Na and F-Ca environments reduces the number of network-modifying cations and, therefore, the number of non-bridging oxygens that could decrease viscosity. The presence of F-Al and F-Si environments is expected to decrease the viscosity due to the replacement of bridging-oxygenes. Because F in the peralkaline melts exists in salt-like environments whose presence can increase viscosity as well as F-Al and F-Si environments whose presence decrease viscosity, the effect of F on viscosity is weaker than in the peraluminous melts where F only exists in F-Al and F-Si environments.
Hydrothermal vents in the Manus Basin were mapped and sampled during cruises with RV *Melville* in 2006 and RV *Sonne* in 2011. Geophysical mapping, rock and fluid sampling, as well as biological studies were conducted in two main working areas (1) North Su at 3°48.0’S, 152°06.05’E in about 1200 m water depth and (2) PACManus at 3°43.5’S, 151°40.4’E in ~1700 m water depth.

At North Su, black smoker systems near the summit of the volcano, white smoker systems on the southern flank, and diffuse vent sites on the northern slope were visited repeatedly. Black smoker vents showed maximum temperatures ranging between 313 and 332°C, the latter corresponding to the boiling temperature of seawater at the ambient pressure (124 bar). White smoker vents revealed copious amount of native sulfur on the seafloor, both in solid and liquid state. The sulfur formed small chimney, and accumulated in m-sized knolls on the seafloor and in sills or buried flows within the volcaniclastic sediment. CO$_2$ bubbling was commonly at the white smoker vents in 2011, but not in 2006. CO$_2$ degassing was also observed during ROV dives at the Satanic Mills site in the PACManus area. Vent fluids there were also boiling at a temperature of 345°C. Lower temperatures (304-314°C) were measured at the Fenway site, where fluid boiling at 356°C was observed in 2006. The preliminary data and dive observations indicate substantial changes in the magmatic-hydrothermal systems. The drastic changes in the volcanic landscape and distribution and style of hydrothermal venting on the south flank of North Su as well as the apparent changes in gas content of the fluids at PACManus indicate first-order transients in the volcano-hydrothermal systems that are driven by dynamic changes in the magma plumbing system and strongly affect metal accumulation at and below the seafloor.

The extraordinary variability in fluid chemistry, on both spatial and temporal scales, provide a glance of the complex magmatic-hydrothermal interplays in systems where polymetallic metal deposits are currently forming. The variety of vent systems encountered represents the surface expression of high- and low-sulfidation epithermal systems. This variability is obviously tied to the changes in magmatic activity including magma degassing of SO$_2$ and CO$_2$. One basin-scale, variability in fluid and deposit composition is related to the proximity of the system to the arc front and linked to basement compositional changes from depleted tholeiites in the west to calc-alkaline arc basalts to rhyodacites in the east.
On the longevity and dynamics of large magma reservoirs in the earth’s crust

Olivier Bachmann
Sarah Gelman
Francisco Gutierrez

Christian Huber, Josef Dufek

1ETH Zurich, baolivie@ethz.ch
2University of Washington, Seattle, sgelman@uw.edu
3Universidad de Chile, Santiago, francisco.gutierrez.ferrer@gmail.com
4Georgia Tech, Atlanta, chuber6@mail.gatech.edu, josef.dufek@eas.gatech.edu

Understanding the timescales and processes involved in the formation and maturation of upper crustal magma reservoirs, ultimately sourcing the largest volcanic eruptions on Earth, is one of the most fundamental goals of volcanology. While such reservoirs are known to assemble incrementally over extended periods of time, debate persists regarding the timescales of melt preservation in the cold upper crust. If rapid cooling individually freezes incoming replenishing intrusions, accumulations of eruptible magma are impossible, precluding caldera-forming eruptions for all but the highest magma emplacement rates. Recent numerical thermal models have been used to assess the viability of upper crustal silicic magma survival, and have suggested that supervolcanic reservoirs must form in geologically short timescales with anomalously high injection rates, and subsist only ephemerally, making them less predictable. Motivated by geological observations suggesting the contrary, we have improved upon these models by incorporating two fundamental features of natural systems not previously considered: (1) a non-linear crystallization-temperature relationship adapted for upper crustal silicic magmas and (2) a temperature-dependent thermal conductivity. We demonstrate that the incorporation of both of these properties can allow an upper crustal reservoir to remain above its solidus for hundreds of thousands of years, on par with estimates from zircon crystallization histories, when fed by magma fluxes typical of large magmatic provinces. While the crystallization-temperature path plays the most significant role in maintaining a large pool of eruptible magma, the incorporation of temperature-dependent thermal properties, together with a deeper emplacement level, significantly extends the lifetime of such reservoirs. These results provide strong support for long-lived upper crustal mushes as a staging ground for accumulation of highly eruptible, crystal-poor silicic magmas, and further assert the evolutionary link between volcanic and plutonic systems.
The gabbro/dike transition of the oceanic crust is one of the most important interfaces of our planet, where magmatic, metamorphic and hydrothermal processes interfere. At fast-spreading ridges, where the crust is generally accepted to be layered and uniform, the gabbro/dike transition is characterized by a decametre-thick horizon made of hornfels formed under metamorphic conditions up to the granulite facies. This zone corresponds to the conductive boundary layer (CBL), a thin (<100 m), hot (>650 °C), impermeable zone predicted by theoretical models, which is sandwiched between the axial magma chamber and the sheeted dikes and across which the heat of the axial magma chamber is exchanged.

In contrast, crust formed at slow- and ultraslow-spreading ridges is highly variable, ranging from emplacement of the mantle directly to the seafloor over broad regions, to local highly magmatic spreading that forms layered crust broadly similar to that from fast-spreading ridges. Due to the lack of systematic investigations, the nature of the gabbro/dike transition of slow- and ultraslow-spreading ridge systems is only poorly constrained. In this study we performed a systematic review of the extensive collections of dredges and dive suites of the Woods Hole Oceanographic Institution (WHOI, Massachusetts, US) containing rocks from the sheeted dike rooting zone from slow- and ultraslow-spreading ridges. The following collections were identified to be relevant for this project: (1) Atlantis Bank at Southwest Indian Ridge; ultra-slow spreading rate; three dives performed with the submersible "Shinkai"; (2) Gakkel Ridge; ultra-slow spreading rate; two dredges sampled by the US icebreaker "Healey"; (3) Kane Megamullian at Mid-Atlantic Ridge; slow spreading rate; one dive performed with the AUV "Jason". From this sample pool, ~ 400 samples were characterized in terms of igneous and metamorphic assemblage, intrusion relationships, deformation textures, veining, and contact relationships, first in hand specimen. 118 thin sections were prepared which were investigated petrographically and with electron microprobe (41 thin sections) in order to unravel the petrographic record of primary magmatic, late magmatic, secondary high-temperature (i.e. granoblastic recrystallization), low-temperature hydrothermal and tectonic processes. Special focus was to discover the presence of the characteristic granulite-facies granoblastic overprint in the corresponding dike basalts - the key for the development of a CBL. Up to now, in none of the thin sections of our sample pool, the characteristic granoblastic overprint was discovered. Instead, our results reveal, at least in those regions of slow- and ultraslow-spreading ridges which were sampled, only relative simple cutting relations of the type "basalt cuts gabbro", in contrast to the more complex intrusive relations known from fast spreading ridges ("gabbro cuts dikes" with evolution of a contact aureole).
Acidity of hydrothermal solutions at submarine vents

Chris Ballhaus,
Steinmann Institut, Universität Bonn, Poppelsdorfer Schloss, 53115 Bonn, ballhaus@uni-bonn.de

Why are submarine hydrothermal solutions at mid-ocean ridges (MOR) so acidic? Where do the compounds come from that acidify the water at mid-oceanic hydrothermal vents to pH values as low as unity? A common assumption is that magmatic melts underneath hydrothermal fields emanate volatile compounds like SO$_2$, H$_2$S und HCl which hydrolyse with seawater and produce low pH values. The problem with this theory is that MORB are notoriously poor in volatiles.

Here I investigate experimentally if the acidity can be generated by boiling seawater boiling near its critical temperature. An autoclave was built that allows seawater to be heated and equilibrated to ~360°C. Coexisting water and vapor phase can be sampled separately at pressure and temperature via a system of microvalves. The autoclave has an internal volume of 200 ml and was manufactured from acid-resistant V4A steel. It is filled with seawater to ~40% (bulk density ~ 0.4 g/cm$^3$) to ensure the water coexists with a vapor phase up to near the critical temperature of seawater (~ 400°C). First results (Fig. 1) show that the vapor phase, after condensation at 25°C, can be highly acidic. The equilibrium controlling the pH values of the water and the condensed vapor phase is

\[
\text{H}_2\text{O} + \text{Na}^+ (\text{water}) + \text{Cl}^- (\text{water}) \rightleftharpoons \text{NaOH (water)} + \text{HCl (vapor)}
\] (1)

With increasing temperature and pressure, the equilibrium is shifted to the right, and HCl and NaOH become increasingly associated. Hydrogen chloride is relatively volatile and fractionates into the vapor phase, while the non-volatile NaOH stays dissolved in the solution. After condensation to 25°C and dissociation of HCl, the condensed vapor phase may have pH values as low as unity.

![Figure 1. The pH of the vapor phase of seawater (3.6 wt.% NaCl equiv.) measured after condensation at 25°C.](image)

When hydrothermal solutions boil at depth, an HCl-enriched vapor phase results. Subsequently, the vapor may mix with cooler seawater and impose on the water extremely acidic pH values. The pH may be so low that ferric iron becomes water soluble. Basaltic rocks in close proximity to a vent may be bleached, and white (near iron-free) pillow pseudomorphs may result as observed in Cyprus near hydrothermal sulfide deposits. If such lithologies are subsequently overprinted at high pressure in a subduction zone, jadeite felses with pillow pseudomorphs may form as observed on the island of Syros.
Seismic Sequence and Depositional Facies Architecture of middle part of Nile Delta, Egypt.

Moataz khairy Barakat

Geology Department, Faculty of Science, Tanta University, Tanta, Egypt.

moatazbarakat@yahoo.com

The Nile Delta basin contains a thick sequence of deposition and subsidence that is inferred to extend from Jurassic to Recent. Many of Structure events and depositional environments varied during this period. The seismic data of a grid of 2D seismic lines (Velocity, and association of seismic facies, amplitude and continuity) and the well logs data were tied to form synthetic seismograms. Five sequences boundaries and various seismic facies were interpreted and dated. A detailed study integrated sequence stratigraphic covers seismic sequence stratigraphic, detailed Sedimentology, structural interpretation, seismic facies architecture and depositional environmental. The available well log data were interpreted, and correlated with seismic sequences boundaries. The characteristic seismic signature of some geological bodies essentially composed of one geological facies.

These sequences represented high frequency cycles of relative change in sea level with variable rate of subsidence and uplift. The dominated deposition from Jurassic to Eocene was carbonate facies and detrital sediments from Oligocene onward. In Miocene time was Deltaic to littoral marine and from Pliocene to recent change from neritic marine to fluvial deltaic. The formation qualifies for definition of sequence as bounded on both side by an unconformity. The depositional sequences determination and geometry definition used as strong helpful tool to minimize reservoir distribution for future hydrocarbon exploration.

The study led to interpretation of the chronostratigraphic, paleogeographic and depositional history of middle part of Nile Delta, Egypt and will greatly help more accurately discover new oil and gas plays and rediscovers old plays.
Light Emitting Diodes (LED) are more and more applied in general lighting in order to save energy. Therein inorganic phosphors, belonging to different mineral groups, are used to convert the blue light of the LED chip into white light. The kind of white light – warm white or cold white light – is described by the Correlated Colour Temperature (CCT). But not only the CCT is important for the general lighting application but also the quality of the colour rendering of the generated light, expressed as the Colour Rendering Index (CRI).

To generate white light, often only one phosphor is used in LEDs; i.e. a yellow light emitting phosphor is used on a blue light emitting LED chip. However, with this setup white light with only a minor CRI can be achieved. In order to obtain white light with a high CRI a mixture of different phosphors has to be applied in the LED.

To achieve the required CCT of a LED, the exact mixture ratio of different phosphors is found out, experimentally. In order to accelerate the development of the phosphor mixture a simple model for calculating the powder and LED emission spectra of the resulting phosphor mixture has been developed. The model is based on the optical properties of the phosphor powders, which can be measured by a fluorescence spectrometer. In a first step only the emission spectra of the single phosphor components has been used for modeling. In further steps the model has been refined by using also the reflection spectra, the excitation spectra and the quantum efficiency. This is necessary to take account of different interactions between light and phosphor particles.

The modeled spectra are compared with the emission spectra of the phosphor mixtures and the LED spectra. With increasing complexity of the model the spectra can be calculated better. However, the model applied is not able to calculate the real spectra, precisely. Important parameters, like particle size distribution, particle shape and morphology, multiple interactions of light with different phosphor particles etc. are not included.

Nevertheless, the model is a useful tool to support the development of phosphor mixtures in the lab.
The Gardar Province developed in a continental rift-related environment that was previously deformed, metamorphosed and intruded during the Ketilidian orogeny approximately 1800 Ma ago. The Gardar intrusions divide in two periods of igneous activity, from ~ 1300 – 1250 Ma and from ~1180 – 1140 Ma. The first period comprises the northern intrusions associated with the oldest approximately W-E to WNW-SEE trending lamprophyric to gabbroic dykes. During the second magmatic event, the southern main intrusions together with WSW-ENE gabbroic to syenitic dykes were emplaced. Some of the intrusions show an exceptional enrichment of rare earth elements (REE’s) and a huge variety of minerals some of which can only be found in this part of the world. To understand the development of the Gardar magmatism from relatively common mafic melts to those of these exceptional intrusions, it is crucial to understand the geochemistry and evolution of the mafic melts, assuming they acted as magma conduits for surface volcanism and major intrusions.

To constrain the regional and time-dependent evolution of the Gardar magmatism, the major and trace element composition of the basic dykes of the older and younger magmatic period were investigated. Additionally, some basaltic lava flows of the older magmatic period were analyzed to verify, whether they represent extrusive equivalents to the mafic dykes.

All investigated rocks can be classified as basalts or basanites after Le Maitre (1989). The oldest generation of dykes is characterized by Ba highs and Nb troughs as well as light REE enrichment. These dykes show regional variations with higher REE concentrations and slight Eu anomalies in the southern parts of the province. In comparison, the rocks of the younger magmatic period show higher alkali and lower SiO₂ contents. They are enriched in Ba, P, Ti and light REE. These data indicate a regional difference in composition of mafic dykes with the higher evolved rocks occurring in the south of the province as well as a time dependent compositional change with the highest degree of fractionation in the rocks of the younger magmatic period. In the latter, trace element signatures also indicate apatite and phlogopite components in the parental magma which could be formed by partial melting of sub-continental mantle lithosphere which had been metasomatised by subduction-related fluids during Ketilidian orogeny (Upton & Emeleus 1987; Koehler 2009).

The geochemical signature of the investigated lava flows show significant similarities with dyke compositions of the older and younger magmatic period, indicating that both dyke systems must be considered as possible sources for these basalts. The obtained data also provides a geochemical link of the basic dyke swarms of the early Gardar magmatism to dyke swarms in the Hopedale block, Labrador giving new evidences for a much more wide spread magmatism.


Deep geothermal reservoirs of the Lower Exter Formation (Upper Keuper, Triassic) in the North German Basin: the geothermal potential of distributive fluvial systems

Gregor Barth¹, Matthias Franz², Carmen Heunisch³, Markus Wolfgramm⁴

¹gregor.barth@geopal.de
²matthias.franz@geo.tu-freiberg.de
³carmen.heunisch@lbeg.niedersachsen.de
⁴markus.wolfgramm@gtn-online.de

The North German Basin (NGB) is the largest geotectonic structure of the Central European Basin (CEB) with most promising opportunities for geothermal heat production. Among the main geothermal reservoirs of the (1) Middle Buntsandstein, (2) Schilfsandstein, (3) Rhaetoliassic, (4) Middle Jurassic and (5) Lower Cretaceous the Upper Keuper (Rhaetian) reservoirs of the Exter Formation have promising potential but up to now a more intensive use is hampered because knowledge about spatial distribution of reservoirs and their properties (porosity, permeability) is rather preliminary.

The reservoirs of the Lower Exter Formation (“Postera-Sandstein”) have been subject to a high-resolution basin-scale study incorporating outcrops, more than 20 cored wells (> 2000 m cored intervals) and more than 400 logged wells. Based on a combined approach of micropalaeontology, palynology and sequence-stratigraphy 3 time-slices were evaluated using sedimentological, petrological and petrophysical methods resulting in 3 high-resolution facies maps for the Lower Rhaetian. Implementation of an extensive data set on petrology and reservoir properties enables the evaluation of potential production sites.

Deposition of the Lower Exter Formation was controlled by two major sedimentary environments a shallow epeiric sea in the western part of the CEB and a large distributive fluvial system (DFS) in the NE part. In the West the early Rhaetian Sea terminated terrestrial clastics of the Norian. Supplied with clastics from Scandinavian source areas a large DFS spread from NW Poland to NE Lower Saxony and was characterised by a distributive network of fluvial channels that decrease downstream in with and depth. Between both a sandy shoreface marked the transition from terrestrial to shallow and restricted marine environments. Within this general setting six lithofacies associations are identified. (I) distributive channels: up to 10 km broad and up to 40 m thick strings of fine- to coarse-grained sandstones of high maturity, (II) sheet sands: up to a few meters thick fine- to medium-grained sandstones of high maturity and immature pedogenic overprint, (III) dry playa: up to several decameter thick reddish to variegated pedogenic overprinted shales often comprising mature calcisols, (IV) wet playa: up to several decameter thick grey to greenish less pedogenic shales and shaly clays with conchostracans, fish- and plant remains, (V) shoreface: up to 10 m thick bioturbated fine- to medium-grained sandstones of high maturity, (VI) offshore: up to several decameter thick dark grey to grey partly bioturbated shales and siltstones comprising a brackish fauna.

Sandstones of distributive channels and shoreface comprise excellent reservoir potentials with porosities between 3.7–41.0 % (average 22.6 %) and permeabilities between 0.1–4.5 D (average 1 D). Although sheet sands have comparable porosities between 1.9–36.8 % (average 22.4 %) and permeabilities between 0.1–3.0 D (average 1.1 D) their low thicknesses exclude their use as geothermal reservoir.
BASIC MAGMATIC FORMATIONS WITHIN THE EASTERN PART OF THE BÜKK MOUNTAINS, HUNGARY

Ádám Bartók

1 University of Debrecen, Department of Mineralogy and Geology, Debrecen; adam1515@freemail.hu

The Bukkium is a paleo-mesosoic tectonostratigraphy unit consists of principally Oligocene and Miocene molass basin sediments bounded by compressional crustal thickening and subduction that forms the basement rock of NE Hungary, and it is a subject of intense research conducted by the University of Debrecen’s Tardona Research Group for 15 years. Basement metasediments intercalated with volcaniclastic successions interpreted to represent the Bukk sedimentary basin. More than 20 000 micro tectonic measurements have been done in this area (Kozák et al 2000). It became apparent that within the platform carbonates of the marine sediment, the basaltoid rocks (basalt, metabasalt, metaandesite) determine their morphological tectonic environment. They strongly contributed to the regional deformation which was caused by the regional compressions of SW, SE and E direction.

The primary subject of the study was the basaltic rocks. These types of formations lie in a curve from Szarvaskő to the city limit of Miskolc and do not form a continuous chain of bodies. The metabasaltic rocks orientations fit into the morphological tectonic direction of the Bükk Mountains. Among them we studied the materials of the easternmost edge around the Szinva spring.

On the east and west sides of the Szinva spring we can observe the basalt bodies along approximately 200 meters (E-W orientation). We examined the area with the size ratio of 1:1000 sufficient detail traversal on the spot. Both sides were examined by micro tectonic observations on the field (Kozák et al 2000) where we also studied the contact, appearance, development, and other structural characteristics of the exposed rocks. On this basis, we collected samples from the matrix environment where the metabasalt and the limestone mix with each other and from the basalt body where the alteration is not so high. They were processed in the laboratory of the Department to be prepared for the microscopic including the stereo-microscopy and geochemical analyses. We would like to answer the following interesting questions:

- Is there any palaeoenvironmental relationship between the embedding environment and the magmatic rocks?
- What kind of plate tectonic and volcanic processes can be reconstructed?
- How can we get a more accurate reconstruction of the region by determining their absolute and relative ages and petrogenesis?

The results of the macro- and microscopic studies show that this body of basalt is tectonically heavily loaded by the changing deformations within the Bukk Mountains, strongly altered by clay minerals mainly chlorite and characterized by hydro-metasomatic alteration.

The geochemical analyses (TG, DTG, DTA) revealed that the original magma could be of mantle origin basalt with high iron and magnesium content (tholeiites, with 10-15% iron and magnesium content).

Due to the periodic transgression which was in the Eocene and Miocene, it pushed into a low lying area covered with sediment, where the surrounding areas were uplifted (like tuffs exposed near Bukkszentkereszt and Bukkszentlaszlo).
Meteoric and marine diagenetic environments controlled by sea level changes in Pleistocene coral reefs, Red Sea coast, Sudan

Hamed Basher¹, Robert Bussert², Wilhelm Dominik³

¹ Faculty of Petroleum and Minerals, Al Neelain University, Khartoum, Sudan - alhajhame@yahoo.com
² Institute of Applied Geosciences, TU Berlin, Germany - r.bussert@tu-berlin.de
³ Institute of Applied Geosciences, TU Berlin, Germany - wilhelm.dominik@tu-berlin.de

Pleistocene emergent coral reefs characterize most of the Sudanese Red Sea coast and form a very well-defined fringing reef complex extending parallel to the coast line. The fringing reef is only sporadically punctuated by narrow streams and alluvial fans. Six coral reef zone schemes were distinguished. They include beach rock, rock reef rim, fore reef, reef flat, back reef and shore zone. Geometry, coral content, field relationship and onlap pattern of the zones were recorded and a total of 15 lithological facies were determined. Four major diagenetic environments were recognized and are interpreted to reflect distinct periods of sea level change.

The beach rock zone is dominated by marine cements. Major types are micritic cement, which forms thin coatings around grains, thick fibrous aragonite isopachous rims, peloidal cement and botryoidal aragonite within boring cavities.

The rock reef framework exhibits intensive boring cavities which are partially or totally filled with internal sediment. Micritic as well as peloidal and aragonitic fibrous cements are abundant. Microcrystalline fringes around grains construct bridges between grains and form meniscus cement fabrics. Vug cavities caused by dissolution are common. Regular coincidence of these diagenetic features suggests that the reef notches were exposed to mixing zone digenetic environment. Oxygen isotopes δ¹⁸ data indicates that the reef in 76,000 B.P., which corresponds to MIS 5a.

δ¹⁸ data indicates that the fore reef and back reef zone were formed during the major highstands of MIS 5e and MIS 7, respectively. Except of the dark micritic lines that characterize trabecular centres of skeletons, most coral species of the zones show no alteration of their primary aragonitic microstructure. A marine phreatic environment, which is represented by fibrous aragonite, botryoidal, dog tooth cement and peloidal cementation, is dominant in the lower part of both zones. The transition into the vadose fresh water environment is indicated by dissolution features as well as meniscus and pendant cements.

The reef flat zone represents the older reef sequence (MIS 13?) and shows prominent diagenetic features indicating a freshwater phreatic environment. Vuggy and moldic porosity produced by solution processes are increasing upward in the zone. Total leaching of aragonite is accompanied by intense calcite cementation. Equant and bladed calcite with circumgranular and isopachous cement fabrics are dominant, while blocky calcite and syntaxial overgrowths also occur. A complete replacement of aragonite by mosaic equant calcite characterizes corals in upper part of the zone. Needle fiber crystals or whisker calcite cement that indicates a vadose environment is present in the upper part of the succession.
After formation of the Gondwana supercontinent and throughout the Paleozoic, a thick pile of mostly clastic sediments has been deposited on the northern Gondwana margin. Deposition took place in a supposed “super fan” (Squire et al. 2006) which was supplied by erosion of the East African Orogen (EAO). The Arabian-Nubian Shield was formed as part of this super orogeny. Although the super fan model has been used to explain the thick Paleozoic clastic sequences in North Africa, its eastern extend has yet to be determined. In this project we aim to use sediment provenance in order to test this model with data from the Arabian Shield and Platform and to estimate the impact of the Paleozoic glaciations on sediment provenance in this region. U/Pb dating on detrital zircons will be used to compare age groups with data from North Africa in order to identify similarities and disparities in sandstone provenance and to discern whether the EAO served as a barrier for the super fan to the east during the lower Paleozoic. Further provenance data will be obtained by quantitative petrology, whole rock geochemistry as well as single grain geochemistry. Low temperature thermochronology (zircon fission track dating/ZFT) will be used to reconstruct uplift and erosion history of the source area(s). So far, there is only scarce data on sediment provenance of Paleozoic clastics from the Arabian Peninsula and only a few zircon U/Pb or ZFT ages exist. Until now, authors have suggested a very proximal sediment source. With our study we aim to improve the understanding of sediment provenance on the eastern Gondwana margin using state of the art techniques not only in the sediment sink, but also in probable source areas. These possible source areas encompass not only the proximal Arabian Shield, but also other, more distal parts of the EAO, like Neoproterozoic clastics in Uganda. In the course of a recently conducted field campaign to Saudi Arabia, over 150 samples were taken from Paleozoic outcrops on the southwestern and central to north-central Arabian Platform, representing the sediment sink, as well as adjacent areas on the Precambrian Shield, which are potential sediment sources. By comparing stratigraphically equivalent samples from two different sink areas we aim to investigate if the Paleozoic deposits in the southern and northern part of the Arabian Peninsula share the same provenance over time, thus belonging to the same catchment system.

Mercury (Hg) is known as a highly critical element for the environment and human. However, the toxicity of Hg strongly depends on its speciation. Particularly historical mining sites are often heavily contaminated with Hg through applied silver or gold amalgamation. The “Patio Process” was the first application of silver amalgamation on an industrial scale. The method was introduced in Mexico in 1554 and was still used until the beginning of the last century. This resulted in considerable quantities of Hg polluted mine tailings remaining in the environment. However, the determination of Hg-speciation in those tailings has not been conducted. Therefore the aim of this study was to determine the speciation, through a detailed geochemical and mineralogical characterization, of Hg in mine tailings of the Patio Process. Samples were taken from an old mining district near the city of Fresnillo in the northern Mexican state of Zacatecas. Further samples were tested from tailings found in the urban area of the city of Cedral in the nearby state of San Louis Potosí. The samples were analyzed using several different methods of X-ray spectroscopy, involving Micro X-ray fluorescence in laboratory and using synchrotron radiation (ANKA Karlsruhe, Germany). Bulk and microdiffraction techniques \( \mu \text{SyXRD} \) were used in order to characterize the geochemical and mineralogical environment. Space-resolved X-ray absorption analysis EXAFS was applied to identify the specification of Hg in the samples. The results show that cinnabar (HgS, trigonal) and meta-cinnabar (HgS, cubic) represent the main Hg-species (> 90 %) with minor portions of Hg-chlorides (Hg2Cl2, HgCl2). The spatial distribution of Hg in the samples is extremely heterogeneous with local concentration maxima (>2 %). Those Hg-hotspots are often associated with high concentrations of As, Cu, Fe, Pb or Zn. Due to its high stability, low mobility and poor bioavailability the toxic potential of cinnabar and meta-cinnabar is low. The main risk results from the minor amounts of Hg-chlorides. Both chloride speciations have a higher solubility in water and thus pose a threat to groundwater and they may be available for methylation.
Hydrothermal dolomites in the Paleozoic of Northern Spain: outcrop analogues for hydrocarbon reservoirs

Thilo Bechstädt¹, Natalia Muñoz Quijano², P. Ronchi³, Fabio Lapponi⁴, Maria Boni⁵

¹bechstaedt@georesources.de
²Natalia.Munoz@geow.uni-heidelberg.de
³Paola.Ronchi@eni.it
⁴flap@statoil.com
⁵boni@unina.it

The Cantabrian Zone, NW Spain, represents a Variscan foreland basin, later affected by post-Variscan orocline formation. Pervasive porous dolomites, situated within tight, mainly Carboniferous carbonates, serve as outcrop analogues for burial dolomite reservoirs elsewhere. Objectives of the DFG- and Eni-funded research are geometry and size of dolomite bodies, types of dolomite, porosity and permeability, and connection of dolomitization to geodynamic evolution.

The dolomite bodies are up to several kms long and hundreds of metres thick. The first dolomite type is replacive, the second porosity-filling. Petrographic, geochemical and FI data are consistent with a burial, hydrothermal origin of the dolomite. Dolomitization was caused by a hypersaline, marine-derived modified brine, which first replaced precursor carbonates, generating new porosity, and then precipitated dolomite cements in an almost isothermal and isochemical process.

Various dolomite types containing macro- and microporosity can be defined according to textures and internal fabrics. Macroporosity is highest in the Vuggy and Zebra types of porosity. Dolomitization strongly improved the poroperm properties of the original tight limestone host rock. In many areas, however, an over-dolomitization affected mainly the Meso Zebra fabric and reduced dramatically the porosity, generated just before. This process could be called “self-cannibalization”: (i) replacive dolomitization created additional new porosity; (ii) hydrothermal fluids were focused into this now highly permeable rock, stabilized it, and (iii) infilled the pores with cements, partly or totally.

Late Variscan lithospheric delamination-induced extensional tectonics and crustal thinning provided the heat required to trigger fluid convection and dolomite precipitation. Fluid circulation was facilitated by the reactivation of highly permeable Variscan and Post-Variscan fault zones, as well as pre- and syn-orocline bending joints. Oversaturation and dolomite precipitation occurred, when the overpressured fluids moved into higher horizons and lost temperature and pressure.

Large bodies of hydrothermal dolomite were favoured by a large reservoir of evaporated sea-water (confined by orocline formation), extensive fracturing and reactivation of tectonic structures, fluid flow pathways, and high heat flow causing thermal convection. The abundance of dolomitization in especially western areas is associated with the high amount of fractures there. Timewise, this hydrothermal pulse seems to correspond to the circulation of hydrothermal fluids in the Stephanian Coal Basins located in the area. Effective fluid flow was only possible at the time of post-Variscan rifting and transtension.
Reservoir Quality in the A2C-Stringer interval of the late Neoproterozoic Ara-Group of the South Oman Salt Basin: Diagenetic relationships in space and time

Stephan Becker¹, Lars Reuning², Peter A. Kukla³, Steffen Abe⁴, Shiyuan Li⁵, Janos L. Urai⁶, Suleiman Farqani⁷, Gideon Lopes Cardozo⁸, Zuwena Rawahi⁹

¹stephan.becker@emr.rwth-aachen.de, ²reuning@geol.rwth-aachen.de, ³peter.kukla@emr.rwth-aachen.de, ⁴s.abe@ged.rwth-aachen.de, ⁵s.li@ged.rwth-aachen.de, ⁶j.urai@ged.rwth-aachen.de, ⁷Suleiman.Z.Farqani@pdo.co.om, ⁸Gideon.G.LopesCardozo@pdo.co.om, ⁹zuwaina.al-rawahi@shell.com

The Ediacaran–Early Cambrian Ara Group of the South Oman Salt Basin consists of six carbonate to evaporite (rock salt, gypsum) sequences. These Ara Group carbonates are termed A0C to A6C from the bottom towards the top of the basin. Differential loading of locally 5 km thick Cambrian to Ordovician clastics onto the mobile rock salt of the Ara Group caused growth of isolated salt diapirs, which resulted in strong fragmentation and faulting of the carbonate intervals into several isolated so-called ‘stringers’. These carbonate stringers represent a unique intra-salt petroleum system, which has been successfully explored in recent years. However, some of the stringers failed to produce at significant rates due to the complex diagenetic history from the shallow to the deep burial realm.

The goal of this study is twofold. Firstly, to unravel the complex diagenesis and its relative timing and link them to the burial history of the salt basin. Secondly, to detect spatial distribution patterns of diagenetic phases and their effect on reservoir properties. Mineralogy, rock fabrics, paragenetic relationships and geochemistry of ~ 400 samples from several petroleum wells from the late Neoproterozoic A2C interval were analyzed and combined with pre-existing data. The spatial distribution of diagenetic phases and petrophysical characteristics will be displayed in field-scale distribution maps. These maps comprise crucial information for better prediction of reservoir quality in the analyzed fields, planning of new exploration wells and better volumetric calculations.

An integration of the paragenetic sequence derived from thin-section analysis with results from finite element and discrete element models further helps to constrain the effect of salt tectonics on fracture formation and fluid evolution within the stringers.
Controls of the water-to-rock ratio on REE distribution in hydrothermal fluids: An experimental study

Oliver Beermann¹, Dieter Garbe-Schönberg¹, Astrid Holzheid¹

¹CAU Kiel, Institute of Geosciences (IFG), Kiel, Germany, e-mail: ob@min.uni-kiel.de

High-temperature MOR hydrothermalism significantly affects ocean chemistry. The Sisters Peak hydrothermal field at 5°S on the slow-spreading Mid-Atlantic Ridge (MAR) emanates fluids >400°C [1] with high concentrations of H₂, transition metals, and rare earth elements (REE) exhibiting ‘atypical’ REE pattern characterized by low LREE and no Eu anomaly [2]. This is in contrast to the ‘typical’ LREE enrichment and strong positive Eu anomaly known from many MOR vent fluids observed world-wide [e.g., 3].

Besides temperature, the seawater-to-rock ratio (w/r ratio) has significant control on the fluid chemistry [e.g., 4, 5]. To understand how vent fluid REE-signatures are generated during water-rock interaction processes we reacted unaltered gabbro with NaCl(aq) or seawater fluid at 425 °C and 400 bar using cold seal pressure vessels (CSPV) at variable w/r (mass) ratios ranging from 0.5 to 10. The run durations varied from 3 to 30d in the NaCl(aq) experiments, and from 3h to 3d in the seawater experiments. The reacted fluids were analysed for major and trace elements by ICP-OES and ICP-MS.

In our experiments, only seawater reacted considerably with the fresh gabbroic solid resulting in a strong enrichment of REE in the fluid, even after only 3h run duration. The ‘atypical’ Sisters Peak REE fluid pattern were obtained at high w/r ratios (w/r = 5 and 10) that might be characteristic for focused fluid-flow along e.g., detachment faults at slow-spreading MOR [6]. In contrast, elevated LREE and positive Eu anomalies similar to ‘typical’ REE pattern have been reproduced at low w/r ratios (w/r = 0.5 to 1). Modeling results show that pronounced Eu anomalies can be produced during the reaction of seawater with altered, REE-leached gabbroic host rock at high w/r ratios (w/r = 5 to 10) and by reaction with ultramafic host rocks [7].

References:
Geodynamic implications from trace element fluxes in subduction zones

Christoph Beier¹, Marcel Regelous¹, Karsten M. Haase¹

¹GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Schlossgarten 5, D-91054 Erlangen, e-mail addresses: christoph.beier@fau.de, marcel.regelous@fau.de, karsten.haase@fau.de

The trace element fluxes in subduction zones are significant over the age of the Earth but are poorly constrained. The ‘subduction component’ that is erupted at island arc volcanoes results from a variety of processes and components that involve the composition of the igneous and sedimentary portion of the subducted slab, the composition of the dehydrating fluids and the composition of the mantle wedge melting. The proportion of the different elements that are released and mixed from the subducting plate and the composition of the residual slab that further enters into the deep mantle are not well known. Here, we present major and trace element data from the Tonga-Kermadec arc which is an 3000 km long arc in the southwestern Pacific along with new and published data from the adjacent Valu Fa, Central and Eastern Lau back-arc basin spreading centers. The distance between the arc and back-arc increases from less than 10 km at 23°S to 150 km at 19°30’S. The subduction component in the back-arc lavas (e.g., high Pb/Ce, Ba/Nb, Th/Nb and U/Nb ratios) decreases with increasing distance of the back-arc spreading axis from the volcanic arc. The subduction zone signature is replaced by a normal, depleted mid-ocean ridge signature to the north.

Arc-back-arc geochemical gradients such as these are often assumed to result from progressive slab dehydration and vertical mass transfer within the mantle wedge. Assuming that Nb is immobile in fluids and that Ba/Nb and Th/Nb ratios are not fractionated during mantle melting, then more than 90% Ba and Th in arc lavas is derived from the slab. Assuming a vertical transfer of Ba and Th, the total mass of subduction derived Ba in the mantle wedge (up to 350 km distant from the trench) is on the order of 1.6 x 10^{15} kg while the mass subducted is 4.9 x 10^{14} kg and the total mass of Th in the wedge is 3.6 x 10^{12} kg while the mass subducted is 2.31 x 10^{12} kg.

The excess of Ba and Th in the mantle wedge therefore cannot be explained by simply vertically rising fluids from a dehydrating slab, if the system is in steady-state. Instead, we propose that overlap of the back-arc melting zone with the melting region underneath the arc allows a horizontal flow of melt from the arc melting zone into the back-arc, i.e. the melts move in the opposite direction of the flow of solid mantle induced by plate subduction at shallow levels in the mantle. Our work shows, for the first time, that melts can be focused from the extreme edges of the melting zone that underlies an active spreading axis over distance of up to 200 km. Our model also provides an alternative explanation for U-excesses observed in back-arc lavas and indicates horizontal melt flow velocities of 0.4-1 m/y.
Annealing induced structural reorganization of metamict titanite and allanite

T. Beirau¹, B. Mihailova¹, C. Paulmann¹, T. Malcherek¹, G.A. Schneider², P. Guglielmi², L.A. Groat³ and U. Bismayer¹

¹Mineralogisch-Petrographisches Institut, University of Hamburg, Germany
²Institute Advanced Ceramics, Hamburg University of Technology, Germany
³Department of Earth and Ocean Sciences, University of British Columbia, Canada

In minerals like titanite and allanite, actinides can occur as natural constituents of the crystal structure. After a period of time the long-range ordered crystal structure is destroyed by self-radiation damage resulting from α-decay events of the radiogenic impurities, and becomes metamict [1]. During an α-decay event in crystalline materials the periodically ordered structure is damaged by two different types of particles, the α-particle and the ‘recoil nucleus’. This radiation induced structural amorphization processes generate the metamict state, which is characterized by a high degree of structural disorder with coexisting defect-rich crystalline and amorphous nanoregions.

We present the results of our Raman-spectroscopic [2], nanoindentation [3], synchrotron XRD [2,3,4] and FTIR-spectroscopic [4] studies of the annealing induced structural reorganization of metamict titanite and allanite. Our results show that radiation-induced periodic faults in the crystalline matrix are related to the disturbance of SiO₄-TiO₆-SiO₄-TiO₆ rings comprising TiO₆ octahedra from different chains. The radiation-induced amorphization includes partial change of Ti coordination from octahedral to pyramidal and/or tetrahedral, which leads to a rising Ti-O bond strength.


Sediment-wave fields on a shelf influenced by large amplitude internal waves, Browse Basin region, Australia

Johannes Belde¹, Stefan Back², Lars Reuning³

¹johannes.belde@emr.rwth-aachen.de
²stefan.back@emr.rwth-aachen.de
³lars.reuning@emr.rwth-aachen.de

As the oceanographic understanding of internal waves is advanced, their role in sedimentological processes has recently become the focus of increasing attention. This study analyses a large section of modern seafloor in a region with a pronounced internal wave regime and explores different possible interpretations for the origin of observed bedforms. To this end, the seafloor geomorphology and shallow-subsurface information provided by a giant (> 12,500 km²) industrial 3D seismic-reflection survey imaging the outer shelf and upper slope of the Browse Basin region on the North West Shelf of Australia is examined. The most prominent seismic-geomorphological features of the modern seafloor are submarine terrace escarpments, scarp of active faults, incised valleys and canyons as well as restricted areas of surface-seismic distortion interpreted as sites of gravity-driven mass wasting. Besides these kilometre-scale features it was also possible to document smaller sedimentary bedforms including sediment waves up to 10 m high. These occur in water depths below 250 m in extensive fields located dominantly at the foot of submerged terraces, along the scarps of modern faults, and at the transition between the outer shelf and the continental slope. Another bedform that commonly characterises the more planar regions of the outer shelf are elongate NW-SE-oriented furrows and ridges. The formation of sediment waves and longitudinal furrows and ridges requires flow velocities between 0.3–1.5 m/s, depending on the local sediment composition. In the studied setting, these velocities can be best explained as being generated by internal waves or internal tides.

In addition to the detection of individual 3D seismic-geomorphological features of the modern seafloor, it was also possible to map buried sediment waves in the seismic dataset down to ca. 500 ms (TWT) below the seafloor. This is – to our knowledge – the first 3D seismic observation of buried, kilometre-scale sediment wave fields, which documents a certain potential for the preservation of such bedforms in the sedimentary record.
Sequence Stratigraphy, Reservoir and Seal Potential
in the Mixed Carbonate-Siliciclastic Mafraq Formation (Oman): an Outcrop Analogue Study

D. Bendias ¹; T. Aigner ²

¹Daniel.bendias@uni-tuebingen.de
²T.aigner@uni-tuebingen.de

This study aims to unravel potential reservoir and seal units of the Lower to Middle Jurassic Mafraq Formation in Oman by understanding the depositional system in a sequence-stratigraphic framework using outcrop analogs in the Oman Mountains. It follows an approach from 1D (outcrop sections) to 2D (lateral logging and correlations) to 3D (potential reservoir dimensions).

The mixed carbonate- siliciclastic Mafraq Formation in Oman has so far barely been studied. It can be subdivided into the Lower and Upper Mafraq formation, unconformably overlies the Triassic Mahil Fm. (Jilh) and is topped by the Dhruma Fm (Figure 1).

Figure 1: Mafraq type section in Wadi Sahtan with Dunham and outcrop gamma ray log.

Extensive fieldwork in the Oman Mountains provided detailed sedimentological, sequence stratigraphic, bio- and chronostratigraphic information. Lateral and vertical facies trends and the interpreted depositional environments were used to characterize the Mafraq in North Oman in terms of reservoir/seal quality. As a result several potential reservoir and seal intervals were identified in the Mafraq which will help to assess its hydrocarbon potential in the subsurface of Oman.
Intracellular calcification by cyanobacteria: a significant controlled biomineralization process

Karim Benzerara¹, Fériel Skouri-Panet¹, Marie Ragon¹, Céline Férand¹, Jinhua Li¹, David Moreira², Purificacion Lopez-Garcia², Muriel Gugger³

¹IMPMC - ERC Calcyan, CNRS & UPMC, 75005 Paris, France, karim.benzerara@upmc.fr
²Ecologie, Systématique et Evolution, UMR 8079 CNRS & Université Paris-Sud, France
³Institut Pasteur, Collection des Cyanobactéries, 75724 Paris Cedex 15, France

Cyanobacteria had a pivotal role on several global geochemical cycles throughout the Earth’s history in particular, by biomineralizing CaCO₃. Calcification by cyanobacteria has so far been considered exclusively as an induced extracellular biomineralization process. However, we recently discovered deep-branching cyanobacteria that form intracellular amorphous Ca-Mg-Sr-Ba carbonates [1]. The existence of such intracellularly calcifying cyanobacteria may modify significantly our view on the past and modern role of cyanobacteria in the formation of carbonate deposits and the degree of control they achieve on this geochemically important process. However, several questions remain open: is this biomineralization process widespread phylogenetically or restricted to one single species? Does it occur under specific or diverse environmental conditions? To what extent do phases formed intracellularly by these cyanobacteria differ from abiotically-formed carbonates?

We will address these questions using diverse approaches including high spatial and spectral resolution spectromicroscoscopies and molecular biology. We will show that intracellularly calcifying cyanobacteria have been overlooked and we will detail some molecular processes likely controlled by intracellularly calcifying cyanobacteria.

Mineralogy of the Medieval Ag-Au ores in Nová Baňa, Banská Belá, Treiboltz, Rabenstein, and Kopanice in the Banská Štiavnica epithermal ore district (Slovakia)

Khulan Berkh¹, Juraj Majzlan², Martin Chovan³, Jaroslav Kozák⁴, František Bakos⁵

¹ Institute of Geosciences, Friedrich-Schiller University, Carl-Zeiss Promenade 10, D-07745 Jena, Germany, email: khulan.berkh@uni-jena.de

Medieval mining sites at Nová Baňa, Banská Belá, Kopanice, Treiboltz, and Rabenstein in the Banská Štiavnica ore district are epithermal Ag-Au occurrences, located in the central zone of a large Miocene andesite stratovolcano within the Central Slovak volcanic field. The mineralogy of the exploited ore has largely been unknown up to date because the richest parts of those mines were exhausted three centuries ago, however, studies of samples from recently completed drillholes and newly acquired samples allowed us to gather new mineralogical data.

According to the bulk chemical analysis, local Au grades are higher than 20 g/t and the Ag content of ore higher than 650 g/t. The mineralisation is hosted by partially hydrothermally brecciated, silicified, and sericitized andesitic-dacitic subvolcanic rocks and is very different depending on the sites. In Banská Belá, the Ag minerals are acanthite, polybasite-pearceite, pyrargyrite, stephanite, rare proustite and freibergite and form mostly inclusions in pyrite. In Rabenstein, pyrargyrite and freibergite are the dominant Ag carriers and occur as intergrowths with galena and chalcopyrite. In Kopanice, the main Ag mineral is acanthite and often rimmed by an unnamed AgFe(Ni) or AgSe(Te) sulfide. At Treiboltz, hessite and benleonardite (both tellurides) are the dominant Ag minerals, both associated with galena. In Nová Baňa, the main Ag carriers are pyrargyrite and miargyrite. Electrum and uytenbogaardtite occur in all sites except for Treiboltz. The precipitation of the precious metal minerals always appears to be postdate the formation of the base-metal sulfides. Some of them were most likely formed by processes of secondary enrichment in the cementation zone.

Preliminary analyses of fluid inclusions on the Nová Baňa samples show that the mineralization formed from fluids of low salinity (0–3 wt% NaCl eq.) at moderate temperatures (190–240 °C). The abundant co-existence of liquid- and vapor-rich inclusions indicates boiling during entrapment. Some of these inclusions show higher homogenization temperatures (up to 350°C), which also reflect heterogeneous nature of the fluids at the time of trapping.
Sequences and stratigraphy of carbonate platforms: some insights from the Maldives

Christian Betzler

christian.betzler@uni-hamburg.de; University Hamburg, Institute for Geology

Carbonate stratigraphic sequences and stacking patterns are controlled by variations in accommodation and sediment supply. Sediment supply in carbonates depends on multiple factors, which largely are a function of environmental conditions; changes in accommodation are seen a consequence of sea-level changes and changes in subsidence. Bank margin geometry also depends on the exposure of the carbonate platform margin to wind and waves. In this context, platform margin stacking patterns, such as aggradation, progradation or retrogradation in seismic data and in outcrop are used to reconstruct reactions of carbonate platforms, mainly to sea-level changes. Sequence-stratigraphic models that tend to ignore the basic observation that sediment accumulation rate is a consequence of rate of creation of accommodation, production rate, and transport rate, however, may lead to erroneous conclusions. This can be exemplified with core and seismic data from the Maldives carbonate platform which show that on a regional scale, a complex carbonate-platform growth can occur. Since the late middle Miocene, this carbonate edifice shows a twofold configuration of bank development of persisting growth, which is accompanied by partial platform drowning and associated localized deposition of contourites and drifts in areas just some kilometer apart. This example implies that a downward shift of clinoform tops and offlapping geometries in seismic profiles of carbonate platforms are not necessarily indicative for a sea-level driven forced regression or that aggrading bank margins reflect sea-level rise. Data indicate that oceanic currents are a major controlling factor of carbonate platform slope geometry and stratigraphy which has not been considered in standard carbonate stratigraphic models so far.
The burial history of the Thuringian Syncline (Central Germany)

Daniel Beyer¹, Alexander Malz², Stephan Donndorf³, Michaela Aehnelt⁴, Thomas Voigt⁵, Marika Götze⁶, Jörg Peisker⁷, Jonas Kley⁸, Reinhard Gaupp⁹

¹daniel.beyer.1@uni-jena.de
²alexander.malz@uni-jena.de
³stephan.donndorf@uni-jena.de
⁴Michaela.Aehnelt@uni-jena.de
⁵thomas.voigt@uni-jena.de
⁶marika.ef@web.de
⁷joerg.peisker@uni-jena.de
⁸jkley@gwdg.de
⁹reinhard.gaupp@uni-jena.de

The Thuringian Syncline is a regional syncline in central Germany. Its stratigraphy is similar to that of the North German Basin from the Permian to Triassic times. The recent structural configuration of the Thuringian Syncline is characterized by a number of northwest trending fault zones, which are mostly extensional with only small displacements. From regional correlations, literature and Lower Jurassic strata bracketed by normal faults, the timing of the extension can be assigned to Lower Jurassic up to Lower Cretaceous times. In some areas it is observable that these grabens and half-grabens were reactivated with a reverse sense. This phase of contractional deformation can be timed to the Upper Cretaceous shortening event that coincides with the heave of the adjacent basement uplifts of the Harz and Thuringian Forest, whose deformation is well constraint by thermochronological data. Syn-tectonic deposits are preserved neither for the extensional nor for the contractional deformation stage, what makes graben inversion difficult to detect. This study is based on thermal maturity investigations, a detailed map analysis, interpolations of stratigraphic surfaces at depth and cross section balancing. Results from vitrinite reflectance measurements were used to reconstruct the variations of the maximum thickness of the eroded overburden. These measurements combined with an analysis of geological maps enabled us to build a geometrical model of the fault zones after extension and to separately analyse the stratigraphic heaves of the extensional and of the later contractional deformation. Our results show that stratigraphic heaves of these fault zones were much higher before graben inversion. Although the composition of the underlying basement influences the later structural evolution by different compaction and the reactivation of existing structures in the basement. Our survey identified a deep, extended and later reactivated palaeo-depression in the central part of the Thuringian Syncline. Assuming that many Central European structures, formerly interpreted as purely extensional with small fault offsets, were affected by much higher subsidence and were later reactivated gives a regionally more consistent picture of the structural evolution, which is comparable with similar structures from the North German Basin. Our project shows how a combined survey using structural modelling integrated with sedimentologic and basin-modelling methods can put close constraints on the geological evolution even with limited subsurface data.
Age and origin of ferroan, high-K A- and S-type granitoids of the Mesoproterozoic Namaqualand Metamorphic Complex (Kakamas Terrane, South Africa)

Julia Bial¹, Volker Schenk¹, Steffen Büttner²

¹ Institut für Geowissenschaften, Christian-Albrechts-Universität Kiel, 24118 Kiel (jb@min.uni-kiel.de)
² Department of Geology, Rhodes University, Grahamstown, South Africa (s.buettner@ru.ac.za)

The Namaqualand Metamorphic Complex (NMC) is a low pressure granulite-facies terrane that surrounds the Kaapvaal Craton to the south. Its formation is related to the Mesoproterozoic amalgamation of the supercontinent Rodinia and represents a segment of Grenville-aged (1.3-1.0 Ga) belts occurring all over the world. The evolution of the belt is characterized by three stages of voluminous granitoid emplacements. The main stage was at 1210-1180 Ma, but emplacements at about 1100 Ma and 1000 Ma are also reported (e.g. Raith et al., 2003, Robb et al., 1999, Clifford et al., 2004). To shed light onto the geodynamic significance of the granitoid magmatism we investigated several granitoid bodies in two spatially separated areas of the central Kakamas Terrane in South Africa and southern Namibia. All granitoids are alkali-calcic to calc-alkaline, peraluminous and show high-K to shoshonitic characteristics; mostly all ferroan. We subdivide the granitoids into two major groups: (1) A-type granitoids and (2) S-type granites. The A-type granitoids (48-75 wt.% SiO₂) have a variable composition ranging from alkali-feldspar-granites to tonalites, containing biotite and/or hornblende or orthopyroxene. They are strongly enriched in REE and LILE and depleted in Ba, Sr, Eu, Nb, Ta and Ti. The S-type granites (68-76 wt.% SiO₂) differ from the A-type group in having strictly granitic compositions, containing biotite and/or garnet/sillimanite and having lower REE and MgO, FeO, CaO, TiO₂, MnO concentrations, but higher Na₂O and K₂O contents. The A-type granitoids display well-defined trends in Harker diagrams and log compatible vs. log incompatible diagrams pointing to fractional crystallization. The negative Eu, Ba and Sr anomalies indicate feldspar fractionation. Nb/Ta and Nb/La vs. Zr/Sm ratios indicate that residual rutile and subordinate residual amphibole is responsible for the Nb-Ta and Ti troughs. Ba/Th vs. Th trends preclude fluid enrichment as the cause of the high enrichment of trace elements in these rocks. Discrimination diagrams show that most of the A-type granitoids have “within plate granite (WPG)” character, whereas the S-type granitoids are of “syn-collisional” chemistry.

The geochemical characteristics of the A-type granitoids are consistent with a differentiation of the melts by crystal fractionation. The residuum of the melts indicate that they derived from deep source rocks (mantle or deep crust). Our new U-Pb zircon data reveal an emplacement of the A-type granitoids into middle to lower crustal levels at about 1200 Ma. The heat input by these granitoids might be the cause for the synchronous regional low pressure granulite-facies metamorphism of the NMC. The S-type granitoids are of the same age and appear to be the product of crustal melts formed by mica dehydration melting. Any geodynamic model of the NMC orogeny has to consider the synchronous A- and S-type magmatism and the HT to UHT metamorphism at ~1200 Ma as the main crust forming event, followed by two weaker magmatic and metamorphic episodes at ~1100 Ma and ~1000 Ma.

Temperature and humidity dependent investigation of a zeolite comprising 8-ring pores

Anna Bieniok¹, SoHyun Park², Uwe Brendel³

¹University of Salzburg, Dept. Geography & Geology, anna.bieniok@sbg.ac.at
²University of Munich, Dept. Environmental and Geo Science, sohyun.park@lmu.de
³University of Salzburg, Dept. Molecular Biology, uwe.brendel@sbg.ac.at

Microporous materials like zeolites are characterized by open framework structures with pore sizes in molecular dimensions and extreme high inner and outer surface area. They are suitable as adsorbents or catalysts when converted to their dehydrated forms allowing the free access to active sites inside their cages. However, during dehydration channels and cages can undergo extreme changes in shape and pore size. Therefore, it is important to be aware of the deformation capability of the water-free framework under special temperature, humidity and gas pressure conditions.

We have studied the structure deformations of paulingite variants by single crystal X-ray diffraction under various temperature and air humidity. Paulingite is a complex 8-ring zeolite providing a unique pore system in which responses upon dehydration and cation distribution of seven distinctly different 8-ring cages can be characterized effectively at once. Our studies on paulingite show that this zeolite belongs to a flexible and collapsible framework structure and resembles the deformation observed in zeolite Rho at high temperatures. The framework is very sensitive to changes in air moisture. The effect of the relative air humidity to the water content of the zeolite structure seems to be much greater than the effect of temperature. If the water content is reduced, cations move from positions inside the three large cages (called grc, pau and plg) to sites near single 6-rings or inside elliptically deformed 8-rings. The cation displacement of Ca in the plg cage is about 2.4 Å. Saddle-shaped 8-rings of small compositional building units (e.g. oto) provide appropriate environment for larger cations like K. According to the water content the framework reacts with distortions of the pore openings to adjust required bonding distances. Therefore it is important to control temperature and humidity conditions during the diffraction experiments.
Geochemical modeling of the Antimony Line at the Murchison Greenstone Belt (MGB), South Africa

N. Blauwbroek¹, W. Bach², U. Schwarz-Schampera³, A. Klügel⁴

¹nikki.blauwbroek@uni-bremen.de
²ebach@uni-bremen.de
³ulrich.schwarz-schampera@bgr.de
⁴a.kluigel@uni-bremen.de

¹²³ University of Bremen, Faculty of Geosciences, Klagenfurter Straße (GEO), 28359 Bremen
²Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) Hannover, Stilleweg 2, 30655 Hannover
³nikki.blauwbroek@uni-bremen.de
⁴wbach@uni-bremen.de

The 3.09 to 2.97 Ga Murchison Greenstone Belt (MGB) represents one of a number of Archean volcano-sedimentary belts within the Kaapvaal Craton and is located in the northeastern corner (e.g. Bougail et al., 1986). The MGB is well known for its numerous precious and base metal deposits, including Sb and Au mineralization along a central structural lineament, the Antimony Line (AL). This is a set of Precambrian Sb-Ass-Hg, located in a complex quartz-carbonate altered brittle-ductile structure (Jaquin et al., 2013). The formation history of the MGB, and in specific the AL, is complex and has attracted attention to many geologists and geochemists for decades. Structural analysis and age determinations have been made to attempt to unfold the formation and relationship of the Rooiwater, Rubbervale and Wiegel unit with the group of surrounding intruded granites (e.g. Vearncombe, 1988; Paupol et al., 1996; Jaquin et al., 2013). This study will attempt to provide a geochemistry-geochemical input - with the main focus on the Sb-Ass-Au-Hg mineralization in the AL. We examine what very little geothermal and geochemical data is available about the very mobile antimony and its mineralization (Stibnite-Sb₂S₃) in the MGB. A combination of fieldwork, exploration and geochemical analysis is used to assess the geothermometry and thermodynamic modeling. To overcome the lack of geothermal data about for Sb, we expanded our 1 kb database for Geochemist’s Workbench and EQ3/6 by key minerals and aqueous species in the database for the Fe-Sb-Ass-Cu-S system. The field observations strongly indicate that the Sb mineralization is located primarily near the contact between a chlorite-rich schist (metagranodiorite) and a talc-rich schist (metakomatiite). Fuchsite-rich rocks are surrounded by metagranodiorite and located near the metakomatiite are also present near this contact. The Sb mineralization (stibnite-berthierite) is primarily developed in fracture filling of quartz-carbonate veins in multiple orientations. The As mineralization (arsenopyrite) is found outside of this zone and within the metagranodiorite, specifically near biotite enrichments and albitionization of the quartz veins. These field observations have been interpreted as a classical black wall metamorphism under greenschist facies conditions between the komatite and granodiorite, which has been overprinted by later deformation and hydrothermal processes. First results of δ¹⁸O measurements of the quartz-carbonate alteration veins indicate temperatures of 140 to 200°C and mantle carbon δ¹³C signatures. The REE patterns of the veins appear to be more similar to the metakomatiite than the metagranodiorite. These results provide an input for initial modeling in an attempt to assess whether the primary mineralization of the stibnite is tied to the metasomatic event causing the blackwall alteration. The model works on the assumption that the Sb is hosted primarily in the granodiorite, which may present an ancient volcanic arc. The fluids are predicted to have high O₂ and S₂ fugacities, and Sb is highly soluble even at T of around 200°C. When percolating into the komatite, these fluids cause serpentinization, which lowers the O₂ and S₂ fugacities and decreases the Sb solubility by two orders of magnitude. The modeling has been preformed for different temperatures and a constant pressure of 1 kbar. The models...
are very robust in predicting greatly increased solubility of Sb in felsic sulfide-bearing rocks over a range of temperatures (150-300°C). In the temperature range, precipitation of Sb from such fluids is expected to occur close to the metasomatic front. Deformation and fluid migration during later stages caused the recrystallization of Sb to stibnite (and berthierite) within the quartz-carbonate alteration veins.

I still have to put references in.
Origin of carbonate minerals in CO$_2$ reservoir rocks
at the Ketzin pilot site (Germany)

S. Bock$^1$, H.-J. Förster$^2$, D. Pudlo$^3$, A. Förster$^4$ and R. Gaupp$^5$

$^1$Susanne.Bock@uni-jena.de
$^2$Hans-Juergen.Foerster@gfz-potsdam.de
$^3$Dieter.Pudlo@uni-jena.de
$^4$Andrea.Foerster@gfz-potsdam.de
$^5$Reinhard.Gaupp@uni-jena.de

At the pilot site Ketzin (Germany), roughly 64,000 tons of CO$_2$ were injected in a mineralogically heterogeneous sandstone reservoir. Core material was recovered in 2007 for a baseline study and again in August 2012 (Ktzi 203 borehole), approximately four years after start of CO$_2$ injection. Different carbonate minerals were detected in the reservoir rocks prior and after contact with the CO$_2$. In sandstones unaffected by CO$_2$, authigenic poikilitic dolomite is present in variable amounts, which has not yet been observed in the sandstones exposed to CO$_2$. In these rocks, minor amounts of small mineral aggregates occur, usually composed of siderite mantled by Ca-rich carbonate (calcite?, hydrocalcite?). Three potential CO$_3^{2-}$ sources for the newly formed carbonates have to be considered: (A) dolomite dissolution, (B) reactions of injected CO$_2$ with the formation fluid, and (C) the drill mud.

Since the mud used during drilling the Ktzi 203 borehole has contained high concentrations of potassium carbonate (220 g/l K$_2$CO$_3$) and has penetrated the reservoir-rock samples to variable depths, both siderite and calcite could have been accidentally formed in response to drill-mud contamination. This possibility demanded to examine the spatial distribution of newly precipitated K-bearing minerals and the carbonate species. To exclude alteration by drill-mud infiltration, the central and outer parts of the cores (10 cm Ø) were studied separately. Whereas calcite and siderite are present throughout the entire core, sylvite (the most likely repository of K released during dissolution of K$_2$CO$_3$) is omnipresent only in the outer zone of the core. KCl accompanies the carbonates in lower amounts exclusively in those inner-core samples displaying high porosity. This observation suggests that the central parts of the drill cores are almost unaffected by the drill mud. Thus, CO$_2$–fluid–rock reactions may have facilitated dolomite dissolution and subsequent (hydro)calcite and siderite precipitation.
Sclerochronological records from Neogene reef corals document decreasing seasonality upon closure of the Central American Seaway

Aron Böcker¹, Thomas Brachert², Markus Reuter³

¹aron.boecker@uni-leipzig.de
²brachert@uni-leipzig.de
³markus.reuter@uni-graz.at

Climate in the western Atlantic region (Caribbean, Gulf of Mexico, Florida) is particularly sensitive to atmospheric oscillations such as ENSO. It is known that Plio/Pleistocene climate was significantly different from the Mio/Pliocene climate due to the closure of the Central American Seaway (CAS) around 3.5 Ma ago. Uplift of the Isthmus of Panama increasingly restricted the exchange of waters from the tropical Pacific waters and North Atlantic/Caribbean. The final closure of the CAS forced warm Caribbean water masses to enter the Gulf of Mexico and pass via Florida Straits into the Atlantic where they form the Gulf Stream.

We use sclerochronological records of corals from Miocene to Pleistocene reefs to document potential changes in seasonal climate associated with CAS uplift and closure. Reef corals of the genus Solenastrea were collected from reefs of the Plio-/Pleistocene age in southern Florida; corals of Pliocene and Miocene age in northern Hispaniola (Cibao Valley, Dominican Republic). Coral skeletons selected for geochemical study were checked for signs of diagenetic alteration using standard methods. Most corals show a clear density banding in X-radiographs which is orientated perpendicular to the axis of maximum growth. REEs and trace element concentrations (Sr, Mg, U, Ba, Y, B) compare well with other fossil and recent coral skeletons. Oxygen stable isotope data (18O/16O) of Plio/Pleistocene Solenastrea from Florida imply seasonal SST changes of 9.5°C. Mio/Pliocene Stephanocoenia and Montastraea from Cibao Valley document seasonal SST changes of ~2°C and ~4°C, respectively, assuming no seasonal change in seawater δ18O composition for all specimens. In contrast, seasonal SST changes inferred from Sr/Ca and Mg/Ca of Solenastrea from Florida amounts 14.4°C and 12.7°C respectively. Stephanocoenia from Cibao Valley record seasonal SST contrasts of 7°C and 4-7°C (based on Sr/Ca and Mg/Ca), respectively. The difference in seasonality derived from oxygen isotope ratios and trace element ratios most likely reflects subannual changes in the 18O/16O of seawater.

The regional SST differences between the Florida and the Cibao Valley corals are related to two phenomena: (1) Cibao Valley is located in an equatorial setting with a low SST seasonality and (2) Florida experienced enhanced interannual variability during the Plio/Pleistocene, because bands of high skeletal density either formed during winter, summer or transitional seasons. Contrasting this, corals grown during Mio/Pliocene before the CAS closure, show only low interannual variability.
Geochemical analyses (Microscopic kerogen type assessment, vitrinite reflectance, TOC, Rock-Eval, GC, GC-MS, etc.) have been performed on numerous sedimentary rocks and oil samples from the central Upper Rhine Graben and compared to literature data to achieve a comprehensive geochemical characterization of the petroleum system Upper Rhine Graben.

Source rock characterization and kerogen type assessment prove excellent source rock properties for the Lias and Fish Shale as well as good qualities for the Pechelbronn Beds and Hydrobia Beds.

Biomarker analyses and carbon isotopes identify four distinct oil families (Gaintchi, 1979; Bruss, 2000). North of the Heidelberg Basin most oil reservoirs are located in the Pechelbronn Beds and dominated by high wax crude oil (generated by the Lower Pechelbronn Beds) and a light oil type generated from marine Tertiary source rocks. The French sectors are dominated by Liassic oil. In the central Upper Rhine Graben all four oil families occur, testified by minor oil reservoirs of a low-mature oil generated by the evaporitic-salinar Lower Hydrobia Beds, several reservoirs generated by the Rupelian Fish Shale, high-wax crudes generated by the Pechelbronn Beds, and major oil fields generated by the Posidonia Shale.
Antimony is a pollutant, ubiquitously present in our environment [1]. When Sb$^{5+}$ enters the soil, it can be adsorbed onto the surface of iron oxides or be incorporated into their structure [2]. During the transformation of iron oxides, such as ferrihydrite (Fe$_2$O$_3 \cdot n$H$_2$O), poorly crystalline feroxyhyte (δ-FeOOH) can be formed when Sb$^{5+}$ is present [3]. Feroxyhyte was first described in 1976 [4], and belongs to the least studied iron oxide polymorphs [5]. Feroxyhyte was first described in 1976 [4], and belongs to the least studied iron oxide polymorphs [5]. Feroxyhyte is built by a hexagonal close packed array of oxygen atoms, with Fe$^{3+}$ residing in the octahedral interstices. In the feroxyhyte structure, pairs of face sharing Fe$^{3+}$-octahedra alternate with pairs of octahedral vacancies along the c-axis [5]. In our study, we focused on the possibly of Sb$^{5+}$ incorporation into the crystal structure of feroxyhyte by replacing Fe$^{3+}$.

2-line ferrihydrite was synthesized after [6]. 5.1 g Fe(NO$_3$)$_3 \cdot 9$H$_2$O was rapidly mixed with 45 mL 5 M KOH solution under constant stirring. The pH of the suspension was brought to 4 with concentrated HNO$_3$. After the addition of 100 mL 0.015 M K$_2$Sb(OH)$_6$ solution, the pH of the suspension was reset to 4 with concentrated HNO$_3$, and sealed in a PET bottle. The suspension was aged for 16 days at 70 °C, filtrated, washed, air-dried and sealed in glass vials.

Bulk chemical analysis was performed with ICP-OES, showing molar Sb:Fe ratios of 0.12. X-ray absorption fine structure spectroscopy (EXAFS) was performed at the Sb-L1 edge at the SUL-X beamline, Angströmquelle Karlsruhe (ANKA), Germany. All spectra were processed with the IFEFFIT software package containing Athena and Artemis [7]. For the fitting, the feroxyhyte model after [8], including changes suggested by [5], was modified by substituting one Fe$^{3+}$-octahedron against one Sb$^{5+}$-octahedron. Our data suggests, that Sb$^{5+}$ can be incorporated into the structure of feroxyhyte following the substitution reaction Fe$^{3+}$O$_6$H$_3 \leftrightarrow$ Sb$^{5+}$O$_6$H$^+ + 2$H$^+$. 

Magma storage conditions of the Heise volcanic field, Snake River Plain – an experimental study -

Torsten Bolte¹, Francois Holtz², Renat Almeev³, Barbara Nash⁴

¹Leibniz University Hannover, Institute for Mineralogy, Callinstr. 3, 30167 Hannover, Germany
²Department of Geology and Geophysics, University of Utah, Salt Lake City, USA

¹t.bolte@mineralogie.uni-hannover.de

The Heise volcanic field is part of the Snake River Plain Yellowstone (SRPY) hotspot track in the Western USA, representing the movement of the North American continental plate over a fixed mantle hotspot over the time span of the last 17 Ma. The Heise volcanic field produced high silicic, voluminous rhyolitic magmas and started 6.62 Ma ago with the eruption of the crystal rich Blacktail Creek Tuff (BCT) and ended 4.45 Ma ago with the nearly crystal free Kilgore Tuff (KT). After a 2 million year break, the eruptive activity moved to the still active Yellowstone plateau 2.05 Ma ago. We conducted an experimental study using natural rock samples representative of BCT and KT units to (1) constrain the internal change of magma storage conditions within the 6.6 – 4.4 Ma Heise volcanic center and to (2) compare these results with former studies from older units of the SRPY hotspot track (e.g. Bruneau Jarbidge volcanic field (12.7 – 10.5 Ma)). We also determined the composition of minerals and glasses (microprobe analyses) of different rhyolites from the Heise volcanic field to determine their pre-eruptive conditions by utilizing a set of available geothermometers (ILMAT, QUILF, Feldspar pairs, Zircon and Apatite solubility, TitaniQ). The study of natural BCT rhyolite, containing Ti-mt, Ilm, Pig, Aug, Akf, Qz and accessory Ap, Zr and Bt, yielded pre-eruptive temperatures varying in a narrow interval between 810 and 850°C (using all methods, except oxide pairs which gave ~50°C higher temperatures). Pre-eruptive pressures, estimated by using TitaniQ model (Huang & Audetat, 2012) and by projecting glass compositions on Qz-Ab-Or ternary plot were estimated to be in the range of 100 – 200 MPa.

Crystallization experiments were performed in the temperature range 670-900°C at 200MPa using cold seal pressure vessels (αH₂O in the range 0.1-1; Ni-NiO buffer) and allowed us to constrain the stability fields of the main mineral phases in the BCT composition. Our experimental data indicate that BCT magmas could be stored under 200MPa pressure and could have pre-eruptive temperatures of ~850°C and melt water contents of 1-3wt% H₂O. This relatively low temperature and the relatively high H₂O contents obtained for 6.62 Ma old BCT eruption are different from those obtained in our previous study for the older 10Ma Bruneau Jarbidge eruptive center (~ 950°C 0.7 – 1.5 wt% H₂O, at pressures of 300 – 400MPa, Almeev et al, 2012). This observation clearly illustrates the change of pre-eruptive conditions with time. Our on-going study of melt inclusions in BCT rhyolite and preliminary experimental results for the younger KT rhyolite indicate that magma storage conditions did not change significantly during the Heise eruptive cycle.

References:
Mixing from below - solving some problems with classical fluid-mixing models

Paul D. Bons¹ & Enrique Gomez-Rivas¹

¹Dept. of Geosciences, Eberhard Karls University Tübingen, Tübingen, Germany. paul.bons@uni-tuebingen.de

Hydrothermal fluids are important carriers of mass and heat in the crust. They form various types of ore deposits, for example, the Ag-bearing deposits in the German Black Forest. Many models for such deposits invoke mixing of surface-derived (meteoric or seawater) fluids and deeper basement-derived fluids. The required simultaneous down- and upward flow of fluids is commonly explained with convection, topography-driven flow, etc. Such models, however, often violate basic hydrodynamic principles. A solution is to separate down- and upwards flow in time. Fluids may infiltrate dry basement rocks below an unconformity. These fluids slowly interact and equilibrate with their host rock and may further modify their signatures by gravitational fractionation (Bons & Gomez-Rivas, 2013). Exhumation and/or heating by igneous intrusions may trigger fluid release (Staude et al., 2009). Fluids from different depths ascend rapidly in short bursts (mobile hydrofractures, Bons, 2001) and mix, and may produce ore deposits. In this model mixing of different fluids does occur, but the fluids all flow up and mix from below.


Complexation of Sr in aqueous solutions equilibrated with silicate melts: Implications for fluid-melt partitioning

M. Borchert1, M. Wilke2, C. Schmidt2, K. Kvashnina3, S. Jahn2

1Deutsches Elektronen-Synchrotron, Hamburg, Germany, manuela.borchert@desy.de
2Helmholtz Zentrum Potsdam GFZ GeoForschungsZentrum, Potsdam, Germany
3European Synchrotron Radiation Facility, Grenoble, France

Fluid-melt partitioning of Sr, Ba, La, and Y strongly depends on fluid and melt composition [1-2]. That is, partition coefficients of these elements increase with i) salinity of the fluid and ii) increasing alumina saturation index (ASI: Al/(Na+K) in moles) of the silicate melt (Fig.1).

Fig. 1. Fluid-melt partition coefficients of Sr, Ba, La and Y as function of melt composition at 750°C, 200 MPa, and using a chloridic fluid.

On one hand, the distinct affinity for chloridic fluids points to a preferential complexation of these elements with chlorine. On the other hand, the strong dependence on melt composition suggests that a different release of melt components into the aqueous fluid in peralkaline systems changes the speciation in the aqueous fluid. Up to now, the exact nature of the complexation in the fluid is not clear.

Here, we present experimental and theoretical data on the complexation of Sr in three fluid-melt systems. X-ray absorption spectroscopy was applied to probe the local environment around Sr in silicate-bearing fluids, i.e., peralkaline or peraluminous melts completely dissolved in the aqueous fluid, and in various model systems, e.g., crystalline compounds, silicate glasses, and aqueous solutions. In order to decode the complexation of Sr in model systems and silicate-bearing fluids, theoretical spectra are calculated either using model structures, by testing several small cluster geometries or based on snapshots of trajectories produced with ab initio molecular dynamics simulation to account for atom movements in aqueous solutions. Experimental data clearly show differences in the local environment around Sr in studied silicate-bearing fluids. Theoretical spectra point to a predominant formation of i) SrO\textsubscript{6} clusters in chlorine-free peralkaline fluids, ii) distorted SrO\textsubscript{6} clusters in chloridic-peralkaline fluids, and iii) complexes that very likely incorporate Cl\textsuperscript{-} in chloridic-peraluminous fluids.

Fe Mössbauer spectroscopy of pantelleritic melts

N. Borovkov¹, K.- U. Hess², K. T. Fehr³, C. Cimarelli⁴, D. B. Dingwell⁵, A. Günther⁶.

¹nikita.borovkov@min.uni-muenchen.de
²hess@lmu.de
³fehr@min.uni-muenchen.de
⁴cimarelli@min.uni-muenchen.de
⁵dingwell@lmu.de
⁶guenther@min.uni-muenchen.de

Fe species in the melt can include [6]-Fe²⁺, [5]-Fe²⁺, [4]-Fe³⁺, and [5]-Fe³⁺. The relative proportions between these species can vary according to bulk glass composition and oxygen fugacity conditions. RedOx state and coordination of Fe can considerably affect important physical properties (density and viscosity) of magma, even where bulk composition and Fe content are constant. A set of silicate glasses with pantelleritic composition have been synthesized at different oxygen fugacity conditions (from air down to IW buffer). Samples were analysed by ⁵⁷Fe Mössbauer spectroscopy (MB). The spectra were taken at 298K in transmission mode and fitted by applying an extended Voigt-based lineshape according to Lagarec & Rancourt (1997). The MB spectra of all samples display three lines which can be described to two different doublets. One doublet with an isomer shift (IS) of 0.87-1.00 mm/s relative to alpha-iron and a quadrupole splitting (QS) of 1.78-2.28 mm/s can be attributed to ferrous iron. The second doublet with IS of 0.26-0.50 mm/s relative alpha-iron and QS of 0.77-0.94 mm/s can be attributed to ferric iron. With decreasing oxidation (Fe³⁺/Fe total from 0.70 to 0.17) the IS of ferric iron increases slightly from 0.26-0.32 mm/s to 0.45-0.50 mm/s. The IS of ferrous iron increases slightly from 0.79-0.85 to 0.95-1.00 mm/s. The QS for both speciations increases slightly with increasing oxidation state like in peralkaline melts (Fehr et al., 2011) and in contrast to ferrobasaltic glasses (Botcharnikov et al., 2005). The transformation of Fe coordination state as a function of oxidation was observed. Ferric iron with IS=0.26-0.37 mm/s is assumed to be network-former (Fe³⁺/Fe total=0.52-0.70) and with IS=0.39-0.50 mm/s (Fe³⁺/Fe total=0.18-0.41) it became network-modifier and is probably [5]-fold coordinated. Ferrous iron probably change over the coordination as well from [5] to [6]-fold. Transformation of Fe coordination and changes of the degree of polymerisation depending on oxidation state can affect the viscosity. These data might be successfully applied for viscosity calculation models.
The Levant Basin has earned its position as a new Frontier gas province due to the recent discoveries that triggered the exploration in this region. One of the major questions that are yet to be answered is related to the potential thermogenic source rocks and their distribution within the Levant Basin and Margin.

The upper Santonian – upper Campanian appears to be a regional potential hydrocarbon source rock along the eastern Mediterranean. However, the extent of these source rocks to the Levant Basin and Margin is still unknown due to the lack of data.

Detailed organic geochemical analyses of the upper Santonian – Campanian rock succession from onshore Lebanon showed that these source rocks include immature algal marine hydrogen rich organic matter deposited under dysoxic conditions. Comparison of these findings with the available regional data, as well as paleogeographic and paleofacies maps suggest that deposition of the organic rich strata of the upper Santonian – upper Campanian was restricted to a productivity zone along the shelf area, while the basinal equivalent is more aerated and probably organic lean. This hypothesis needs better testing using different techniques (e.g. foraminiferal assemblages and abundances), more data concerning the regional distribution and organofacies mapping of these potential source rocks (e.g. in Syria and NW Iraq), as well as a better understanding of the structural control on the organic matter distribution.
Neritic carbonate production is highly diverse, and both skeletal and non-skeletal in origin. Non-skeletal material seems to form in warm-water settings only, and as such to be diagnostic for the “tropical zone”. In contrast, the skeletal factory extends from the tropics to the polar zone and is highly diverse. Two large biotic systems have been identified for the warm water (Photozoan carbonates) and cool-water zones (Heterozoan carbonates). Because this binary classification is too simple for significant paleoclimatic reconstructions, various attempts have been made to refine the classification.

In this contribution I will introduce the “Critical Temperatures Approach” (CTA) into palaeoecology and carbonate sedimentology to make more specific temperature estimates from shallow-water carbonates. We assume maximal carbonate precipitation of the calcifying biota to occur at their specific optimum temperature and to decrease towards their minimum and maximum temperature of distribution. Identification whether maximum calcification occurred in winter or summer allows estimates to be made, whether a taxon occurred under optimal or warm/cold suboptimal conditions. I will illustrate the potential of the CTA with two case studies on carbonate production in the Photozoan System (Plio-Pleistocene/ Florida, Late Miocene/Mediterranean region). In these, the model is relevant for all poikilothermic carbonate producers in reefs and platforms, and has implications for judging geographic distributions and causes of declining growth of corals, benthic carbonate communities and entire carbonate systems. With regard to the causes underlying expansion and demise of carbonate platforms and reefs in geological history, I expect the model predictions to help for a deeper understanding of biotic responses during hyperthermals or coolings, and possibly also for identifying regions in the modern ocean where corals are endangered or taking advantage of global warming.
Quantification of dissolved CO₂ in silicate glasses using Micro-Raman spectroscopy.

Richard Brooker¹, Yann Morizet² and Bruce Kjarsgaard³

¹richard.brooker@bristol.ac.uk School of Earth Sciences, University of Bristol, BS8 1RJ, UK.
²yann.morizet@univ-nantes.fr LPGN UMR CNRS 6112, Université de Nantes, 44322 France.
³bruce.kjarsgaard@nrcan.gc.ca GSC, 601 Booth Street, Ottawa, ON, K1A 0E8. Canada

We investigate the potential use of Confocal Micro-Raman spectroscopy for the quantification of CO₂ in geologically relevant glass compositions (Morizet et al, in press). A calibration is developed using a wide range of both natural and synthetic glasses, that have CO₂ dissolved as carbonate (CO₃²⁻) in the concentration range from 0.2 to 16 wt.%. Spectra were acquired in the 200 and 1350 cm⁻¹ frequency region that includes the v₁ Raman active vibration for carbonate at 1062-1092 cm⁻¹. This peak is fitted and the intensity compared to the total area of other fitted peaks representing the glass structure. The most precise and accurate calibration is found when carbonate peaks are compared to aluminosilicate spectral features in the high frequency region (HF: 700-1200 cm⁻¹). This area can be simulated with several Gaussian peaks, mainly related to different structural Q species in the glass as well as the carbonate peak. In some samples the ‘dissolved’ CO₃²⁻ appears to have two different Raman bands, one sharper than the other. This may be consistent with previous suggestions that CO₃²⁻ has several structural environments in the glass, unrelated to any precipitation of crystalline carbonate from the melt during quenching (Brooker et al., 2001). The calibration derived using the HF peaks is linear for both the full range of glass composition considered and the range of CO₂ concentrations, even when multiple carbonate peaks are involved. The amount of carbonate (expressed as wt% CO₂) is 15.17 times the CO₃/ HF ratio (the fitted areas of the v₁ carbonate peak(s) at 1062-1092 cm⁻¹ over the remaining aluminosilicate envelope from 700-1200 cm⁻¹). This technique is similar to the Raman calibration recently developed for water (Le Losq et al., 2012), but is complicated by the overlapping of these two fitted components. Using error propagation, we propose the calibration accuracy is better than ±0.4 wt.% CO₂ for our dataset, and the lower detection limits is around 0.2 wt% CO₂. As with the water calibration, the apparently composition-independent linear relationship with the Q-species HF peaks is unexpected.

The v₁ Raman peak position for carbonate is not constant and appears to be correlated with the density of the melt (or glass) in some way, rather than the cation composition.

Refs


New insights on the maturity distribution and shale gas potential of the Lower Saxony Basin, NW-Germany

Bruns, Benjamin¹, di Primio, Rolando², Berner, Ulrich³, Littke, Ralf¹

¹ RWTH Aachen University, EMR - Energy & Mineral Resources Group, Aachen, Institute of Geology and Geochemistry of Petroleum and Coal, Lochnerstr. 4-20, D-52056 Aachen, benjamin.bruns@emr.rwth-aachen.de
² Deutsches GeoForschungsZentrum GFZ, Sektion 4.3, Organische Geochemie, Telegrafenberg B 428, D-14473 Potsdam, rolando.di-primio@gfz-potsdam.de
³ Bundesanstalt für Geowissenschaften und Rohstoffe, Geochemie von Erdöl und Kohle, Stilleweg 2, D-30655 Hannover, ulrich.berner@bgr.de

Due to its economic relevance the Lower Saxony Basin, NW-Germany, has already been intensively investigated. Consequently, it can be regarded as a well-known example of a sedimentary basin that experienced strong inversion. Oil and gas source rocks of economical importance comprise Upper Carboniferous coals as well as Jurassic (Lias) and Cretaceous (Wealden) marls.

Extensive 1D and 2D basin modeling has already been performed in this area, while no high resolution 3D model was accomplished so far. 1D and 2D basin models usually lack the effect that 3D geometry has on temperature and pressure simulation results. This includes, for example, overpressure generation/pressure outflow below impermeable layers or lateral heat flow influence and heat accumulations in anticlinal structures.

Thus, we developed a fully integrated, 3D high resolution numerical petroleum systems model (500 m² grid cell size; PetroMod software suite) incorporating the Lower Saxony Basin, the Pompeckj Block, and parts of the Münsterland Basin with special emphasis on the maturation reconstruction as well as adsorption capability and shale gas potential of the Jurassic Posidonia Shale.

Based on thermal calibration with vitrinite reflectance and borehole temperature data at a great number of locations within the study area, erosion and basal heat flow maps were compiled. The Posidonia Shale has been locally buried to depths of more than 7000 m equaling maturities exceeding 4 % VRr. These maximum values apply, however, only to small parts of the basin centre. The burial depth, temperature, and maturity distribution throughout the whole study area is in fact highly variable.

This study offers new insights on the thermal evolution through time and maturity distribution of the Lower Saxony Basin and adjacent areas. An independent reappraisal of the erosional amounts and maturity distribution in the study area was performed, providing the highest resolution of erosional amount distribution achieved so far, thus also supplying a highly differentiated image of maturity distribution. Based on the refined heat flow and erosion maps, maturity maps and information on the maturity evolution through time can be delivered for all important source rocks in NW-Germany. The accurate reconstruction of maturation through time is an important necessity to assess petroleum generation. Thus, by adding experimentally derived sorption parameters and applying refined kinetic data on petroleum generation to the source rock members, this model is able to show a distinct picture of hydrocarbon formation and sorption, thus enabling quantification of shale gas potential.
Early evolution of the Albert Rift: insights from basal fluvio-lacustrine sediments along new road cuts in the Middle to Upper Miocene (Uganda)

D. Brüsch1, S. Schneider1, M. Hinderer1, J. Hornung1, R. Petschick2

1 Institute of Applied Geosciences, TU Darmstadt, Schnittspahnstrasse 9, D-64287 Darmstadt, bruesch@geo.tudarmstadt.de

2 Institute for geosciences, Goethe University Frankfurt; Altenhoferallee 1, D-60438 Frankfurt

The development of the East African Rift System (EARS) during the past 20 million years is thought to influence the regional climate in Africa. Sedimentary deposits of continental rift basins exhibit a record of these changes together with the tectonic evolution of the rift. Our study focus on the western branch of the EARS in western Uganda where rift flanks are extremely uplifted, in particular the up to 5000m high Rwenzori Mountains. A new large road cut in the Kisegi-Nyabusosi (Semliki) was studied during the dry season 2012 exposing Middle Miocene sediments, hence representing the base of the syn-rift succession in the Albert Rift. The aim was to reconstruct the palaeoclimatic and palaeoenvironmental conditions during the initiation of the rift and to provide new insights into the Miocene terrestrial record of Africa, which has been rarely studied so far. We logged 3 sections at a centimeter to decimeter scale of together 180 m with sedimentological and geophysical methods (natural spectral gamma-radiation, magnetic susceptibility) and analyzed lithofacies types and facies associations making up architectural elements. In total almost 27 samples of fine-grained sediments have been taken for further analysis of mineralogical composition, clay minerals, and palynology. Time control and stratigraphic correlation will be based on established gastropod assemblages of East Africa, palynomorphs and cycle analysis. First results show that a fluvial setting in the beginning changed with time to fully lacustrine conditions and again to a transitional system of near shore environment in the end. The sequence is characterized by 11 distinctive lithofacies that build up 9 architectural elements. The mesoscale cyclic patterns after Roller et al. (2010) could be confirmed by the study of this succession indicating that the cyclic signatures could be found in a more regional context over laterally widespread areas, which gives the chance to establish a sequence stratigraphic framework for the Albertine basin. In general a climatic trend from arid to a more humid climate within the documented succession can be observed. These findings are further validated by first XRD results showing a considerable decrease of smectites and increase of kaolinites. The frequent iron crusts within the uppermost part of the succession also point to a more humid climate and increased mobilization of iron from chemical weathering of the crystalline source rocks. Moreover, the recorded gamma ray survey also support this trend, e.g. thorium increases in costal mudflat deposits representing more chemical weathered clays towards the top of the succession. A Th/U ratio less than 2 is caused by uranium fixation under reducing conditions whereas ratio values greater than 7 implying uranium mobilization through weathering and/or possible terrestrial environments. Together with the field observations this supports the assumption that the clay packages in the lower third of the top were deposited in a reducing, lacustrine environment. In contrast to the uppermost costal mudflats, here oxidizing conditions were dominant and the insoluble Th$^{4+}$ was enriched whereas the U$^{6+}$ could be mobilized.

Reference:

Basement brines are in many cases invoked to play a major role in the formation of various types of hydrothermal ore deposits, since they may contain appreciable amounts of dissolved base metals (e.g., Fe, Cu, Zn, Pb). Mixing of deep crustal brines with shallower formation or meteoric waters is thought to be the key for instantaneous mineral precipitation where these two fluid types encounter.

Those basement brines are globally characterized by high salinities (approximately 25 wt.%) and show in many cases distinct chemical signatures (e.g., Cl/Br, Na/Ca and Na/K ratios). Whether these signatures originated by rock-buffered water-rock interaction within the basement itself or if they are inherited from shallower/earlier processes is still poorly constrained and widely discussed. Another important aspect of this study concerns the provenance of metals in such fluids, which were involved in basement-related hydrothermal ore deposits.

To investigate the potential of typical basement-rocks as fluid buffers and metal source, leaching experiments on different rock types from the crystalline basement of the Schwarzwald were carried out. Three different lithologies including granite, orthogneiss and paragneiss as representatives for typical basement rocks were used. For each lithology two different grain fractions (63-125 µm and 2-4 mm) were leached in ultrapure MilliQ-water for durations between 1 minute and 4 weeks at 25°C. Major cations and anions were analysed using ion chromatography and alkalinity titrimetry was used to quantify dissolved carbonate. Trace metals were analysed using Total Reflection X-ray Fluorescence.

The absolute concentrations and the relative abundances of the major cations and anions depend on the used grain fraction. Concentrations of Ca, Mg and SO\textsubscript{4} are independent of the used grain fraction, while Na, K, Cl and F show elevated initial concentrations in the leachates were the fine fraction was used. Element concentrations still increase after leaching durations of 26 days indicating that equilibrium conditions were not yet obtained. Our preliminary data show that Cl/Br ratios (by weight) in the leachates lie between 55 and 110 and are not a function of time. In contrast, other chemical ratios (e.g. Cl/F, Na/Ca and Na/K) display systematic variations with time. We intend to carry out further experiments testing the efficiency of base metal mobilization under variable experimental conditions (e.g., pH, temperature and initial salinity of the leachates). Additionally, mineral separates (mica, feldspar, sulphides) will be used instead of whole-rock powder to identify the source and the process of metal mobilization by water-rock interaction in detail.
Fe-bearing carbonates in the Earth’s lower mantle

Valerio Cerantola - valerio.cerantola@uni-bayreuth.de
Catherine McCammon – catherine.mccammon@uni-bayreuth.de
Leonid Dubrovinsky – leonid.dubrovinsky@uni-bayreuth.de
Bayerisches Geoinstitut, University of Bayreuth, Germany

Recent studies showed Fe-bearing carbonates to be potential carbon carriers down to the deep lower mantle. Indeed, the presence of iron influences the stability of these phases at high pressures and high temperatures (HPHT), partly due to the spin-pairing of Fe-d electrons. The high-spin (HS) to low-spin (LS) transition is responsible for a net volume decrease of the carbonate phases, affecting the elements partitioning between them and the main mantle components. Our goal is to identify which phases may be the dominant carriers of carbon into the deep mantle at the relevant conditions of oxygen fugacity, pressure and temperature. To perform our experiments, we achieve HPHT conditions using externally heated or laser heated diamond anvil cells, which enable us to reach pressures and temperatures down to the core-mantle boundary. Our studies involve in situ and ex situ analyses on carbonates using X-ray diffraction, Mössbauer, Raman, XANES and IR spectroscopies. Samples analyzed after quenching to room P and T are also investigated using SEM, electron microprobe, and TEM. Carbonate solid solutions are enriched in $^{57}$Fe to ensure a strong signal for Mössbauer spectroscopy. Solid solutions are synthesized where the ratio between Fe and Mg is varied, starting from the pure Fe end-member FeCO$_3$ to the composition that is believed to be representative for carbonates in the lower mantle, Mg$_{0.9}$Fe$_{0.1}$CO$_3$. Also the presence of Ca must be taken into account. Indeed, the effect of Ca on the redox stability of iron-bearing carbonates at HPHT is still unknown. Recent results on siderite (FeCO$_3$) at HP and RT using Mössbauer and Raman spectroscopy confirmed the spin crossover of iron between 40-48 GPa. The quadrupole doublet of Fe (octahedral coordination) becomes a singlet after the spin transition. This behaviour was expected and already observed in ferropericlase (Fe,MgO), due to the reduction in the splitting of the energy levels in the Fe-d shell. Moreover, Raman spectra showed the loss of the external vibration at 200 cm$^{-1}$ (RP) after the spin transition, which is consistent with a slight structural change between Fe and the CO$_3^{2-}$ ions, which may induce a change in the polarizability. We are currently investigating the phase stability of Fe-bearing carbonates at lower mantle conditions using X-ray single crystal diffraction, Mössbauer and Raman spectroscopy. The presentation will focus on our most recent results.
Melt inclusions in migmatites and granulites

Bernardo Cesare

1 Department of Geosciences, University of Padova, Italy, bernardo.cesare@unipd.it

The study of melt inclusions is a recent, small-scale approach to a better understanding of melting in the continental crust. It builds on the discovery of glassy inclusions and their crystallized counterparts (nanogranites) in garnet and other host minerals from anatectic crustal enclaves in lavas and from regional migmatites and granulites.

Produced by an incongruent melting reaction, e.g., Bt+Sil+Pl+Qtz=Grt+liquid±Kfs, a growing peritectic phase (i.e. garnet) can trap droplets of the anatectic melt that is being formed by the same reaction. Hence, anatectic melt inclusions are trapped during the prograde history of magma formation and, therefore, they differ from the “classic” inclusions found in minerals from igneous rocks, that are trapped during magma crystallization upon cooling.

As the composition of anatectic inclusions is representative of that of the bulk melt in the system during crustal melting, these tiny objects (rarely exceeding 15 μm) represent embryos of anatectic granites. With an appropriate characterization and analytical strategy they can provide the missing information on the primary composition of natural crustal melts before they undergo modification processes such as cumulus, fractional crystallization, mixing or entrainment of exotic material.

In slowly cooled, regional migmatites, melt inclusions are generally completely crystallized as nanogranite: a cryptocrystalline aggregate of quartz, feldspars and micas. After the first discovery in the granulites of the Kerala Khondalite Belt (India), in the last decade we have studied inclusions from a dozen of occurrences worldwide: while glassy inclusions can be directly analysed with minimal sample preparation, nanogranites need to be remelted to a homogeneous liquid and then quenched. Such remelting is achieved in a piston cylinder apparatus, to prevent the decrepitation of inclusions and loss of volatiles.

We have analysed inclusions for major and trace elements, and also for H₂O: the melts are all leucogranitic and peraluminous, but show important variations in normative Qtz-Ab-Or proportions, as well as in H₂O contents, and generally differ from minimum melts.

Since H₂O is one of the main parameters determining melt viscosities and, in turn, the strength of partially melted rocks, the characterization of the fluid contents of nanogranites provides more realistic constraints to the rheological behaviour of the deep crust, and to the timescales of melt extraction from it, and allows better constrained numerical modelling.

Melt inclusions have opened new perspectives both for the microstructural approach to partially melted rocks and for the chemical characterization of natural crustal melts. These perspectives can now be transferred to different systems (e.g. mafic protoliths) and different settings (e.g. subduction zones and melting at HP conditions).
Empirical equation on minimum water content of a ryolitic melt as a function of temperature and pressure

Jakub Ciazela, Francois Holtz

1jakub.ciazela@gmail.com
2f.holtz@mineralogie.uni-hannover.de

Water content influences the composition and the amount of first melt generated during partial melting. In crustal melting processes, one main source of water comes from the hydrous mineral phases such as muscovite or biotite and melting is often assumed to occur as a result of dehydration reactions (fluid-absent dehydration melting). In such fluid-absent melting conditions and at a given pressure, the water content in melts coexisting with quartz and feldspar (eutectic melt) is dependent on the temperature at which dehydration melting occurs. This minimum water content decreases with the temperature of dehydration melting. Thus, the temperature, the minimum water content of melts and the amount of hydrous minerals which break down will control the melt fraction in crustal systems, if the role of external fluids is neglected.

The effect of temperature on the amount of water in silicate melts at fluid-absent conditions was determined experimentally by Holtz et al. (2001) for the synthetic Qz-Ab-Or system at selected pressures. Based on that work, we provide in this study an empirical equation, which is predicting the minimum water content of ryolitic melt:

\[
H_2O \text{ wt\%} = -0.38\sqrt{(T - 640)} + 0.216P \\
+ (7 \times 10^{-5}) (T - 640)^2 + 0.01(T - 640) + 3.1(0.018P^2 + 0.26P) + 6.68
\]

with P given in kbar and T given in °C. The equation is valid for the temperature range 641-1150 °C and the pressure range 0.12 - 10 kbar. The predicted water content can be as high as 11% H_2O at high pressure and low temperature. The estimated error of the equation relative to the experimental data is 0.1 H_2O wt%. In the low temperature field, the validity of the equation is constrained by the water-saturated solidus curve since melt cannot exist below this curve.

The equation is useful for many petrological applications. It can be used to estimate the melt fraction in rocks in case of fluid-absent melting conditions (if pressure and temperature are known). For example, a quartzo-feldspathic gneiss containing 10 wt% muscovite (containing 4 wt% H_2O) undergoing muscovite dehydration melting at 750°C and 500 MPa is expected to produce 7.2 wt% melt. On the other hand, the same rock containing 10 wt% biotite (containing 3.5 wt% H_2O) will only melt at ~ 850 °C and is expected to produce ~ 10.3 wt% melt. The equation can also be used to constrain the water content of eutectic melts generated at fluid-present conditions, if the fluid is composed of water only. It is emphasized that the established relation cannot be used to predict the H_2O content of melt coexisting with a mixed fluid phase composed for example of H_2O and CO_2. However, the equation is useful to constrain the water content of melts coexisting with mixed fluids at conditions just above the solidus.

Flow, transport, and reactions in pores and fractures – the remarkable and uncertain world of crustal fluid rock interaction

Christoph Clauser¹, Gabriele Marquart¹, Christian Vogt¹, Christian Kosack¹,², Wolfgang Rabbel³, Eva Szalaiova³

Institute for Applied Geophysics and Geothermal Energy, E.ON Energy Research Center, RWTH Aachen University, Germany, cclauser, gmarquart, cvogt @eonerc.rwth-aachen.de

²E.ON Gas Storage GmbH, Essen, Germany, christian.kosack@eon-gas-storage.com

³Christian-Albrechts-Universität Kiel, Germany, wrabbel@geophysik.uni-kiel.de

Assessment of heat and species transport in the subsurface often – if not always – requires understanding the nature of subsurface flow systems. These may occur in pore or fracture networks, individual larger fractures, or a combination of both. Accordingly, different flow laws may apply. However, the geometry of flow paths and their individual contribution is most always poorly known. A well-established way for approaching this uncertainty is upscaling and analyzing the integral effect of smaller structures. An alternative approach is provided by stochastic models which propagate the uncertainty in input data into an uncertainty of the prognostic variables.

Case studies in sedimentary and hard rock reservoirs illustrate the benefits and limitations of the applied Monte Carlo, Bayesian, and Ensemble Kalman Filter approaches. Highlights presented are

– a successful pre-drilling temperature prediction for a sedimentary basin at a depth of 2 500 m;
– the reduction of the uncertainty of a temperature prediction in a sedimentary reservoir at a depth of 4 500 m to one quarter of the a priori value;
– the successful fit of a tracer curve in fractured bedrock and derivation of a plausible distribution of hydraulic permeability;
– derivation of fracture permeability in basement rock from 3-D reflection seismics and appraisal of its suitability for geothermal power production.
Upper-crustal kinematics of continental plateau formation in the southern Central Andes inferred from fault-slip analysis

Heidi Daxberger¹, Ulrich Riller²

¹daxberh@mcmaster.ca
²ulrich.riller@uni-hamburg.de

Elucidating the tectono-morphologic evolution of the Central Andes is important for understanding the mechanical behavior of non-collisional orogens at convergent plate boundaries. Fault-kinematic data from the southern Central Andes are generally interpreted in terms of changes in plate (boundary) kinematics or vertical-axis rotation associated with the formation of the Andean orocline. However, none of these hypotheses accounts adequately for Neogene to Recent horizontal extension and vertical shortening of upper crust documented from the Puna Plateau and the adjacent Eastern Cordillera. Based on new and compiled fault-kinematic data, in total 4746 brittle faults at 317 stations, we propose that strain axis configurations in the southern Central Andes are controlled by (1) local deformation kinematics, (2) overall WNW-ESE horizontal shortening imposed by plate convergence and (3) differences in crustal thickness and respective surface elevation, i.e., gravitational potential energy. Specifically, the Puna Plateau and Eastern Cordillera have been undergoing horizontal shortening and gravitational spreading of upper crust, whereas the topographically lower Pampean Ranges continue to undergo horizontal shortening only. Although less apparent in the fault-kinematic data than E-W and NW-SE extension, orogen-parallel extension is inherent to the Puna Plateau and Eastern Cordillera and compensates likely for overall WNW-ESE shortening of thickened crust. The importance of orogen-parallel extension in the kinematics of topographically elevated parts of the southern Central Andes is underscored by the strike-slip components on prominent reverse or thrust faults. The data supports geodynamic interpretations in which topography and crustal thickness influence significantly upper-crustal kinematics of the southern Central Andes.
Metal mobility in hydrothermal fluids: experimental investigations and analytical advances

I. T. Derrey*, M. Albrecht, R. E. Botcharnikov, I. Horn, S. Weyer And F. Holtz

Institut für Mineralogie, Leibniz Universität Hannover, Germany (*correspondence: i.derrey@mineralogie.uni-hannover.de)

Hydrothermal fluids are crucial in the formation of ore deposits, as they are the main transport medium leading to the selective concentration of elements in the Earth’s crust and, among others, metals of economic interest. Fluid inclusions in minerals do not just enable us to probe natural fluids from depth, but also provide an opportunity to investigate fluids in high P/T experiments [1]. With the development of LA-ICP-MS techniques it has become possible to analyze major, minor and trace element concentrations in fluid inclusions [2].

Thus, synthetic fluid inclusion studies are an ideal tool to study metal transport and partitioning in hydrothermal fluids and to provide key data necessary for the quantification of transport properties. Partly due to difficulties in producing decent sized synthetic fluid inclusions at low temperatures, previous studies were mostly focused on conditions above. By combining the two current methods of host mineral pretreatment (thermal cracking [1] and HF etching [3]), we are able to synthesize fluid inclusions in quartz with a size in excess of 20 µm at T down to at least 400 °C. This gives us the opportunity to study the conditions and processes responsible for the mobility of metals at low temperatures. Experiments are conducted in cold seal pressure vessels at T=400-800 °C and P up to 200 MPa with the aim to unravel the transport and partitioning of metals occurring in granite related ore deposits.

We have been implementing a new technique to analyze fluid inclusions by LA-ICP-MS, which is based on the combination of a femtosecond laser with a sectorfield ICP-MS. We are able to successfully analyze fluid inclusions in excess of 10µm up to a depth of ca. 50µm in quartz with a success rate of ca. 75%. The analytical error is <20% for the investigated elements. We are further testing a method to extend the signal length of the inclusion by freezing the fluid in a heating-freezing cell during the ablation. The inclusion remains frozen until entirely evaporated, resulting in a considerably longer signal time. This might allow us to further reduce the analytical error on the analyzed element concentrations.

Results for Au, Mo and W solubility in fluids of varying composition obtained at different P, T, fO₂ and fS₂ will be presented.

Development of the deep geothermal project Geretsried-North and results of the first well, GEN-1

Sebastian Dirner¹, Dr. Franz Boehm², Alexandros Savvatis³

¹dirner@erdwerk.com
²boehm@erdwerk.com
³savvatis@erdwerk.com

The deep geothermal project “Geretsried-North” is located south of Munich between the towns Wolfratshausen and Geretsried. It is planned to produce thermal water with a doublet, for power generation and district heating. The first well GEN-1, with a planned depth of almost 5.000 m TVD and 6.000 m MD is one of the deepest geothermal wells currently drilled in the German Molasse basin. The upper Jurassic Malm carbonates with a thickness of up to 500 - 600 m represent the thermal reservoir. It is planned to drill the reservoir with a 1.400 m long and highly deviated well. In July to August 2013 the well will be completed with an extensive borehole logging program within the reservoir section and a sub-sequent short term production test.

In preparation of the drilling, a reservoir model was set-up on the basis of a new 3D-seismic and promising drilling-targets were identified. The Malm is a highly heterogeneous reservoir and can be differentiated from seismic data into swells (reef facies) and troughs (lagoonal facies). For the identification of reefal- and lagoonal facies seismic texture analysis, reflector termination and a variety of seismic attributes were utilized.

Geothermal wells drilled on a reef complex show a higher productivity than wells drilled on a lagoonal trough. Recent research on the basis of 16 geothermal wells in the greater area on Munich postulates, that reef complexes are more prone to dolomitization- and karstification processes, hence developing favorable reservoir characteristics.
Provenance indications of detrital zircon from metasedimentary rocks of the Zábřeh Crystalline Complex and the Mirov "Culm" in the northeastern Bohemian Massif

Kerstin Drost¹, Jan Košler², Jiří Konopásek²

¹ Department of Geoscience, Eberhard Karls University Tübingen, Wilhelmstr. 56, 72074 Tübingen, Germany, kerstin.drost@uni-tuebingen.de
² Department of Earth Science and Centre for Geobiology, University of Bergen, Allégaten 41, 5007 Bergen, Norway

The Zábřeh Crystalline Complex is situated in the northeastern Bohemian Massif, where several crustal domains (Moldanubian Zone, Saxothuringian Zone/Lugicum, Teplá-Barrandian unit, Moravo-Silesian Zone) are juxtaposed. The Zábřeh Crystalline Complex is made up of variably metamorphosed volcanosedimentary successions and intrusives and overlain by diastrophic Givetian to ?Lower Carboniferous sedimentary rocks of the Mohelnice Formation (Mirov "Culm"). The nature of the contact between basement and overlying siliciclastic rocks of the Mohelnice Formation are not quite clear; both an angular unconformity and a tectonic contact have been discussed. The siliciclastic rocks of the Mohelnice Formation were interpreted to be derived from equivalents of the underlying volcanosedimentary successions.

Two samples of siliciclastic rocks were taken in order to analyse detrital zircon age spectra and Hf isotope compositions of detrital zircon grains by LA-ICP-MS and LA-MC-ICP-MS, respectively: one fine-grained metagreywacke from the southern part of the Zábřeh Crystalline Complex and one conglomerate from the overlying Mohelnice Formation. The results allow comparisons among both samples and with data from the surrounding crustal domains.

Despite of the small overall grain size of the metagreywacke sample both samples yielded zircon grains of up to >300µm length. Detrital zircon age spectra are plainly overlapping but with distinct differences in the abundance of the individual age groups as well as in the ages of the youngest grains. Zircon from the metagreywacke sample of the Zábřeh Crystalline Complex comprises 39% Neoproterozoic ages that are chiefly Ediacaran but not younger than ~570Ma. A huge proportion of the analysed grains gave Paleoproterozoic (41%) and Archean (20%) ages. In contrast the conglomerate sample from the Mohelnice Formation yielded 9% Early Paleozoic zircon grains with the youngest age being 480±15Ma. Neoproterozoic - mostly Ediacaran - detritus makes up 55%. One Mesoproterozoic grain was found. Paleoproterozoic ages are frequent (33%), but Archean ages are rare (2%).

According to the U-Pb dating results an affinity with the Moldanubian Zone and the Teplá-Barrandian unit can be expected for both sampled units. However, a relationship with the Saxothuringian Zone/Lugicum is not impossible too. In contrast an affinity with the Moravosilesian Zone is unlikely for both sampled units because Pre-Neoproterozoic detrital zircon age spectra do not match. The rocks of the Mohelnice Formation may in part have been derived from equivalents of the rocks of the Zábřeh Crystalline Complex.
New mineral-chemical evidence for the epigenetic formation of the REE mineralization in the Blackbird district, Idaho, USA

M. Duchoslav¹, T. Wenzel¹, J. Slack², R. Mertz³, G. Markl¹

¹Eberhard Karls Universität Tübingen, Mathematisch-Naturwissenschaftliche Fakultät, FB Geowissenschaften, Wilhelmstrasse 56, D-72074 Tübingen, Germany
(*correspondence: Marguerita.duchoslav@student.uni-tuebingen.de)
²U.S. Geological Survey National Center, 12201 Sunrise Valley Dr., MS 954, Reston, VA 20192 U.S.A., jfslack@usgs.gov
³Johannes Gutenberg Universität Mainz, Institut für Geowissenschaften, Johann-Joachim-Becher-Weg 21, 55099 Mainz, Germany, mertzrc@uni-mainz.de

The Blackbird district in east-central Idaho (USA) is classically referred to as a Co-Cu-Au deposit locally enriched in Bi and Ni. This ore deposit consists of multiply metamorphosed Mesoproterozoic stratabound veins within sedimentary units in the vicinity of Mesoproterozoic to Eocene intrusions. Based on recently discovered high whole-rock contents of REEs (up to 3.66 wt.%), especially MREEs and HREEs, this district attracts special attention.

Two syngenetic models (Mesoproterozoic VMS, SEDEX) and two epigenetic models (Mesoproterozoic IOCG, Cretaceous metamorphic) have been proposed. The first two models infer ore formation coeval with sedimentation, either by volcanogenic or sedimentary-exhalative mineralization. According to the IOCG-model, this deposit formed distal from Mesoproterozoic granitic intrusion by magmatic-hydrothermal and basin-derived fluids. The last model attributes ore formation to Cretaceous metamorphic fluids.

REEs mainly reside in xenotime (Xnt), monazite (Mnz), gadolinite (Gad), and allanite (Aln). The many different textures of Xnt include patchy, concentric, and oscillatory zoned, as well as brecciated and re-cemented grains in addition to inclusions within Mnz and Py (pyrite) and unzoned grains in different mineral associations. Hence, there are at least four different generations of Xnt to distinguish.

All textural varieties of the REE minerals were analyzed by EMPA (REEs + Y, Si, Ca, P, Al, Fe, Mn, Mg, Ti) and LA-ICP-MS (REEs + Y, P, Si, Co, Cu, As, Bi, Pb, U, Th) in order to better understand the formation processes of the Blackbird district deposits and the contained REE mineralization.

Our results indicate that the few different textures of Mnz with very similar REE patterns are strongly enriched in LREEs (La/Yb = 687.6) with slightly different negative Eu anomalies (log Eu* 0.77 to -0.13). In contrast, much more abundant Xnt shows distinct variations in REE patterns with strong enrichment in HREEs (La/Yb = 0.0008), negative to almost no Eu* (log Eu* 0.79 to -0.09), and a Y/Ho ratio between 0.72 and 1.04.

The high REE contents of the Blackbird deposits are not indicative of the syngenetic models. The different zoning features suggest more than one mineralizing event. Based on the presence of cobaltite inclusions within early growth zones of Xnt, the IOCG model is considered more likely than the other models.
Theriak_D is a new add-on of the open source Theriak/Domino software package. The package provides a wide range of thermodynamic equilibrium calculations and illustration facilities (de Capitani & Petrakakis, 2010), based on the Gibbs free energy minimization (de Capitani & Brown, 1987), but is restricted to its own environment. The Theriak_D add-on allows the user to process thermodynamic data, calculated by Theriak/Domino, outside the package. Thus, the add-on provides the opportunity to calculate thermodynamic properties within every programming environment like MATLAB® or SCILAB®, calling up Theriak/Domino within a script. The tool allows the user to compute chemical and physical parameters (like the solid rock density/volume/weight, the amount of free fluids or the molar amount of stable mineral phases) along any pressure–temperature (P-T) path or P-T grid. To demonstrate the applicability, an example is given in which the solid rock density, the amount of free fluids and the molar amount of garnet is calculated of a 2D-temperature-pressure grid, portraying a simplified subduction zone. In this way, the use of Theriak_D opens up thermodynamics to people with only a basic knowledge of phase diagrams and similar thermodynamic illustration techniques, e.g. by illustrating thermodynamic properties in a more familiar setting like subduction zones. As a result, the tool will hopefully support other ideas combining thermodynamics and geodynamic models and can be used for a variety of purposes.

This presentation introduces Theriak_D and includes typical examples of its functionality. The Theriak_D add-on is still under development and will soon be freely available online.
Cyclic variations in climate such as glacial-interglacial cycles strongly influence the dynamics and character of sedimentary processes in alpine landscapes. For example, shifts from aggradation to incision can be associated with changes in the overall climate conditions and the resulting fluctuations in the amount of sediment supply. Possible mechanisms for such swings in sediment input include variations in sediment production from the alpine headwaters, driven by modulation of glacial extent and glacial erosivity, and variations in the weathering and soil production rates in the subalpine catchments controlled by swings in temperature and precipitation.

Here, we use data from the Colorado Front Range to demonstrate how glacier fluctuations control the sediment supply to the fluvial system and the range-bounding basin. We explore the spatial pattern of sediment transport from the glacial headwaters to the adjacent basin and establish the timing of basin incision.

Our results show that sediment transport rates vary greatly through time leading to nonlinear basin incision rates. It appears that incision rates are related to glacial-interglacial cycles with high sediment input to the fluvial system during glacial times and a reduced sediment input during interglacial times.
Relationship between seawater density and cold-water coral carbonate mounds in the northeast Atlantic through time

Wolf-Christian Dullo¹, Andres Rüggeberg², Sascha Flögel³, Jacek Raddatz⁴, Volker Liebetrau⁵

¹cdullo@geomar.de
²arueggeberg@geomar.de
³sfloege@geomar.de
⁴jraddatz@geomar.de
⁵vliebetrau@geomar.de

Cold-water coral reefs are marine benthic ecosystems that act as important hot spots of biodiversity and living resources. They are at risk due to ongoing global environmental change. In the NE Atlantic, the reefs form giant coral carbonate mound structures of several hundred meters of elevation. The development of these coral carbonate mounds is paced by Northern Hemisphere climate variability, from about 2.7 Ma onwards. In this study we demonstrate that cold-water coral ecosystems only thrive under specific oceanographic conditions, among which seawater density plays an important role. Paleo-seawater densities are reconstructed for two different NE Atlantic coral carbonate mounds, Challenger Mound (Belgica Mound Province, IODP Expedition 307) and Propeller Mound (Hovland Mound Province), based on oxygen isotope ratios in benthic foraminifera. Our results indicate that the development of coral carbonate mounds is closely linked to mid-depth bottom water densities. Thriving coral growth is predominantly found at seawater densities (sigma-theta, σΘ) between 27.2 and 27.7 kg m⁻³. Comparable to present-day conditions, we interpret the reconstructed density envelope as a pycnocline serving as boundary layer, on which horizontal currents develop carrying nutrients and possibly enabling the distribution of larvae. The reconstruction of seawater density highlights the importance of pycnoclines as a controlling factor favoring coral carbonate mound growth. Furthermore, it provides a tool to study the sensitivity of these ecosystems with respect to environmental changes and has potential in paleoceanographic reconstructions of water-mass dynamics. These results will be discussed further applying modeling results of the paleo-bathymetry of the pycnocline.
Nano-scale Element and Isotope Analysis for Interface Characterization and Dating with APT

U. Ehrke¹, R. Ulfig², D. Larson³, T. Kelly⁴, D. Lawrence⁵, D. Olson⁶, D. Snoeyenbos⁷, and J. Valley⁸

¹Ulrich.Ehrke@ametek.com
²Robert.Ulfig@ametek.com
³David.Larson@ametek.com
⁴Thomas.Kelly@ametek.com
⁵Dan.Lawrence@ametek.com
⁶David.Olson@ametek.com
⁷Kyanite@mac.com
⁸Valley@geology.wisc.edu

Atom probe tomography (APT) can determine chemical identity (mass/charge ratio) and 3D position of individual atoms in metals, semiconductors, dielectrics, and composite materials including minerals with sub-nanometer resolution. Recently, this unique capability has been applied to geological applications and the 3D chemical and spatial information has provided new insights into the age and thermal history of minerals.

SIMS (IMS-1280) analysis was used to identify and age a 2.4Ga Albion-Raft R-Grouse Ck core complex, Utah, (Strickland et al. 2011). Higher spatial resolution analysis with APT (LEAP 4000X HR™) was used to demonstrate that incompatible elements, including Pb and Y, were concentrated in ~5-10nm diameter domains, spaced ~50 nm apart, while U is homogeneously distributed[1]. The analyzed domains suffered 4-8 x 10¹⁵ α-decay events/mg due to U and Th decay and yet the zircon analyzed was found to be >97% concordant (U-Pb ages) by SIMS, suggesting annealing of radiation damage during the life of the zircons. The 207Pb/206Pb ratios for these nm-scale domains, as measured by APT, average 0.17, in good agreement to the previous SIMS analysis, thus Pb in this particular zircon is radiogenic. The implications of these findings will be discussed.

In a compositional interface in a natural zircon crystal [(Zr,Hf)SiO₄], a region of the specimen with an unusual concentration of rare earth elements was mapped for Th by SX5 FE-EPMA (7kV, 100nA) to reveal the surface position of this otherwise cryptic feature of interest. Superposition of the mapping data on a BSE image of the specimen guided the specific site selection for FIB-based specimen preparation for APT analysis. The feature of interest was successfully captured within a 100nm long APT analysis, and the Th Mα signal observed by EPMA was found to emerge from a 25nm thick band containing 0.2at% Th. The other rare earths included an inhomogeneous distribution of U, Y along with P, and Al and subnanometer compositional analysis revealed this interface to be a core/overgrowth fossil resorption front[2].

A synergy has been found between FE-EPMA, SIMS and APT, especially in these geological applications, to identify regions of scientific interest and then use the nano-scale 3D information to help date and detail giga-year geological events.

The Mesoproterozoic basement of the Mount Painter Inlier (South Australia) consists of metasedimentary rocks and A-type granites. Both units occasionally contain meter-sized patches or layers dominated by highly aluminous minerals such as phlogopite with corundum, spinel, sillimanite, cordierite or sapphirine. Quartz is not present in the assemblage. Zircon, monazite and anatase/rutile are common accessory phases, whereas hogbömite is rare.

The zircon population in the hyperaluminous lithologies found within the granitoids has the same age and Hf isotopic distribution as the zircons found within the granitoids themselves. It is therefore likely that desilication is the petrogenetic process responsible for the formation of the hyperaluminous rocks. Zircon data, in combination with major element trends, point towards mafic dykes being the precursor to the hyperaluminous rocks found within the metasediments. The spatial distribution of the hyperaluminous rocks argues against their interpretation as a palaeosol, as is often assumed in the case of highly aluminous rocks.

Isocon diagrams indicate significant mass loss during desilication, mainly represented by loss of SiO$_2$, CaO and Na$_2$O, while K$_2$O and MgO increased.

The range in mineralogical assemblages can be shown to be dominantly controlled by variations in the activity of SiO$_2$, MgO and K$_2$O. Petrographic observations, such as the relic presence of diaspore, seem to indicate that desilication took place at relatively low temperature, and that metamorphism was a later event. Dating of monazite and zircon rims indicates new growth of these minerals around 460-500 Ma, which we interpret to reflect high-temperature metamorphism. The prior desilication event could therefore have happened during the development of the Adelaide Rift Sequence in the Neoproterozoic, with hydrothermal fluxing of seawater through the Mesoproterozoic basement.
New frontiers: exploration of the geothermal Malm reservoir below folded Molasse and alpine thrusts south of Munich

Elsner, M. ¹ and Böhm, F. ²

¹martin_elsner@gmx.de
²boehm@erdwerk.com

Late Jurassic carbonates, the ‘Malm’, are the most important reservoir for hydrothermal resources in the North Alpine Foreland Basin. Dipping gently southwards, their top reaches a depth of 5.000 m at the northern margin of the alps. In the area of greater Munich (Bavaria, Germany), located in the center of the basin, the depth of the reservoir is between 2.000 m north of the city and 4.000 m south of it. The Malm reservoir here is covered by rocks of Cretaceous age, which reach from regressive, locally evaporitic sediments (Purbeck, Berriasian) to glauconitic shelf sands (Aptian to ?Cenomanian) and highstand marls (Cenomanian to Turonian). [Anzahl] projects have been carried out since [Jahr; wann gings los? Riem?] either for heating only or for both, production of electricity and heating. So far, both the geological understanding of the reservoir and the drilling capabilities increased. Thus, new claims are lying increasingly close to the alps, where a higher depth of the reservoir stands for a higher temperature, but also for higher risks during exploration and drilling. To eliminate risks regarding depth, structure, facies and stratigraphy of the Cretaceous overburden of the reservoir, it is necessary to evaluate information not only from the two deep drillings in the region (Staffelsee 1 and Miesbach 1), but also from allochthonous alpine nappes of the Helvetic unit.

Towards the south, the thickness of the Cretaceous overburden becomes considerably higher, and stratigraphic gaps are less frequent and smaller. In addition, the facies changes gradually to the Helvetic facies known from the allochthonous Helvetic nappes. Here, the Berriasian does not contain evaporates as farther north, but consists of marls and limestones containing quartz detritus, indicating lowstand conditions. Within the Valanginian and Hauterivian, oolitic limestones have been proved; they may be hydraulically connected to the Malm and form part of the reservoir. The Barrêmeian and early Aptian consists of argillaceous marls (Drusbergschichten) and the Schrattenkalk unit – a shallow water limestone consisting of bioclasts and ooids. It was karstified during exposure prior to deposition of the next unit, the greensands of the Garschella Formation (late Aptian to Albian). Pelagic limestones of the Seewen Kalk (Cenomanian to early Turonian) form the next higher unit, which is covered by argillaceous marls and greensands of the late Turonian.

Regarding the depth of the reservoir, a significant increase of the dip has not been observed; thus it can be assumed to dip consistently under the alpine thrust pile. However, the synthetic and antithetic faults dominating the structure in the foreland give way to reverse faults and minor thrusts.

Most important consequences for exploration are the possible extension of the Malm reservoir towards overlying strata of early Cretaceous age. The seismic reflector of top Purbeck thus may lose its importance for exploration and drilling. For planning wells, the presence of permeable Schrattenkalk needs to be identified in seismic surveys, as here a loss of drilling fluids is possibly. The underlying Drusbergschichten are better off behind the casing, before drilling into the reservoir that may cover early Cretaceous intervals.
Spatial and temporal variation in rock exhumation in the St. Elias Mountains: Insights from multiple thermochronometer techniques.

Eva Enkelmann¹

¹eva.enkelmann@uc.edu

Department of Geology, University of Cincinnati, 500 Geology-Physics Building, Cincinnati, OH, 45221, USA

The Yakutat – North American collision zone in southeast Alaska is one of the most active tectonic regions on Earth and formed the highest coastal mountain range – the St. Elias Mountains. Large ice fields and glaciers cover more then 50 % of this regions surface and shape the landscape by actively eroding material that is transported into the Gulf of Alaska. The St. Elias Range is an excellent natural laboratory to study interaction between surface and tectonic processes and has attracted many scientists that generated a large dataset of geophysical and geological observations. Various geo- and thermochronometric ages derived from bedrock and detrital material have been produced over the past 15 years, revealing the complex pattern of differential rock exhumation across the orogen. The rock exhumation correlates with structures as well as with climatic patterns, but the syntactical region of the St. Elias Mountains, where the Yakutat plate corner is colliding and strike-slip motion transients into convergence, stands out as it reveals the most rapid and deep exhumation then elsewhere in the region.

New thermochronometric results from the St. Elias syntaxis region are presented that give evidence for a larger region of rapid and deep-seated exhumation then previously known. Based on these new data we evaluate various exhumation models that have been proposed for the St. Elias, and compare the observational data with those from the eastern and western Himalayan syntaxes. Endogen processes appear to be the main driver for the exhumation pattern, but a strong interaction with surface processes is also observed. Efficient glacial erosion and evacuation of material results in differential exhumation rates recorded by the exposed bedrock on the mountain ridges and the detritus that originates from underneath the ice. These processes lead to a strong bias in the termochronological dataset, which make the St. Elias Mountains to a unique setting and challenge fore thermochronometric studies. Besides the information about rock exhumation as a result of the interplay between tectonic and surface processes, the dataset provides also insights about the removal, transport, and deposition of glacial material, which will guide future studies in other regions that are glaciated or have been glaciated in the past.
Temperature cycling as a powerful tool to enlarge melt pools and crystals in experiments

Martin Erdmann* and Jürgen Koepke

Institut für Mineralogie, Leibniz Universität Hannover, Callinstraße 3, 30167 Hannover, Germany

*corresponding author: m.erdmann@mineralogie.uni-hannover.de

Experiments in high silica systems at temperatures close to the solidus often show to small minerals and melt pools, leading to problems for in-situ analysis. Mills et al. (2011) showed that oscillating temperature during an experimental run speeds up recrystallization of a magma analog by dissolving small and enlarge larger crystals, dramatically changing the crystal size distribution. This principle is also believed to occur in nature, indicated by thermochronological data (e.g. Davis et al., 2011).

Here we show that temperature cycling has the potential to significantly enlarge melt pools and crystals in a fluid saturated andesitic system. In the framework of a detailed phase relation study with a natural andesitic sample from the Pacific Antarctic Rise, crystallization experiments applying temperature cycling were performed systematically for two different temperatures and different water activities. Internally heated pressure vessels were used for runs at 950°C (with $aH_2O=1, 0.5, 0$), cold seal pressure vessels for experiments at 800°C (with $aH_2O=1, 0.6$). Comparative experiments at equilibrium conditions with constant temperature were performed for both approaches. For all other experiments temperature was cycled with amplitudes of 20K for different time intervals but constant total run duration after initial equilibration at constant temperature. Additionally, for one experiment at 800°, the temperature was increased several times by 50K to study the potential to dissolve tiny crystals in the matrix.

Observed effects are striking, at least for silicate phases (i.e. clinopyroxene and plagioclase). Tiny crystals in the matrix are mainly dissolved, leading to large melt pools without mineral inclusions enabling microprobe analysis using a defocused beam. Clinopyroxene crystals are up to 5 times larger, plagioclase crystals even up to 10 times when comparing to experiments performed at constant temperature. Grain sizes of FeTi-oxide phases are less influenced by this technique. An essential requirement for applying this technique routinely is an identical phase composition in runs with constant and cycled temperature. For all studied temperatures and water activities the phase assemblage is the same and compositions of all phases are identical within the analytical error. Thus, the temperature cycling technique opens interesting perspectives, especially in facilitating in-situ analysis in near solidus systems.


Trace element contents of experimental hydrous partial melts from the MOR magma chamber roof: evidence for crustal contamination and felsic melt generation

Martin Erdmann\(^1\)*, Lennart A. Fischer\(^1\), Lydéric France\(^2\), Etienne Deloule\(^2\), and Jürgen Koepke\(^1\)

\(^1\)Institut für Mineralogie, Leibniz Universität Hannover, Callinstrasse 3, 30167 Hannover, Germany

\(^2\)CRPG; UMR 7358, CNRS; Université de Lorraine, 15 rue Notre Dame des Pauvres, 54501 Vandœuvre-lès-Nancy, France

*corresponding author: m.erdmann@mineralogie.uni-hannover.de

Felsic lithologies in the oceanic crust formed at fast spreading ridges occur commonly close to the base of the hydrothermally influenced sheeted dike complex and, thus, near to the axial magma chamber. To decipher the possible crustal processes that may be correlated to felsic melt generation such as fractional crystallization, partial melting, melt-rock interactions, and contamination, a detailed experimental study using six different natural samples from the lower part of the sheeted dike complex of the IODP site 1256 (East-Pacific Rise, EPR) was performed. In order to test the hypothesis that felsic lithologies at the dike/gabbro transition are of anatectic origin, we performed melting experiments using rock powder (125-200 μm) of the chosen starting materials under conditions similar to those prevailing at the base of the sheeted dike complex (i.e. 100 MPa, 910 to 1030°C, \(f\text{O}_2=\Delta\text{QFM}+1\)). The starting material varies from relatively fresh basalt with clinopyroxene, plagioclase and FeTi-oxides as primary magmatic phases, to highly hydrothermally altered basalts, to contact metamorphic overprinted basalts in granulite facies with characteristic granoblastic textures. While the major element compositions of the starting materials vary only slightly (e.g., Si\(_2\)O\(_4\) 48.56-51.53 wt%; Al\(_2\)O\(_3\) 12.07-14.95 wt%), trace element pattern of the whole rocks vary significantly from typical N-MORB to more depleted compositions. Especially the starting materials with granoblastic texture from the sheeted dike/gabbro transition are strongly depleted in the light rare earth elements (LREE) with a positive Eu anomaly implying that these rocks correspond to residues from a former partial melting event.

In order to test whether the generated melts have the potential to contaminate primary MORB by assimilating, trace element compositions of the melts were obtained by SIMS (CRPG, Nancy, France). Anatectic melts of experiments using fresh and altered basalts at temperatures \(\leq 970^\circ\text{C}\) match the compositions of natural dacies from the EPR in terms of major and trace elements. Low degree partial melting (< 20%) results in a significant enrichment in Zr-Hf, most distinctive for LREE, and in a depletion in Sr, Ti and V. Such melts have the potential to contaminate primary MORB significantly. The use of granoblastic basalts as starting material reveals at the same temperature a smaller degree of melting. Moreover, corresponding partial melts are much more depleted in incompatible trace elements with low potential to contaminate primary MORB.
Depositional effects on the molybdenum isotopic composition of carbonates

S. EROGLU, R. SCHOENBERG, N. BEUKES AND M. WILLE

suemeyya.eroglu@uni-tuebingen.de, schoenberg@ifg.uni-tuebingen.de, nbeukes@uj.ac.za, martin.wille@uni-tuebingen.de

The exact timing of changes in the redox state of Earth’s atmosphere and oceans, particularly around the 2.40–2.32 Ga great oxidation event (GOE), which marks the dramatic shift from reducing to oxidizing conditions, are a highly debated topic in Geosciences. Recent studies showed that variations in the isotopic composition of the redox-sensitive transition metal molybdenum in sedimentary archives are a suitable tool to constrain redox fluctuations of the atmosphere-hydrosphere system even before the GOE [1, 2].

In our study we are investigating the Transvaal Basin in South Africa, which contains one of the best preserved carbonate platforms of the Archaean. This platform, which was deposited shortly before the GOE between ~2.58 and 2.50 Ga, is very similar to modern tidal areas and is composed of alternating stromatolithic carbonates and shales [3]. Sedimentological features of the Transvaal Basin point to changing depositional environments, in particular the water depth, which influenced this organo-sedimentary precipitation of the carbonates, resulting in various types of lithified microbial mats.

Here, we determined the Mo concentration and δ⁹⁸/⁹⁵Mo values from Transvaal Basin samples and obtained very distinct Mo isotope signatures throughout the various formations of the platform. Our measurements confirm previous studies reporting heavy δ⁹⁸/⁹⁵Mo values of carbonates and black shales from the slope of the Griqualand West Basin in South Africa, which can be well-correlated to the Transvaal Basin [4, 5]. Most of the Transvaal carbonates are characterized by low Mo concentration of around 20 ppb and δ⁹⁸/⁹⁵Mo values ranging between +0.2 and +0.6‰. Some samples, however, show highly variable δ⁹⁸/⁹⁵Mo signatures between -0.7 and +1.4‰ on the cm-scale and indicate an influence of the depositional environment of the stromatolites on their Mo isotopic composition. Tidal flat shales from the Transvaal Basin yield concentrations between 0.6 and 1.7 ppm and δ⁹⁸/⁹⁵Mo values between +0.1 to +0.6‰. It has been shown that strong redox gradients develop within modern microbial mats [6], which could promote variable scavenging of the redox sensitive element Mo from seawater, possibly also depending on differences in the depositional environment, such as water depth. This observation might be an important aspect for future interpretation of Mo isotopic compositions of chemical sediments.

Investigations on metamorphic tourmalines

Ertl, A.¹, Henry, D.J.², Hughes, J.M.³, Giester, G.⁴, Meyer, H.-P.⁵, Körner, W.⁶, Schuster, R.⁷

¹andreas.ertl@a1.net
²dhenry@geol.lsu.edu
³jmhughes@uvm.edu
⁴gerald.giester@univie.ac.at
⁵hans-peter.meyer@geow.geow.uni-heidelberg.de
⁶wilfried.koerner@univie.ac.at
⁷ralf.schuster@geologie.ac.at

Approximately 40 tourmalines from metamorphic rocks, which experienced different metamorphic conditions (<150 to 750°C), were structurally and chemically investigated. In many cases also the whole rock chemistry of these samples, which contained the tourmalines, was determined. The lattice parameters vary from $a = 15.94$, $c = 7.16$ Å and $a = 15.93$, $c = 7.18$ Å up to $a = 16.03$, $c = 7.27$ Å. Usually, the Z site is occupied by Al and by significant amounts of Mg. Usually only tourmalines with $c \geq 7.21$ Å contain significant amounts Fe at the Z site (≥0.1 apfu). The highest amounts of Fe at the Z site (~0.7 apfu) was found in tourmalines with $c = 7.27$ Å. The average composition of crystals, used for structure determination, varies from 1.5-3.0 wt% Na₂O, ≤2.2 wt% CaO, 3-12 wt% FeO$_{\text{total}}$, 3-11 wt% MgO, ≤0.8 wt% MnO, 0.1-1.4 wt% TiO$_2$, 0.1-0.8 wt% F, and up to 0.3 wt% SrO, 0.1 wt% ZnO, 0.1 wt% NiO, 0.1 wt% K₂O and 0.2 wt% Cr₂O$_3$. Only two samples contained a highest amount of FeO (~15 wt% FeO$_{\text{total}}$) and the lowest amount of MgO (~0.4 wt%). With increasing metamorphic temperature conditions the tourmalines can contain higher amounts of Mg at the X site. Contrary, tourmalines which crystallized below 500°C contain only up to ~0.4 wt% CaO. It seems that the Ca content in tourmaline depends mainly on the temperature during crystallization and less on the whole rock chemistry. The amount of TiO$_2$ varies strongly in some crystals, but no clear trend between TiO$_2$ and the metamorphic grade was observed. Yet we are at the beginning of this extensive investigation and will hopefully find some more relationships between metamorphic conditions, crystal structural data and whole rock chemistry.
Tetrahedrally-coordinated Al in Mn-rich liddicoatite from a pegmatite-marble contact in the Austroalpine basement units

ANDREAS ERTL¹, EKKEHART TILLMANNS¹, RALF SCHUSTER², JOHN M. HUGHES³, HANS-PIETER MEYER⁴, THOMAS LUDWIG⁴ AND HEINRICH MALI⁵

¹Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Althanstrasse 14, 1090 Vienna, Austria andreas.ertl@a1.net, ekkehart.tillmanns@univie.ac.at

²Geologische Bundesanstalt, Neulinggasse 38, 1030 Vienna, Austria, Ralf.Schuster@geologie.ac.at

³Department of Geology, University of Vermont, Burlington, VT 05405, USA, jmhughes@uvm.edu.

⁴Institut für Geowissenschaften, Universität Heidelberg, Im Neuenheimer Feld 236, 69120 Heidelberg, Germany, hans-peter.meyer@geow.uni-heidelberg.de, thomas.ludwig@geow.uni-heidelberg.de

⁵Institut für Geowissenschaften, Montanuniversität Leoben, Peter Tunner-Strasse 5, 8700 Leoben, Austria, heinrich.mali@unileoben.ac.at

ABSTRACT

Light green tourmaline from the border zone of a pegmatite of the Austroalpine basement complex, from Altes Almhaus, Stubalpe, Styria, has been characterized by crystal structure determination and chemical analyses (EMPA, SIMS). A crystal structure refinement of this liddicoatite in combination with the chemical analyses gives the optimized formula

$$X(\text{Ca}_{0.51}\text{Na}_{0.43}\square_{0.06})Y(\text{Al}_{1.27}\text{Li}_{0.82}\text{Mn}^{2+}_{0.41}\text{Fe}^{2+}_{0.19}\text{Mg}_{0.02}\text{Zn}_{0.01}\text{Ti}^{4+}_{0.01}\square_{0.27})Z\text{Al}_6^T(\text{Si}_{5.72}\text{Al}_{0.28})\text{O}_{18}(\text{BO}_3)_3^V(\text{OH})_3^W[\text{F}_{0.58}(\text{OH})_{0.29}\text{O}_{0.13}],$$

with $a = 15.907(1)$, $c = 7.119(1)$ Å, $R = 0.018$. The <T-O> distance with 1.624 Å is consistent with ~0.28 apfu Al at the T site. This is the first verification of liddicoatite from Austria and the first verification of significant amounts of $^{[4]}\text{Al}$ in liddicoatite. The tourmaline- and spodumen-bearing pegmatite crosscuts a marble from where Ca was mobilized, which is also responsible for the crystallization of this Ca-rich tourmaline (liddicoatite). Usually tourmalines from the border zone of the pegmatites of the Rappold Complex were characterised as dravite (Ertl et al., 2010). Such pegmatites were formed by anatectic melting of mica schists and paragneisses in Permian time. These tourmalines, including this liddicoatite, crystallized from the pegmatitic melt, influenced by the metacarbonate and metapelitic host rocks. 

INDIRECT BIOMINERALIZATION OF GREEN RUST BY NITRATE-REDUCING BACTERIA IN THE PRESENCE OF Fe(II)

M. Etique¹, A. Zegeye², B. Grégoire³, C. Ruby⁴, F.P.A. Jorand⁵

¹marjorie.etique@univ-lorraine.fr
²asfaw.zegeye@univ-lorraine.fr
³brian.gregoire@
⁴christian.ruby@univ-lorraine.fr
⁵frederic.jorand@univ-lorraine.fr

The microbial activity of iron-oxidizing bacteria may have a major role on the geochemistry of the Earth’s crust by taking part in the biogeochemical cycle of iron under both oxic and anoxic conditions. Discovered over the last 20 years, they can gain energy from the ferrous iron oxidation in anoxic environments at neutral pH using Fe(II) as an electron donor. Amongst these, iron-oxidizing nitrate-reducing bacteria combine the oxidation of Fe(II) with the reduction of nitrate [1]. A variety of secondary iron minerals (SIM) can be formed during this process such as green rust (GR) – a layered Fe(II)-Fe(III) double hydroxides – recently identified as an intermediate compound during the oxidation of Fe(II) by the iron-oxidizing nitrate-reducing Acidovorax sp. strain BoFeN1 [2]. Due to their low solubility at neutral pH, these SIM precipitate rapidly in the immediate vicinity of cells leading to their encrustation which apparently limits further cell growth and Fe(II) oxidation. However, the parameters that control the formation of SIM have not yet been clearly defined as well as the contribution of nitrate and nitrite towards the oxidation of Fe(II), despite the fact that GR is known to be reactive with NO₃⁻ and NO₂⁻ [3].

Our work was dedicated to investigate nitrate-reducing bacteria under neutral pH and anoxic conditions with different Fe²⁺/NO₃⁻ ratios and cell densities. We actually shown that GR was produced even bacteria were not able to oxidize Fe(II) thereby suggesting that this secondary iron mineral is the result of the oxidation of ferrous iron by nitrite. Moreover, NO₂⁻ from the nitrate bioreduction is converted into NH₄⁺ by GR. Therefore, we can assume that GR’s reactivity towards nitrite could directly compete with the denitrification process.

That is why the formation of GR could result from iron-oxidizing as well as nitrate-reducing bacteria. This should have been accounted by now for the nitrogen and iron biogeochemical cycles.

Ferrihydrite, a poorly crystalline Fe oxyhydroxide, is known to be highly reactive towards soil organic matter (OM). The interaction with OM may affect crystal size, aggregation and stability of ferrihydrite by changing its surface properties and the accessibility of the original oxide surface.

We performed microbial reduction experiments using Geobacter bremensis and ferrihydrite-organic matter associations produced by adsorption and coprecipitation. As a surrogate for dissolved soil organic matter we used the water-extractable fraction of a Podzol forest-floor layer under spruce. The objectives were (i) to investigate whether coprecipitated ferrihydrites differ in their reactivity from ferrihydrites with adsorbed OM and (ii) to understand how the amount of associated OM influences the reaction.

When ferrihydrite formation takes place in the presence of dissolved OM coprecipitation may occur. In contrast to adsorption of OM on pre-existing ferrihydrite surfaces, coprecipitation may lead to adsorption and occlusion of organic molecules. Moreover the presence of dissolved OM impairs ferrihydrite growth, affecting crystal size, crystal structure and the aggregation behavior of ferrihydrite. As coprecipitated ferrihydrites differ in many properties from pure ferrihydrites and as some of the associated OM may be occluded instead of adsorbed, we assume that also their reactivity may differ from ferrihydrites with adsorbed OM.

We observed that increasing amounts of associated OM led to decreasing initial reaction rates and a decreasing degree of dissolution. Small amounts of associated OM resulted in a higher degree of dissolution than compared to the organic-free control ferrihydrite, whereas high amounts of associated organic matter impeded dissolution. Coprecipitated ferrihydrites were slightly more reactive than ferrihydrites with adsorbed OM.
Rapid and deep-seated exhumation at the Yakutat plate corner, southeast Alaska/southwest Yukon Territory

Sarah Falkowski¹, Eva Enkelmann², Todd A. Ehlers³

¹sarah.falkowski@uni-tuebingen.de
²enkelmea@ucmail.uc.edu
³todd.ehlers@uni-tuebingen.de

This study investigates the spatial and temporal patterns of exhumation along the northernmost part of the transpressive Fairweather Fault in the St. Elias Mountains, southeast Alaska/southwest Yukon Territory. The dextral Fairweather transform fault forms the eastern boundary between the obliquely colliding Yakutat Terrane and the North American Plate. The subduction-collision of the Yakutat Terrane created the St. Elias orogen, which became a prime location to study active convergent orogens, terrane accretion processes, and climate-tectonic interactions. We focus on the plate corner region, where the Fairweather Fault bends and tectonics transitions into convergence and flat-slab subduction to the west. The plate corner is the region characterized by the highest topography (up to 5959 m), extreme relief (up to 5000 m), high seismicity (M>7), and heavy glaciation. It is also the area, where deep-seated, rapid exhumation has been discovered beneath the high Seward Ice Field by detrital zircon fission-track analyses (~2 Ma age populations; closure temperature of 250±40 °C). Additionally, relatively deep exhumation has been suggested to occur in a ~20 km-wide corridor along the Fairweather Fault. However, those data are dominated by apatite (U-Th)/He cooling ages (closure temperature of 55-65 °C) from bedrock samples from high elevations above the ice cover.

We collected 26 samples from modern glacio-fluvial sand deposits to gain a better spatial coverage for the cooling signals in the glaciated region of the northernmost Fairweather Fault and the plate corner region. To investigate the long-term exhumation history we conducted zircon fission-track analyses, which yielded 2718 new single grain ages that range between 0.2 Ma and 293 Ma. Each detrital sample contains three to five age populations with peak ages between 1.2±0.7 Ma and 267±64 Ma (1σ). The age distributions show distinctly different exhumation signals for the upper (North American Plate) and lower (Yakutat Terrane) plate of the subduction-collision zone with dominantly Eocene and older cooling on the lower plate and Miocene and younger cooling on the upper plate.

We show that rapid exhumation around the northernmost Fairweather Fault is not uniform and that the area of rapid deep exhumation is larger and extends farther east than previously expected. Furthermore, we suggest a large-scale flower-structure that developed since the earliest Pliocene around the northern Fairweather Fault to accommodate strain localization at the plate corner.
Phase equilibria experiments on a trachyte and a trachybasalt from the Campi Phlegrei Volcanic District (Italy)

Sara Fanara¹, Roman Botcharnikov¹, Danilo M. Palladino², Anika Husen¹, Simone Righi², Gabriele Macchi Ceccarani², Marius Stranghöner¹ and Harald Behrens¹

¹ Institut für Mineralogie, Leibniz Universität Hannover, Callinstr.3, 30167, Hannover, Germany
(e-mail: s.fanara@mineralogie.uni-hannover.de)
² Dipartimento di Scienze della Terra, Università La Sapienza di Roma, P.le Aldo Moro 5, 00185, Roma, Italia

Phase equilibria experiments were conducted on H₂O-CO₂ saturated trachytic and trachybasaltic melts from the Campi Phlegrei Volcanic District (CPVD) (Italy). These two compositions were selected to represent respectively the most and the least evolved compositions of the CPVD.

Phase equilibria experiments were performed at 100, 200 and 300 MPa and at temperature between 850°C and 1050°C for trachyte and from 950°C to 1150°C for trachybasalt in the Cold Seal Pressure Vessel (CSPV) and in the IHPV under relatively oxidizing conditions (log fO₂=QFM+3.3 for IHPV; log fO₂=QFM+1 for CSPV). To probe the effect of oxygen fugacity, a set of additional experiments at 200 MPa were conducted on trachytic samples with addition of several bars of hydrogen to the pressure medium. The oxygen fugacity was in this way adjusted to more reducing conditions (fO₂=NNO). Run products were analyzed by electron microprobe, spectroscopic techniques and Karl-Fischer titration.

For comparison natural samples from the juvenile parts of the Solchiaro and the Campanian Ignimbrite deposits were collected around the city of Naples and on the island of Procida. The collected products were analysed with the same techniques used for the experimental ones. A close comparison between the experimental phase assemblages and their compositions, and the phenocryst assemblages of the natural samples were found in H₂O-CO₂ saturated liquids (50%H₂O; 50%CO₂), suggesting that besides H₂O also the CO₂ was present in the fluid phase. In a first attempt, experimental trachytic samples undergoing more reducing conditions show an anomalous abundance of mineral phases that are normally rare or not present in the natural assemblage (i.e. apatite more abundant than magnetite; presence of amphiboles). Thus relatively oxidizing conditions are expected in the magma storage prior to the Campanian Ignimbrite eruption.

Experiments on the trachyte show that the most common natural phenocrysts assemblage (with phenocrysts of magnetite, clinopyroxene, feldspar, biotite and apatite) could have been formed prior to the Campanian Ignimbrite eruption at temperature between 850°C and 1000°C and equilibrated at a minimum pressure of 200 MPa, in liquidus with a wide range of H₂O content (appr. 2.5 - 5.5wt%).

Harker diagrams of experimental and natural samples were used to reconstruct the evolution of the CPVD melt. It is suggested that the crystal fractionation via differentiation plays a major role during the evolution of the magma prior to the Campanian Ignimbrite eruption.
Production of metaluminous melt during fluid-present anatexis of the Maghrebian basement (La Galite Islands, Central Mediterranean Sea)

S. Ferrero 1*, R. Braga 2, M. Berkesi 3, B. Cesare 4, N.L. Ouazaa 5

1 Universität Potsdam, Institut für Erd- und Umweltwissenschaften, Germany; * sferrero@geo.uni-potsdam.de
2 Università di Bologna, Dipartimento di Scienze della Terra e Geologico-Ambientali, Italy
3 Eötvös University, Department of Petrology and Geochemistry, Hungary
4 Università di Padova, Dipartimento di Geoscienze, Italy
5 Université Tunis El Manar, Département de Géologie, Tunisie

At La Galite Archipelago peraluminous granitoids contain abundant entrained material. The plutons are related to Miocene anatexis of the crystalline basement buried beneath the Maghrebian Chain (Fourcade et al., 2001). Two types of enclaves, garnet-bearing tonalites and garnetites (garnet ≥ 85 % modal) have been investigated. Primary fluid (FI), melt (MI) and mixed inclusions occur at the garnet core, evidence for fluid-melt immiscibility during host growth. The coexisting mineral inclusions assemblage consists of Ti-rich (~6 wt%) Bt+Pl+Qtz+Ilm, with Wm+Chl pseudomorphs after Crd and minor Kfs. Microstructural constraints and phase assemblage are consistent with a peritectic origin of the garnet.

FI and MI study provide data on the products of anatexis. FI are one phase at room temperature, and contain a CO2-rich fluid (T_melting = -70/-60 °C). Homogenization to liquid (L+V→L) occur at T= -14°C / +11°C. Raman investigation at different temperatures (25-400 °C) showed that FI contain a complex fluid system consisting of CO2 (70.1–77.5 mol%), H2O (11.2–14.4 mol%), N2 (8.8–11.1 mol%) and CH4 (2.5–4.0 mol %). Siderite and an OH-bearing phase, identified by Raman and IR spectroscopy, occur in every analyzed inclusion. They have been interpreted as products of a post entrapment fluid-host reaction. MI vary from glassy inclusions to fully crystallized (nanogranites, Cesare et al., 2009; Ferrero et al., 2012). The latter ones consist of Pl+Kfs+Qtz+Bt±accessories (e.g. Zrn, Ap). The average melt composition is metaluminous (aver. ASI=1) and leucogranitic, with fluid content ~2.3 wt% (equal to the deficiency from 100% from chemical analysis) and peralkalinity index of 0.000. This is the first finding of a non peraluminous melt, almost peralkaline, produced via partial melting in natural samples.

Conventional geothermometry on Grt-Bt (Kleeman & Reinhardt, 1994) gives 620–670 (±50) °C for the Grt-bearing tonalite and 700–790 (±50) °C for garnetite. P values were estimated as 0.3–0.35 GPa and 0.2–0.3 GPa respectively (Hoisch, 1990). Low pressure anatexis is also reported in the Edough metamorphic core complex (NE Algeria, around 100 km toward SW from La Galite) by Caby et al. (2001) coeval with respect to granitoids emplacement at La Galite archipelago.

References


Kinetics of Sulfur Degassing and Sulfur Isotope Fractionation during Decompression of Silicate Melts

Fiege A. 1*, Holtz F. 1, Behrens H. 1, Shimizu N. 2, Mandeville C.W. 3

1Institut für Mineralogie, Leibniz Universität Hannover, Germany; a.fiege@mineralogie.uni-hannover.de
2Woods Hole Oceanographic Institution, Woods Hole, USA; nshimizu@whoi.edu
3U.S. Geological Survey, Reston, USA; cmandeville@usgs.gov

Sulfur (S) is a major volatile in magmatic systems and large amounts of S can be released to the atmosphere during volcanic eruptions as well as in-between two eruption events. Hence, a good knowledge of S degassing mechanisms in magmatic systems and of fluid-melt S-isotope fractionation is a pre-requisite to allow one to interpret volcanic gas signatures and, thus, to improve monitoring of active volcanic systems. However, data on S fluid-melt distribution is rare and, to date, no experimental data on the kinetics of S degassing during decompression has been published. In addition, experimental data on S-isotope fractionation between aqueous fluids and silicate melts at high temperatures (T>1000°C) is, to our knowledge, entirely lacking.

We conducted isothermal decomposition experiments with volatile-bearing (H2O-S±Cl) andesitic and basaltic melts at 1030 to 1250°C and various oxygen fugacities fO2 (log(fO2/bar) = QFM to QFM+4; QFM: quartz-fayalite-magnetite buffer). In these experiments, pressure (p) was released continuously from ~400 to ~70 MPa at a constant rate of ~0.1 MPa/s. The samples were annealed for tA = 0 to 72 h at final p-T conditions after decompression to allow us to investigate the kinetics of S (and S-isotope) degassing.

Experiments with andesitic composition conducted under oxidizing conditions (>QFM+3) and at ~1030°C revealed a strong decrease of the S(fluid)/S(melt) ratio with increasing tA (S(fluid) = wt% S in the fluid; S(melt) = wt% S in the melt). The data show that fluid-melt near-equilibrium conditions were achieved shortly after decompression; i.e. within ~5 h. Such a kinetically controlled transient release of large amounts of S during fast decompression was not observed at lower fO2 (~QFM+1 to ~QFM+1.5) in andesitic systems and was not detected at all (i.e. independent of fO2) in basaltic systems.

The S-isotope composition of selected glasses before and after decompression was measured by secondary ion mass spectrometry. Gas-melt isotopic fractionation factors (αg-m) were estimated via mass balance calculations (103 ln(αg-m) ≈ Δ34Sg-m). The obtained data indicated no detectable effect of tA on αg-m. Δ34Sg-m was found to vary strongly as a function of fO2. For closed system degassing of S-bearing silicate melts at ~1040°C a Δ34Sg-m of about +3.7 ‰ was determined for reducing conditions (~QFM to ~QFM+1) and of about -1.5 ‰ for oxidizing conditions (>QFM+3). Δ34Sg-m was found to decrease notably with increasing T; e.g. at 1200°C Δ34Sg-m ≈ +3.0 ‰ under reducing conditions and Δ34Sg-m ≈ -1.3 ‰ under oxidizing conditions. The data show that fluid-melt S-isotope fractionation in magmatic systems can be significantly larger than predicted by previous models [e.g. 1], at least for reducing conditions.

High-resolution well core sonic logging – applications to clastic reservoir characterization and natural building stone quality evaluation

Claudio M. Filomena 1, Harald Stollhofen 2

1 claudio.filomena@fau.de
2 harald.stollhofen@fau.de

Petrophysical properties and their heterogeneity within sandstone bodies are key parameters for the evaluation of both, reservoir rocks and building stones. However, common tools applied to constrain e.g. porosity distribution pattern in borehole cores are often time consuming, destructive or suffer from a resolution limited to the metre- to decimetre-scale. As an alternative, we test the applicability of non-destructive, high-resolution sonic (HRS) logging of well core sections at the cm-scale for hydrocarbon reservoir characterization and the evaluation of natural building stone quality.

The study uses an ultrasonic device, equipped with conical-shaped piezoelectric stainless steel p-wave transmitter and receiver probes facing towards each other in a way that enables measurements in plane with the sedimentary bedding. The application of a 40 dB pre-amplifier and a contact pressure of 3 bars avoid the use of signal-enhancing couplant materials and maintain a constantly high sonic transmitter strength (Filomena and Stollhofen, 2011).

The Middle Solling Sandstone Member (MSSM), a gas-bearing reservoir in the southern North Sea offshore from the Netherlands, provides the first test sample. It almost entirely consists of "clean", cross-bedded to massive aeolian dune and dry sandflat deposits which are salt-plugged to variable degrees. Plots of HRS logging data versus core plug porosity values show a positive linear relationship. Once calibrated for a particular facies type, this correlation enables the calculation of porosity proxy data from sonic transit time values, acquired at centimetre steps. Also, plots of closely spaced HRS logging derived porosity proxy data significantly improve interpolation between single, wider spaced core plug porosity data points. HRS logging thus contributes a reliable and time-efficient, highly spatially resolving quantification of reservoir heterogeneity (Filomena et al. 2012).

Our second test sample is the so-called Worzeldorf Sandstone, a natural building stone quarried nearby the city of Nürnberg, Germany. Within the scope of an exploration campaign for potential quarry enlargement, HRS logging was applied to the coarse-grained pebbly sandstones of the Late Triassic Löwenstein Formation (Middle Keuper). P-wave sonic velocity ranges from 1.8-4.4 km/s and correlates well with measured compressive strength of 2-104 MPa and Young’s modulus of elasticity (5-36 kN/mm²). Therefore, non-destructive HRS logging provides quantitative and reproducible proxy data which constrain elastic rock properties of mineable sandstone quality (Filomena et al., in review).

References:


The whole is greater than the sum of its parts: intrinsic variability in reaction rate and the prediction of reactivity of mineral and rock bodies

Cornelius Fischer¹, Rolf S. Arvidson², Andreas Lüttge³

¹cornelius.fischer@uni-bremen.de, ²rsa4046@uni-bremen.de, ³andreas.luttge@uni-bremen.de

There is an emerging view that simple averages of reaction rate and reactivity cannot be used to reconstruct the history of fluid-rock interaction, reaction paths, etc., as such values contain no information of the distribution of rates in time and space. In any three dimensional body of rock, the bulk rate integrates the flux of material liberated from all the different reactive surface sites. The distribution of contributors to the bulk rate may be neither simple nor Gaussian. Thus, in place of mean values, we preserve this information by using the concept of rate spectra: the quantification of all contributors to the bulk rate (Fischer et al. 2012).

On the molecular scale, chemical reaction kinetics are fundamentally stochastic, governed by the dynamical behavior of molecules (e.g., Gillespie, 2007). On larger scales, this reacting framework is superimposed on a multitude of physical discontinuities. Examples include the variety of crystal defect structures as well as domain boundaries. Reaction kinetics on this scale are governed primarily by the distribution of defects, such as screws and related dislocations. For example, in situ microscopic observations of reacting mineral surfaces have shown that the creation and destruction of kinks and the resulting movement of steps are fundamental to mineral dissolution and growth, and have provided a significant increase in our understanding of these processes. However, it is also clear that larger structures such as twinning and other intergrowth discontinuities, grain surfaces in porous networks, and depositional boundaries (facies, bedding, etc.) define the physical heterogeneity of the system on larger scales. Thus our ability to integrate molecular scale theory with observations of reacting mineral surfaces, and apply these to macroscopic geological bodies constrain any quantitative prediction of “whole rock” reactivity (Lüttge et al., 2013).

We discuss results of experimental observations in light of the contributors to the bulk rate using the concept of rate spectra. These spectra allow for an analysis of surface sections of contrasting reacting behavior and thus, contrast in reactivity. Frequency analysis of rate spectra over time provides deeper insight into the role of distinct surface sites. The analysis of reacting surfaces as a function of crystal size variations enables analysis of superimposed bounding conditions in terms of overall surface energy variation. Addressing the sensitive portions of the rate spectra will ultimately increase our predictive understanding and the applicability of the rate spectra concept to complex geological systems.

References:
Experimental study on hydrous partial melting of hydrothermally altered dolerite: Generation of felsic melts within fast-spreading oceanic crust

L.A. Fischer¹, M. Erdmann¹, L. France², E. Deloule², J. Koepke¹

¹Institut für Mineralogie, Leibniz Universität Hannover, Callinstraße 3, 30167 Hannover, Germany
²CRPG; UMR 7358, CNRS; Université de Lorraine, 15 rue Notre Dame des Pauvres, 54501 Vandœuvre-lès-Nancy, France

E-Mail: lennartfischer@gmx.de

Felsic lithologies in recent oceanic crust and ophiolites may be formed by different magmatic processes, as fractional crystallization of MORB and partial melting of mafic lithologies. The latter is discussed as a major process at the gabbro/dike transition of fast-spreading ridges, where the axial melt lens is directly beneath the sheeted dikes. An upward moving of the axial melt lens roof may trigger a melt intrusion within the previously altered sheeted dikes, which is consequently reheated, and may potentially suffer hydrous partial melting. To quantify the influence of partial melting on the generation of felsic magmas in the sheeted dike complex, high pressure-high temperature experiments were performed. Therefore, a natural sample of a typical sheeted dike complex from the IODP drilling at Site 1256 (equatorial East Pacific Rise) was used as starting material. The sample is a moderately altered dolerite containing plagioclase (An₅₀₋₅₇), clinopyroxene (Mg# 0.55-0.60) and quartz, with chlorite as secondary phase; sulfides and Fe-Ti-oxides are present as accessory minerals.

The partial melting experiments were performed in an H₂-controlled IHPV at different temperatures (940°C - 1030°C), a pressure of 100 MPa, corresponding to a mid-crustal level, and at a fO₂ corresponding to QFM +1 (QFM = quartz-fayalite-magnetite oxygen buffer). All experiments ran in Au-capsules under water saturated conditions. The experimental products were analyzed with EPMA (Institut für Mineralogie, Hannover) and SIMS (Centre de Recherches Pétrographiques et Géochimiques, Nancy). First results on phase relations and mineral compositions are presented. The experimental phases are olivine + plagioclase + clinopyroxene at 1030°C. At lower temperatures orthopyroxene crystallizes at the expense of olivine as well as Fe-Ti-oxides. The analyzed melts vary in their SiO₂ contents between ~50wt% (1030°C) and ~68wt% (940°C) and can be classified as basaltic respectively dacitic. The pyroxenes show a wide range in chemistry and most of them are zoned with relictic cores. In general, the newly formed clinopyroxene is depleted in Fe and enriched in Mg and Ca. Trace elements of the melt pools were investigated with SIMS. Preliminary results show trace element patterns which correspond to those of naturally formed felsic lithologies found in the gabbro/dike transition zone of fast-spread crust.

For further investigation a detailed evaluation of the SIMS measurements is in progress. Further experiments are in preparation to investigate phases at temperatures beneath 940°C to get more evolved melt pools and for refining the present results.
Evidence for rapid fluid exsolution in primitive lavas from the Troodos ophiolite (Cyprus)

Raúl O. C. Fonseca1, Chris Ballhaus1, Maria Kirchenbaur2,1, Carsten Münker2, and Thorsten Geisler1

1Steinmann-Institut, Universität Bonn, Poppelsdorfer Schloss, 53115 Bonn
2Institut für Geologie und Mineralogie, Universität zu Köln, Zülpicher Strasse 49b, 50674 Köln, Germany

The Troodos Massif in Cyprus is a 90-93 Ma old supra-subduction zone ophiolite complex, thought to be a relic of the closure of the Tethys Ocean. The uppermost portion of the Troodos ophiolite comprises a lower sequence of evolved tholeiitic arc andesites and dacites that is overlain by primitive basalts, picrites and boninites (upper pillow lavas - UPL). The complex’s magmatic lithologies display ubiquitous features that can be directly linked to their over-saturation in an H2O-rich fluid phase and its subsequent exsolution from the melt. Invariably, these features assume the shape of obicular-like textures found at various scales (micro- to macroscopic), that can be found at a variety of crustal levels, ranging from Moho-emplaced podiform chromitites to relatively shallow primitive basalts and picrites. However, the processes that lead to fluid-exsolution as well as the origin of the exsolved fluid (magmatic versus ambient ocean water) are still not well known.

Here we present the results of a multi-disciplinary study of a suite of primitive basalts to andesitic boninites from the UPL. Samples consist of cm-sized nodules of pristine glass with phenocrysts of olivine laden with fluid inclusions. Glass textures range from vitrophyric to spinifex-like at the 10 to 100 μm scale. Interestingly, some samples display skeletal crystals of high-Al quench clinopyroxene (cpx) whose crystallization appears to have stopped ‘on its tracks’ prior to completion. Cross-sections of the glassy nodules have been analyzed for their HFSE, LILE, and REE abundances over rim-core-rim line profiles via LA-ICP-MS. Core and rim samples of these nodules were additionally analyzed for their Sm-Nd, Lu-Hf and Sr isotope systematics via MC-ICP-MS. Initial results show that there are no significant variations in the investigated isotope systems from core to rim, nor in differently sized nodules. The ‘quench’ cpx in these samples and the surrounding glass were characterized by micro-Raman spectroscopy. First results indicate that the cpx crystals show preferred crystal orientation, corroborating the notion that these phases have been ‘frozen’ before fully crystallizing into equilibrium cpx. When taken together, these initial results suggest that UPL lithologies lost water rapidly via fluid exsolution. The resulting rapid heat loss led to the very efficient cooling and quenching of these glasses, and may have also prevented trace element patterns from becoming disturbed. Our results may potentially provide us with insights on how fluid exsolution affects crystallization and elemental mobility in water-saturated magmatic settings.
Detrital zircons in the late Carboniferous of Northern Germany: orogenic recycling of Baltica-derived Devonian shelf sediments

Wolfgang Franke and Christian Dulce (ExxonMobil, Hannover)

w.franke@em.uni-frankfurt.de

ICP-MS laser dating of zircons from late Carboniferous sandstones of northern Germany (foreland basin of the Rheno-Hercynian Variscides) has revealed late Proterozoic, early Ordovician and Devonian through to early Carboniferous age groups. Like detrital mica ages from the same rocks (Küstner 2000, Neuroth 1997), these zircons are derived from sources in the Variscan belt. In addition, there are frequent zircons derived from sources in Baltica and the Mazury High. At first sight, these results would suggest a river system with tributaries from the North and South. This model is not feasible, because
• early Carboniferous ages of detrital zircon are still present in the Carboniferous of the Oslo Graben (Dahlgren & Corfu 2001) and
• zircons from the two source regions also occur in South-derived flysch turbidites of the Namurian B at the northern margin of the Rhenish Massif.

The zircon spectra can be interpreted, instead, by accretion of Baltica-derived Devonian shelf sandstones to the NW-ward prograding Rheno-Hercynian tectonic front (see already Engel et al 1983, with earlier refs. to the composition of synorogenic clastics). Since, in most of the Rhenish Massif, the Devonian sandstones are still sealed by Carboniferous deposits, recycling was only possible from the Taunus Unit and areas further South.

The frequency of Baltica-derived zircons in the late Carboniferous foreland basin suggests that an important part of the Carboniferous catchment area consisted of accreted Devonian shelf sediments. These recycled shelf sediments have to be added to the width of the Rheno-Hercynian passive margin (see also Doublier et al 2011). Ongoing studies are expected to reveal the earliest occurrence of recycled material and to establish comparisons between the detrital zircons and the presumed source rocks in the southern Rhenish Massif.

We gratefully acknowledge fruitful discussions with Suzanne Kairo (ExxonMobil, Houston) and the zircon analyses of Paul O’Sullivan (Apatite to Zircon Inc., Viola, Idaho)

References
A new clay mineral in phosphorite: trioctahedral analogue of illite (Tal Group, Lesser Himalaya, India)


1gerhard.franz@tu-berlin.de
2dorothee.hippler@tu-berlin.de
3rhede@gfz-potsdam.de
4wirth@gfz-potsdam.de
5dhirajmohanbanerjee@gmail.com

Illite as a common constituent in sedimentary rocks is referred to as a non-expanding, dioctahedral, aluminous, K-bearing 2:1 sheet silicate mineral of the mica group, which has ionic substitutions in both the octahedral and the tetrahedral sites and an interlayer charge between 0.8 and 0.6. It is classified as ‘dioctahedral interlayer-deficient mica’ or as ‘hydromica’ and can be described chemically as intermediate between pure muscovite and pyrophyllite with approximately 0.65 K pfu and 3.35 Si pfu. The occurrence of a trioctahedral analogue of illite is debated, but the term ‘trioctahedral illite’ is used frequently in the literature for weathering products of biotite or for illite material with a large proportion of trioctahedral smectite layers.

Here we describe a true interlayer deficient, trioctahedral, non-expandable K-Mg- and F-rich mica (K-deficient F-phlogopite) as a neoformation in sedimentary phosphorites, using HRTEM on focused ion beam samples in combination with energy dispersive electron microprobe analysis and XRD data. The mineral can be described as a trioctahedral analogue of illite, chemically intermediate between F-phlogopite and talc. It was found in the phosphate-carbonate matrix of organic-rich phosphorite from the Mussoorie Syncline in the Lesser Himalaya. The rocks are from the Neoproterozoic-Cambrian boundary and are black shales, chert beds and pyritiferous phosphorites known as the Tal Group. Phosphorite beds vary in thickness from few cm to 15 m at places and show massive, laminated, granular and fragmentary textures. The rocks are brittle deformed but without signs of metamorphism. Other minerals present are F-carbonate-apatite, dolomite, calcite, illite, pyrite, rutile, rare sphalerite and organic carbon. The formula (WDS microprobe analysis and analytical TEM, assuming 22 negative charges) is $K_{0.5}(Mg_{2.8}Fe_{0.01}V_{0.01})[Al_{0.7}Si_{3.3}O_{10}[F_{1.4}OH]_{0.6}]$, with small amounts of NH4. Powder XRD data clearly show that it is non-expandable, and HRTEM imaging of the lattice fringes confirm the regular 10 Å-spacing. Mica aggregates are up to 5 µm x 100 µm large, but layer packages are extremely fine-grained with ~10 layers per package. They are intimately intergrown with organic carbon, which according to HRTEM imaging is very poorly crystallized. Textural arguments favor a formation of the mica during dolomitization.
Eustatic control on coeval development of Anisian/Ladinian carbonate platforms at the NW Tethyan shelf and epeiric carbonates in the CEB

Matthias Franz¹, Sandra Kaiser², Jan Fischer¹,³, Carmen Heunisch⁴, Friedrich W. Luppold⁵

¹matthias.franz@geo.tu-freiberg.de; ²sakaiser@uni-bonn.de; ³jfischer1@yahoo.de; ⁴Carmen.Heunisch@lbg.niedersachsen.de; ⁵FriedrichWilhelm.Luppold@lbg.niedersachsen.de

Correlations of Anisian/Ladinian strata from the NW Tethyan shelf (f. e. Dolomites) and the epeiric Central European Basin (CEB) are constrained by only a few biostratigraphic markers. Thus, application of sequence-stratigraphic methods can make valuable contributions to improved correlations. The late Anisian (Illyrian) transgression from Tethyan waters via so-called gates resulted in flooding of the CEB. Superimposed by rapid subsidence the transgressive trend of 3rd order Anisian/Ladinian sequence An 5 resulted in rapid vertical up building of narrow platforms. Subsequent to its maximum flooding surface (MFS) in the latest Anisian chiesense subzone the regressive trend forced a pronounced lateral progradation of platforms up to the late Ladinian archelaus zone. In the CEB the rapid Illyrian transgression culminated with the MFS of the Upper Muschelkalk Sea in the lower conodont zone 2 (sequences/pulcher to philippii/robustus zones) of latest Anisian age. Afterwards regressive trends favoured the step-by-step progradation of coastal to fluvial plain environments extending up to South Germany in the late Ladinian and resulting in the most diachronous facies shift of the entire Germanic Triassic. The correlation of sequence boundaries, systems tracts and MFS reveal a coeval development from aggrading to prograding platforms at the NW Tethyan shelf and from retrogradational to progradational stratal pattern architecture of epeiric carbonates in the CEB.

In the CEB the overall T-R trend of sequence An 5 as well as a stacking pattern of “smaller scale sequences” can be demonstrated by coeval variations in lithofacies, biofacies, Sporomorph Eco Groups (SEG), δ¹⁸O_p values and ⁸⁷Sr/⁸⁶Sr ratios obtained from fossil bioapatite of fish teeth, semiaquatic amphibian teeth, brachiopods and conodonts. The interval around the MFS is dominated by autochthonous aquatic SEG of marine, lagoonal and brackish-freshwater environments. Towards the top allochthonous terrestrial SEG of coastal, pioneer, drier lowland, wetter lowland, river and upland environments become more dominant. Accordingly, δ¹⁸O_p values of 18.9-21.8 ‰ VSMOW around the MFS in South Germany are comparable with Tethyan δ¹⁸O_p values of 18.3-21.8 ‰ VSMOW (late Anisian) and ⁸⁷Sr/⁸⁶Sr ratios of 0.7078-0.7079 are only slightly higher than a proposed seawater ⁸⁷Sr/⁸⁶Sr ratio of 0.7075. Thus, the Upper Muschelkalk Sea at maximum flooding stage can be considered euryhaline marine in South Germany. Higher up δ¹⁸O_p values successively decrease down to 17.6 ‰ VSMOW and ⁸⁷Sr/⁸⁶Sr ratios rise up to 0.7083. Compared Tethyan δ¹⁸O_p values from the Tethyan of 20.3-21.3‰ VSMOW (late Ladinian) the up to ~3.5 ‰ fractionated δ¹⁸O_p values suggest successive freshening following the stage of maximum flooding. A freshening trend from South Germany towards Thuringia can be deduced from ~1 ‰ fractionated δ¹⁸O_p values within individual time-slices. As this is already the case at the stage of maximum flooding only the southern parts of the Upper Muschelkalk Sea can be considered euryhaline marine.
Rare earth elements (REE) share many similar properties resulting in similar geochemical behavior. However, the technical demand for REEs and thus the metal prices are heavily skewed towards two light rare earth elements (Nd, Pr) and the three heavy rare earths (Dy, Eu, Tb) as well as Y, that are commonly used in magnets in the renewables industry. It is expected that short supplies of HREEs will be driving up their price and shifting the economies of mining projects in favor of companies that can produce sufficient quantities of HREEs. The generally accepted notion is that the HREEs are less common and therefore rarer and more valuable than the LREEs. Most REE ore bodies are typically enriched in LREE (La – Gd) and most REE ores are depleted in the HREEs (Tb-Lu). Ores that contain xenotime or zircon as the principal REE mineral are relatively enriched in heavy REE but of minor abundance. HREE reserves are almost all in ion-adsorption type ore deposits in southern China, whereas LREE can be obtained from carbonatite and/or alkaline igneous complexes in many other countries. Thus, the chief differences can be seen in the relative proportion of LREE to HREE which asserts a great effect on the viability of a REE prospect. To have the economically favorable elemental distribution is, therefore one of the key factors to consider when analyzing the potential of exploration projects and this has to be accounted for when calculating the value of REE ores.

For example, the value of polymetallic ores is generally provided by the “net smelter return” a figure that sums up individual prices for all salable metals present in the ore. In analogy to that the so-called “basket-price” is used for calculating the value of REE ores. The basket price (in US$/kg) is the theoretical price that could be obtained for one kilogram of fully separated rare-earth oxides, containing rare-earth oxides in the same proportions as found in-situ within the deposit.

Especially the south Chinese ion adsorption clay deposits of Longnan, Xunwu and Xinfen contain high grades and amounts of HREE. The relative distribution (±100%-normalized value) of in-situ REO of the Longnan-1 deposit is around 87 wt-% HREE+Y with high grades of Dysprosium with 8.9 wt-% [1]. The average distribution of all Longnan deposits is around 85 wt-% HREE+Y. However, there are only two deposits not located in China with equal high grade of HREE+Y, which are the deposits of Browns Range-Wolverine (Australia) and Lofdal (Namibia). The relative distribution of in-situ REO of the Browns Range-Wolverine deposit is around 84.5 wt-% HREE+Y and 85.5 wt-% HREE+Y for the Lofdal deposit[1]. Finally, Browns Range and Lofdal have a high HREE potential and, therefore, they can become an alternative to the Chinese deposits.

[1] REE World, Proedgewire
Magma storage conditions and melt evolution of the basanites-phonolite series from Cumbre Vieja Volcano (La Palma, Canary Islands): An experimental approach at 400, 550 and 700 MPa

P. Fuchs1*, T. Wengorsch1, R. Almeev1 AND A. Klügel2

1Institute of Mineralogy, Leibniz University Hannover, Germany (*p.fuchs@mineralogie.uni-hannover.de)
2Geosciences Department, University of Bremen, Germany

Eruptive products of the recent Cumbre Vieja volcano (CV) cover a large spectrum of alkali-rich rocks ranging from basanites to phonolites. A model of the magma plumbing system is largely based on barometric studies of phenocrysts and xenoliths and includes three major intervals of magma stagnation and fractionation at mantle and crustal depths [1]. However, the relative influence of intensive thermodynamic parameters on phase equilibria is still unknown. We present results of an experimental study aimed at evaluating the p-T-αH2O/αO2 conditions in the genesis of a basanite-tephrite-phonolite system. High pressure and temperature phase equilibria experiments (700, 550 and 400 MPa; 1000-1175°C) in the presence of H2O-CO2 fluid (XH2O varied between 0 and 1, keeping fO2 between ~FMQ and FMQ+3.3) were conducted in an internally heated pressure vessel using two natural basanites with 13.7 wt.% and 9 wt.% MgO and a tephriphonolite (400 and 200 MPa; 950-1100°C) with 2.8 wt.% MgO, respectively, representing three differentiation stages in the evolution of CV magmas.

The mineral assemblage of the basanitic starting material (Ol+Cpx+Sp), with similar compositions as in the natural starting material, was reproduced at 700, 550 and 400 MPa, 1150-1100°C and 0.7-2.9 wt.% H2O in the melt (H2Om) for the primitive basanite and at 550 and 400 MPa, 1175-1125°C and 1.5-2.7 wt.% H2Om for the evolved basanite. Tephritic residual melts were produced by Ol+Cpx+Sp crystallization at 400, 550 and 700 MPa, 1100-1150°C and low to intermediate H2Om (1.4-4.2 wt.%). Phonotephritic melts were generated by Cpx+Ol+Krs+Mt crystallization at 400 MPa, 1075-1100°C and 0.7-3.1 wt.% H2Om. Tephriphonolitic melts were produced by Cpx+Pl+Krs-Mt+Ap crystallization at 400 MPa, 1050°C and 0.7-1.1 wt.% H2Om. The natural mineral assemblage of the tephriphonolite (Cpx+Krs+Pl+Mt+Ap) in the compositional range of natural minerals, was reproduced in equilibrium with a phonolitic melt at 400 and 200 MPa, 1000°C and 0.6-0.7 wt.% H2Om.

Our results indicate that single-step differentiation from basanites to phonotephrites is possible in a pressure range of 400 to 700 MPa at least. At 700 MPa Pl crystallization in basanites is suppressed, indicating that tephriphonolitic or phonolitic melts can only be generated at lower pressures or from parent more evolved than basanite. From our experimental data we can assume that genesis of tephriphonolitic and phonolitic magmas can occur up to pressures of 400 MPa at least, which is in contrast to the relatively low pre-eruptive storage pressures of phonolites from comparable systems (e.g. >200-250 MPa for Kerguelen [2] and 130 MPa for El Abrigo, Tenerife [3]). One of the major phases controlling the evolution of CV magmas is Krs, which is an amphibole that can be stable even in melts with <1 wt.% H2Om (>0.1 XH2O), suggesting that CV melts are H2O-poor even in evolved magmas. The formation of phonolitic melts also requires low fO2 (~FMQ): because higher fO2 results in extensive Mt crystallization leading to Qz-normative residual liquids instead of Ne-normative.

Siderite in Archaean Banded Iron Formations - a biosediment?

Fabian M. Gäb¹, Chris Ballhaus², Dieter Garbe-Schönberg³

¹fgaeb@uni-bonn.de
²ballhaus@uni-bonn.de
³dgs@gpi.uni-kiel.de

Siderite in Archaean banded iron formations has been a mineral of considerable interest and subject of intensive studying for some time. Siderite is been thought to be a CO₂ sensor for the Archaean atmosphere (Ohmoto et al. 2004) as well as a biomarker for early life on Earth (Köhler et al. 2013). In this study we take both hypotheses to the experimental test. We check if siderite can be precipitated inorganically under conditions that are considered to be realistic for the formation of banded iron formations (BIF). If it can be shown that siderite cannot be precipitated inorganically, a biological origin would become inevitable. Additionally that would make siderite obsolete as a CO₂ sensor for the Archaean atmosphere, because it was not in equilibrium with the atmosphere at the time of its precipitation. We designed experiments based on the inorganic precipitation reaction

\[ \text{Fe}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{FeCO}_3 + 2\text{H}^+ \]

We equilibrated an Archaean seawater proxy containing 3.5 wt.% NaCl and 4500 µmol/kg carbonate alkalinity with a reducing N₂:H₂:CH₄ atmosphere with varying CO₂ content (0, 1000, 5000 ppmV). When exchange equilibrium was reached, variable amounts of ferrous iron were added as FeCl₂, ranging from 50 to 500 ppm. Following reaction with the atmosphere for another 24h, a blue-green precipitate formed. The remaining solution was then titrated for alkalinity. The result of titration quantifies the amount of carbonate removed from the solution via precipitation of an insoluble complex with Fe²⁺ ions. This is directly linked to the amount of „siderite“ formed. We also analyzed the remaining solution for its Fe content with ICP-OES. The precipitate was analyzed with Raman spectroscopy and was characterized as an iron-carbonate-hydroxide-complex. Both parameters, i.e. remaining carbonate alkalinity and Fe content in solution gave closely matching results. The higher the CO₂ partial pressure of the atmosphere, the less Fe carbonate is precipitated because a high CO₂ partial pressure destabilizes the carbonate ion in solution and lowers the pH. With 5000 ppmV of CO₂ in the atmosphere 500 ppm of Fe²⁺ (aq) must be added in order to precipitate an Fe carbonate-hydrate. High CO₂ contents of the Archaean atmosphere (> 50,000 ppmV) derived from the above equilibrium (Ohmoto et al. 2004) seem unrealistic in view of these results. In a second series of experiments the same setup was used but added MnCl₂ was added instead of FeCl₂. No difference was found between Fe²⁺ and Mn²⁺ regarding the precipitation of carbonate. Two conclusions can be drawn from the study. (1) Siderite in BIF cannot be a primary inorganic precipitate from seawater, and (2) siderite should not be used as indicator mineral to derive CO₂ partial pressures of the Archaean atmosphere. We concur with Köhler et al. (2013) that siderite microbands in BIF formed by reduction of ferric iron hydroxide with organic carbon, perhaps outlining bacterial or algal mats at the seawater-sediment interface. Siderite is indeed a biosediment and indicates the existence of life on earth in the Archaean.

Magnetic nanoparticles (MNPs) are used in important applications, such as cancer treatment, as MRI contrast agents and in high density data storage. These nanoparticles must have a monodispersed size and shape distribution for use in technology, as this ensures that they have a consistent and known magnetic behavior. The synthesis of uniform MNPs usually requires the use of harsh chemicals heating to hundreds of degrees Celsius, neither of which can be considered green. In nature, biomineralization proteins direct the formation of about 60 different biomaterials to form specific crystal phases and structural morphologies, all under ambient synthetic conditions. The magnetic bacteria are able to use biomineralization proteins to template uniform magnetic nanoparticles within lipid vesicles called magnetosomes. Some biomineralization proteins and bioinspired peptide mimics can template the formation of consistently uniform nanoparticles from at low temperatures, and under mild, aqueous reaction conditions in vitro. Therefore, biomineralization proteins and peptides offer a far greener approach to nanoparticle synthesis than the methods currently used in industry.

The processes used by magnetic bacteria to synthesize their magnetic particles in vivo are still not well understood. It is only by developing a better understanding of these processes, and by careful characterization of the properties of the biotemplated materials, that we can hope to develop biomineralized materials for use in technology. In previous work, it has been shown that magnetosome templated magnetite nanoparticles from magnetic bacteria are formed extremely rapidly within the cells, and are of very high quality. Here we have undertaken a study to characterize the materials and magnetic properties of biotemplated magnetic nanoparticles using techniques such as x-ray magnetic circular dichroism (XMCD) and vibrating sample magnetometry (VSM). The biotemplated magnetite was formed under mild, aqueous reaction conditions and is of a high quality. We have explored the effect of doping in different elements (cobalt, copper and manganese) into the biotemplated magnetite nanoparticles, so the effect on the magnetic properties of the materials will be discussed. By using the magnetic bacteria to template doped magnetite nanoparticles, the magnetic properties of the nanoparticles can be tuned for use in a range of applications.

A tale of two viscosities: the case of partial melting

Ganzhorn A.C. (1,2,3,4,5), Llorens M.G. (6), Gomez-Rivas E. (6), Bons P.D. (6), Labrousse L. (1,2), Roessiger J. (6)

1UPMC Univ Paris 06, UMR 7193, ISTeP, F-75005 PARIS.
2CNRS, UMR 7193, ISTeP, F-75005, PARIS.
3Université d’Orléans, UMR 7327, ISTO, F-45071 ORLEANS.
4CNRS/INSU, UMR 7327, ISTO, F-45071 ORLEANS.
5BRGM, ISTO, UMR 7327, F-45071 ORLEANS.
6Department of Geosciences, Eberhard Karls University Tübingen, Germany

Field evidences and experimental data show that partial melting of crustal rocks during their burial of subsequent exhumation is acting as a weakening mechanism. Nevertheless, no unified estimate of this weakening effect has been computed so far, and all possible curves between Reuss and Voigt averages have been proposed. In order to numerically assess the effect of partial melting on crystalline aggregates viscosity, we describe here a series of 24 two-dimensional simple shear numerical experiments on two-phase linear viscous material. One phase is designed to be a solid similar to quartz and the other represents silica rich melt. Relative abundance of each phase, wetting angle of melt and grain boundary migration velocity were systematically varied to test the effect of those parameters on the bulk flow behaviour.

In numerical experiments without grain boundary migration, the system first shows hardening (until $\gamma=1$) followed by softening (until $\gamma=2$) before steady state is reached. Strong and weak phase show equivalent stretching rates and single-phase strain ellipsoids compare. Strength curves and strain patterns are insensitive to wetting angle values.

When grain boundary migration occurs, bulk flow behaviour depends on wetting angle. At low wetting angle (30°) and fast grain boundary migration, melt pockets are connected and elongated perpendicular to shear direction whereas they trend oblique to shear direction at slower grain boundary migration. At high wetting angle (180°) and fast grain boundary migration, the initial rounded melt pockets stay circular whereas they become elliptic for slow grain boundary migration. Aspect ratio of strong phase grains is also sensitive to the same parameters: fast grain boundary migration and high wetting angles induce higher elongation of grains for equivalent bulk shear. Strength curves also show the effect of surficial tension vs grain boundary migration. At low wetting angle (30°), the system is subject to softening whereas at high wetting angle it is subject to hardening for the melt pockets remain unconnected.

Numerical textures obtained at low wetting angles and high grain boundary migration velocities better match natural examples of partially molten rocks showing synkinematic melt segregation, implying that such combination is relevant for migmatites.
Textural and geochemical aspects of Upper Critical Zone rocks of the eastern Bushveld Complex at Two Rivers Platinum mine, South Africa

R.J. Giebel¹,², C.D.K. Gauert ², M. Schannor³

¹ Institut für Geologische Wissenschaften, Von-Seckendorff-Platz, Martin-Luther-Universität Halle-Wittenberg, Germany
² Department of Geology, University of the Free State, Nelson-Mandela-Drive, Bloemfontein, R.S.A;
³ Institut für Geologische Wissenschaften FU Berlin, Germany

The study concentrated on the mineralogy of the Merensky Reef and the UG-2 chromitite units in the Upper Critical Zone of eastern Bushveld Complex (BIC) at Two Rivers Platinum mine (TRP), south of the Steelpoort Fault zone. Variations in thickness and textures of both units south of the Steelpoort fault zone allowed the classification of four and three facies types, respectively. The density of pegmatoidal pipe development was also investigated, revealing to an increase in the frequency of ‘pegmatoid’ occurrence and disturbances of the magmatic layering on approach of the Steelpoort fault zone from a southerly direction.

An evolving lithological sequence of chromitite → pyroxenite → norite → anorthosite is observed in both units with increasing stratigraphic height. The origin of the chromitite layer can be explained by a model of repeating magma influxes and a mixing of the magmas. Cumulate facies changes in thickness and composition of UG-2 and MR units within lateral distances of 100s of meters at TRP mine probably reflect changes in the liquid line of descent, the intensity of magma convection, the pulses of replenishment, and contamination and volatile content of the magma. Cumulate thickness variations, as noted in the vertical distance of UG-2 and Merensky reef in the northern sector of the eastern Bushveld with increasing distance from the fault zone, are probably caused by basement morphology induced compartmentalization.

Within different areas of the TRP mining lease single layers are absent and foot and hanging wall lithologies change. Such variations in the mode of occurrence of the layers are probably caused by influxes of smaller portions of magma through multiple feeders.

Vertical whole rock major element-oxide and mineral compositions indicate a normal fractionation trend with reversals at the base of the reefs confirming a repeated magma influx. Both the Merensky Reef and the UG-2 chromitite layer contain three PGE concentration peaks which occur in the basal, central and the upper part of the reefs.

Incompatible trace elements in the interstitial trapped liquid are generally located within the reefs, crystallizing as late stage post-cumulus mineral phases. Most of these minerals are formed in the UG-2 chromitite layer or in the Merensky pyroxenites next to the chromitite stringers. Disequilibrium textures of adjacent plagioclase and orthopyroxene as well as the anorthite / enstatite content relationship confirm this disequilibrium and are considered to confirm magma mixing.
High temperature synthesis of iron-, sodium- and halogen-rich silicate glasses: experimental and analytical challenges

CHRISTOPHER GIEHL*,1, CHRISTIAN SCHRÖDER2, THOMAS WENZEL1 AND MARCUS NOWAK1

1Fachbereich Geowissenschaften, Eberhard Karls Universität Tübingen, Germany
2Biological and Environmental Sciences, University of Stirling, Scotland, UK

*correspondence: christopher.giehl@uni-tuebingen.de

Natural silicate glass compositions can be used to investigate magmatic processes and synthetic glasses are important materials for industrial processes. Moreover, both types of glasses are commonly used as starting material for phase equilibrium experiments in experimental magmatic petrology. However, loss of Cl and F to the vapor phase during high T silicate glass synthesis was reported from melting of rock powders and silicate glass syntheses (Lukkari & Holtz 2007, Giehl et al. 2013).

To quantify Cl and F loss, ten anhydrous peralkaline Fe- (3.5 – 15.1 wt% FeO*) and Na-rich (8.1 – 13.5 wt% Na2O) phonolitic glasses with high Cl (0.1 – 0.5 wt%) and F (0.2 – 2.8 wt%) concentrations were synthesized. Syntheses were performed at ambient pressure, 1200 – 1400 °C and 2 – 8 h dwell time using platinum (Pt) or graphite (C) crucibles. The Fe3+/Fe2+ ratio (XFe3+), composition, homogeneity and loss of Cl and F to the vapor phase of glasses were investigated with Mössbauer spectroscopy and electron microprobe analyses (EMPA), respectively.

Glasses synthesized in Pt crucibles show significantly higher XFe3+ (0.61 – 0.96) compared to those synthesized in C crucibles (XFe3+= 0.0 – 0.45), some of them coexisting with native iron, depending on synthesis T, dwell time and XFe3+ of starting powder. EMP glass analyses yield homogeneous compositions within one sample. However, increasing synthesis T and dwell time increases loss of Cl and F to the vapor phase.

Na has long been known to migrate when analyzed with electron microbeam techniques (Lineweaver 1963). Recent studies recommend procedures to minimize Na loss for haplogranitic glasses. However, Na loss in glasses was suggested to aggravate through depolymerization, increased alkalinity, dissolved H2O and additional fluxing components such as Cl, F and Br (e. g. Morgan & London 2005). To obtain reliable H2O concentrations using the by-difference method in Fe- and Na-rich glasses, knowledge about XFe3+ as well as the extent of Na migration is crucial (Devine et al 1995). To investigate the effect of current density, additional EMP analyses with variable beam diameter (10-30 µm) and probe current (4-50 nA) were performed to quantify Na migration. We found a linear relationship between current density (0.03 – 0.13 nA/µm²) and Na loss (up to 14 % relative). This linear relationship is in agreement with previous data for current densities below 1 nA/µm² (Morgan & London 2005). However, Na loss is more severe compared to anhydrous haplogranitic glasses and high F concentration in glasses was found to further increase Na loss.
An experimental study on phase relations in peralkaline iron-rich melts: the influence of halogens and implications for geothermometry and trace element partitioning

CHRISTOPHER GIEHL*1, MICHAEL MARKS1 AND MARCUS NOWAK1

1Fachbereich Geowissenschaften, Eberhard Karls Universität Tübingen, Germany

*correspondence: christopher.giehl@uni-tuebingen.de

High concentrations of Cl and F are known to affect phase relations in magmatic rocks. In this study, we present phase equilibrium experiments investigating a peralkaline iron-rich phonolitic composition with variable Cl and F content. The starting material resembles a potential parental melt composition of the peralkaline Ilímaussaq plutonic complex/South Greenland (Marks & Markl 2003).

Nominally dry and H2O-bearing experiments were performed at 100 – 150 MPa, 1000 – 650 °C and variable fO2 in an internally heated argon pressure vessel and in hydrothermal rapid-quench cold seal pressure vessels. To cover the large T interval of crystallization we applied a three-step fractional crystallization strategy. Stable mineral phases are titanomagnetite, fayalitic olivine, clinopyroxene, alkali feldspar, nepheline and aenigmatite (± native iron). Increased Cl and F concentrations additionally stabilize fluorite (CaF2), hiortdahlite ((Ca,Na)6(Zr,Ti)2Si4O14F4), sodalite (Na8Al6Si6O24Cl2) and eudialyte (Na4Ca2(Fe,Mn)ZrSi8O22(Cl,OH)2). Furthermore, selected experiments were repeated using a starting glass doped with trace elements.

In the Ilímaussaq rocks, magmatic clinopyroxene shows a gap between Ca-rich and Na-rich compositions. This gap may be induced by Ca-rich hiortdahlite and fluorite at the expense of Ca-rich clinopyroxene by reason of increasing F content in the residual melt. Na-rich clinopyroxene, not influenced by Ca-F phases, is then stabilized coexisting with a more evolved melt at lower T. Both the Cl/OH ratio in eudialyte and the Mn partition coefficient between clinopyroxene and eudialyte/aenigmatite show a systematical decrease with T. The comparison with existing data indicates that these ratios may have the potential for geothermometers, rarely available for evolved peralkaline phase assemblages. In experiments with additional trace elements (Nb, La, Ce, Y, Sr), aenigmatite, hiortdahlite and eudialyte were found to incorporate up to 13 wt% REE’s and an additional wöhlerite group mineral is stabilized. However, phase relations are basically unaffected. This also supports the reliability of experiments based on simplified starting compositions.

Microapatites on dissolved dolomite crystals as an indication for the origin of dolomite sands in the Franconian Upper Jurassic

Axel Gillhaus1 Rolf D. Neuser2 Detlev K. Richter3

1Axel.Gillhaus@ruhr-uni-bochum.de 2 Rolf.Neusser@ruhr-uni-bochum.de 3 Detlev.Richter@ruhr-uni-bochum.de

The origin of dolomite sands in the Upper Jurassic of the Franconian Alb commonly is attributed to dissolution processes in the deeply weathered Franconian dolomite under humid conditions of a tropical climate (Schnitzer 1963, Burger 1989, Menckhoff 2006) which prevailed during the Paleogene and early Neogene (Peterknecht 2011). Scanning electron microscope (SEM) pictures of three dolomite sand deposits (Druidenhain S, Moggast, Röbling NE) give a reference in different states of dolomite conservation including all transitions from unspoiled dolomite crystals to dolomite crystal relics. Due to the dissolution processes rounded corners, edges and microcaverns are common properties of these dolomite crystals. However, especially on crystal surfaces and in microcaverns small minerals of hexagonal prismatic shape occur. According to Energy Dispersive X-ray spectroscopy (EDX) analyses these prisms contain Ca, P, and O which is an indication of being apatite minerals. Cathodoluminescence (CL) investigations reveal a multi-phase composition of the Franconian dolomite: The cores of the dolomite crystals show blotchy red CL colours with relics of brownish-beige CL-zones whereas the crystal edges emit a homogeneous red CL. As the crystals of the dolomite sands often are stronger cavernous inside than outside it is obvious that the multi-phase composition of the dolomite crystals has an effect on the dissolution behavior of the dolomite crystals. Certainly the dissolution of the Franconian dolomite initially starts at the crystal boundaries but during successive dissolution the multi-phase composition of the crystals plays an important role - among the rhombohedral cleavage and the inclusion content. The growth of the microapatites finally is attributed to organic acids from the decay of extensive vegetation in Tertiary soils above the Franconian dolomite. Such organic acids as component of weathering fluids increase the dissolution of dolomite and provide the phosphorus for the precipitation of microapatites during retention in the dolomites porosity.

Literature:


Sizes, shapes, and patterns of coral reefs in the Maldives, Indian Ocean:
the influence of wind, storms, and precipitation

Eberhard Gischler¹, Dominik Schmitt², David Storz²

¹gischler@em.uni-frankfurt.de, Institut für Geowissenschaften, Goethe-Universität, 60438 Frankfurt am Main
²schmittdominik@gmx.net, Institut für Geowissenschaften, Goethe-Universität, 60438 Frankfurt am Main
david.storz@em.uni-frankfurt.de, Institut für Geowissenschaften, Goethe-Universität, 60438 Frankfurt am Main

The Maldives are among the largest reef areas in the world. The Maldives archipelago is located in the NW Indian Ocean and extends for about 1,000 km from N to S and is some 150 km wide. The archipelago consists of 21 atolls (14 larger and 7 smaller ones) and 4 reef-fringed islands (small atolls with completely sediment-filled lagoons) that cover a total area of 21,370 km². In order to get a better understanding of the variety of reef forms in this major carbonate platform location, reef areas, reef types, and other geomorphological elements such as channels through marginal reefs, lagoons, faroes (smaller circular reefs that are found in lagoons and at marginal reefs), and lagoon patch reefs were quantified using satellite images and British admiralty sea charts. These numbers were compared to each other and related to environmental parameters such as precipitation, wind stress, current strength, and storm impact. Sizes and abundances of geomorphological elements show many statistically significant correlations. For example, total reef area covaries with reef and channels areas and abundances. Lagoon depth correlates with atoll area and precipitation rates, probably as a result of limestone dissolution during sea-level lowstands and the fact that larger catchment areas may produce larger karst reliefs. Apart from precipitation, the influence of wind and wind-induced waves appears to be of great importance for spatial patterns of reef types in the Maldives. From S to N within the archipelago, i.e., away from the equator the influence of the Indian Monsoon reversal and storms increases. In the same direction, the abundance of lagoonal reefs and channels through marginal reefs increases. The pattern is not as clear for faroes, which are so typical for the Maldives. Both the numbers of lagoonal and marginal faroes reach maxima in the north-central part of the archipelago and decrease towards the north, for reasons not entirely clear. Faroes, the formation of which has been disputed, form via processes of lateral sand transport during the reversing monsoon and subsequent colonization of sand spits by corals. Wind stress appears to be correlated with faro development as it increases from S to N and slightly decreases again in the very N, just like the abundance of faroes. In addition, the destructive influence of cyclones, which only reaches as far south as the N° Maldives, might be detrimental to faro development. Given that dissolution during glacial sea-level lowstands also plays a role in faro development, the decreasing precipitation rates (as proxy for glacial limestone dissolution) might hamper faro formation towards the N of the archipelago.
Recent developments in remote sensing (tectonic) geomorphology

Richard Gloaguen and the Remote Sensing Group

1 RSG Helmholtz Institute Freiberg of Resource Technology, Halsbruekerstr. 34, 09599 Freiberg r.gloague@hzdr.de

2 RSG TU Bergakademie Freiberg, 09599 Freiberg

The access to recent satellite sensors and increasing computing power has led to the development of new methodologies to quantify Earth's surface processes. During the past decade, we, at the Remote Sensing Group, have contributed to the advance of remote sensing based methods for 3 specific aims:

1. The extraction of image discontinuities from remote sensing images and digital elevation models and the statistical analysis of inferred faults allow us to characterize the geometry of the deformation field, the intensity of recent tectonic activity and even physical properties of the deformed medium (e.g. rock strength, brittle layer thickness). The extraction of faults is difficult and we have taken several approaches (e.g. object oriented classifications, Hough transform), none of them being ideal. We then use the specific distribution (e.g. fractal, Weibull) of fault dimensions to determine characteristic physical properties.

2. The calculation of geomorphic parameters enables us to characterize the relative intensity of erosion and to localize neotectonic activity. We automatically extract the drainage network from high resolution DEMs and derive informations about the intensity of incision from geometric properties of river profiles. The quantification of the geometrical properties the Earth's surface gives insights about relative surface uplifts or base level changes and the localization of deformation.

3. The determination of the water balance and pathways. We are now able to quantify the amount of specific precipitation involved in the transport of sediment and river incision and erosion with high resolution and accuracy. We use distributed models fed exclusively by remote sensing data to quantify daily runoff. We use in-situ data to calibrate rating curves that allow use to quantify sediment discharge.

These techniques rely on the recent availability of sensors measuring climatic features such as precipitation and temperature with high temporal and spatial resolution as well as very high resolution imagery and DEMs over very large areas and with good accuracies. These methods also benefit from the somehow recent introduction of advanced quantitative methods in Earth Sciences. We thus make a heavy use of nonlinear analyses and machine learning methods.

I will illustrate the potential of remote sensing for quantitative (tectonic) geomorphology using examples of our last projects. Without being exhaustive I hope to convince the audience, that the nonlinear analysis of remote sensing data has now become an essential tool for the quantification of Earth's surface processes.
Deciphering the driving forces of short-term erosion in glacially impacted landscapes, an example from the Western Alps

C. Glotzbach¹, P. van der Beek², J. Carcailler³, R. Delunel³

¹Institute of Geology, Leibniz University Hannover, Germany (glotzbach@geowi.uni-hannover.de)
²Institut des Science de la Terre, Université Joseph Fourrier Grenoble, France (pvdbeek@ujf-grenoble.fr, julien.carcaillet@ujf-grenoble.fr)
³Institute of Geological Sciences, University of Bern, Switzerland (romain.delunel@geo.unibe.ch)

Tectonic uplift is the main driver of long-term erosion, but climate changes can markedly affect the link between tectonics and erosion, causing transient variations in short-term erosion rate. Here we study the driving forces of short-term erosion rates in the French Western Alps as estimated from in-situ produced cosmogenic 10Be and detrital apatite fission-track thermochronology analysis of stream sediments. Short-term erosion rates from 10Be analyses vary between ~0.27 and ~1.33 mm/yr, similar to rates measured in adjacent areas of the Alps. Part of the data scales positively with elevation, while the full dataset shows a significant positive correlation with steepness index of streams and normalized geophysical relief. Mean long-term exhumation and short-term erosion rates are comparable in areas that are exhuming rapidly (>0.4 km/Myr), but short-term rates are on average two-three (and up to six) times higher than long-term rates in areas where the latter are slow (<0.4 km/Myr). These findings are supported by detrital apatite fission-track age distributions that appear to require similar variations in erosion rates. Major glaciations strongly impacted the external part of the Alps, increasing both long-term exhumation rates as well as relief. Based on our data, it seems that glacial impact in the more slowly eroding internal part is mainly restricted to relief, which is reflected in high transient short-term erosion rates. The data further reveal that normalized steepness index and ridgeline geophysical relief are well correlated with (and could be used as proxies for) short-term erosion, in contrast to slope, corroborating studies in purely fluvial landscapes. Our study demonstrates that climate change, e.g. through occurrence of major glaciations, can markedly perturb landscapes short-term erosion patterns in regions of tectonically controlled long-term exhumation.
Early exhumation of the Aiguilles Rouges and Mont Blanc massifs, European Alps

C. Glotzbach\textsuperscript{1}, M. Danišík\textsuperscript{2}, M. Rahn\textsuperscript{3}, P. van der Beek\textsuperscript{4}, C. Spiegel\textsuperscript{5}

\textsuperscript{1}Institute of Geology, Leibniz University Hannover, Germany (glotzbach@geowi.uni-hannover.de)
\textsuperscript{2}Department of Earth & Ocean Sciences, University of Waikato, New Zealand (martind@waikato.ac.nz)
\textsuperscript{3}Swiss Federal Nuclear Safety Inspectorate ENSI, Switzerland (Meinert.Rahn@ensi.ch)
\textsuperscript{4}Institute des Science de la Terre, Université Joseph Fourier Grenoble, France (pvdbeek@ujf-grenoble.fr)
\textsuperscript{5}Department of Geosciences, University Bremen, Germany (cornelia.spiegel@uni-bremen.de)

Although the exhumation history of the external crystalline massifs of the European Alps has been extensively studied, the timing and kinematics of the initiation of exhumation is little understood. Here we present new zircon/apatite fission-track and apatite (U-Th-Sm)/He data from the central Aiguilles Rouges massif, which are combined with existing data in an attempt to investigate the (early) exhumation history of the Aiguilles Rouges and Mont Blanc external crystalline massifs. The exhumation history is reconstructed by various methods, including 3D thermal-kinematic modelling. Although we applied simple 1D interpretation approaches, only 3D thermal kinematic-modelling could accurately refine the burial and exhumation scenario, suggesting rapid burial at \~0.6 km/Myr between \~33 Ma and \~20 Ma, followed by rapid exhumation (>1 km/Myr) that started at \~19 Ma, decreased to \leq0.5 km/Myr at \~13 Ma, and finally increased to \geq1 km/Myr during the last million years. A strong gradient in burial and early exhumation normal to the strike of the orogen is predicted, with burial/exhumation rates in the Mont Blanc massif being approximately twice as high as in the more external Aiguilles Rouges massif. Initial rapid exhumation occurred contemporaneously with major movements along the Simplon Fault Zone, suggesting a kinematic link. Based on our data and modelling results we suggest that orogen-perpendicular and -parallel doming occurred at or slightly after \~20 Ma. It was governed by thrusting along individual crustal-scale faults within the external crystalline massifs in combination with transtensional movements in the Rawil depression located between the Mont Blanc-Aiguilles Rouges and Aar-Gotthard culminations.
Provenance of Quaternary sediments deduced from fission track analyses

C. Glotzbach¹, J.J. Hertel¹, F.S. Busschers², J. Winsemann¹

¹Institute of Geology, Leibniz University Hannover, Germany (glotzbach@geowi.uni-hannover.de, winsemann@geowi.uni-hannover.de, johanna_hertel@gmx.de)

²TNO – Geological Survey of the Netherlands, Utrecht, The Netherlands (freek.busschers@tno.nl)

Quaternary sediments blanket a large portion of the Earth’s Surface. The provenance of these sediments is traditionally deciphered by heavy mineral and geochronological (e.g. U-Pb dating) analyses, but as with most provenance methods, similarities in the source signal and repeated recycling of older sediments often complicate or even prevent a robust interpretation. In this study we investigate the potential of apatite and zircon fission track (AFT and ZFT, respectively) analyses to unravel the provenance of fluvial and glacigenic Pleistocene sediments in the Lower Rhine Embayment and the northeastern Netherlands. Measured detrital AFT and ZFT age distributions are compared to in situ AFT and ZFT ages of potential source areas in central and northern Europe. Due to differing cooling histories of these regions, it should theoretically be possible to distinguish five source regions (from young to old): the Alps, the Black Forest and Vosges Mountains, Late Cretaceous inversion structures (e.g. Harz Mountains, Bohemian Massif), the Rhenish Massif and the Fenno-Scandinavian region. Analogous to accompanied heavy mineral analyses the observed AFT and ZFT age distributions reveal a more or less pre-dominant provenance from the Alps, suggesting that the majority of sand was originally deposited by the River Rhine. The drainage basin of the River Rhine also comprises the Black Forest and Vosges Mountains and the Rhenish Massif, which according to our AFT and ZFT results make up only a minor source in the majority of analyzed sediments. Some samples, especially in the Münsterland Embayment and northeastern Nederland also contain grains from Fenno-Scandinavian source regions. Based on these results, we suggest that detrital thermochronology, such as AFT and ZFT methods, are capable to unravel the provenance of Pleistocene deposits. Advantages compared to alternative methods such as heavy mineral analyses are: i) the provenance signal (age distribution) is less influenced by the grain size of sampled sediments, and (ii) although source regions are composed of similar lithologies and/or crystallization ages (e.g. widespread Variscan basement rocks in Central Europe), variable cooling histories result in distinguishable cooling ages. We yield valuable information about the previously unresolved or poorly defined provenance of Middle Pleistocene fluvial sediments in the Lower Rhine Embayment and the northeastern Netherlands. In addition, heavy mineral and fission track results challenge the straightforward usage of augite as an index mineral for Rhine provenance in the northern Netherlands.
Refining the Margin of the Zimbabwe Craton: New U-Pb Zircon ages from the Dete-Kamativi Inlier, NW Zimbabwe

Glynn, S.M1, 2, Master, S1, 3, and Frei, D4
1School of Geosciences, University of the Witwatersrand, Johannesburg, South Africa 2GeoForschungsZentrum, Telegrafenberg, Potsdam, Germany (sarahg@gfz-potsdam.de) 3Sharad.Master@Wits.ac.za 4Central Analytical Facility & Dept. of Earth Sciences, University of Stellenbosch, South Africa (Dirkfrei@sun.ac.za)

We have recovered zircons from a wide variety of sample materials collected from the Dete-Kamativi Inlier near the Zimbabwe-Zambia border. Laser ablation ICP-MS analyses of these samples both greatly refine the deformational history of the Dete-Kamativi Inlier as well as clarify key chronological relationships between the Zimbabwe Craton and basement units to the west below the Kalahari sands.

Data from two late, undeformed granites both yielded similar concordia intercept ages of 2.0 to 2.1 Ga. Though collected only 4 km from each other, the two granitic samples have distinctly different petrologies – which is also reflected by distinct differences between the inherited zircon populations. Zircons from sample Z DK-2 (coordinates 18°31’53”S 27°04’29”E) define tightly an age of 2.02 Ga, interpreted as the unit’s crystallization age. In contrast, zircons from sample Z DK-1 (18° 33’ 59”S 27°03’18”E) fail to define a precise magmatic age; rather the zircon population is dominated by older, commonly concordant components ranging between 2.6 and 3.3 Ga. The observed age spectrum for Z DK-1 is consistent with patterns observed further to the east and south in terrains clearly assigned to the Zimbabwe Craton.

Published zircon ages obtained from both outcrop and drill core samples from across central Botswana are dominated by ages similar to our 2.0 to 2.1 Ga population. It therefore seems that our study area occupies an important tectonic position between the Zimbabwe Craton and Palaeoproterozoic terrains forming the basement further to the west.

Laser Ablation ICP-MS results for the two granites, Z DK-1(left) and Z DK-2 (right).
In this study we investigated the Fe isotopic composition of metal, sulphide grains and chondrules, in ordinary and CB chondrites, and CO3 chondrite Kainsaz, as well as iron meteorites. Recent studies [1-3] found variations in δ⁵⁶Fe of up to 1.2‰ in bulk chondrules or mineral grain fractions which were manually extracted and dissolved. LA-MC-ICP-MS scanning revealed Fe isotopic zoning in CB metals of several ‰ [4]. Here we represent the first high precision in situ Fe isotope analyses conducted by femtosecond laser ablation-MC-ICP-MS. Instrumental mass bias was monitored with a Ni standard solution, which was simultaneously aspirated during laser ablation. This method provides δ⁵⁶Fe reproducibilities of 0.04 to 0.06 (2 SD) for replicate analyses of homogeneous standards with a spatial resolution as low as 20 μm on iron rich phases. Prior to isotope analyses metal and sulfide grains were characterized with EMPA.

The analyses of over 100 metal and sulphide grains in OCs revealed δ⁵⁶Fe values with a total variation of 1.6‰, ranging from -0.8‰ to +0.8‰, relative to IRMM-014. The analyzed sulphide grains (all troilite), revealed an average δ⁵⁶Fe of -0.47‰. Metal grains consist to 80% - 90% of kamacite, with average δ⁵⁶Fe of 0.05‰, and 10% - 20% of taenite, with average δ⁵⁶Fe of +0.49‰. In CB chondrites, large metal aggregates (>500 µm) are chemically and isotopically unzoned (with chondritic δ⁵⁶Fe). Several smaller grains, however, show a strong zoning in both, Ni concentrations and Fe isotopes, with high Ni and δ⁵⁶Fe as low as -7‰ in the metal core, similarly as previously observed by [4]. A profile across an olivine grain of a small type II chondrule of Kainsaz (CO3) revealed a positive correlation of δ⁵⁶Fe and FeO with a total range in δ⁵⁶Fe of 1.2‰. Kamacite in iron meteorites is unfractionated (δ⁵⁶Fe = 0) and our in situ results agree with solution based bulk analyses (e.g. [5]).

The in situ isotope analyses of this study show that mineral phases and components in meteorites have heterogeneous Fe isotopic compositions and are frequently zoned. This makes solution-based Fe isotope analyses difficult to interpret, as representative sampling is challenging. In the case of CB chondrites the coupled chemical and isotopic zoning in several metal grains indicates Fe isotope fractionation during condensation, either from the solar nebular or from an impact-related gas cloud [4]. The chemical and isotopically zoned olivine in a chondrule of Kainsaz was likely generated by Fe diffusion into the olivine during chondrule formation. The systematic Fe isotope fractionation between metal, taenite and troilite in OCs more likely indicate re-equilibration during cooling on the parent bodies. The large Δ⁵⁶Fe_{metal-troilite} of 0.6‰ – 0.8‰ in OCs may indicate a very low troilite-metal equilibration temperature of <300°C (calculated after [1] and [6]).

Structural controls on stratabound hydrothermal dolomitization: insights from the Benicàssim case study (Maestrat basin, E Spain)

Enrique Gomez-Rivas1, Paul D. Bons1, Juan Diego Martín-Martín3

1 Department of Geosciences, Eberhard Karls University Tübingen, Wilhelmstr. 56, 72074 Tübingen, Germany; enrique.gomez-rivas@uni-tuebingen.de, paul.bons@uni-tuebingen.de

2 Group of Dynamics of the Lithosphere, Institute of Earth Sciences “Jaume Almera” (CSIC), 08028 Barcelona, Spain; jdmartin@ictja.csic.es

Hydrothermal dolomitization is a fundamental process in enhancing or degrading carbonate porosity and permeability. Upon burial, high-temperature hydrothermal dolomite forms when fluids hotter than the host rock are advected and interact with limestones. Typically, fluids forming hydrothermal dolomite are seawater-derived or deep brines that are transported upwards along faults and fractures (i.e. feeding structures). The geometry, extent and connectivity of dolomitized geobodies can vary depending on the original depositional facies distribution, pre-dolomitization diagenesis and presence of structures such as fractures and stylolites. Fault-related dolomitization geometries typically range between two end members: (1) dolostone appears in irregular patches around faults and (2) dolostone appears in layers that extend away from faults. In the second case only some layers are preferentially dolomitized, while the others remain unaltered. There are still many open questions on what are the main factors controlling the transition from these two end members.

The Upper Aptian to Lower Albian Benicàssim ramp carbonates (Maestrat basin, E Spain) are an excellent case study for improving the current knowledge on hydrothermal dolostone distribution. In this area, seismic-scale stratabound hydrothermal dolomitized bodies extend for several kilometers away from large-scale faults, replacing syn-rift shallow-marine carbonates. Field and petrographic data indicate that grain-dominated facies are preferentially replaced while mud-rich facies are less frequently dolomitized. However, grainstone and packstone facies appear occasionally unaltered between dolostones, suggesting that depositional facies is not the main dolomitization control. There is a very high density of sedimentary (i.e. layer-parallel) stylolites in the area, as well as several sets of fractures of different ages. Dolomitization fronts are always very sharp, and in most cases follow sedimentary stylolites and outcrop-scale fractures. They weave up and down following consecutive stylolites, suggesting that these structures acted as barriers to the dolomitizing fluid, and constrained the reaction to only one side of the stylolite. The degree of stylolitization (stylolite density and stylolite teeth height) does not significantly change between limestones and dolostones, although it is slightly higher in the first ones. However, strongly anastomosing stylolites in some limestone layers create a network of connected stylolites that acted as flow barriers preventing dolomitization.

In order to complement field observations, we present fluid flow numerical simulations with the aim of analyzing the impact of stylolite and fracture network properties on dolomitizing fluid flow. The simulations illustrate how dolomitizing fluids can be channelized depending on the geometry and connectivity of stylolites and fractures, thus suggesting that these structures can be the main control on the formation of stratabound dolomitization.
Orthopyroxene (opx) in oceanic spinel peridotite is a useful proxy for water contents in the upper sub-oceanic mantle. Because of the large grain size of opx (compared to olivine), it is less affected by secondary diffusional water loss due to decompression. Contrasting water contents were found in opx of oceanic spinel peridotite, comparing samples from the Mid-Atlantic Ridge near 15°N (ODP-Leg 209) and those near 23°N (ODP-Leg 153).

Orthopyroxene from ODP-Leg 209 contains 15 wt.-ppm H$_2$O, incorporated as OH groups in the mineral structure. In contrast, H$_2$O contents in opx from ODP-Leg 153 are one order of magnitude higher, with typical values of 270 wt.-ppm. These latter values agree well with both the H$_2$O contents known from sub-continental spinel peridotite xenoliths and the water storage capacity of opx at pressures typical of the spinel peridotite facies. The water contents in opx from the sub-oceanic mantle at the Mid-Atlantic Ridge, ranging from 15 (= highly depleted) to 270 wt.-ppm (= water saturation in opx), compare well with the highly variable water contents of Atlantic MORB glass that also scatter over one order of magnitude.

Mineral trace element data indicate different degrees of partial melting: 18% for Leg 209 peridotite and 12% for Leg 153 samples. The mantle equilibrium temperature differs by 200 °C: Leg 209 = 1150-1200 °C, Leg 153 = 950-1000 °C). The opx water contents of Leg 209 are compatible with residual values after c. 18% partial melting of a peridotitic source with original bulk rock water contents of 120-130 wt.-ppm and original opx water contents of 300 wt.-ppm, respectively. In contrast, the water content of 270 wt.-ppm in opx of Leg 153 peridotite cannot be reconciled with residual amounts to be expected after 12% partial melting. This is because an unrealistically high initial water content of 3500 wt.-ppm would be required for the original opx – exceeding the water storage capacity of opx at an ambient pressure of c. 20 kbar by one order of magnitude. The data imply that – following melt depletion – the water contents of Leg 153 peridotite re-equilibrated in the spinel-peridotite facies. This may have been facilitated by a longer mantle residence time of Leg 153 peridotite (compared to Leg 209) after partial melting and prior to tectonic exhumation from c. 60 km depth. An extended mantle residence time is compatible with isobaric cooling from >1200 °C to 950-1000 °C (at c. 20 kbar) as documented by Leg 153 peridotite, and it facilitates re-introduction of water from less or non-depleted mantle regions due to the high diffusivity of H.

Acknowledgements. Financial support by DFG is gratefully acknowledged. This project used samples provided by ODP/IODP.
In-situ monitoring of reaction band formation using synchrotron radiation

L.C. GÖTZE¹, R. MILKE¹, S. SCHORR¹, R. DOHMEN², R. WIRTH³

¹Free University of Berlin, Institute of Geological Sciences, Berlin, Germany
²Ruhr University Bochum, Institute for Geology, Mineralogy & Geophysics, Bochum, Germany
³GFZ German Research Centre for Geosciences, Potsdam, Germany

Diffusion reaction couple experiments are an essential tool in order to understand corona microstructures and underlying processes in metamorphosed and igneous natural rocks. By employing a heating attachment and synchrotron radiation we monitored the initial and transient stages of an in-situ reaction band formation at the nanoscale. Additionally, by miniaturising the experimental setup using thin films we could lower the temperatures and test durations that are usually applied in diffusion couple experiments.

As a model system the reaction between corundum (Al₂O₃) and periclase (MgO) that forms spinel (MgAl₂O₄) was chosen. The diffusion couples consisted of single crystal substrates of either (0001) oriented corundum with an amorphous MgO thin film on top or (111) oriented periclase which reacted with an Al₂O₃ thin film. Thin films were produced by laser ablation, and their thickness was always less than 300 nm. Experimental temperatures were varied from 700 to 1000 °C, and test durations ranged from 5 minutes to 3 hours. The texture of the in-situ grown spinel, i.e. the crystallographic relationship between substrate and thin film, was subsequently analysed using a four-circle diffractometer to obtain pole figures. As complementary methods to the X-ray diffraction techniques transmission electron microscopy (TEM) and atomic force microscopy (AFM) were employed.

When using corundum substrates no spinel formation could be observed at 700 and 800 °C, but the originally amorphous reaction layers crystallise oriented on the substrate. Spinel formation occurs at a moderate rate at 900 °C, and is rapid at 1000 °C. The time series conducted at 1000 °C points to an interface-controlled reaction regime, i.e. the thickness of spinel grows linearly with time. Reaction kinetics are considerably faster when using periclase as substrate, where moderate spinel formation occurs already at 800 °C. Microstructures within the spinel, as revealed by TEM, suggest 'counter-diffusion of the cations' as the diffusion mechanism. For this specific scenario, the reaction volume is positive at the moving corundum/spinel interface, and correspondingly, TEM bright field pictures show parabolic strain contrasts that extend into the corundum substrates. On the other hand, at the periclase/spinel interface the reaction volume is negative, and a porous layer at this phase boundary is visible. The observed discrepancy of reaction kinetics is supposed to be due to the different reaction volumes, as a positive reaction volume induces mechanical force to the substrate and thus reduces the thermodynamical driving force for the reaction.

Diffraction spectra and particularly the pole figures show that the spinel crystallises and grows epitactically on and into the substrates.
Kinetics of phlogopite rim growth on olivine in phonolite melt at upper mantle / lower crust conditions

Thomas B. Grant¹, Ralf Milke², Bernd Wunder³, Richard Wirth⁴, Dieter Rhede⁵, Luiz Morales⁶

¹grant@gfz-potsdam.de
²milke@zedat.fu-berlin.de
³bernd.wunder@gfz-potsdam.de
⁴richard.wirth@gfz-potsdam.de
⁵dieter.rhede@gfz-potsdam.de
⁶luiz.morales@gfz-potsdam.de

The Heldburg Phonolite, central Germany contains olivine xenocrysts from spinel lherzolite origins. Dis-equilibrium with the melt lead to dissolution of olivine and the growth of phlogopite + diopside reaction rims. The reaction rims are small-scale analogues of a potential metasomatic reaction with evolved alkali enriched melts in the mantle. This work aims to reproduce the reaction rims experimentally, to determine the rim growth rates for estimates of xenocryst residence times and to work out how the properties of rim grain boundaries are affected by increasing the bulk water content of the melt.

We were able to experimentally reproduce reaction rims of phlogopite on olivine using synthetic forsterite olivine and phonolite melt at conditions of 10kbar and 950°C. Rim growth is parabolic with time, indicating a diffusion controlled reaction. No measurable concentration profiles were observed in the host olivine or the melt suggesting that diffusion controlled growth was limited by grain boundary diffusion in the rims. Increasing the bulk water content of the melt produced dramatically increased rates of rim growth. From 4-8 wt.% H₂O in the melt and an observed reaction rim of 100µm, the estimated residence times can vary from around one week to several years.

Transition electron microscopy (TEM) analysis of phlogopite grain boundaries shows the presence of sub micron pores of fluid and micron to sub micron melt inclusions throughout the rims. The connectivity of both fluid and melt pockets appears to be limited and the phlogopite-phlogopite rim grain boundaries show no signs of a fluid or melt film. It is most likely that atomically bound hydrous species are present at phlogopite grain boundaries and that increasing the bulk water content of the melt increases the level of grain boundary hydration and fluid saturation. This then increases the rates of transport during reaction, giving faster rim growth rates.
Tourmaline-supergroup minerals are ubiquitous accessory minerals in rocks of the Earth’s crust. They are stable over a wide pressure-temperature (P-T) interval [1]. Despite their potential for use as a geothermobarometer, experimental thermodynamic data for the tourmaline group minerals are very limited.

In this study, calorimetric and P-V-T data of synthetic Al-rich tourmaline (olenite) have been obtained. Analytical data on a sample prepared at 25 kbar, 600°C, show excess boron and water relative to the theoretical formula NaAl$_3$Al$_6$[Si$_6$O$_{18}$](BO$_3$)$_3$O$_3$(OH), coupled with deficiencies in Si, Al, and Na. Thus, a provisional structural formula was derived as (Na$_{0.65}$$\square$$_{0.35}$)(Al$_{2.72}$$\square$$_{0.28}$)(Al$_{5.42}$Si$_{3.28}$) [Si$_{3.73}$B$_{2.27}$O$_{18}$](BO$_3$)$_3$(OH)$_{3.87}$O$_{0.13}$ [2]. The volumetric behaviour of this sample has been determined in situ up to 8.5 GPa and 700°C using a MAX 80 cubic anvil high-pressure apparatus (DESY, HASYLAB, Hamburg, Doris III, Beamline F.2.1). The samples were mixed with vaseline to ensure hydrostatic pressure transmitting conditions; NaCl served as an internal standard for pressure calibration [cf. 3]. Energy dispersive diffraction patterns were collected at a fixed 20 angle (0 ≈ 3.67°). By fitting a Birch-Murnaghan EOS to the data, the bulk modulus of olenite was determined as 91.18 ± 4.84 GPa, (K’ = 4), $V_{T=0}$ = (1484.93 ± 3.79) Å$^3$ exp $[(0.137 ± 0.090) \times 10^{-4} dT]$, $(\partial K'/\partial T)_P = 0.023 ± 0.017$ GPa K$^{-1}$. The $V_0$ value is in good agreement to the values obtained from Rietveld refinement of two different samples by Marler et al. [4].

The standard entropy of another sample (No. V 81, [5]) was derived from low-temperature heat capacity measurements using a physical property measurement system (PPMS) in the temperature range 5 K $< T < 300$ K: $S^0_{298}$ (olenite V81) = 574.2 ± 2.0 JK$^{-1}$mol$^{-1}$ assuming the composition of the first sample [2]. Additionally, DSC measurements with a Perkin Elmer Diamond DSC in the temperature range 270 K $< T < 760$ K were performed to check the reproducibility of the PPMS measurements around ambient temperature.

References

Metamorphic and magmatic events in the Transuralian zone – a U-Pb LA-Q-ICP-MS zircon study

L. Gronen¹, S. Sindern², Yu. Ronkin³, R. Winkler⁴, B.A. Schulte, J. Glodny, U. Kramm

¹lars.gronen@rwth-aachen.de
²Sindern@rwth-aachen.de
³y-ronkin@mail.ru
⁴Rebecca.Winkler@rwth-aachen.de

Granites and an amphibolite facies leucosome from the Mariinskiy Complex as well as a tonalite from the Nishniy Sanarskiy Complex (Southern Urals) were investigated to define the evolution of the western Transuralian Zone along the Kazakh Continent during the Uralian Orogeny. U-Pb-isotope analyses of zircon were performed at RWTH Aachen University using an ElanDRCe quadrupole ICP-MS (PerkinElmer) coupled to a NewWave UP193FX ArF laser ablation system (ESI). The Plesovice standard was used to correct for laser induced inter-elemental fractionation and instrumental mass discrimination. Raw data were processed using the PepiAge software by I. Dunkl (Göttingen). Major and trace element analyses of whole rock samples were carried out using XRF (RWTH Aachen) and SF-HR-ICP-MS (IGG Ekaterinburg) techniques. The granitoids are magnesian, calcic to calc-alkalic and metaluminous to mildly peraluminous. The mineralogy of the samples and their chemical composition of major and trace elements indicate granite formation by mixing of slab-derived melts and melts generated in the crust, which is most consistent with an Andean type magmatic arc setting. This together with the compositional characteristics of subalkaline basaltic rocks support ideas that the Transuralian zone contains remnants of the Valerianovka Andean type magmatic arc along the margin of the Kazakh continent. Zircon crystals of the granitoid rocks are elongated and have well developed prism and bipyramid faces. Magmatic formation is indicated by oscillatory growth zonation in BSE and CL images. U-Pb age determination of zircon yields ages of 364 +/- 14 Ma for the Mariinskiy granitic intrusion and 357 +/- 2.5 Ma for the tonalitic intrusion of Samarskiy. Amphibolite facies host rocks of the granitoids record minimum T conditions near 500 °C. Zircon crystals from a leucosome of these rocks are elongated and show core-rim structures with oscillatory growth zonation at the grain edges. These crystals are considered to have formed in the leucosome and to represent peak metamorphic conditions. LA-ICP-Q-MS U-Pb analyses yield an age of 353 +/- 6 Ma, which indicates that HT metamorphism occurred during the Uralian orogenesis. The granitoids of the western Transuralian zone are similar, in age and composition, to subduction-related intrusives of the Magnitogorsk and Easturalian zone to the west of the study area. This points to contemporaneous subduction of the east Uralian oceanic domain in a westward direction underneath the Magnitogorsk arc as well as in an eastward direction underneath the Kazakh continent in late Devonian to early Carboniferous times.
Zircon is an accessory mineral, which is often used for constraining rock-forming processes in various ways. Next to it wide-spread use in geochronology it is also important for the geochemical cycle of high-field strength elements (HFSE), particularly the geochemical twins Zr and Hf. Finally, the Ti content found in zircon can be used for estimating the temperature of formation (Watson et al. 2006).

Here, we present data on a series of samples synthesized across the zircon-hafnon join (zircon, hafnon, and five intermediate compositions), which were grown from a Pb-silicate melt after the method of Watson et al. (1997). We will present a reconnaissance study on the properties of the zircon-hafnon solid solution using XRD and Raman spectroscopy. The crystals synthesized so far show sizes from about 20 to more than 100 µm across. Most crystals, especially at intermediate compositions display sector and growth zoning. Yet, there are domains sufficiently large and homogeneous for Raman measurements. Preliminary examination showed systematic shifts of the four main bands at >300 cm\(^{-1}\) produced by internal vibrations of the SiO\(_4\) tetrahedra, whereas the bands <300 cm\(^{-1}\), commonly referred to as lattice modes (Nasdala et al. 2003), show a more complex behaviour within the zircon-hafnon join.

In the calibration of the Ti-in-zircon thermometer Watson et al. (2006) could not synthesize zircon at temperatures below 1000°C. In order to calibrate the thermometer also for lower temperatures, they had to rely on natural samples, where the temperature of formation was determined independently. We successfully synthesized zircon in rutile and quartz-saturated experiments at temperatures between 800 and 1100°C and 200 – 1000 MPa. To enhance transport and reaction, Na-Si-glass was dissolved in the coexisting aqueous solution (Wilke et al. 2012). Crystal sizes range from 40 µm at 1100°C to 10 µm at 800°C, sufficiently large to be analysed by electron microprobe and LA-ICP-OES or SIMS. Resulting Ti contents will be compared to Watson et al. (2006) and used to complement the Ti-zircon thermometer.

Earthquake-cycle deformation, long-term fault slip and the growth of fault-bounded mountains

Andrea Hampel

Institut für Geologie, Leibniz Universität Hannover; hampel@geowi.uni-hannover.de

In tectonically active regions, crustal deformation and surface processes act in concert to shape Earth’s landscapes. During earthquakes, faults accumulate displacement, which leads – over geological timescales – to the growth of mountain ranges. The surface deformation associated with individual intra-continental earthquakes has recently been recorded by GPS, which revealed hitherto unrecognized contrasts between the slip patterns on normal and thrust faults. I will present three-dimensional numerical models including discrete faults, which shed light on the relationship between coseismic slip, cumulative displacement acquired over several earthquake cycles and the growth of fault-bounded mountain ranges.

The first model set investigates the differences in the co- and postseismic slip patterns of normal and thrust fault to explain the contrasting surface deformation patterns observed in the GPS records of recent intra-continental earthquakes. In the hanging wall of the thrust fault ruptured during the 2003 Chengkung (Taiwan) earthquake, a divergent displacement pattern was recorded. In contrast, a convergent slip pattern was observed in the hanging wall of the normal fault that produced the 2009 L’Aquila (Italy) earthquake. Remarkably, such convergent slip patterns are also evident in field records of cumulative fault slip in central Italy, which underlines the coseismic origin of the latter. Our finite-element models demonstrate that the observed fault-parallel motions are a characteristic feature of the coseismic slip pattern on normal and thrust faults (Hampel et al., Geology, vol. 41, p. 299-302, 2013). Modeled slip vectors converge toward the center of normal faults whereas they diverge for thrust faults, which causes contrasting fault-parallel displacements at the model surface. The model also predicts divergent movements in normal fault footwalls, which were recorded for the first time during the L’Aquila earthquake. During the postseismic phase, viscous flow in the lower crust induces fault-parallel surface displacements, which have the same direction as the coseismic displacements but are distributed over a larger area that extends far beyond the fault tips. Hence, detecting this signal requires GPS stations in the prolongation of the fault’s strike. Postseismic velocities vary over several orders of magnitude depending on the lower-crustal viscosity and may reach tens of millimeters per year for low viscosities. Our study establishes the link between coseismic and cumulative slip patterns on normal and thrust faults and emphasizes that understanding fault-parallel slip components and associated surface displacements is essential for inferring regional deformation patterns from space-geodetic and fault-slip data.

The second model set investigates how temporal changes of the friction coefficient of the fault plane affect coseismic and cumulative fault slip (Hampel & Hetzel, Terra Nova, vol. 24, p. 357-362, 2012). Such changes may arise from processes that alter the strength of fault rocks either by progressive weakening or strengthening. By using three-dimensional numerical models with a thrust fault that is alternately locked and released, it is shown that variations in the friction coefficient affect both coseismic and long-term fault slip. Decreasing the friction coefficient by 5% while keeping the duration of the interseismic phase constant leads to a four-fold increase in coseismic slip, whereas a 5% increase nearly suppresses slip. A gradual decrease or increase of friction over several earthquake cycles (1–5% per earthquake) considerably alters the cumulative fault slip. In nature, the slip deficit (surplus) resulting from variations in the friction coefficient would presumably be compensated by a longer (shorter) interseismic phase, but the magnitude of the changes required for compensation render variations of the friction coefficient of >5% unlikely.

For the third model set, the fault models were coupled to a landscape evolution model to investigate the growth of mountain ranges by continuous slip accumulation of the fault at depth. In different experiments, fault length and dip as well as the diffusion constant and fluvial erosion parameter were varied. The modelled landscapes show that the mountain range developed above the thrust has a continuous crustline that acts as a drainage divide, i.e. rivers flow both toward and away from the fault surface trace. At the fault tips, rivers are deflected by the growing range. In contrast, in the normal fault model, rivers flow through the rising range, which indicates that river incision is able to keep pace with rock uplift. As a result, the range is dissected by rivers. The results of the parameter study reveal the relative contribution of diffusive and fluvial erosion to the evolution of the model landscape. The fluvial erosion parameter, which ultimately reflects the effect of precipitation, exerts control on the number and the spacing of the channels. Our preliminary results indicate that the bow-shaped topographic envelope shape of the fault-bounded mountain range is maintained also when surface processes modify the shape of the range, in accordance with observations from natural mountain ranges, e.g. at the margin of the Tibetan Plateau or in the Basin-and-Range Province.
Rapid coastal subsidence in the central Ganges–Brahmaputra Delta (Bangladesh) since the 17th century deduced from submerged salt-producing kilns

Hanebuth T.J.J.1, Kudrass H.R.1, Linstädter, J.2, Islam, B.3, Zander, A.M.4

1 MARUM – Center for Marine Environmental Sciences, University of Bremen, Leobener Strasse, 28359 Bremen, Germany, thanebuth@marum.de
2 Institute of Prehistoric Archaeology, University of Cologne, Weyertal 12, 50923 Köln, Germany
3 Department of Geology and Mining, University of Rajshahi, Rajshahi 6205, Bangladesh
4 Institute of Geography, University of Cologne, Albertus-Magnus-Platz, 50923 Köln, Germany

The densely populated low lying Ganges-Brahmaputra Delta is highly vulnerable to the global sea-level rise. In order to estimate the subsidence of the delta over historical time scales, we examined submerged salt-producing kiln sites in the coastal Sundarbans.

These kilns were built just above the previous winterly spring high-tide level, but are currently located ~155 ± 15 cm below the corresponding modern level. According to optically stimulated luminescence (OSL) dating, the kilns were ultimately fired ~300 years ago (1705 ± 35 AD) and salt production was terminated abruptly by a catastrophic event (major cyclone), which affected the kiln sites at different levels and locations. Two particular buried mangrove root horizons 80 cm below this kiln level also indicate catastrophic scenarios (probably subsidence events related to a regional earthquake). AMS-14C ages measured on the charcoal layers at the kiln’s bases and on these associated mangrove stump horizons support the OSL dates.

Based on the respective elevations of these kiln and mangrove palaeo-horizons and on the ages, the 300-year-average rate of sinking of the outer delta is 5.2 ± 1.2 mm/a, which includes 0.8 mm/a of eustatic sea-level rise over this historical period. Expecting further acceleration of the eustatic sea-level rise of up to 7 mm/a, we calculate a rise in relative sea level of up to 8.9 ± 3.3 mm/a for the next few decades, which will dramatically aggravate the already present problematic situation.

Only a prudently-managed control of sediment accretion will keep southern Bangladesh above the sea level.

(Published in the September issue of Geology.)
Inclusions in sanidine megacrystals from the Quaternary volcanic field of the Eifel, Germany

Nicole Hanold¹, Jürgen Schreuer², Bernhard Stöckhert³

¹nicole.hanold@ruhr-uni-bochum.de
²juergen.schreuer@ruhr-uni-bochum.de
³bernhard.stoeckhert@ruhr-uni-bochum.de

Sanidine megacrystals weighing up to 10 kg are found at several eruption centers of the Quaternary Eifel volcanic fields, Germany. The origin of these highly perfect sanidine megacrystals is poorly understood. Insight into environment and conditions of crystallization is provided by inclusions, which mostly contain both solids (minerals, glass) and fluid phases. Internal microstructure of inclusions, arrangement, shape, and size are studied with polarization and scanning electron microscopy, chemical composition of solids is analyzed using EDX, composition and density of fluid phases by microthermometry. Cathodoluminescence microscopy is used to reveal inhomogeneities and zoning in host sanidine and solid inclusions. Entirely solid single crystal inclusions comprise apatite, pyroxene, biotite, titanite, zircon, pyrochlore and nosean. Primary inclusions containing solid and fluid phases are of two types with respect to the solids: Type 1 inclusions show a rim of idiomorphic crystals, which protrude into the cavity. Type 2 inclusions show an additional glass film coating these idiomorphic crystals. The glass film has a composition similar to sanidine. With respect to fluids filling the remaining cavity, microthermometric analysis allows further subdivision into four groups. Group A shows melting of ice at a temperature of -9 °C to -2 °C. In group B dissociation of clathrate is observed at temperatures between +6 °C and +15 °C, indicating additional CO₂. Group C inclusions contain CO₂ and H₂O as separate phases at room temperature. In group D inclusions no phase transitions can be observed. In addition to primary inclusions, secondary fluid inclusions formed by crack healing, in part stranded in an incipient stage. Healed cracks are irregularly distributed without preferred orientation. Volume proportions of different phases in primary group C fluid inclusions are estimated to 20-30 % glass, 60-70 % aqueous solution, and up to 10 % CO₂. Density of glass with composition similar to sanidine is assumed as 2.5 g/cm³. Density of CO₂ is about 0.65 g/cm³ on average, that of aqueous solution about 1.1 g/cm³. Bulk density of primary inclusions calculated from estimated density of the different phases and their volume proportions is similar to 1.4 g/cm³. Our preliminary results indicate that sanidine megacrystals grew in a dense aqueous mother phase with minor amount of CO₂ and solute proportions approximately corresponding to sanidine. Presumably, this phase had accumulated at the roof of a stagnant magma chamber. Irregularities during crystallization of sanidine caused trapping of small aliquots of the mother phase as inclusions. As there is no indication of decrepitation during explosive eruption, the tiny containers seemingly remained intact and represent the quench product of the phase from which sanidine megacrystals grew, and probably also original density.
Many climate reconstructions in the South China Sea are based on highly resolved core interpretations by means of clay minerals. For long time periods, the classical stratigraphic principles may be true, but how orderly is deposition of sinking particulate matter during much shorter time intervals? How much do lateral advection, sorting and mixing of sediments from different sources contribute to local sediments? And how do these current driven mechanisms distort climatic signals, which we actually want to know from specific drainage basins or regions? How big are the impacts of variations in riverine sediment flux amounts and their compositions related to weathering compared to the variations of particulate matter distribution through current activity? To learn more about the complex network of mechanisms involved in recent sedimentation, we aim to distinguish the cause of variations by geochemical and mineralogical fluxes and compositions within sinking particulate lithogenic matter.

Annual means of geochemical and clay mineralogical compositions of sinking particulate lithogenic matter, monthly collected by sediment traps in the South China Sea, show at least three types of geochemical and clay mineralogical facies above the continental shelves. They are comparable to those of riverine sediments as described in previous publications; a northwestern facies derives from the taiwanese and southern chinese rivers, a southwestern from the Sunda shelf and surrounding drainage basins as well as Mekong, Red and smaller vietnamese rivers, and a northeastern from Luzón rivers. Varying contributions of two of those particle clouds to a local sediment are documented by seasonal variations in clay mineralogical and geochemical properties at the mooring station SCS-W. The two clouds shift over the mooring station opposed to monsoonal surface current direction changes.

In other regions of the SCS and in greater depth, contribution of the source regions and their variations of compositions follow a less regular pattern. Especially in the central basin the network of mechanisms is more complex. At nearly all mooring stations, smectite contents increases downwards to the continental slope or basin floor, though geochemical properties of the particulate matter varies differently. We suspect that in some regions, additional smectite altered autochthonously of formerly deposited volcanic ashes, while in other regions it may be laterally advected from the continental slope or enriched by gravitational differentiation.
Geological evolution of the North Sea: a dynamic 3D model including petroleum system elements

Sabine Heim1, Rüdiger Lutz2, Dirk Kaufmann3, Lutz Reinhardt4

Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 2, 30655 Hannover, Germany

1Sabine.Heim@bgr.de; 2Ruediger.Lutz@bgr.de; 3Dirk.Kaufmann@bgr.de; 4Lutz.Reinhardt@bgr.de

This study investigates the sedimentary basin evolution of the German North Sea with a focus on petroleum generation, migration and accumulation. The study is conducted within the framework of the project “Geoscientific Potential of the German North Sea (GPDN)”, a joint project of federal (BGR, BSH) and state authorities (LBEG) with partners from industry and scientific institutions.

Based on the structural model of the “Geotektonischer Atlas 3D” (GTA3D, LBEG) and recent research work of the northwestern part of the German North Sea, the so called “Entenschnabel” area, three dynamic 3D models are developed. Geological information, e.g. lithostratigraphy, facies and structural data, was provided by research institutions and industry partners or taken from published research projects and the literature.

Numerical modeling of the central part of the German North Sea was carried out for a sedimentary succession containing 19 stratigraphic layers, representing the sedimentary deposition from the Devonian until Present. Structural details have been considered in terms of simplified faults and salt structures, as well as main erosion and salt movement events. In particular, the models require salt doming processes of Zechstein evaporates during a time period between Late Triassic and Cretaceous, for single diapirs until Present. Lithology, facies and the boundary conditions e.g. heat flow, paleo water-depth and sediment water interface temperature were assigned. The system calibration is based on geochemical and petrological data, such as maturity of organic matter (% VRr) and present day temperature.

Due to the maturity of the sedimentary organic matter Carboniferous layers are the major source rocks for gas generation. Main reservoir rocks are the Rotliegend sandstones, furthermore, sandstones of the Lower Triassic and Jurassic can serve as reservoir rocks in areas where the Zechstein salts are absent. The model provides information on the temperature and maturity distribution within the main source rock layers as well as information of potential hydrocarbon generation based on kinetic data for gas liberation.

Finally, these dynamic 3D models offer a first interpretation of the current data base and an estimation of the structural- and burial evolution of the German North Sea area, including information on the petroleum system elements. It provides information about possible migration pathways, oil and gas accumulations, as well as the type of generated hydrocarbons and non-hydrocarbons.
The Early Mesozoic Ayú Complex in Mexico: constraints for the western margin of Pangea-A

Maria Helbig¹, Duncan Keppie², Brendan Murphy³, Luigi Solari⁴

¹maria.helbig@gmail.com, ²keppie@eastlink.ca, ³bmurphy@stfx.ca, ⁴solari@unam.mx

Various paleogeographic models have been proposed concerning the Late Paleozoic to Early Mesozoic configuration of Middle America. Constraining the paleo-position of southern Mexico is crucial for evaluating the validity of the proposed models and has important implications for the paleogeography of Pangea. The Triassic–Jurassic Ayú Complex in southern Mexico, formerly inferred to be part of the Paleozoic Acatlán Complex, consists of the Chazumba Lithodeme, the Magdalena Migmatite, the San Miguel intrusive rocks and the mafic to ultramafic Tepejillo and Tultitlán lenses. The study area crops out in a horst and is in fault contact with contemporaneous, unmetamorphosed and mildly deformed continental fluvial sedimentary rocks. The Chazumba Lithodeme comprises a polydeformed, middle to high-grade, siliciclastic, turbiditic succession that is intercalated with boudinaged ortho-amphibolites. In the south, the metasedimentary protoliths are affected by ca. 171 Ma partial melting which formed the Magdalena Migmatite. Migmatisation was accompanied by 171–168 Ma intrusions of granodioritic, dioritic, and granitic dikes and sheets as well as pegmatite bodies, which are characterised by inherited zircon populations of ca. 290–260, 360–320, 480–420, 880–990, and 1250–1080 Ma. U–Pb detrital zircon dating of seven metasedimentary samples from the migmatized and unmigmatized Chazumba Lithodeme yielded youngest detrital zircons and clusters of 192, 198, 214, 250, 266, and 291 Ma, and are interpreted to reflect the Late Triassic–Middle Jurassic deposition of the turbiditic rocks of the Chazumba Lithodeme. Whole-rock rare earth element (REE) geochemistry of the ca. 170–200 Ma ortho-amphibolites suggests a composition ranging from alkalic and transitional basalts to normalised mid-ocean ridge basalt (N-MORB) tholeiites. Initial εNd values (t = 190 Ma) of the amphibolites range from +9.01 to –2.16. Alkaline basalts have negative εNd values, suggesting derivation from an older subcontinental mantle source (TDM = 877 and 791 Ma). Group II–IV amphibolites have positive εNd values ranging from +2.31 to +9.01, indicating a transition from an older to a relatively juvenile mantle source that is typical of a back-arc setting. The geochemistry of the metasedimentary protoliths suggests mainly derivation from an acid-arc source. Sm–Nd systematics indicate that most samples were derived from cratonic basement and plot within the Oaxacan Complex envelope with εNd values (t = 195 Ma) ranging from –5.53 to –7.65.

Our data are consistent with sedimentation in a back-arc environment along a rifted passive margin, close to a magmatic arc. The Chazumba Lithodeme is possibly correlative with various western Mexican Triassic–Jurassic mafic suites and the Potosí fan sedimentary rocks that formed along the western, rifted margin of Pangea. It is probable that flattening of the subduction zone led to subduction erosion during the Early–Middle Jurassic and underthrusting of the Chazumba Lithodeme. Steepening of the subducting slab and diachronous rifting within the Gulf of Mexico contributed to extensional tectonics recorded on the Mexican mainland and facilitated the tectonic exhumation accompanied by migmatization of the Chazumba Lithodeme. More generally, the documentation of arc-back arc assemblages in the Ayú Complex requires deposition adjacent to a subducting ocean, and thus supports a Pangea-A reconstruction.
Constraints on the formation conditions of syn-late orogenic Co-Ni-Cu-Au mineralization in the Rhenish Massif, NW-Germany

Hellmann, A., Peters, M., Wohlgemuth, C., Meyer, F.M.¹²³⁴

¹andre.hellmann@rwth-aachen.de
²meike.peters@rwth-aachen.de
³christoph.wohlgemuth@rwth-aachen.de
⁴m.meyer@rwth-aachen.de

Co-Ni-Cu-Au mineralization in the Siegerland District of the Rhenish massif is structurally controlled and postdates the main D₁-folding event and the formation of synorogenic D₁ siderite-quartz veins.

Structural investigations on the regional- and mine scale as well as ore body modeling with CAE-Studio 3 shows, that the mineralization is closely related to the formation of D₂ reverse faults and imbricate zones. On the mine scale, the mineralization is largely controlled by the presence of D₁-siderite-quartz veins, which became reactivated by reverse, oblique reverse and locally normal faults.

Fe-Co-Ni-sulpharsenides and chalcopyrite are the main ore minerals. Siegenite may be present. Subordinate arsenopyrite and marcasite formed early in the paragenetical succession and are replaced by alloclasite, cobaltite and cobaltite-gersdorffite. Fe-Co-Ni sulpharsenides host invisible Au, Ag and Bi. The gangue is quartz. Alteration minerals comprise chlorite, muscovite and quartz, forming narrow alteration envelopes in the surrounding low-grade metasediments.

Fluid inclusions are of the aqueous biphase type (L+V) with Tₜ (L) = 170-250°C (202°C mean) and show a narrow range in Tₘ between -8 to -3°C, corresponding to 5 - 10 mass-% NaCl eq. (mean: 8.2 mass-%). Isochore calculations, combined with the paleo-geothermal gradient deduced for peak metamorphic conditions (Oncken, 1991) shows that the trapping temperature of the fluid is likely in the range between 220-300°C. The Co-Ni-Cu-Au mineralization has formed at the district scale from a relative homogeneous, aqueous fluid of moderate salinity, which may have been derived from the devolatilization of the sedimentary pile in deeper crustal regions.

Despite the common occurrence of siderite in synorogenic siderite-quartz veins, carbonate is absent in the alteration assemblage, suggesting a low CO₂-activity in the fluids. The presence of marcasite in reactivated siderite-quartz veins indicates slightly acidic formation-conditions at the onset of the mineralization, pointing to fluid-neutralization as one possible mechanism for ore precipitation. Co, Ni, Cu as well as Au may have been transported predominantly as chloride complexes at T >200°C (i.e. Migdisov et al., 2011), although the role of As in complex formation is still unknown.

References:
Connectivity of pore space in Boom Clay as visualized by Wood’s metal injection experiments, in combination with BIB-SEM, and 3D FIB-SEM investigations

- Relevance for radioactive waste disposal issues -

Susanne Hemes¹, Guillaume Desbois² and Janos L. Urai³

¹ s.hemes@ged.rwth-aachen.de
² g.desbois@ged.rwth-aachen.de
³ j.urai@ged.rwth-aachen.de

Characterizing the porosity in Boom Clay is of major interest in the evaluation of the material as a potential host rock formation for the deep geological disposal of high and medium-level, long-lived radioactive waste in Belgium and the Netherlands. A detailed analysis of the pore space (i.e. pore morphologies, pore orientations, pore-size distribution and pore interconnectivity) is crucial in understanding transport processes, such as diffusion and fluid flow, and accessing transport relevant parameters, such as permeability.

In the present study we use scanning electron microscopy (SEM) in combination with Wood’s metal injection, cooled (40°C) broad-ion-beam (BIB) milling and focused-ion-beam (FIB) serial cross-sectioning to visualize, analyze and characterize the effective pore space in representative samples of the Boom Clay Formation. Pore networks are extracted from the 2D segmentation of porosities in FIB-SEM image-stacks, to show the connectivity of the pore space in 3D and to be able to discriminate between pore bodies and pore throats.

Results show a highly interconnected pore space, down to several nm in pore throat diameter. Total connected porosities are between 10-20 % in the different samples investigated. Small, unconnected pores are frequent, but do not account for a major fraction of the total porosity volumes. Comparing our results to Mercury injection Porosimetry (MIP) data, shows a difference of ~ 15 % in interconnected porosities. This discrepancy was first explained by the different resolutions of MIP (~ 3 nm pore throat diameter) and BIB-/FIB-SEM investigations (~ 7-15 nm). However, comparing total interconnected porosity volumes at identical resolutions, still shows a difference of ~ 10 % between MIP and Wood’s metal - BIB-SEM/FIB-SEM data. We interpret this to be due to sample compression, taking place during high pressure MIP experiments, and compaction of the actual accessible pore space, which are erroneously attributed to MIP volumes. Indications of sample compression and pore space compaction become evident from high resolution BIB-SEM image analysis of Wood’s metal injected Boom Clay, showing a deformation (i.e. compaction) of the fine-grained clay-matrix, especially around larger grains in the fine-grained clay-matrix. A combination of the above described methods is necessary to be able to interpret results correctly and further research needs to be conducted on the actual processes taking place during MIP and Wood’s metal injection experiments.
Baseline characterization of sandstone reservoirs in the framework of hydrogen underground storage

Henkel, S.¹, Pudlo, D.², Ganzer, L.³, Reitenbach, V.⁴, Albrecht, D.⁵ and Gaupp, R.⁶

¹henkel.steven@uni-jena.de
²dieter.pudlo@uni-jena.de
³leonhard.ganzer@tu-clausthal.de
⁴viktor.reitenbach@tu-clausthal.de
⁵daniel.albrecht@tu-clausthal.de
⁶reinhard.gaupp@uni-jena.de

The H2STORE project investigates potential geohydraulic, petrophysical, mineralogical, microbiological, and geochemical interactions induced by the storage of hydrogen in sandstone reservoirs. Detailed analytical methods (e.g. XRF, ICP-OES/MS, XRD, SEM, EMPA, CLM, AFM, µ-CT) are applied to investigate the geochemical and mineralogical rock alteration and its relevance to rock porosity and permeability caused by the presence of hydrogen in such reservoirs. The sandstones were derived from well cores, which represent reservoir sandstones and sealing mudstones of various compositions from the Tertiary of Bavaria, the Late Triassic of Brandenburg, the Early Triassic of Lower Saxony and Thuringia and the Rotliegend of Saxony-Anhalt. The selection of these stratigraphic units covers the main clastic reservoirs of Germany. The presented investigations are conducted on silt- and fine grained sandstone samples, which are, except for the Bavarian Tertiary, characterized by almost similar depositional and transport (~ playa-like) conditions. According to QFL-classification the sandstones vary from arkoses (Thuringia) to litharenites (Bavaria). We compared whole rock geochemistry from the different sample sites and show a connection to rock porosity and permeability, cement abundances and the authigenic formation of different types of clay minerals. By polarized light microscopy, EPMA and XRD we identified blocky cements like quartz, anhydrite, dolomite, calcite and albite. Authigenic clay minerals are present as illite, chlorite and kaolinite. The abundance of major elements shows regional and stratigraphic variations, like e.g. the iron content of the rocks. Thereby Late Triassic and Permian samples show a higher amount of iron than Early Triassic rocks. Generally rock porosity and permeability show a wide scatter. However, due to their different source areas and therefore their different rock compositions the sandstones exhibit specific stratigraphic and regional-dependent variations, which are expressed as distinct correlations of petrophysical and mineralogical/geochemical data. By outstanding autoclave experiments we want to show, how these mineralogical/petrophysical features will interact with the site-specific residual pore waters, reservoir gases and microbiological biocenoses in the presence of hydrogen. Thereby e.g. iron oxidation (of discrete minerals and of Fe-bearing clay coatings), sulfate reduction (of pore-filling blocky cements), hydrogen adsorption by clay minerals and biological induced fermentation processes are most likely of special importance as potential reactants during fluid (hydrogen)-rock processes.
Geothermal potential of medium depth reservoirs in the Northern German Basin - Geochemical conditions of Cretaceous Wealden sandstones at the geothermal well Groß Buchholz Gt1, Hanover

Hesshaus, Annalena¹; Houben, Georg² & Kringel, Robert³

¹Annalena.Hesshaus@bgr.de
²Georg.Houben@bgr.de
³Robert.Kringel@bgr.de

Formations of medium depth have a considerable potential for geothermal energy supply for heating purposes. While only moderate temperatures would be obtained, much lower investment costs are to be expected compared to deep geothermal wells.

The sandstones of the Early Cretaceous Wealden formation in the Northern German Basin are highly to moderately porous up to 20% and therefore fairly permeable. Thus suitable flow rates of 10 to 40 1 s⁻¹ could be achieved. As a result of their depositional facies, the non-marine sandstones are found only locally throughout the Northern German Basin. Sandstones at an adequate depth are only occurring in the regions of Osnabruck, Hanover and Brunswick. Since the Wealden formation in the Northern German Basin is a target formation for mineral oil production, conflicts in use need to be considered.

Here, the geochemical properties of the formation brine are discussed. We will focus on the brine recovered from the Wealden formation at the well Groß Buchholz Gt1 in Hanover. The Wealden formation, here located at a depth interval from 1,200 to 1,350 m was intended to provide a storage for hot water recovered from the approx. 3,700 m deep target horizon. The approx. 4 km deep geothermal well was drilled to provide thermal energy for the geocentre in Hanover (office complex with a heat demand equivalent to 2 MW). As the brine of the target horizon (Middle Buntsandstein) is oversaturated with respect to halite at surface conditions, the Wealden formation moved into focus as an alternative source of thermal energy.

The formation contains a highly saline Na-Ca-Cl brine with 200 g l⁻¹ total dissolved solids at a density of 1.13 g cm⁻³. After degassing and without oxidation, a pH value of 5 to 6 at an alkalinity of 1.8 meq l⁻¹ was measured. The exsolved gas from the brine contained traces of hydrocarbons and traces of pyrite were found in the reservoir rocks. Therefore, and with high concentrations of iron and manganese in the water, the reservoir is strongly anoxic. With oxygenation of the brine, massive precipitation of iron hydroxide would occur. Because of the presence of swellable clay minerals in the reservoir rocks, one has to consider clay swelling and hence a reduction of porosity when injecting unconditioned fresh water. At temperatures of around 70°C bacterial activity could be stimulated as well. This could promote corrosion as well as precipitation.
Interpreting the early history of our planet to the public: The Barberton-Makhonjwa Geotrail (Archean, South Africa)

C. Heubeck¹, K. Lane², L. Lane², N. Oosthuizen¹, T. Ferrar³

¹. Freie Universitaet Berlin, Germany, christoph.heubeck@fu-berlin.de
². Hamilton-Fynch, mail@hamiltonfynch.com
³. Barberton Tourism and Biodiversity Corridor (BATOBIC) Programme, South Africa, tonyferrar@lantic.net

Our science remains ineffective if its message does not reach the intended audience, usually ultimately the tax-paying public funding our efforts. Ineffective communication slows down the positive effects of our insights, reduces their reach, our visibility, funding and institutional clout, and degrades the public acceptance of our profession and agendas. This is particularly the case in countries in which the geosciences are perceived as single-issue (e.g., dedicated to the extraction of mineral resources) and in which the level of general education is uneven; commonly, however, it is just in these countries that exemplary and justly world-famous locations relevant to the understanding of Earth history or Earth processes are located.

We here present efforts at explaining the relevance of the Barberton Greenstone Belt, South Africa, to the public. This orogen (~3.6-3.2 Ga), morphologically expressed by the Makhonjwa Range, preserves the oldest well-preserved sequence of volcanic and sedimentary rocks on Earth, including globally unique information about the Earth’s early surface conditions, volcanism, meteorite flux, plate tectonics, the formation of continents, the origin and spreading of life, and the composition of the early atmosphere and hydrosphere. Long-term preservation of relevant outcrops and access to them for future generations of Earth scientists will ultimately depend on us successfully installing a chain of public awareness, acceptance, appreciation, and stewardship. This, in turn, necessitates the effective transfer of scientific insights and their relevance to the general public and to policy makers. In order to address this issue, a local group of local and regional stakeholders (naturalists, nature conservation authorities, tourism managers, community activists, property owners, communication consultants, mining representatives and scientists) designed and implemented a 36 km-long “Geotrail” along a scenic paved road across the Makhonjwa Range which showcases a cross-section of the natural (mostly geological) features at 15 sites. Interpretative panels were installed, targeted at the traveler who may be interested in nature and geology, by employing appropriate language and images. Design followed a layered approach which used multiple criteria, including aesthetics, readability, and content for individual demographics and differing interest levels. Panels embed geological information in their ecological, historical and cultural context and relate to local and institutional features. Parking areas and recreational facilities provide infrastructural support; a local visitor center serves as information hub and for capacity training. Concerns to date pertain to vandalism, the chances of reaching responsible acceptance from the local population, and maintenance.
**Multiple element complementarities in carbonaceous chondrites.**

Dominik C. Hezel¹, Maike Becker¹, Toni Schulz², C. Münker¹ and Herbert Palme³

¹Institut für Geologie und Mineralogie, Universität zu Köln, Zülpicher- trasse 49b, D-50674 Köln.
²Department of Lithospheric Research, University of Vienna
³Forschungsinstitut und Naturmuseum Senckenberg, Senckenberganlage 25, D-60325 Frankfurt am Main, Germany.
Corresponding author: dominik.hezel@uni-koeln.de

Carbonaceous chondrites (CC) are primitive meteorites that contain components that formed in the protoplanetary disk prior to planet formation. Two major components are chondrules and matrix, often contributing >95 vol%. The formation of chondrules is arguably among the most important and long standing questions in cosmochemistry. Various mechanisms have been proposed in the past. A still controversial, key constraint to support certain mechanisms and exclude others is whether chondrules and matrix formed in the same or in different regions of the protoplanetary disk. A number of studies pointed out that chondrules and matrix have different element ratios (e.g. Mg/Si), while the bulk chondrite is CI chondritic (Wood, 1985; Klerner & Palme, 1999; Hezel & Palme, 2008,2010). This became known as the chondrule - matrix complementarity. The cause of this complementarity holds the clue to whether chondrules and matrix formed in the same or in different regions of the protoplanetary disk. Zanda et al. (2006), for example, suggested that chondrules and matrix formed in different regions of different elemental compositions. Subsequently, chondrules and matrix were mixed together. Klerner & Palme (1999), Hezel & Palme (2008,2010) and others argued that chondrules and matrix formed in the same region, and complementarity is the result of fractionating certain phases into chondrules (e.g. forsterite) while others end up in the matrix (e.g. pyroxene, feldspar, Fe-rich olivine).

Multiple complementarities in a single chondrite or CC group are a strong argument for the formation of chondrules and matrix in the same region. We currently conduct a systematic study of complementary relationships in CC, and found e.g. additional complementarities in Fe/Mg and Hf/W (cf. table & figure), supporting the formation of chondrules and matrix in the same region of the protoplanetary disk.

![Graph showing complementarities in CC](image)

**References**

Structural Diagenesis in an Upper Carboniferous Tight Gas Sands Reservoir Analogue, Piesberg Quarry, NW-Germany

M. Höhne¹, P. Steindorf⁴, B. Koehrer², P. Bertier³, K. Schurk¹, C. Hilgers¹

¹christoph.hilgers@emr.rwth-aachen.de
²bastian.koehrer@wintershall.com
³pieter.bertier@emr.rwth-aachen.de

¹Reservoir-Petrology, EMR | Energy and Mineral Resources Group, RWTH Aachen University, ²Wintershall Holding GmbH Germany, 49406 Barnstorf, ³Clay & Interface Mineralogy, EMR Group, RWTH Aachen University

Uncertainties in reservoir characterization of tight gas sandstones can be significantly reduced by using quantitative data from outcrops. The active Piesberg quarry near Osnabrück exposes Upper Carboniferous strata and therefore provides a reservoir outcrop analog to the gas-bearing tight gas fields in NW-Germany. This study focused on variations of sedimentary facies, porosity, diagenesis and structural inventory in the quarry.

The Westphalian C/D of the Piesberg consists of three third-order coarse- to fine-grained sandstone cycles, each some 50 m thick, separated by anthracite coal seams, siltstones and mudstones. Tight sandstones are strongly cemented, faulted and jointed. Petrography shows shale-, mudstone and clay rip-up fragments squeezed into primary porosity during eodiagenesis. Sandstone types commonly show low porosities (<10 %) and very low permeabilities (<0.01 mD) mainly due to intense quartz cementation. Scarce authigenic carbonates are euhedral ankerites formed during burial. Secondary porosity resulted mostly from detrital carbonate leaching and limited dissolution of feldspars. Within a zone of up to several meters around faults, porosity is much higher and the matrix porosities can increase to up to 25%. Both joints and faults were mapped throughout the quarry and strike, slip and throw of the latter were documented. Joints were analyzed in a 50 x 50 m section of the quarry wall using LIDAR (Light detection and ranging) laser scanning, which allows the characterization of the lithology and quantitative measurement of bedding and fracture orientation data in inaccessible areas. Cemented fractures prevail around faults and may thus be associated with the structural and diagenetic evolution of the Upper Carboniferous of the Piesberg area.

Our high resolution field data enables a better understanding of tight sands reservoir properties at a subseismic scale, considering both the alteration and evolution of pore space during diagenesis and the formation of structures. Combined with well-log and core data, results may be used to develop improved exploration and development strategies and to reduce uncertainties in 3D-reservoir modeling of analogous subsurface tight gas reservoirs.
The challenges of quantitative analysis of poorly ordered minerals in soils and sediments

Stephen Hillier¹, The James Hutton Institute, Craigiebuckler Aberdeen AB34 4TL and Department of Soil and Environment Swedish University of Agricultural Sciences (SLU), P.O. Box 7014, SE-750 07 Uppsala

¹stephen.hillier@hutton.ac.uk

““The determination of the composition and mineral content of soils and sediments is an important means of understanding soil properties, formation and (land) use-capabilities.”” So began Chapter 11 ‘Chemical allocation for soil minerals’ of M. L Jackson’s classic tome “Soil Chemical Analysis Advanced Course” (Jackson 1956). Thus, it has long been known that in addition to recording the processes and rates of soil formation, the minerals in soils are central components to what nowadays is often termed the ‘environmental functions’ performed by soils. For example, a soils’ capacity for buffering, filtering, binding, nutrient retention, nutrient supply, and substrate provision all have dependencies that relate to its mineralogy, and particularly to the more poorly ordered minerals it may contain. There are many reasons, therefore, why a quantitative rather than just a qualitative knowledge of the mineralogical composition of soils may be required.

Methods for mineralogical analysis are diverse. They range from direct instrumental based methods on the one hand to indirect methods such as selective chemical dissolution on the other. Most are readily employed in a qualitative manner for mineral identification. They may also be used extensively for further characterization, especially when the focus is one or a group of related minerals such as the clay minerals or the iron oxides. Quantitative mineralogical analysis across such groups of minerals, or indeed across the broader spectrum of minerals that may occur in a given soil or sediment, is a much more challenging task. Indeed, arguably, soils represent the most difficult of all mineralogical materials to analyze quantitatively. This is because, as well as containing a wide variety of minerals often of various origins, many of the minerals found in soils and recent sediments are poorly crystalline, highly disordered and frequently intimately admixed with variable amounts of organic matter. Some of the earliest attempts to obtain quantitative mineralogical analyses of soils relied heavily on wet chemical methods and an informed allocation of chemical elements to different mineral groups. Despite the relatively good accuracy of such wet chemical procedures the widespread application of such elaborate schemes was never likely, although allocation rather than direct schemes still remain popular.

Evidence from round robins indicates that X-ray diffraction (XRD) based methods offer probably the best all round methods for quantitative analysis of the mineralogical composition of soils and sediments. A variety of approaches using XRD will be outlined; their strengths and weaknesses highlighted, particularly in relation to poor crystalline minerals including the clay minerals, and the many challenges that remain for quantitative analysis of soils and sediments will be discussed.

Jackson, M.L. 1956. Soil chemical analysis - advanced course. Published by the author, Dep. of Soil Science, Univ. of Wisconsin, Madison, WI.
Additional provenance source of the Triassic Buntsandstein in Central Germany revealed by field, petrographic, and geochemical data

Ulrike Hilse¹, Marcus Meyer², Cindy Kunkel³, Carita Augustsson⁴, Michaela Aehnelt⁵, and Reinhard Gaupp⁶

¹Ulrike.Hilse@uni-jena.de
²Marcus.Meyer@uni-jena.de
³Cindy.Kunkel@uni-jena.de
⁴Carita.Augustsson@uni-jena.de
⁵Michaela.Aehnelt@uni-jena.de
⁶Reinhard.Gaupp@uni-jena.de

We investigate sandstones of the Lower and Middle Buntsandstein of Early Triassic age in the Thuringian Basin and in NE Hesse, Central Germany. Special regard is given to the influence of the Eichsfeld Swell for the provenance and sedimentation. In Central Germany, the terrestrial Buntsandstein is dominated by paleoflow directions towards the north. Correspondingly the detritus is thought to have been transported from late Variscan rocks of the Bohemian Massif, the Vindelician High and the French Massif Central. Nevertheless, locally - and especially in NW Thuringia and NE Hesse - paleoflows vary, with transport towards northwest and east. The regional occurrence of these directions indicates different source areas. Here, the Eichsfeld Swell, a structural high separating the study area in two subareas, may have influenced the fluvial pathways.

For provenance determination, geochemical (ICP-MS, ICP-OES, XRF) and petrographic (microscopy, cathodoluminescence of quartz, light and heavy minerals) methods were used. Paleoflow directions from outcrops and the literature were also combined for our transport model. The analyzed sandstones are fine to medium grained subarkoses, lithic subarkoses, and arkoses predominantly with a moderate to good sorting. The most common detrital grains are monocrystalline quartz, potassium feldspars, and polycrystalline quartz. Plagioclase and rock fragments are relatively rare (5-10 vol%). Heavy minerals are accessory and dominated by zircon, tourmaline, apatite, rutile, and chlorite.

First results of geochemical bulk-rock analysis reveal K/Rb ratios and Eu anomalies of 216.0 and 0.92 respectively in the west and 247.2 and 0.77 in the east (data are median values). Furthermore, metamorphic, polycrystalline quartz grains (Qp > 3) and pelitic rock fragments are more common in the west, and quartz grains of metamorphic origin, as revealed by microscopic and cathodoluminescence investigations. In the east the dominance is more pronounced for magmatic, felsic rock fragments and non-undulous quartz of igneous origin. This proposes that sandstones in the Thuringian basin (east of the Eichsfeld Swell) have higher contents of clasts with felsic origin than sandstones in NE Hesse (west of the swell). These results suggest an additional provenance for the western part of the study area, probably the Rhenish Massif. In the Thuringian basin, the mineralogical composition and paleoflow directions indicate a quartzose to felsic igneous provenance that is in accordance with source rocks in the Bohemian Massif.
Neotectonic analysis in the Central Andes, NW Argentina: evaluating the influence of climate on fault mechanics

Kathrin Hincke¹, Moritz Kirsch², Ulrich Riller³

¹kathrin.hincke@uni-hamburg.de
²moritz.kirsch@uni-hamburg.de
³ulrich.riller@uni-hamburg.de

The climate controls atmospheric circulation patterns and the hydrologic cycle, and thus exerts an influence on erosion and sedimentation, surface uplift, and the exhumation of rocks. If and in what way climate also affects the mechanics of thin-skinned deformation is under discussion, but there are only few systematic investigations. The Puna Plateau and the Eastern Cordillera, two geomorphological provinces of the neotectonically active Central Andes in NW-Argentina, exhibit contrasting climatic conditions and thus offer a natural laboratory to find answers to this problem. Our aim is to investigate the mechanics of crustal deformation on different scales and evaluate, if there is a correlation between specific fault characteristics and different climate zones.

In a first phase of the study, field-based structural investigations, as well as petrographic and microstructural analyses are conducted, focusing on two fault systems in the Eastern Cordillera, namely the Calchaquí Fault and the El Toro Muerto Fault of the northern Calchaquí Valley, and the Refugio Fault and the Cachi Fault of the southern Luracatáo Valley, respectively. In both valleys Late Neoproterozoic to Paleozoic rocks are thrust over Cretaceous to Tertiary sedimentary strata along north-south striking faults. The fault zones vary in width between several tens up to a hundred meters and faulting is predominantly localized within the Late Neoproterozoic to Paleozoic rocks. Only a few centimeters of the footwall rocks are incorporated in the fault zone. The Refugio fault zone exhibits multiple breccia generations, which indicate different phases of movement. Whereas the deformation in the Refugio Fault Zone is brittle-ductile, it is brittle in faults of the Calchaquí Valley. This suggests that deformation occurred in a shallower crustal level for the faults of the Calchaquí Valley than for the Refugio Fault.

In a second phase of the study, the mechanical properties of active faults in the Puna Plateau will be documented. Furthermore, parameters such as displacement and slip rate will be determined by means of balanced cross-sections, remote sensing analysis and known exhumation rates. These results should ultimately allow us to assess differences in the activity and the mechanism of faults in the Puna Plateau and the Eastern Cordillera.
Chemical denudation rates in the humid tropics of East Africa and comparison with $^{10}$Be-derived erosion rates

Matthias Hinderer$^1$, Dorthe Pflanz$^1$, Sandra Schneider$^1$

$^1$Institute of Applied Geosciences, TU Darmstadt, Schnittspahnstrasse 9, D-64287 Darmstadt, hinderer@geo.tu-darmstadt.de

Chemical denudation is largely controlled by rock types, runoff, and soil shielding [1]. Basically, the tropical regions of Africa provide favorable climatic conditions for mineral weathering because of permanent high temperatures and humid conditions which stimulate soil flushing and chemical leaching. Nevertheless, rivers in Africa show some of the lowest chemical denudation rates in the world, e.g. dissolved yield of the Congo River is only ca. half of the world average. The widespread inhibition of chemical weathering is usually interpreted as a combination of weakly weatherable old cratonic crystalline rocks and intense soil shielding. Active tectonic rift settings are supposed to change this scenario by landscape rejuvenation i.e. enhanced erosion and acceleration of chemical weathering via liberation of fresh rock material. We tested the role of these factors in the western branch of the East African Rift System (Uganda) which shows a pronounced topography, is tectonically active, and located at the transition between the Congo Basin and the East African Plateau. Based on 2 years hydrochemical monitoring of 15 rivers in the western East African Rift, together with geochemistry of soils, river sediments, and bedrocks we calculated chemical denudation rates and tracked shifts of major cation ratios via chemical weathering. In contrast to previous studies emphasizing low chemical denudation rates in tropical cratonic areas we also found relative high rates for silicate bedrocks up to 33 mm/ka due to more easily soluble Quaternary volcanic tephras and to a minor degree due to amphibolites. Quartz-derived $^{10}$Be erosion rates fail to predict these high rates because major sources of solutes are provided by tephras and mafic minerals. Although cosmogenic denudation rates significantly increase with increasing topography this is not reflected in chemical rates. Hence, the strong tectonic rejuvenation in this rift setting does not significantly accelerate chemical denudation. Cation ratios show distinct fractionation pattern for all rock types. Soils are depleted in Ca and Na, and enriched in K and Mg, whereas river sediments and to a lesser degree also river waters are enriched in Ca and Na compared to rock signatures.
Implications of the February 2013 Mw 6.7 "Indigirka-Zyryanka" earthquake and recent seismicity for the tectonics of Northeast Russia and the Ulakhan fault

David Hindle¹, Kevin Mackey²

¹University of Göttingen, dhindle@gwdg.de
²Michigan State University, mackeyke@msu.edu

The February 2013 Mw 6.7 earthquake located at E142.51° N67.65° is the largest recorded earthquake in the northwestern Okhotsk region. It has an almost pure thrust mechanism which is likely to be directed towards the northeast on a moderately steeply dipping thrust plane (324°/43°NW from Harvard CMT). It occurs north of the what has traditionally been seen as the trace of the Ulakhan fault, which is itself often considered to be the North America (NAm) Okhotsk (Okh) plate boundary. The region of the earthquake is also quite close to the likely position of the triple junction between NAm, Okh, and Eurasia (Eur), to the north of which begins extension and spreading of the Arctic-North Atlantic ridge system. The earthquake was preceded (November 2011 and January 2013) by two earthquakes close to or upon the Ulakhan fault's trace. The larger of these (Mw 5.6) has a strike slip mechanism, and occurred 1 month prior to the Indigirka-Zyryanka event. In the light of these new data, existing models of both earthquake recurrence and frequency, as well as tectonic schemes for how the Okhotsk plate accommodates deformation in its northwestern region, can be updated and revised. Preliminary investigation suggests that weakly demonstrated "abnormal" $\beta$ values from the log-log seismic moment-frequency relationship continue and are possibly strengthened. These low values ($\beta \sim 0.4-0.45$) have a critical effect for some models of likely future seismicity and maximum earthquake potential as well as seismic versus aseismic deformation in the region. The nature of the event challenges the tectonic block models of strain partitioning within the Okhotsk plate, and suggests a more complex behaviour in the region of the triple junction than previously considered. Finally, the large thrust earthquake suggests that the Ilin-Tas anticlinal structure which has overthrust and deformed the adjacent Tertiary sediments of the Indigirka-Zyryanka Basin may well be still actively growing today, and its structural relief may have accumulated entirely since Pliocene times.
The Jura-Molasse fold-thrust belt is the most external portion of the western Alpine deformation system. It forms an arc, with a change in strike of nearly 90 degrees and a significant shortening gradient along its length. It is generally recognised as a classic example of thin-skinned tectonics, with deformation rooting in Triassic evaporites whose isopachs correspond closely with the final shape and westernmost limits of the Jura mountains. It is also apparent that the present day Molasse Basin which is sometimes called the Jura mountains "indenter" was transported passively, in almost piggy-back style and undergoing little significant deformation as the Jura mountains accumulated shortening further to the west. The relatively undeformed nature of the Molasse Basin, which sits between the Subalpine Molasse thrust, marking the Oligo-Miocene position of the Alpine thrust front, and the Jura Mountains which contain up to 27km post-late Miocene shortening has been recently suggested to be due to the narrowing taper of the Mesozoic and Tertiary material due to flexure of the alpine foreland european lithosphere in response to both shortening in the alpine hinterland and additional loading due to the wedge of Tertiary, foreland basin sediments that comprise the Molasse series. The Tertiary wedge tapered from approximately 5km thickness beneath the Subalpine Molasse thrust to a few 10's of metres ~125km further west and also depressed the underlying Jurassic and Triassic carbonates (1-2km thick) by the same amount. The pre-deformation geometry of the basin formed an above-critically tapered wedge, above a very weak evaporitic (mostly salt) detachment. Current models suggest this allowed concentration and conservation of force and stress applied to the wedge along its western edge, with little to no loss due to basal shear. Low differential stress gradients with depth were well below rock strength in the thick, steeply tapered, Molasse region, but due to conservation of integral force, vertical stress gradients with depth (and differential stress) increased as the taper narrowed until they exceeded rock strength. It has been suggested this occurred at approximately the position of the easternmost thrust of the the Jura system. We test this hypothesis with a 2d numerical, elastic-plastic model, based on the balanced and restored Jura-Molasse system to which we apply the amount of shortening suggested by cross section balancing. We thus invert the restored geometry with a mechanical model which allows spontaneous "thrust" localisation, and formation of what can be described as "pseudo-folds". Overall, the broad geometry of the Jura-Molasse system, including frequency and length and spatial distribution of overthrusts, can be quite well matched using reasonable rock parameters. The peak stresses supported by the Jura-Molasse during their evolution are monitored whilst varying boundary conditions, particularly basal shear strength of the Triassic detachment and suggest that a simple model of total conservation of stress and force is not strictly applicable for their formation. Nevertheless, some degree of stress concentration is likely. Too high a basal friction leads to thrusting in the Molasse Basin, effectively "missing" the Jura entirely. To completely match present day geometry, both unbending of the european lithosphere and some form of erosion at the surface also prove necessary. The mechanical reason for the former and the timing of the latter may also be linked.
Earth’s Deep Volatile Cycles
Marc M. Hirschmann

A key parameter influencing the geodynamical, geochemical, and climatic evolution of a terrestrial planet is the relative proportion of major (C-H-O-S-N) volatiles sequestered in the deep interior as compared to that available to near-surface reservoirs including the crust and fluid envelopes. Mantle and basalt geochemistry establish that a significant fraction of Earth’s hydrogen and carbon reside in the mantle, and surface geology strongly suggests that this has been so for much of Earth’s history. Plate tectonics outgasses large amounts of volatiles volcanogenically and ingasses similarly large fractions by subduction and though the two fluxes are not in perfect balance, together they produce near-surface and deep volatile reservoirs that have been stable for much of Earth’s history. This simple set of observations raises enormous questions for which we presently only have partial answers, including:

Are deep Earth cycles dynamic? Though deep Earth volatile cycles are strongly linked to plate tectonics, we don’t really understand the effect of volatile cycles on tectonics. Deeply stored volatiles influence chemical and physical properties of the mantle, including the locus of melting and the rheology (though the importance of the latter has been disputed recently). Thus, at this point we cannot say with certainty whether deep Earth volatiles are a product of plate tectonics or plate tectonics a product of deep Earth volatile cycles. Put another way, how does the cycling of volatiles in the deep Earth “tune” geodynamic tempos?

How are major volatiles stored in the mantle and what role do they play in mantle melting? Seismic evidence suggests widespread deep features seemingly attributable to melting, ranging from discontinuities at the lithosphere-asthenosphere boundary of mature oceanic lithosphere to regions of low shear wave velocity atop the 410 km discontinuity. Melts cannot be stable in these regions without considerable volatile concentrations. How do these melt regions arise and what role do they play in deep Earth dynamics and mass fluxes?

What were the initial conditions? The violent events associated with the accretion and differentiation of the early Earth were likely to have outgassed a large portion of terrestrial volatiles, creating a massive early atmosphere. But now a large portion of these volatiles are in the mantle. How and when were the large-scale interior reservoirs accrued? At least in some scenarios, deep volatiles are required for the kinds of dynamical processes (such as breaking the lithosphere) required for ingassing of surface volatiles.

What proportion of Earth’s major volatiles are in the core? Though C, H, N, or S may not be the principal light elements in the core, all are moderately to strongly siderophile, and even modest concentrations could dominate bulk Earth inventories. Further, some models of core formation suggest that metal could have incorporated virtually all the available C, H, N and S during core formation. If so, then the inventory of volatiles in the mantle and surface reservoirs derive chiefly from a late veneer. However, there is considerable evidence contrary to this scenario, which leaves unanswered the question of how core formation partitioned volatiles between the metal and non-metal terrestrial reservoirs.
Stable isotope palaeoceanographic proxies

Hoefs Jochen

jhoefs@gwdg.de

One of the most promising tools in tracing back the history of the oceans is the analysis of stable isotope ratios of suitable samples having preserved their primary isotope ratio. Hoefs (1981) has summarized existing data at that time. Recently, the introduction of the MC-ICP-MS technique allows the investigation of new isotope systems with high precision. Detailed age profiles of 5 elements covering ages up to 120 Ma are of particular interest in this connection: S in barytes (Paytan et al. 2004), Li in foraminifera (Misra and Froelich, 2012), B in foraminifera (Pearson and Palmer, 2000), Ca in foraminifera (Gussone et al. unpubl) and Tl in Fe/Mn crusts (Nielsen et al. 2009). Observed variations in these age curves can be explained by changing isotope compositions or concentrations of marine sources and/or sinks. The goal is linking the causes of isotope variations with globally important geological processes.

Chemical and isotopic compositions of the ocean are generally described by simple box models, in which input sources are rivers and hydrothermal systems while output fluxes are represented by chemical sediments and interactions with the oceanic crust. Changes in the input sources by varying weathering rates are often taken as the major parameter inducing changes in the oceanic composition. On the other hand, output processes show the largest isotope fractionations of the elements under consideration suggesting that they are the main drivers in a non-steady state ocean.

As the temporal resolution of the presented “age curves” has increased relative to earlier attempts, the rate of isotopic change may be faster than the residence time of the particular element. This is the case for sulfur where short term changes require unreasonable large changes in S-fluxes and isotope composition. In this case, special assumptions about oceanic basins separated from the whole ocean are needed. The Tl isotope curve strongly correlates with the S isotope curve indicating that both systems respond to similar mechanisms. A marked increase in organic carbon burial leading to higher pyrite burial rates may be responsible for the striking similarity of both systems.


Nielsen SG and others (2009) Earth Planet Sci Lett 278: 297
Constraints on the origin of the 3450 Ma Tsawela Gneisses, Ancient Gneiss Complex, Swaziland

Hoffmann, J.E.1,2, Kröner, A.3,4, Hegner, E.5, Hofmann, A.6

1Institut für Geologie und Mineralogie, Universität Köln, Germany
2Steinmann Institut, Universität Bonn, Germany
3Institut für Geowissenschaften, Universität Mainz, Germany
4Department für Geo- und Umweltwissenschaften, LMU München, Germany
5Faculty of Science, Department of Geology, University of Johannesburg, South Africa

The ca. 3450 Ma Tsawela gneiss constitute a well-preserved tonalite suite within the Palaeoarchaean to Mesoarchaean Ancient Gneiss Complex (AGC), Swaziland. The Tsavela gneisses have intruded the >3480 Ma tonalitic to granitic Ngwane gneisses as well as greenstone remnants that represent the oldest lithologies of the AGC. In contrast to the strongly deformed and partly migmatized Ngwane gneisses, the Tsawela only show a weakly hornblende-biotite-fabric and often preserve a medium- to coarse-grained magmatic texture. Widespread are centimetre to decimetre-sized hornblendite inclusions that either represent mafic cumulates or greenstone fragments.

To constrain the origin of the Tsawela gneisses and their relationship to the Ngwane gneisses and greenstones, we obtained major and trace element analyses combined with Hf-Nd whole-rock, Hf-in-zircon and high-precision HFSE analyses, and additional analyses of both suites as well as from greenstone remnants of the AGC.

The initial εHf(t) values of the Tsavela gneisses range from +1.1 to +4.2, whereas the initial whole-rock εNd(t) values are rather uniform ranging from +0.1 to +1.5.

Interestingly, the most juvenile Tsawela gneiss with an εHf(t) of +4.2 has the lowest MgO and the highest SiO₂ content and the highest La/Yb ratio, compared to the other samples, and also yielded the lowest Cr, Ni and Cr contents. With decreasing initial εHf(t) values, MgO, Cr, Ni increase and La/Yb decreases. In a diagram of Sr vs. La/Yb, the samples follow mixing trends with mafic crust as one endmember similar the greenstone remnants of the AGC. Slight offsets from the modeled arrays may be explained by admixture of the older Ngwane gneiss TTGs following assimilation-fractional-crystallization (AFC) trends. Modelling of the 176Lu/177Hf ratios suggests that that the admixed crust was of mafic composition, rather than felsic. Hf isotopes of this component, possibly representing the hornblendite inclusions in the Tsawela gneisses, suggest an age of ca. 4000 Ma.

The geodynamic setting in which these magmatic processes occurred is difficult to constrain and several scenarios are possible.
TEM investigations of the assembly of the calcium carbonate crystals of *Emiliania huxleyi* coccoliths

R. Hoffmann¹, A. Wochnik², C. Heinzl³, S. Betzler⁴, S. Matich⁵, E. Griesshaber⁶, C. Scheu⁷ and W.W. Schmahl⁸

¹ Hoffmann.Ramona@lrz.uni-muenchen.de LMU Department of Earth and Environmental Sciences 80333 Munich Germany

² Angela.Wochnik@cup.uni-muenchen.de LMU Department of Chemistry 81377 Munich Germany

³ Christoph.Heinzl@cup.uni-muenchen.de LMU Department of Chemistry 81377 Munich Germany

⁴ Sophia.betzler@cup.uni-muenchen.de LMU Department of Chemistry 81377 Munich Germany

⁵ Sonja.Matich2@wsi.tum.de TUM Walter-Schottky-Institut 85748 Garching Germany

⁶ E.griesshaber@lrz.uni-muenchen.de LMU Department of Earth and Environmental Sciences 80333 Munich Germany

⁷ Christina.Scheu@cup.uni-muenchen.de LMU Department of Chemistry 81377 Munich Germany

⁸ wolfgang.schmahl@lrz.uni-muenchen.de LMU Department of Earth and Environmental Sciences 80333 Munich Germany

Marine organisms with a skeleton composed of calcium carbonate (CaCO₃) becoming more and more interesting for material science, because of their outstanding functionality in comparison to inorganic CaCO₃ phases [1]. Within this study the assembly of the CaCO₃ shell of the single celled marine coccolithophore species *Emiliania huxleyi* was investigated. Since their skeletal elements possess sizes smaller than 5 µm high resolving methods like transmission electron microscopy (TEM) are required. For this method very thin samples are needed. Cross-section samples were prepared by focused ion beam (FIB) sectioning and plane-view samples by droping the samples onto a copper holey carbon TEM grid and etching them afterwards.

According to Young et al. [2] the coccoliths, these are CaCO₃ plates which build up the coccosphere, are composed of two different units with alternating orientation of the crystallographic c-axis: the radial R-unit and the vertical V-unit. Using mainly electron diffraction, bright field and high resolution imaging in the TEM we could image and analyze the R- and V-unit and found the crystallographic c-axis of the R-unit parallel and of the V-unit perpendicular to the coccolith plane oriented. Hence the R- and V-model for *E. huxleyi* could be confirmed. To detect orientation changes within the elements of the R-unit diffraction experiments were applied. One area of the coccolith element was tilted to a zone axis and by keeping the Goniometer angles diffraction pattern of the whole element were taken and afterwards overlain. Considering the accuracy of the method we could show that the elements within the R-unit of *E. huxleyi* have a single crystalline character.


[3] The authors thank goes to J. Young, H. Schulz and M. Kučera for providing the samples. This project is funded by the German Science Foundation (DFG, Grant Nr. SCHM 930/15-1).

[4] The authors acknowledge financial support from the German Science Foundation DFG. R.H. is grateful for a stipendium by the Bayerische Eliteförderung (BayEFG).
Recent seismological studies have strengthened the case that the Hawaiian hotspot is generated by a deep mantle plume. Nevertheless, fundamentally contradictory interpretations of the isotopic compositions of Hawaiian basalts persist, even among authors who accept the plume model. One view holds that the regional isotopic pattern of basalts from the two parallel lines of Hawaiian volcanoes reflects large-scale heterogeneities within the plume, and these are derived from even larger-scale geochemical structures in the basal thermal boundary layer of the mantle. In addition, the temporal geochemical evolution of a given Hawaiian volcano progressively samples first the front edge, then the more central region, and finally the other peripheral side of the plume. Thus the geochemistry of the basalts “maps” the geochemistry of the plume and, ultimately, its source region at the base of the mantle.

The alternative view is that the plume resembles a uniformly heterogeneous “plum pudding”, with small (<< 5km) fertile plums (or veins) of pyroxenite and/or enriched peridotite scattered in a matrix of more refractory peridotite. In a rising plume, the plums melt before the matrix, and the final melt composition is solely controlled by the bulk melt fraction. We test the geochemical consequences of this plum pudding model and show that it is inconsistent with several geochemical observations, (1) the relative melt fractions inferred from La/Yb ratios in shield-stage basalts of the two parallel (Kea- and Loa-) volcanic chains, and (2) the systematic Pb-isotopic differences between the chains, and the absence of such differences within each chain. The most serious failure of the plum pudding models is that all of them predict a shift toward enriched Nd-Sr isotopic compositions during the final, “rejuvenated” stage of Hawaiian volcanism when melt fractions are lowest, but actual Nd isotopic compositions become consistently more depleted during this stage. We conclude that plum pudding models may well account for many of the short-term compositional fluctuations of Hawaiian eruptions, but the geochemical differences between Kea- and Loa-trend volcanoes, as well as those between early and late stages of volcanism clearly reflect the larger-scale internal geochemical structure of the Hawaiian plume.

To interpret the origin of the rejuvenated basalts, which erupt after a hiatus of up to 2 Ma after the shield stage, we extend our previous modeling of conduit formation and melt extraction from the plume head to include much lower melt fractions, relevant to rejuvenated basalts. We find that these melts are formed at the previously unmelted underside of the plume, 200 to 400 km from the shields, from material that originally constituted the uppermost part of the thermal boundary layer at the base of the mantle.
The Archean Moodies Group, Barberton Greenstone Belt (BGB), ~3.2 Ga, represents Earth's oldest-known tidally influenced siliciclastic sequence and includes well-preserved microbial mats. Detailed stratigraphic sections measured along 15 km strike length demonstrate that the microbial communities colonized three major habitats: (periodically inundated?) coastal floodplain, supra- and intertidal environments.

We investigated the microbial microstructures of crinkly intertidal and tufted supratidal mat facies, both preserved as abundant kerogenous laminae ~1mm thick, overlying individual depositional events in medium- to coarse-grained sandstones. Intertidal mats are widely underlain by enigmatic, nearly monomineralic chert layers up to 40 cm long and few mm thick. Microbial tufts 1-2 cm in height and vertically stacked microbial domes are also internally partially silicified. XRF elemental scanning of fresh slabbed and polished hand samples showing well-preserved microbial mat structures indicates that (1) the monomineralic layers underlying the mats and tufts likely once consisted of pure carbonate, and that (2) Fe is enriched in the kerogenous mat laminae. Electron microprobe analyses show that carbonate remnants in the chert layers are mostly composed of internally zoned rhombic dolomite. SEM observations of freshly exposed kerogen surfaces document interwoven, bundled and twisted filaments 1-3 µm in diameter, confirming mat biogenicity.

The close association of (now largely silicified) carbonates and overlying microbial mats in a siliciclastic environment suggests that mat metabolic activity promoted carbonate precipitation, pointing at autotrophic metabolisms such as CO2 fixation which increase sub-mat pore fluid alkalinity and thus induce carbonate precipitation. Alternatively or additionally, carbonate could have formed as a byproduct of a Fe-reducing metabolic pathway.

We conclude that Middle Archean photic-zone filamentous microbial mats may have been metabolically tiered and, at least in its upper layers, employed a photosynthetic strategy.
Patterns of seismically induced mass wasting and the mass balance of earthquakes

Niels Hovius¹, Odin Marc² and Patrick Meunier³

¹hovius@gfz-potsdam.de
²omarc@gfz-potsdam.de
³meunier@biotite.ens.fr

Shallow earthquakes form local relief and build mountain ranges. They can also cause considerable sediment production and erosion. Triggered mass wasting is one of the principal causes of damage and loss of life due to earthquakes in upland areas; the attendant erosional flux can affect patterns and rates of sedimentation in fluvial systems and beyond; and the mode and rate of mountain building in frontal ranges may be determined by the balance of seismic surface deformation and erosion. In this contribution, we show that these effects are systematic and predictable, due to strong links between earthquake mechanisms, seismic wave propagation and slope instability.

Patterns and rates of seismically induced mass wasting in upland areas are set by earthquake strong ground motion and the propensity to failure of local slopes. This gives rise to landslide density patterns that reflect the distribution of fault slip in shallow earthquakes and the directionality of seismic wave fields. Static effects of earthquakes on hill slopes may be long lived, causing rates of mass wasting to remain high after seismic events. While the spatial effects of earthquakes on mass wasting are now well established, geomorphic relaxation and post-seismic sediment fluxes remain poorly constrained. Nevertheless, we are now in a good position to estimate the mass balance of earthquakes. We have done this for 10 intermediate and large earthquakes in continental, compressional settings. Accounting for earthquake location and substrate susceptibility, we have found a strong correlation between seismic moment and landslide volume. The mass balance of an earthquake, then, is determined primarily by the distance to the seismic source, the dip of the seismogenic fault, the rake of the co-seismic slip, and the modal slope of the epicentral topography. Very shallow dip-slip earthquakes on a steep thrust fault dissecting steep topography can have a negative mass balance for moment magnitudes >6.0, but for more common frontal thrust scenarios the transition from constructive to destructive occurs at higher earthquake magnitudes. With this knowledge, links between seismicity and erosion can now be considered explicitly in numerical models of landscape evolution and mountain building, although such models should also take into account the contributions from inter-seismic and aseismic processes.
Concurrent $\mu$-XRD$^2$ & DTA: Real-time Monitoring of the De- and Rehydration of Bassanite

N. Huber$^1$, C. Berthold$^2$, K. G. Nickel$^3$

University Tübingen, Faculty of Science, Department of Geosciences, Applied Mineralogy

$^1$nadja.huber@uni-tuebingen.de
$^2$christoph.berthold@uni-tuebingen.de
$^3$klaus.nickel@uni-tuebingen.de

The time- and temperature-resolved combination of two-dimensional X-Ray Diffraction (XRD$^2$) and Differential Thermal Analysis (DTA) has high potential for the detailed characterization of temperature dependent processes like phase transitions, recrystallization phenomena and decomposition reactions with or without structural changes. An in-house designed DTA-heating chamber allows constant heating and cooling of samples from room temperature up to 600°C. A commercially available Bruker DISCOVER microdiffractometer ($\mu$-XRD) was used in this study, equipped with focusing polycapillary lens optics and a large two-dimensional detector. The focusing polycapillary optics provide a high intensive spot of ~200 $\mu$m in size, enabling measurement times down to a few seconds (as shown in [1]). Due to these short XRD measurement times it is now possible to survey processes with the time and temperature resolution needed for DTA-experiments, in which heating and cooling-rates in the order of 10 K/min are used. Additionally, our setup includes a large two-dimensional VÅNTEC-500 detector with an active area of 140 mm diameter, which covers around 40°2Θ and 40°$\psi$ in one measurement ($\mu$-XRD$^2$) without moving the detector. This gives the opportunity to observe texture and crystallinity changes of the sample directly during the heating and cooling process of a coupled $\mu$-XRD&DTA experiment, which is essential to avoid misinterpretations of intensity changes in the X-ray patterns.

To demonstrate the potential of this coupled setup we examined the dehydration process of gypsum (CaSO$_4$·2H$_2$O) to anhydrite (CaSO$_4$) in the temperature range from room temperature up to 450°C [2]. During heating the well-known intermediate phases hemihydrate/bassanite (CaSO$_4$·0.5H$_2$O) and the water-free bassanite structure (in the literature often referred to as $\gamma$-anhydrite or anhydrite-III) were observed. Concerning the reversible, temperature-dependent dehydration and hydration process of the bassanite structure, we will now present detailed heating and cooling studies under controlled wet and dry atmospheres with the coupled $\mu$-XRD$^2$ & DTA setup.

It is shown that the simultaneously achieved additional information by coupling $\mu$-XRD$^2$ and DTA is indispensable for a proper evaluation of the occurring processes and avoids the uncertainties of results from stand-alone DTA and XRD devices.


Several studies have shown that cementation may be driven by variations in pore size of the host rock. However, experimental approaches are lacking. To better understand the underlying process, we developed a transparent microreactor for diffusion-controlled cementation experiments under the microscope. We studied the effect of different pore sizes and surface charges of solid material at different pH, using rock analogs. High-resolution videos allowed to analyze the nucleation from solution, pore cementation and growth rates of cements.

Pores were cemented with salt, which is well known to form pore-size dependent seals in siliciclastic reservoirs. Mass transport was driven by diffusion, which is considered the major mass transport during burial diagenesis.

While halite precipitated primarily in pores larger than 200 μm, alum nucleated in smaller pores. The growth rate of alum (10^{-5} mm/s) was one order of magnitude higher than that of halite. However, the dissolution rates of both minerals were similar at about 10^{-6} mm/s. Newly formed euhedral halite grains migrated against the bulk diffusion transport direction, towards the higher-temperature reservoir. Halite growth rates increased by one order of magnitude to 1.8 × 10^{-5} mm/s, if the phase boundary was vapor-liquid. In comparison, nucleation in a two-phase porous rock analog showed no difference in cementation pattern at a pH 7. However, at a pH of 10.5 the surface energies of the two different solids are altered, and porosity was significantly reduced.

Our experiments showed that pore size dependent nucleation and cementation is a process, which may also take place in layered sedimentary rocks of different grain sizes. Our experiments in transparent microreactors can now be developed towards reservoir conditions and establish the processes at elevated p-T conditions.
Experimental simulation of the magma differentiation beneath Shatsky Rise oceanic plateau

Anika Husen1*, Renat Almeev1, Francois Holtz1

1Institut für Mineralogie, Leibniz Universität Hannover, Germany (*A.Husen@mineralogie.uni-hannover.de)

Understanding of the magma ascent, storage and differentiation beneath large igneous provinces (LIPs) is of the great interest, since their formation mechanisms are still under debate. Mainly two competing models are explaining the formation of LIPs: 1) the arrival of a deep sourced mantle plume in the lithosphere, and 2) decompression melting of unusually fusible mantle beneath fast-spreading ridges. The Shatsky Rise is a unique oceanic plateau, because its tectonic evolution along the Pacific-Farallon-Izanagi triple junction is well known.

In comparison to MORB, Shatsky Rise magmas are high in FeO (Fe8: 10.2-11.3) and low in SiO₂ and Na₂O (Na8: 1.5-1.8), indicating higher amounts of partial melting at greater depth. Compared to other oceanic plateaus, as e.g. Ontong Java and Kerguelen, the Shatsky Rise glass compositions have very similar differentiation trends. The high CaO/Al₂O₃ ratios in the evolved natural glasses are most likely indicative of low pressure cotectic differentiation. Although this assumption was supported by our thermodynamic calculations (200-50 MPa), there are no experimental studies on such MORB-like compositions with high FeO and low Na₂O contents up to date. Here we present results of our crystallization experiments conducted in internally heated pressure vessels using synthetic analogues of three representative Shatsky Rise compositions: AH6 - the most primitive starting material with 8.6 wt% MgO (melt inclusion found in fresh olivine (Fo87) from Ori Massif), AH3 - an intermediate composition with 8.0 wt% MgO (most magnesian sample recovered at Ori Massif) and AH5 - an evolved basalt with 6.4 wt% MgO (most magnesian sample recovered at Tamu Massif). The capsules with these three starting materials were run simultaneously in two sets of experiments with different H₂O concentrations in the experimental samples. The experimental pressures were 100, 200, 400 and 700 MPa and the applied temperatures varied between 1075°C and 1225°C. In the first experimental setup, C-Pt double capsules were used to maintain nearly anhydrous conditions (<0.2 wt% H₂O, FTIR data) along the CCO-buffer (FMQ-1 – FMQ-2 depending on pressure). The second set of experiments was performed under “nominally dry” conditions in Fe-presaturated Au₈₀Pd₂₀ capsules (~0.5 wt% H₂O, FTIR data) along FMQ.

Our experimental results indicate that the magmas could evolve in different reservoirs beneath Shatsky Rise. The most evolved basaltic melts (Tamu and Ori Massif) have formed under low pressure differentiation of the more magnesian Ori-like parental magmas. These crystallization conditions have been successfully reproduced in our crystallization experiments at 200 MPa and “dry” conditions. The crystallization of the AH-6 at low pressures of 200-400 MPa also leads to the formation of the most evolved Shatsky Rise compositions. The intermediate compositions were produced only partially at 700 MPa. However, the differentiation trend of the intermediate compositions (Ori Massif basaltic glasses) cannot be reproduced by isobaric differentiation. Our experiments under “nominally dry” conditions are still in progress and will help to envisage the role of the small amounts of melt H₂O on phase stabilities, temperatures and conditions of multiple saturation in LIP basalts.
Kinetic fractionation in orthopyroxene reaction rims between doped forsterite and quartz - first experimental results

Sarah Incel¹, Ralf Milke², Bernd Wunder³

¹sarah.incel@zedat.fu-berlin.de
²milke@zedat.fu-berlin.de
³wunder@gfz-potsdam.de

¹,² Freie Universität Berlin, AB Mineralogie-Petrologie, Malteserstr. 74-100, 12249 Berlin
³ Helmholtz Zentrum Potsdam, GFZ, Telegrafenberg, 14473 Potsdam

When reaction rims form between mutually incompatible minerals, e.g. Opx rims between Ol and Qtz, local equilibrium is maintained between the major chemical components, but to achieve local equilibrium for the minor components additional mass transfer is necessary. Competition between grain boundary and volume diffusion during these mass fluxes leads to kinetic fractionation of chemical components.

There is a large body of experimental work on mineral rim growth in the Mg(Fe)-Si-O system in the literature, but additionally present chemical components have been out of focus, except Fe and Ni in the study of Milke et al. (2011). Ni is retained in Ol, whereas excess Fe completely leaves the replacement zone via grain boundaries and is enriched at the Qtz-Opx interface. This effect was explained by an interplay of volume and grain boundary diffusion in Fo and Opx and different partition coefficients for Ni and Fe between those two phases. We study the partitioning of other transition metals like Co, Mn, Zn, and Ti that are more or less compatible in the forsterite structure.

Forsterite start materials were synthesized doped with Ni, Co, Mn, Zn, and Ti, respectively, with concentrations high enough for electron microprobe analysis. The rim growth experiments were done in a piston cylinder apparatus at 1.5 GPa. The five setups, doped forsterite plus quartz powder enclosed in a Pt-capsule, were put to reaction under “dry” conditions with crushable alumina as pressure medium and under “wet” conditions with CaF₂. The wet runs were heated up to 950 °C and lasted 2 d, and the dry runs to 1400 °C and lasted 5 d. The minimum rim widths under “wet” conditions are ca. 8.7 and 7.5 micrometers for Co and Ni respectively and the Mn- and Zn-rims are around 3.8 and 7.4 micrometers thick. If the rim width is proportional to the square root of time, the rims should be ca. 6.9 microns large. Preliminary results indicate that only a few weight percent of one trace element can inhibit, e.g. Mn, or promote rim growth e.g. Co and Ni. The chemical zoning patterns differ between each chemical component e.g. Cobalt shows both an enrichment front in the forsterite at the Fo-Opx interface and at the opposite side in the orthopyroxene at the Opx-Qz interface. This implies that one part of the excess Co diffuses back into the forsterite and the other part diffuses via grain boundaries in the polycrystalline Opx rim towards the Opx-Qtz interface.

Kinetic fractionation is a fundamental aspect of metasomatism. Our study aims at reactions relevant to mantle metasomatism. Further experimental study is necessary to identify the order of importance for the boundary conditions (diffusion and distribution coefficients) and other so far unconsidered quantifiable factors.

Recent sedimentary facies of the Dry Tortugas, Gulf of Mexico, South Florida

Isaack, A.\textsuperscript{1} and Gischler, E.\textsuperscript{2}

\textsuperscript{1}anja-isaack@stud.uni-frankfurt.de

\textsuperscript{2}gischler@em.uni-frankfurt.de

Several studies have investigated carbonate built-ups, distribution of coral communities, and sediment textures of the Dry Tortugas (24° N, 82° W), a small (8 x 5 km), shallow–water carbonate platform that is part of the Florida Reef Tract, based on mapping, drilling, grain–size analysis and geophysical methods. Systematic studies focussing on the composition and facies distribution of carbonate sediment are rare. Based on the quantitative analysis of 159 surface sediment samples and subsequent statistical testing, we identified seven modern facies that characterize the Dry Tortugas including algae–mollusk packstone–wackestone, mudstone, algae–coral grainstone, algae–mollusk grainstone, algae–rich grainstone, coral–mollusk grainstone, and coral–rich grainstone. Commonly, grain–supported sediments are found on the shallower banks and shoals, whereas the deeper platform area mainly comprises mud–supported sediment. The interior lagoon areas are covered by algae–mollusk packstone–wackestone, mudstone is found in the western part of the lagoon deeper than 15 m. Marginal shoals, smaller banks and patch reefs are characterized by coral–rich, coral–mollusk, algae–coral and algae–rich grainstone. Beachrock, that occurs on the seven small islands of the Dry Tortugas, is composed of algae–coral and algae–rich grainstone. In general, sediment is moderately to poorly sorted. Only beach sediment is moderately well to very well sorted. Correlation analyses shows r–values for water depth and components of sediment between 0.28–0.64 (p<0.0003–p<0.0001) with the most significant correlation between water depth and the mud–sized fraction. The Dry Tortugas show a complex facies pattern, which appears to be mainly influenced by the lack of a continuous, surface–breaking reef system and clear zonations, i.e., irregular submarine topography that produce currents and counter currents resulting in a variable high energy system. Frequent hurricane and storm actions favor undirected sediment distribution, however, indications for massive sediment redepositon are largely lacking.
Deformation and Evolution of the Western Margin of the Indian Plate

Ishtiaq A. K. Jadoon, Department of Earth Sciences, COMSATS Institute of Information Technology, Abbottabad, Pakistan, e-mail: jadooni@ciit.net.pk

Matthias Hinderer, Technische Universität Darmstadt, Institut für Angewandte Geowissenschaftern, Schnittspahnstrasse 9, 64287 Darmstadt, e-mail: hinderer@geo.tu-darmstadt.de

Combined surface geology (field geology and Landsat image interpretation) and subsurface geophysical (seismic reflection, gravity, and seismicity) data reveals the deformation and the evolution of the active, lobate Sulaiman fold belt along the western margin of the Indian plate. A regional 800 km long, NNW-SSE crustal-section, shows tectonic units across the margin (N to S) as the Afghan block, the left-lateral strike-slip Chaman fault (since the early Tertiary), the Khojak flysch basin (Eocene-Miocene), the Muslimbagh ophiolites (late Paleocene-early Eocene), and the Sulaiman fold belt (Triassic-Eocene platform and Neogene molasses sedimentation). The broad (>300 km) and gentle (<1°) Sulaiman fold belt is characterized with the presence of about 10 km strata of stratigraphic thickness, without any thrust fault, at the deformation front. This is interpreted with a, thin-skinned, duplex-style deformation over a weak detachment. The duplex sequence, of Paleozoic to Jurassic strata, is topped by a hinterland vergent roof-sequence, of Cretaceous and younger strata. The roof sequence is breached by a set of exposed thrust faults, of limited displacement, both with foreland and hinterland vergence in the internal part of the system. This zone is reflected by the highest degree of seismic activity at the western margin of the Indian plate. The Landsat data shows the presence of right-lateral strike-slip faults of EW orientation, obliterating former fold-and-thrust structures in this zone. They are apparently representing the youngest Quaternary deformation with anticlockwise block-rotation in the system. We have calculated shortening of about 349 km with convergence rates of about 18mm/yr, since about 20 Ma across the Sulaiman fold belt, south of the Muslimbagh ophiolites and the Khojak flysch basin along the margin.

With gravity data, the crust is modeled as thinner (15-27 km thick) along the Sulaiman fold belt and a thicker (~57 km) along the Afghan block across the Chaman fault. This implies presence of a preserved passive margin along the western terminus of the Indian plate. Deformation partitioning, with transpression in the sedimentary wedge above a decollement and pure translation of the lithosphere with indentation of the Afghan block is considered in our model. The pattern of deformation is supported by the focal-mechanism solutions, and represents active evolution of the Himalayas at the western oblique margin of the Indian plate.
Structure and properties of refractory oxide melts and glasses

Sandro Jahn
Deutsches GeoForschungsZentrum GFZ, Telegrafenberg, 14473 Potsdam, Germany

Calcium and magnesium aluminates are refractory materials of technological importance and significant components of the Earth's crust and mantle. They have a very high melting point, which makes an experimental investigation of the structure and physical properties of their melts challenging. While liquid calcium aluminates \((\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}\) can be quenched into a glass for a range of compositions, the melt of \(\text{MgAl}_2\text{O}_4\) crystallizes in the spinel structure. Experimental approaches to study the structure of aluminate melts and glasses include container-less x-ray and neutron diffraction [1], Raman, x-ray absorption and NMR spectroscopy [2]. They are often complemented by atomic-scale simulations, which provide three-dimensional structure models for these disordered phases [3]. Here, we follow up on a recent combined experimental and computational study of \(\text{CaAl}_2\text{O}_4\) [4], which dealt with the structural changes accompanying the transition from the melt to the glass phase. By analyzing the results of molecular dynamics simulations over a time scale of a few nanoseconds, the structural evolution of calcium and magnesium aluminate melts during quench from 2500 K to room temperature will be discussed. This includes the changing abundance and linkage of structural motifs, such as \(\text{AlO}_4\) tetrahedra and Ca- or Mg-centered polyhedra. From the same simulations, transport properties such as self-diffusion coefficients and the viscosity are extracted. This allows to link the atomic structure to important physical properties and to get new molecular scale insight into the origin of the strong super-Arrhenius behavior of the viscosity of fragile glass-forming systems.

Biomineralization of the green rust, a reactive Fe\(^{II}\)-Fe\(^{III}\) hydroxysalt

Frédéric P.A. Jorand\(^1\)

\(^{1}\)frederic.jorand@univ-lorraine.fr

It is well known that iron oxide reduction by iron reducing bacteria promotes the formation of Fe\(^{II}\) bearing minerals, such as the mixed Fe\(^{II}\)-Fe\(^{III}\) hydroxysalt green rusts (GRs), in anoxic conditions. Other bacterial activities such as iron-oxidizing and/or nitrate-respiring bacteria were found to promote GR formation. Although the microbial-promoted generation of GRs is widely demonstrated, the mechanisms and factors governing the GR formation as the main secondary iron mineral at the expense of other products in lab-scale investigations or environmental systems are largely unknown. As GR is an effective reductant for several contaminants the mechanism controlling the formation routes of GR merit investigation, from both the environmental and engineering points of view.

Some factors such as cellular material (i.e. autoclaved cells and/or bacterial polymers), synthetic anionic polymers or oxyanions have been identified to control the route of the GR mineralization as secondary mineral at the expense of other products such as magnetite.

The arrangement mode of the heterogeneous aggregates resulting from the interactions between bacterial cells, iron oxide particles and polymers was suggested to influence the routes of formation of secondary iron minerals by limiting the diffusion of reactive species and thus creating favorable microenvironment for GR formation. In these aggregates, the electron transfer from cells to iron oxides is supported by organic electron shuttles.

On the other hand, anionic polymers, colloidal and aqueous silicates were found to also influence the nature of the secondary iron minerals through the stabilization of the GR crystals.

These results indicate clearly that the bacterial cells drive indirectly the nature of the secondary Fe\(^{II}\)-bearing mineral. Moreover, they give new insights into the understanding of the mechanisms of « biogenic » mineral formation based on the electron transfers from bacteria towards iron oxides. Finally, this work contributes to our understanding of the processes leading to green rust formation in environmental systems, such as soils or aquatic systems biofilms, in which a very high cell density can be found at a micro-scale level, associated to exo-cellular polymers and natural silica mineral composites.
Schwertmannite compared to other sulphate-bearing Iron Oxides –

A XANES Study

P.M. Kadletz¹, W.W. Schmahl¹, A.J. Götz¹, J. Göttlicher², R. Steininger²

¹ Ludwig-Maximilians-Universität Munich, Dept. of Earth and Environmental Sciences, Munich
² Karlsruhe Institute of Technology, ANKA Synchrotron Radiation Facility, Karlsruhe

Schwertmannite (SHM) is a poorly crystalline iron-oxyhydroxy-sulphate with a non-stoichiometric composition that is close to $\text{Fe}_8\text{O}_8(\text{OH})_{4.8}(\text{SO}_4)_{1.6}$ [1]. Removing Fe(II), sulphate and arsenate from contaminated waters [2] SHM is precipitating in environments affected by acid mine drainage (AMD) [1] [2] and open pit mining waste water [3].

Due to its low crystallinity the structure of SHM is still a matter of debate. We synthesised SHM by different biotic and abiotic pathways. The products show different particle morphologies and slightly varying XRD profiles. The characteristic “hedgehog” morphology has been obtained by both biotic and abiotic syntheses [4]. The quasi amorphous structure is commonly assumed to be related to akaganéite with sulphate instead of chlorine in the tunnel structure. Our Mössbauer spectra show that Fe is entirely octahedrally coordinated Fe(III). Our Rietveld refinements with the Fernandez-Martinez et al. 2010 [5] structure model gave a good fit when anisotropic crystallite size broadening was applied.

Bigham et al. 1994 assumed that sulphate is both adsorbed to the surface and incorporated into the tunnels of SHM [1]. We performed x-ray absorption fine structure spectroscopy (XAFS) measurements at the SUL-X beamline, ANKA Karlsruhe, with particular focus on the x-ray absorption near edge structure (XANES) of sulphur. We analyzed (1) SHM-like compounds in which the sulphate is partially substituted against arsenate and vanadate and (2) different SHM samples in comparison to other sulphate bearing Fe-oxides.

(1) XANES spectra of SHM-like samples with varying arsenate and vanadate content show isosbestic points indicating that a mixture of different configurations is present meaning the anions occupying different sites in the SHM structure.

(2) XANES spectra of SHM samples have been compared to spectra of other sulphate containing Fe(II)-oxides and Fe(III)-oxides, respectively, (e.g. melanterite, coquimbite, jarosite) and to spectra of goethite with sulphate adsorbed. Alike SHM all minerals containing Fe(III) show a pre-peak feature before the actual absorption edge which all Fe(II) containing minerals do not. We attribute this feature to a symmetrical distortion of the sulphate tetrahedra due to the stronger attractive potential of Fe(III) compared to Fe(II). The goethite samples with sulphate adsorbed give a different pattern than SHM. This indicates that sulphate anions are directly bonded to Fe octahedra and therefore incorporated in the (tunnel-)structure of schwertmannite.

Comparing the annealing dependency of Al/Si distribution in Sanidine megacrysts from Volkesfeld/Eifel with X-ray and neutron diffraction methods.

Johannes Kähn\(^1\), Susan Schorr\(^2\)

\(^1\)johannes.kaehn@helmholtz-berlin.de
\(^2\)susan.schorr@helmholtz-berlin.de

The alkali feldspar Sanidine (K\(_2\)Na\(_2\)Ba)[Al\(_{13}\)Si\(_{8}\]O\(_{30}\)] is part of the solid solution series Albite-Orthoclase with a typical composition within the range from Al\(_{13}\)Si\(_{6}\)O\(_{30}\) to Al\(_{15}\)Or85. The monoclinic tectosilicate (space group C2/m) occurs at two different modifications, low- and high-Sanidine, which differ only in their Al/Si ordering. While disordering is usually acquired by long-term annealing at temperatures of 900°C and above, it is apparently possible to reach a nearly disordered state of Al/Si distribution at considerably lower temperatures and shorter annealing times, when annealing Sanidine megacrysts from Volkesfeld/Eifel [1].

In order to investigate this unusual behaviour and to compare the various approaches to find out the Al/Si distribution we studied Sanidine samples from different locations around the Eifel volcanic region and determined the Al/Si order with direct and indirect methods. These experiments include X-ray and neutron diffraction of both powder and single crystal samples.

The Sanidines were annealed for up to 24 hours at temperatures ranging from 750°C to 1050°C. Neutron powder diffraction experiments were performed at the Berlin Research Reactor BERII using the fine resolution neutron diffractometer (E9) (\(\lambda=1.7982\) Å), single crystal neutron diffraction was done at the 4-circle diffractometer (E5) (\(\lambda=0.8960\) Å). Subsequently, the Al/Si order was determined directly, refining site occupancies of the tetrahedral sites by applying Rietveld refinement to powder diffraction data and using XTAL for data of single crystal experiments. However, this approach is not applicable when using data collected by X-ray diffraction, due to similar atomic form factors of Al\(^{3+}\) and Si\(^{4+}\). Thus indirect methods as introduced by Kroll\&Ribbe [2,3] as well as Salje\&Carpenter [4] have to be applied. X-ray powder diffraction (\(\lambda=1.5406\) Å) was performed at a PANalytical X’pert Pro MPD diffractometer at Helmholtz Centre Berlin for Materials and Energy, single crystal X-ray diffraction (\(\lambda=0.7107\) Å) was done with an Oxford diffraction 4-circle diffractometer at the Ruhr-University Bochum. The data from X-ray powder diffraction and single crystal X-ray diffraction were processed using Rietveld refinement and ShelXL software, respectively. The Al/Si distribution was calculated from lattice constants [2,3] and bond lengths [4].

It was possible to verify, that a decrease in the Al/Si order is dependent on increasing annealing times and temperatures. We observed that different methods to determine the Al/Si distribution provide different results with a variation of 10% for untreated as well as annealed samples. We want to present the results of these investigations and discuss possible reasons for the anomalous Al/Si re-ordering as well as for the differences between the results of the used methods.

Unraveling the PT-time history of polymetamorphic granulites: Texturally controlled EMP monazite dating of granulites from the East Sahara Ghost Craton

S. Karmakar1 and V. Schenk1

1Institute for Geosciences, Christian-Albrechts-University, Kiel, Germany (*shreya196@gmail.com)

Monazite is a robust geochronometer, wherein, due to slow element diffusion rate, crystallization ages can be preserved in discrete compositional domains with sharp boundaries, through a long history of geological events. When these compositional domains can be related to specific mineral or reaction textures, monazite helps to place timing constraints on the P-T history of its host rock. Examples from two different granulite terrains in the East Sahara Ghost Craton will highlight the effectiveness and importance of texturally controlled electron microprobe (EMP) dating of monazites.

The enigmatic East Sahara Ghost Craton lies in northeastern Africa, between the Arabian-Nubian Shield (ANS) in the East, the Tuareg Shield in the West and the Congo Craton in the South. Its northern margin, along with most parts of the craton itself, is obscured under Phanerozoic cover. Metapelitic granulites, from a locality between Jebel Uweinat and Jebel Kamil, SW Egypt-NW Sudan, in the central part of the Ghost Craton, reveal two distinct metamorphic events separated by 700 Ma. Inclusions of Spr and Qtz in Grt porphyroblasts indicate a UHT stage of metamorphism (in the deep crust at 10-12 kbar) followed by isobaric cooling resulting in the assemblage Grt+Sil+Opx. Small, rounded, compositionally homogeneous monazite grains included within the Grt porphyroblasts constrain the age of this UHT metamorphism at 2.6 ± 0.02 Ga. Subsequently, near isothermal decompression (to 6-8 kbar, at ca. 1000°C) led to replacement of porphyroblastic Grt by coronitic Opx+Sil+Spr+Crd / Opx+Spr+Crd / Opx+Crd symplectites, followed by regrowth of Grt at the expense of the symplectite phases with formation of late Bt, Spr and Opx during cooling. Larger grains of monazite occurring in the matrix and the symplectites show complex compositional zoning, which sometimes corresponds to an age zoning, where low-Th (~2 wt%), Y-rich (0.3-0.5 wt%) cores giving Archean ages (2.6 ± 0.02 Ga) are rimmed by domains of Paleoproterozoic ages (1.9 ± 0.01 Ga) with high-Th (4.5-14 wt%) and low-Y (0.1-0.2 wt%) contents. This indicates that the isothermal decompression leading to symplectite formation and the subsequent cooling occurred during a separate Paleoproterozoic orogenic event. In contrast, earlier geochronological studies (Rb/Sr, Sm/Nd, Nd model ages and U/Pb zircon ages) were able to recognise only crust formation during Archean and HT reworking during Paleoproterozoic times.

At Sabaloka, north-central Sudan, close to the ANS/Ghost Craton boundary, enclaves of metapelitic granulites in migmatitic Bt-gneisses have a peak metamorphic assemblage of Grt-Sil-Crd and Grt-Opx-Crd (800-850°C at 4-5.5 kbar). Low-Th (2-5 wt%), Y-rich (2-3 wt%) cores of associated monazite grains indicate the time of Grt growth under MP-HT Sil-grade conditions during 780-720 Ma. The subsequent partial replacement of Grt-Opx-Sil by Crd-Spl / Crd-Spl-Sil assemblages occurred about 170 Ma later during a second LP-HT metamorphic event at 602 ± 4 Ma, as is evident from the Th-rich (6-10 wt%), Y-poor (<1wt%) rims of the monazites. Previously, a crystallization age of ca. 719 Ma from igneous zircons was used to possibly reflect timing of ‘the granulite event’ at Sabaloka, while a Rb/Sr age of ca. 570 Ma from migmatites was interpreted as indicating hydration, retrograde metamorphism and anatexis.

Thus, in both studied areas, Uweinat and Sabaloka, EMP dating of monazites serves as a key tool to not only identify and analyze the domains of monazite grains but more importantly to maintain a ‘textural control’ on the data in order to unravel the polymetamorphic nature of the terrains, hitherto unknown.
Deformation architecture and structural evolution of the Paikon Massif (Axios Zone, Central Macedonia, Greece): a new tectonic interpretation

Kattrivanos E.¹, Kilias A.² and Mountrakis D.³

¹ekatrina@geo.auth.gr
²kiliias@geo.auth.gr
³dmountra@geo.auth.gr

The Paikon Massif is part of the Axios Zone and consists of Triassic to Jurassic marbles intercalated with schists and phyllites, overlain by volcanoclastic and carbonate rocks of Jurassic to Early Cretaceous age, as well as ophiolites. Transgressive Upper Cretaceous limestone and flysch overlie discordantly all the above-mentioned units of the Paikon Massif. Polyphase deformation and metamorphism affected all Paikon units. We distinguish six main deformational events (D₁ - D₆). Deformation started in the Middle to Late Jurassic during subduction, but no structures were preserved from this stage (D₀). Ophiolite obduction and the tectonic emplacement of the volcanoclastic series of the Paikon Massif took place during the Late Jurassic and D₁ event. Top-W movement occurred mainly during D₁. Syn-D₁ metamorphism did not exceed greenschist facies conditions (M₁). D₁ affects the Triassic units of the Paikon Massif and the overlying volcanoclastic series. A HP-LT metamorphism (M₀) recognized in the lower tectonic units of the Paikon Massif predates the D₁ event and is possibly related to subduction and collision. Compressional tectonics and intense thrusting with a southwestward sense of movement continued in Lower Cretaceous time, affecting all pre–Upper Cretaceous units and the obducted ophiolites (D₂). D₂ is associated with a M₂ metamorphism in low grade greenschist facies conditions. Deposition of the Upper Jurassic-Lower Cretaceous carbonate sediments may be related to extension before D₂ and perhaps during the late stages of D₁. During the Late Cretaceous, basin formation and sedimentation of the Upper Cretaceous shallow-water limestone and flysch are probably linked to extension (D₃). During the Paleocene to Eocene, intense imbrication of all tectonic units towards SW takes place again (D₄). In the western Paikon, during D₄, the obducted ophiolites were thrust back towards NE over the Upper Cretaceous limestones and flysch. Extensional collapse and exhumation took place during Oligocene to Miocene, associated with brittle low-angle normal faults, with a main top-to-the-SW sense of movement (D₅). Top-NE movement also occurred during D₅. In Miocene to recent times, brittle high-angle normal and strike-slip faults are formed in an extensional to transtensional strain regime (D₆), associated with Neogene to Quaternary basin formation. The Paikon Massif is regarded as a multiple tectonic window, probably of Pelagonian origin.
The Paleoproterozoic Ubendian Belt in SW Tanzania has been subdivided into eight lithological blocks (Daly, 1988), among which the Lupa and Katuma Blocks host significant gold and base metal mineralizations. In the Katuma Block, gold occurs in sulphide-carbonate-quartz veins hosted within orthogneisses, metapelites and metabasites. Proximal to the ore bearing veins the amphibolite- to granulite-facies host rocks show hydrothermal alteration, muscovite formation and an increase in sulphide disseminations. Recent studies revealed that the Paleoproterozoic Ubendian Belt experienced two subsequent Proterozoic orogenic reworking events, which affected the different blocks to a different degree. This indicates that in post-Paleoproterozoic time the blocks underwent separate geodynamic evolutions. Our study aims to unravel the geodynamic evolution, the age and the origin of the gold mineralization in the Katuma Block. We determined the geochemistry of metabasites, gabbros and orthogneisses, deduced the metamorphic history and dated the formation and metamorphism of the host rocks and the hydrothermal alterations near the veins with zircon (LA-ICP-MS) and monazite (CHIME). The internal textures of the zircon grains in combination with the U-Pb ages indicate that the magmatic formation of the protoliths of the orthogneisses and metabasites in the Katuma Block occurred in Neoarchean time (~2.71 - 2.65 Ga). During this magmatic phase, the rocks also experienced their earliest metamorphism.

Subsequently, the deposition of sediments in the Katuma Block occurred between 2.58 and 1.97 Ga. Geochronological and petrological data suggest that during Paleoproterozoic time the Katuma metapelites experienced a clockwise P-T evolution (Ky-Sil type) reaching granulite-facies metamorphism (6.5 kbar and 785°C). Metabasites experienced P-T conditions of 7.3 kbar and > 660 °C during a near isobaric cooling within the deep crust. U-Th-total Pb dating of recrystallized monazite of a hydrothermally altered metapelite gave a Mesoproterozoic age (~1.2 Ga) for the hydrothermal alteration and gold mineralization event, which correlates with the age of the first high grade metamorphism of sediments in the adjacent Wakole Block. This suggests a possible link between this metamorphism and generation of hydrothermal fluids responsible for the formation of gold bearing veins in the Katuma Block. The Neoarchean metabasites, gabbros and orthogneisses are sub-alkaline in composition with a REE and trace element geochemistry akin to those rocks formed in arc settings. HFSE-ratios like Zr/Y, Ta/Yb, Th/Yb, Th/Hf, Ta/Hf and Th/Ta suggest a continental arc setting for the formation of the precursor rocks of the metabasites, gabbros and orthogneisses in Neoarchean time.

Our new age data point out that the Katuma Block of the Paleoproterozoic Ubendian Belt consists dominantly of Neoarchean rocks that experienced their main metamorphism during Paleoproterozoic orogenic events.
Zoned supergene assemblages during weathering of galena: stability relations among pyromorphite, cerussite and anglesite

Maximilian F. Keim¹, Gregor Markl¹

¹Universität Tübingen, Mathematisch-Naturwissenschaftliche Fakultät, FB Geowissenschaften, Wilhelmstrasse 56, D-72074 Tübingen, Germany

maximilian-felix.keim@student.uni-tuebingen.de
markl@uni-tuebingen.de

Galena (PbS) is a common sulfide mineral in lead-bearing ore deposits. If the mineral is exposed to near-surface conditions, supergene alteration produces thermodynamically more stable secondary lead phases. In this work we investigated 41 thin-sections of weathered galena and adjacent country rock. The samples are from the Schwarzwald ore district (SW Germany) and were investigated using polarized light microscopy and electron microprobe analysis.

Common identified secondary lead phases are cerussite (PbCO₃), anglesite (PbSO₄) and pyromorphite group minerals (PyGM) (pyromorphite Pb₅(PO₄)₃Cl, mimetite Pb₅(AsO₄)₃Cl and vanadinite Pb₅(VO₄)₃Cl). These supergene phases formed in a spatially well ordered zoning texture around the preexisting/relic galena. Part of the galena is dissolved leaving empty cavities behind. Cerussite and anglesite occur either as in-situ replacement of galena and/or as euhedral crystals in the cavities formed during the same or an earlier event of weathering. The PyGM are either located as a thin crust at the margin of the former/relic galena or they occur as infiltration-products in the vicinity of galena in the host rock or gangue minerals. Growth zoning in PyGM indicates a periodic growth during weathering and dissolution of galena, which most probably happened discontinuous. In many samples, various generations of the supergene minerals are present and young PyGM may even form pseudomorphs after earlier cerussite. This again points to discontinuous processes, which may be related to changes of water availability or changes in biological activities. Formation and/or dissolution of cerussite and anglesite might supply lead ions for PyGM formation during the later stages of supergene mineral formation, after galena is mostly or completely consumed. We interpret the supergene mineral textures to reflect differences in solubility products of the various secondary lead phases in combination with changing or variable ion activities in the supergene fluids. The solubility products K are: K_{Anglesite} > K_{Cerussite} > K_{PyGM} (e.g., Näsänen et al. 1961, Nriagu 1972). Accordingly, the spatial arrangement generally shows cerussite and anglesite at the place of former galena, while pyromorphite forms at the margins and outside of it. The very low solubility products of PyGM explain their presence in spite of extremely low PO₄ concentrations in analyzed water –samples from various Schwarzwald mining localities, and they explain their textural position at the rim of the former galena crystal. In terms of temporal evolution of the secondary textures, one observes interesting changes: during further weathering, the secondary –lead –mineral with the highest solubility (anglesite) typically disappears first. With proceeding evolution, also Cerussite dissolves and finally, only the highly insoluble PyGM persist as a perimorphose around a cavity representing the former galena or as pseudomorph after cerussite. The investigation of these secondary Pb assemblages reveals details of weathering processes in ore related systems, records discontinuous processes going on in the critical zone close to the surface and allows to judge the “maturity” of weathered system based on textural arguments.

Magma fractionation and evolution of the submarine Monowai volcanic system, northern Kermadec Island Arc (SW Pacific)

Fabian Kemner¹, Karsten Haase¹, Christoph Beier¹, Sarah Freund¹, Philipp Brandl¹, Ulrich Schwarz-Schampera², Christian Timm³

¹GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Schloßgarten 5, D-91054 Erlangen, e-mail addresses: fabian.kemner@fau.de, karsten.haase@fau.de, christoph.beier@fau.de, sarah.freund@fau.de, philipp.brandl@fau.de

²Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 2, D-30655 Hannover, e-mail address: U.Schwarz-Schampera@bgr.de

³GNS Science, PO Box 30-368, Lower Hutt 5010, New Zealand, e-mail address: c.timm@gns.cri.nz

The Monowai volcanic system (MVS) is part of the 2550 km long Tonga-Kermadec island arc in the southwestern Pacific. The MVS represents one of the largest volcanic systems in the world. It consists of two large Calderas. There are at least two stages of magmatic activity recognized at the MVS, the Caldera forming stage and a resurgent dome and major cone forming stage. The rock samples cover a wide range in SiO₂ and MgO contents. The younger dome-forming stage consists of basalts and basaltic andesites with SiO₂ ranging from 47 to 56 wt.% and MgO ranging from 1.2 to 6.3 wt.%, respectively while the older caldera flank lavas mainly consist of more evolved basaltic-andesitic and andesitic to dacitic rocks with SiO₂ content up to 65 wt.% and MgO contents ranging from 5.2 to 7.9 wt.%, respectively. Sulfur and Cl display significantly higher concentrations with increasing SiO₂, which could indicate assimilation of some hydrothermal material at the older magmatic stage. Zinc and Pb concentrations increase with increasing SiO₂. Incompatible elements like K and Zr show increasing contents with increasing SiO₂ but all lavas have comparable (La/Sm)N between 0.6 and 0.7 and Ba/Nb between 260 and 400 implying a strong subduction zone influence. Nickel decreases from 30 ppm to 5 ppm whereas Co remains constant in the basalts but decreases in the andesitic lavas. Compositions of olivines in the Monowai main cone fall into a narrow range between Fo₇₆ and Fo₈₃ indicating a homogenous magma composition. In contrast An-contents in plagioclase show a large variation being indicative of variable degassing where water loss leads to variable melt-crystal distribution coefficients. The older more evolved lavas of the caldera are product fractional crystallization processes. They are part of a large shallow magma reservoir in the crust where the parent magma resided leading to eruption of andesitic to dacitic lavas. This magma chamber collapsed forming the caldera. Younger lavas show a more mafic, very homogenous composition, forming a young dome in the center of the caldera probably right after the collapse as well as two cones southwest of the caldera that show recent activity. The magma system changed considerably with younger magmas rising without significant residence time in the crust to the surface. Interestingly, the youngest material from the recent eruptions is similar to that on the cone sampled in 1998 implying that melts over the past decade are product of a very homogenous mafic melt reservoir.
The surficial transformation from tetragonal to monoclinic Zirconia, induced by mechanical, chemical or thermal treatment, is a beneficial property on small scales but becomes detrimental when high degrees of transformation are attained. The applicability of Zirconia for medical implants is therefore still controversial, due to the eventual transformation-induced loss of favorable material properties on aging and the potentially resulting catastrophic failure. Predictions of life-time stability thus requires knowledge about the transformation kinetics.

As the transformation is known to be a slow process at room temperature, we examined the transformation progression and phase development on hydrothermally aged samples at elevated temperatures of 134°C under saturated water vapor pressure. We used X-Ray diffraction as well as Raman Spectroscopy for phase determination, complemented by analyses of cross-sections – cut with Focused Ion Beam methods – by EBSD and SEM. Combining all these methods, we can show that the transformation starts at near-surface areas and that the transformed layer proceeds continuously into the bulk following strictly linear kinetics without gradual decrease and a sharp boundary between layer and unaffected material.

The correct interpretation of quantified XRD-data with the known kinetics leads to a model which is also valid for samples aged at 37°C, mimicking human body temperature conditions. This provides insight into the in vivo aging process and transformation progression at low temperatures and for the first time allows realistic forecasts of life-time stability.

We show that phase transformations become significant even at low temperatures without active external triggering. This aging is a slow process over tens of years. However, implanted material is exposed to complex loading conditions including chewing movements in dental material, which may accelerate the aging and wear behavior. Therefore the issue of ageing remains an important topic for Zirconia biomaterial research.
Borehole Image logs to solving primary and secondary porosity in view of geological and petrophysical characterization in carbonate reservoir rocks; a case study, Sarvak Formation, Zagros, Iran

Mehdi Khoshnoodkia¹, Mohammad Rahim Karimi², Liela Fathiyan³

Department of Geological Reservoir Research, NISOC, Ahwaz, Iran

¹m_khoshnoodkia@yahoo.com
²Karimi.m@nisoc.ir
³fathiyan@gmail.com

This article discusses type of heterogeneities and looked how they may be detected and analyzed. Recently, most carbonate formation evaluation methods rely on traditional resistivity and porosity logs. Therefore, the conventional porosity logs (density, neutron, and sonic) often appear somewhat uniformly distributed and under-estimated or overlooked. But, borehole electrical images, Formation MicroImager tool (FMI) in particular, resolve quantitatively the heterogeneous nature of primary and secondary porosity of reservoir. So, with a technique converts electrical borehole images into a porosity map of the borehole interior and the classic Archie saturation equation was used to transform such conductivity data to a porosity map. Through this technique, porosity distribution and quantity of vugs / moulds fraction could be obtained.

In this study, Sarvak formation is a carbonate reservoir which has a complex dual porosity system with widely varying proportions of primary and secondary porosity. The secondary porosity contains vugs, moulds, channels, and fractures. Moreover, some homogeneous matrix / intergranular primary porosity become patchy through selective cementation of the matrix.

The result of FMI interpretation shows that, the dominant structural dip in the Sarvak formation is gentle. Fracturing is not very significant. There are vuggy fractures, some open and closed fractures. Secondary / leached porosity is observed in most of the Sarvak interval as well as total porosity is well developed and is 0-5%. The secondary porosity (possibly due to dissolution) is low. There are many vugs and diagenetic features visible on the image log in the study. In some intervals, secondary porosity is better developed. The FMI images revealed heterogeneity across the whole interval. In clean carbonates, the conductive heterogeneities are due to porous areas (i.e., patches of intergranular and intercrystalline porosity, mouldic / vuggy porosity and, natural open fractures) of different size, shape and conductivity. While in dense carbonates, the conductive heterogeneities due to argillaceous material are observed largely due to clay seams.

The resistive heterogeneities are due to dense/cemented areas of lower or zero porosity.

FMI permeability indicator shows quite a few zones with high permeability index. There are zones with relatively high raw permeability index (>10 md) for Sarvak reservoir of Ahwaz Field.
The use of spectrometry gamma ray and neuro-fuzzy logs for evaluation of total organic carbon contents: A case study from the Gadvan Formation in the South Pars field of the Persian Gulf, Iran

Mehdi Khoshnoodkia¹, Liela Fathiyan², Mahmood Jamilpour³, Omeid Rahmani⁴, Hassan Mohseni⁵

Department of Geological Reservoir Research, NISOC, Ahwaz, Iran

M_khoshnoodkia@yahoo.com
fathiyan@gmail.com
Mahmood_mi@yahoo.com
Omeidrahmani@gmail.com
Mohseni@basu.ac.ir

Total organic carbon (TOC) can be assessed using of conventional geological logs, for example resistivity, sonic, density, neutron, and gamma ray logs. The TOC content of the Gadvan Formation, as a source rock candidate in the South Pars field, was evaluated using spectral gamma ray such as uranium (U), thorium (Th), and potassium (K). In this study, the TOC content was calculated via ∆ LogR technique using conventional geological logs and compared with geochemistry analysis of Rock-Eval. The results obtained via using spectral gamma ray were trained with neuro-fuzzy technique for prediction of TOC. The content of the K confirmed the origin of the source rock as a pure carbonate, whereas the low content of the Th was indicative of the percentage of clays. There was high U content, which established the Gadvan Formation was not deposited in a good reducing environment for conservation of OM. ∆ LogR and neuro-fuzzy methods confirmed that the Gadvan Formation was a relatively poor source rock in the oil-prone well C from the South Pars Gas field. There are no significant differences between the results based on Rock-Eval data and conventional geological logs for assessment of the TOC content.
Composition and phase relations of the complex hydrothermal Fe-Ni-Co arsenide and sulfarsenide minerals from Dobšiná (Slovakia)

Stefan Kiefer1,* and Juraj Majzlan2,*

1Institute of Geosciences, Friedrich-Schiller-University Jena, Germany

1Stefan.Kiefer@uni-jena.de

2Juraj.Majzlan@uni-jena.de

The Dobšiná ore field has been known since the 13th century and even though there is no longer any industrial mining activity, it is still famous for its remarkable supply of Fe-Ni-Co sulfarsenide and arsenide minerals, representing the most important mineralization type within the deposit. The Fe-Ni-Co arsenides and sulfarsenides found in nature are a large and variable group of minerals, which – as experimental studies have shown – are very complex (e.g. Hem and Makovicky 2004a, b). The chemical composition of these minerals changes rapidly on a micrometer scale due to extensive substitution on the cation and anion sites as well as broad polymorphism. The Fe-Ni-Co ores were deposited during the quartz-sulfide period of the mineralization with formation conditions of 200-300 °C and 3.6-4.4 kbar (Hurai et al. 2002). Although the five-component system Ni-Fe-Co-As-S has been examined in comprehensive studies, the extent of the compositional and stability fields within the system at lower hydrothermal temperatures is not yet understood in detail. Within this research, we present extensive optical studies, microprobe analyses and electron backscatter diffraction data and attempt to reach a better understanding of the low-temperature phase relations, chemical variations and polymorphism in the system. Especially the microprobe studies show broad variations particularly in the As and S content. Nevertheless, the chemical analyses show that the mineral composition within one phase system (e.g. FeAsS-NiAsS-CoAsS) confirms a chemical trend and shows possible miscibility gaps.

References

Hem SR, Makovicky E, 2004a: The system Fe-Co-Ni-As-S. I. Phase relations in the (Fe,Co,Ni)As0.5S1.5 section at 650 ° and 500 °C. Can. Mineral., 42, 43-62.

Hem SR, Makovicky E, 2004: The system Fe-Co-Ni-As-S. II. Phase relations in the (Fe,Co,Ni)As1.5S0.5 section at 650 ° and 500 °C. Can. Mineral., 42, 63-86.

The Olympic Dam giant ore deposit – a fossil nuclear reactor?

MARIA KIRCHENBAUR1,2, KATHY EHRIG3, ROLAND MAAS4, VADIM KAMENETSKY5, CHRIS BALLHAUS2, CARSTEN MÜNKER1

1Institut für Geologie und Mineralogie, Universität zu Köln, Germany
2Steinmann-Institut, Universität Bonn, Germany; Kirchenbaur@uni-bonn.de
3BHP-Billiton, Adelaide, South Australia, Australia
4School of Earth Sciences, University of Melbourne, Australia
5CODES, University of Tasmania, Hobart, Australia

The Olympic Dam (OD) supergiant Cu-U-Au-Ag deposit in the Gawler Craton of South Australia occurs within tectonic-hydrothermal breccia hosted by 1.59 Ga granite of the Gawler silicic large igneous province. With probable reserves of ~200000 t of U, OD is one of the world’s largest U deposits. The high uranium content and a possible Proterozoic age of mineralization raises the possibility of Oklo-style fossil nuclear reactor activity, although a much smaller degree of burn-up, similar to that documented in many other Proterozoic and Phanerozoic U deposits, is more likely, given the low average U concentration (450 ppm) at OD. We explore this possibility using U-Sm-Nd isotope data.

High-precision U isotope data for 43 samples with U concentrations up to 10.5% were obtained by MC-ICPMS at Cologne/Bonn, employing both double spiking and standard-sample bracketing to correct for instrumental mass bias. \( \delta^{238}\text{U} \) (relative to a \( ^{238}\text{U}/^{235}\text{U} \) of 137.856 for REIMEP 18a) ranges from -0.5‰ to +0.2‰ (average \( \delta^{238}\text{U} = -0.2‰ \)). Only four samples yield the positive \( \delta^{238}\text{U} \) expected from consumption of \( ^{235}\text{U} \) in sustained nuclear fission, well below \( \delta^{238}\text{U} \) found at Oklo (up to 560‰), but consistent with the minute isotopic effects reported for other old U deposits. Depletion of \( ^{149}\text{Sm} \) by slow neutron capture, observed in many U deposits, reaches 1.5 \( \varepsilon \)-units and only occurs in the few samples with positive \( \delta^{238}\text{U} \). Isotope ratios of Nd are indistinguishable from normal. We conclude that OD contains U with a near-natural abundance of \( ^{235}\text{U} \), but some U-rich domains appear to have experienced a small degree of induced \( ^{235}\text{U} \) fission with associated neutron capture effects in other elements.

The vast majority of our samples (10-8000 ppm U) exhibit slightly negative \( \delta^{238}\text{U} \). Consistently negative \( \delta^{238}\text{U} \) (-0.3 to -0.7‰) was previously found for ‘magmatic’ U deposits, defined to include hydrothermal (200–400°C) deposits [1]. \( ^{238}\text{U} \) depletion in such deposits is thought to reflect natural isotope fractionation during U deposition.

A Mid–Late Triassic tectonothermal event in the eastern Acatlán Complex, southern Mexico: tectonic uplift and magmatic shutdown

Moritz Kirsch¹, Maria Helbig², J. Duncan Keppie³, J. Brendan Murphy⁴, James K. W. Lee⁵, Luigi A. Solari⁶

1 Institut für Geologie, Universität Hamburg, GER; email: moritz.kirsch@uni-hamburg.de
2 Centro de Geociencias, Universidad Nacional Autónoma de México, MEX; email: maria.helbig@googlemail.com
3 Departamento de Geología, Universidad Nacional Autónoma de México, MEX; email: keppie@eastlink.ca
4 Department of Earth Sciences, St. Francis Xavier University, CAN; email: bmurphy@stfx.ca
5 Department of Geological Sciences and Geological Engineering, Queen's University, CAN; email: lee@geol.queensu.ca
6 Centro de Geociencias, Universidad Nacional Autónoma de México, MEX; email: solari@unam.mx

Basement rocks exposed in the Acatlán Complex of the Mixteca terrane in southern Mexico record a polyphase metamorphic history and provide an excellent opportunity to investigate the Paleozoic to Mesozoic tectonic evolution of the North American Cordillera in the context of subduction-related processes following the amalgamation of Pangea.

Two dominant tectonothermal events have been recognized in rocks of the Acatlán Complex: (i) a Devonian–Mississippian (ca. 365–318 Ma) event, recording extrusion and exhumation of high-pressure rocks; and (ii) an Early to Middle Permian (ca. 289–263 Ma) event, involving N–S dextral shearing, transtensional deformation and local S-vergent thrusting in a magmatic arc environment.

We document the existence of an additional, regionally significant, tectonothermal event during the Middle to Late Triassic by presenting ⁴⁰Ar/³⁹Ar step-heating laser probe data for muscovite, biotite and amphibole from two Late Paleozoic low- to medium-grade units in the northeastern part of the Acatlán Complex. These units include (i) the Amarillo unit, consisting of metasedimentary rocks intruded by mafic dikes; and (ii) the Pennsylvanian–Middle Permian, clastic-calcareous, arc-related Tecomate Formation. U-Pb LA-ICP-MS data yield an age of 339 ± 6 Ma for the youngest population of detrital zircon grains in the Amarillo unit. Lithogeochemical and Sm-Nd isotopic data for the Amarillo unit dikes are very similar to those of other Carboniferous meta-igneous rocks in the eastern and southwestern part of the Acatlán Complex, displaying affinities transitional between MORB and continental tholeiites, and initial εNd (t = 339 Ma) values from -6.6 to +6.4, indicating both depleted and enriched mantle sources, as well as variable contamination by continental crust or by subduction-related processes.

The ⁴⁰Ar/³⁹Ar plateau ages range between ca. 239 and 219 Ma and are interpreted to indicate rapid cooling due to tectonic uplift. Moreover, the ages coincide with an apparent hiatus in magmatic activity in southern Mexico, as suggested by a paucity of Mid- to Late Triassic igneous rocks and detrital zircon ages. As both the Carboniferous to Early Triassic, as well as the Early Jurassic tectonothermal history of southern Mexico is to a large part influenced by subduction-related processes, the inferred phase of uplift may perhaps be due to a change from steep to flat subduction, causing magmatism along the arc to temporarily shut down.
Metamorphism and fluid-rock interactions during subduction and accretion – an example from the Western Alps (Valtournenche, Italy)

Kirst, F.¹, Nagel, T.J.² & Froitzheim, N.³

¹fredster@uni-bonn.de
²tnagel@uni-bonn.de
³niko.froitzheim@uni-bonn.de

Subduction zones and accretionary wedges are settings where high-pressure metamorphism of deeply buried units is often linked to metasomatic alteration by fluids released at depth. In the Western Alps a stack of ocean- and continent-derived units, assembled during Late Cretaceous – Early Tertiary subduction and accretion, is exposed. We investigate a garnet-bearing, quartz-rich metasediment sample from a small continental sliver at the Becca d’Aver in the western Valtournenche of Italy. The fragment is interpreted as an extensional allochthon incorporated into the Combin Zone, the accretionary wedge at the Adriatic continental margin, during SE-directed subduction. In the analysed sample, prograde metamorphism and fluid-rock interactions during subduction and accretion have been recorded.

The sample consists of garnet + quartz + calcite + phengite + epidote/allanite + chlorite. Garnets are Mn-rich with up to 52 mol% spessartine-component in cores (Sp₅₂ Al₃₂₅ Gr₃₂ Py₁) and 16 mol% at the rims (Sp₁₆ Al₃₂₅ Gr₃₂₉ Py₃). Distribution maps of major bivalent elements show a growth zonation with decreasing Mn and increasing Mg, Fe, and Ca from core to rim. Most garnet grains display honeycomb-shaped intergrowths with quartz and/or contain large quartz inclusions. The rims of quartz inclusions sometimes define a euhedral garnet crystal shape indicating concomitant growth of quartz and garnet hosts. Some intergrowths display a circular pattern suggesting rotation during formation. Quartz inclusions are occasionally highly strained parallel to the foliation indicating synkinematic crystal growth. Equilibrium phase diagrams were calculated to confine pressure and temperature conditions for mineral compositions and assemblages. Garnet isopleth thermobarometry yields 1.1 GPa and 390°C for core compositions and 1.56 GPa and 450°C for rim compositions. All of the observed minerals, except for chlorite, are stable at peak pressure conditions around 1.7 GPa and 500°C.

Microstructural relations between garnet and quartz indicate contemporaneous growth of these phases in a highly dynamic environment. Thermodynamic modelling suggests garnet growth within a relatively narrow temperature range on the prograde path during blueschist-facies metamorphism. Garnet/quartz intergrowths are interpreted as high-pressure precipitates from a Mn- and silicate-rich fluid released during subduction. Differences in style of inclusion patterns and degree of quartz deformation can be explained by coupling/decoupling of garnet hosts with respect to the local stress field due to the presence of a fully-wetting fluid. Prograde metamorphism in the analysed sample was strongly coupled to fluid-rock interactions during subduction-related shearing. Information on PT-conditions can be used to constrain and quantify the early metamorphic evolution of the continental fragment and the Combin accretionary wedge.
Carbontate dissolution during glacial/interglacial conditions

Jens Kirstein\(^1\), Helge Hellevang\(^2\), Reinhard Gaupp\(^3\)

\(^1\)Jens.Kirstein@uni-jena.de
\(^2\)Helge.Hellevang@geo.uio.no
\(^3\)Reinhard.Gaupp@uni-jena.de

In the past four decades a variety of literature concerning the geochemical kinetics of carbonate dissolution was published. Despite these extensive datasets the attention to glacial carbonate environments is limited. Key aspect of this study is the investigation of dissolution reactions of Triassic limestones (Lower Muschelkalk, Germany) at mineral-water-interface under glacial/interglacial conditions. Our comparison of geochemical modeling, laboratory experiments and field work provide additional information to previous studies and expand the knowledge of: (1) weathering rates of natural carbonate rocks as a function of low-temperature (5-25°C); (2) carbonate weathering over glacial/interglacial times and (3) the role of terrestrial carbonate weathering to the global carbon cycle.

To enhance the understanding of calcite dissolution kinetics, three types of experiments were performed: (1) batch; (2) flow-through and (3) reactive percolation experiments. We will present our results of dissolution rates of micritic calcium carbonate samples (homogeneous, non-porous, fossil-free Triassic Muschelkalk) and different heterogeneous, porous, bioclastic and oolitic limestones in comparison to measurements of vertical scanning interferometer.

This study is part of the project “Timing of long-term carbonate mobilisation in a limestone aquifer” at the International Max Planck Research School for Global Biogeochemical Cycles in cooperation with the Friedrich Schiller University Jena. The goal is to deliver basic data for a quantification of carbonate export and carbon dioxide consumption within the Thuringian basin Muschelkalk aquifer during the Late Quaternary. Finally it acts as a case study for the carbonate transects from land to the sea in the global carbon cycle.
The depth at which rhyolitic magmas are stored in magma chambers prior to eruption is difficult to constrain and remains mainly unknown because the classical mineral assemblages in the rhyolitic systems are not suitable for geobarometry. As an alternative to mineral compositions, the silica content of rhyolitic melts can be used to constrain pressure, provided that the silicate melts have cotectic compositions (melts coexisting with quartz and feldspar). From studies in synthetic systems, it is well known that the silica content of cotectic melts decreases with increasing pressure and that it may be used as barometer. However, the evolution of silica content with pressure is not calibrated for natural rhyolitic systems containing up to 2 wt% CaO and 4 wt% FeO.

In order to calibrate cotectic melt compositions coexisting with quartz or/and feldspars in natural rhyolitic systems, crystallization experiments have been performed at 200 MPa and in a temperature range of 790 to 850°C and the results have been projected onto the haplogranitic Quartz-Albite-Orthoclase diagram (Qz-Ab-Or). The starting materials were composed of glasses with various proportions of the Qz, Ab and Or components; all glasses contained 1 wt% FeO, 3.5 wt% An component and 0.2 wt% TiO₂. Four rhyolitic glasses were synthesized at 1 atm and mixed with each other to get ten starting compositions. The mixed glasses were pre-hydrated with 3 wt% H₂O in an Internally Heated Pressure Vessel. The crystallization experiments were conducted in Cold Seal Pressure Vessels. The water content of the pre-hydrated starting glasses were checked by Fourier transformed Infrared Spectroscopy (FTIR) and Karl-Fischer-Titration. The experimental results (glasses and crystals) were analyzed via Electron microprobe. Results show that the cotectic line separating the quartz primary field from the feldspar primary field is shifted towards the Qz apex by 6 wt% Qz when compared to the water-undersaturated haplogranitic system (containing 3 wt% water). The minimum composition is shifted towards the Qz-Or sideline when compared with the haplogranitic system. The results also indicate that the approach proposed by Blundy and Cashman (2001) to account for the effect of An content on the position of the cotectic lines in the system Qz-Ab-Or is qualitatively correct, but that the shift of the cotectic line is more pronounced than predicted by Blundy and Cashman (2001).

Constraining chromite formation through oxygen isotopes: a study of the UG2 unit (Rustenberg Layered Suite, Bushveld Complex, South Africa)

Ilka C. Kleinhanns\(^1\), Hilde Koch\(^2\), Heinrich Taubald\(^3\), Ronny Schoenberg\(^4\)

\(^{1,2,3,4}\) Universität Tübingen, FB Geowissenschaften, Wilhemstrasse 56, D-72074 Tübingen, Germany

\( ^{1}\)kleinhanns@ifg.uni-tuebingen.de, \(^{2}\)hilde.koch@student.uni-tuebingen.de

\(^{3}\)taubald@uni-tuebingen.de, \(^{4}\)schoenberg@uni-tuebingen.de

The Rustenberg Layered Suite (RLS) hosts the mafic-ultramafic components of the Bushveld igneous complex in South Africa and contains the (yet discovered) most important magmatic ore deposits yielding about 75% of the global Pt production and ca. 50% of the global Cr production. The RLS is further subdivided into a Marginal, Lower, Critical, Main and Upper zone. Within the Critical Zone three sets of chromitite layers are observed that are the Lower Group (LG) 1-6, Middle Group (MG) 1-4 and Upper Group (UG) 1-3 layers. Especially the UG2 layer is of great economic importance and exploited throughout the Bushveld complex. Nonetheless, chromite formation is not well understood and a number of different models are debated. The groundbreaking work of Irvine (1977) \([1]\) who showed that mixing of silicate melts into a hybrid melt can lead to chromite as sole cumulus phase promoted the so-called in situ cumulate models. This process, however, cannot explain the amount of chromite (~7-10 m in total) observed in the RLS as for example silicate melts can only host up to 2-3 wt% \(\text{Cr}_2\text{O}_3\). A different approach to explain chromite formation is used by the intrusive models. These argue for an intrusive origin of the chromitite layers and circumvent the “missing silicate” problem through formation of chromite in structural traps beneath the main magma chamber. Within these traps chromite forms as cumulate phase by (traversing) hybrid silicate melts and accumulates with time. These trapped chromites are remobilized through, for example, larger rising magma batches and transferred into the magma chamber to spread laterally forming layers. Both types of models have in common that the strong metasomatic alteration of the surrounding silicate rock units is used for a great number of arguments in both directions. With the means of mineral oxygen isotope composition it is possible to deduce if certain mineral phase grew in equilibrium with each other. Since the cumulate models argue for in situ production of all minerals these should be in equilibrium with each other. The intrusive model argues for at least two different source regions now combined in close proximity ((1) direct silicate crystallization in the magma chamber and (2) chromite crystallization in deeper lying traps). By comparison of oxygen isotope data of the chromites and neighbouring silicate phases (and comparing cumulus and intercumulus phases) it should be possible to deduce, which model is more realistic to explain chromite formation.

\[1\] Irvine TN 1977, Origin of chromite layers in the Muskox intrusion and other stratiform intrusions; A new interpretation. Geology 5: 273-277
Meso-Cenozoic intraplate shortening in Central and Western Europe

Jonas Kley\textsuperscript{1} Fabian Jähne\textsuperscript{2} Alexander Malz\textsuperscript{3}

\textsuperscript{1}jkley@gwdg.de Geowissenschaftliches Zentrum, Universität Göttingen
\textsuperscript{2}fabian.jähne@bgr.de Bundesanstalt für Geowissenschaften und Rohstoffe (BGR)
\textsuperscript{3}alexander.malz@uni-jena.de Institut für Geowissenschaften, Universität Jena

From the British Isles to Poland, Europe was affected by contractional deformation in Late Cretaceous and Paleogene time. The closest plate margins were the incipient Mid-Atlantic rift in the west and northwest, and the Mediterranean system of subduction zones in the south. Each of these plate margins was located more than 1000 km away from the site of deformation. This tectonic event represents an outstanding example of large-scale intraplate shortening and may serve as a template for comparison with active intraplate deformation. Its effects are seen in a ca. 500 km wide strip that stretches in NW-SE-direction along the Tornquist Line, a regional fault zone separating thick lithosphere of the Baltic Shield from much thinner lithosphere to the southwest. Most faults and folds also trend NW-SE, but some large N-S-striking transfer zones are present. In the southeast, the shortening structures are truncated by the Neogene Carpathian thrust front. In the west, they fan out into more northerly trends in the Central North Sea and more easterly trends in the Channel area before dying out on the shelf. Late Cretaceous (ca. 90-70 Ma) shortening dominates from Poland to the North Sea, while the main shortening event in Southern Britain is of Paleogene age. Many Late Cretaceous to Paleogene structures have been conditioned by Permian or Triassic through Early Cretaceous extensional faulting. The structural styles range from typical inversion structures where grabens were uplifted along their reactivated normal faults to grabens which have been overthrust, folded and faulted but not uplifted. A few large basement uplifts and reverse faults have no demonstrable inheritance from earlier extension. The thick, mobile Zechstein salt has modified extensional and contractional structures, but both extend beyond its depositional borders. Even where thick evaporates underlie the Mesozoic sedimentary cover, the basement is typically involved in the deformation, except for localized thin-skinned imbricate thrusting or salt-cored anticlines. Different structural styles do not appear to control the magnitude of shortening which is similar for transects across the inverted Lower Saxony Basin and areas with predominant basement thrusting. Bulk contraction of the entire deformed belt is unlikely to exceed a few tens of kilometers, corresponding to $<<10\%$ of horizontal shortening. Fold orientations, fault slip data and stylolite teeth indicate rather uniform kinematics, i.e. predominantly SSW-NNE-directed thrusting and folding. This shortening direction is consistent with the convergence direction of Africa, Iberia and Eurasia that was established between ca. 120 Ma and 85 Ma due to a reorganization of global plate motions. The European pulse of intraplate deformation coincides with tectonic events as distant and diverse as early Andean shortening and uplift of passive margins around the South Atlantic.
Archaeometallurgical studies of Athenian owls

Oliver Baehre¹, Gerald Eisenblaetter¹, Gert Kloess¹

¹ Leipzig University, Faculty of Chemistry and Mineralogy, Institute of Mineralogy, Crystallography and Materials Science, Scharnhorststr. 20, 04275 Leipzig. o.baehre@studserv.uni-leipzig.de

Five tetradrachms, two drachms and two hemidrachms dating to the fifth century BC are part of the archaeometallurgical study. The ancient silver coins are stored at the Bibliotheca Albertina in Leipzig.

In comparison with known data from prior archaeometallurgical studies the origin should be investigated. The chemical composition of the used alloy should state whether the coins are made of silver from the Laurion mines in Attica or not.

XRF analysis and density measurements indicate a typical lead content as estimated for authentic Athenian issues. In contrast very low or missing contents of copper, gold or bismuth are detected. As stated by Gale (1980) there should be a gold content below 0.05 mass-% for typical Laurion silver. Further investigations, especially with X-Ray computed tomography, are planned to discuss the variation of the gained density data.

Figure 1: Lead vs. silver content of ancient silver coins (a) and density data (b)

Many thanks to Professor Dr. Ulrich Johannes Schneider and Dr. Christoph Mackert from Leipzig University Library and to Professor Dr. Reinhard Denecke and André Eilert for XRF support.

References:


We identified three Holocene paleo-tsunami event layers in atoll lagoonal deposits of the Maldives. Holocene coastal sediments have been studied as archives for past tsunami events by several authors. Comparable sedimentological studies of mid ocean atoll lagoons are rare.

We have been investigating Holocene sediments of a circular atoll lagoon, located in the center of the Maldives archipelago, as archive for sedimentological events. The small (40 km$^2$), enclosed lagoon of Rasdhoo Atoll is appropriate for the study of Holocene tsunamis, because several meters of carbonate mud have accumulated during the past ca. 10 kyrs in which coarser-grained event beds potentially stand out. In the region close to the equator cyclones can largely be ruled out as trigger of event sedimentation, but earthquakes generating tsunamis are common off the Indonesian coast.

Sedimentological data like grain-size distribution, skeletal sediment composition, and age data were used to identify potential paleo-tsunami events. Forty-two cores were drilled with a Rossfelder electrical vibracorer. Seventeen cores, located along the margin and in the center of the lagoon, were chosen for detailed sedimentological analyses. All cores consist of carbonate sediment that was dated radiometrically with accelerated mass spectroscopy (AMS); one core recovered soil and peat at the base defining the beginning of Holocene inundation. In ten cores, we found coarser layers mostly with redeposited corals like Acropora and Seriatopora; Fungia is less common. These corals derive from the marginal reef and have been transported into the lagoon. Other corals like Porites and Leptoseris, as well as Acanthastrea characteristically live in lagoonal waters, and we assume that they have not been transported. Coarser layers classified as coarse-grained wackestone, floatstone, or rudstone consisting of reef faunal components like coralline red algae, reef foraminifera (e.g., Amphistegina spp., Calcarina sp.), and redeposited corals, which may also be correlated among several cores, were interpreted as tsunami-event layers. Based on these premises, three event layers around 1.3 kyrs BP, 3.0 kyrs BP, and 4.0 kyrs BP qualify as paleo-tsunami events.

Confirming our results, the tsunami-event at 1.3 kyrs BP was also identified during other studies at the western coast of Thailand, northern Sumatra, eastern India, and southern Sri Lanka.
Effect of $fO_2$ on the coordination and oxidation state of iron in silicate glasses

Enter the authors here.

1. Jaayke Knipping jaayke.knipping@web.de
2. Harald Behrens h.behrens@mineralogie.uni-hannover.de
3. Paola Stabile paola.stabile@unicam.it
4. Gabriele Giuli gabriele.giuli@unicam.it
5. Adrian Fiege a.fiege@mineralogie.uni-hannover.de

In this study the effect of oxygen fugacity $fO_2$ on speciation and coordination of Fe in two different alkali-trislicates ($K_2Si_3O_8$; $Na_2Si_3O_8$) was investigated. The starting materials were synthesized by mixing $K_2CO_3$ and $Na_2CO_3$, respectively, in a 1:3 ratio with $SiO_2$ and adding ca. 5 wt% $Fe_2O_3$. This mixture was molten two times at 1500 °C to achieve homogeneity within the starting material. After relaxing the glasses, they were cut in rectangular chips (1x1 cm) to fit into sample holders. The sample holders were either Re-boats for experiments at very reducing conditions ($fO_2< QFM-1; QFM=quartz-fayalite-magnetite-buffer$) or Au/Pd-boats at more oxidizing conditions ($fO_2>QFM-1$), as both metals have very low solubility of iron at the respective conditions. Most of the experiments were conducted at ambient pressure in a gasmixing furnace. The $fO_2$ conditions of the experiments ranged from air atmosphere ($log fO_2/bar): -0.67$) to $H_2/Ar$ atmosphere ($log fO_2/bar): -13.80$). Intermediate conditions were achieved by using either Ar gas or $Ar/H_2/H_2O$ mixtures. In the latter case, the $H_2O$ partial pressure was adjusted by passing the $Ar/H_2$ stream through a thermostat-controlled water reservoir. By observing the EMF values in the furnace, using a lambda-probe, it was possible to control $fO_2$ during the experiment. The compositions of the experimental glasses were checked by electron microprobe. Glasses produced at more oxidizing conditions (especially the $K$-bearing samples) are very hygroscopic and developed already secondary minerals at the surface even if the thin section was always stored in an exsiccator and no reliable microprobe data could be obtained. Cross-contamination between the sodium- and the potassium bearing glasses were observed in particular under reducing conditions. Due to higher alkali vapor pressures at reducing conditions the alkalis became partly volatile and were able to interact with the counterpart melt. Consequently, the Na/K ratio rises in the K-Fe-Si-O glass from 0.01 in the starting material up to 0.22 at the most reducing condition ($Ar/H_2$ atmosphere), while K/Na increases in the Na-Fe-Si-O glass even from 0.01 up to a value of 0.50. The density of each experimental product was measured using the buoyancy method with ethanol as immersing liquid. The glasses ran at more oxidizing conditions show higher densities (e.g. 2.51 g/cm$^3$ for the Na-Fe-Si-O glass in air atmosphere), when compared with its counterparts ran at more reducing conditions (2.45 g/cm$^3$ in Ar/H$2$ atmosphere). The iron speciation ratio of each sample was checked by a colorimetric wet chemistry method, which indicates a continuous increase in $Fe^{2+}/Fe_{total}$ towards more reduced conditions ($Fe^{2+}/Fe_{total}$: 0.07 in air and 0.87 in Ar/H$2$ atmosphere). Further investigation on the structure of the glasses will be done by several spectroscopic methods like IR, UV-Vis, Raman, Mössbauer and XANES (X-ray absorption near edge structure) spectroscopy.
Fracturing, Healing and High Fluid Pressures in Rocks

Daniel Koehn¹, Anna Vass¹, Irfan Ghani²

¹School of Geographical and Earth Sciences, University of Glasgow, UK, daniel.koehn@glasgow.ac.uk
²Tectonophysics, University of Mainz, Germany

Fracturing of rocks due to tectonic stresses or high fluid pressures and the formation of fluid pathways is important for a whole range of industrially relevant processes in the Earth’s upper crust reaching from groundwater transport, hydrocarbon migration to geothermal systems. Fracturing and the opening of fluid pathways become especially important in tight rocks where fluid migration through the rock matrix is restricted. In addition, observations show that fractures are often sealed and occur as veins in geological systems. Depending on the boundary conditions, geological systems can go through a whole range of processes that change their permeability and also the dynamic behavior of flow. Fluid flow through tight rocks leads to high fluid pressure gradients and fracturing, opening of permeability to pressure drops and precipitation so that systems seal again. In order to understand these phenomena and the behavior of a fracturing and resealing reservoir, we developed a numerical model where material fractures and reseals as a function of tectonic stresses and fluid pressure gradients and compare the results with observations of natural systems. The numerical model shows that a rise in fluid pressure in tight rocks will lead to a rise in fluid pressure gradients until the system fractures enough to account for fluid migration. Once sealing of fractures is added to the system, the behavior becomes more complex. Sealing in general will lead to the buildup of new fluid pressure gradients if the fluid pressure source remains to feed the system. Thus, the system will start to re-fracture depending on how fast sealing is occurring. The location of new fractures in the healed system and also the general style of fracturing depend on the strength of the healed material relative to the matrix. Weak veins will be the preferred sites for new fractures whereas strong veins will most probably not re-fracture. This will lead to two effects, first of all, healing will be much more dispersed in a system where veins are strong whereas healing will stay localized in a system with weak veins. Second of all, the system with strong veins will become stronger as a whole, that is the rock itself will become stronger on average and the new fractures will be more localized. In the extreme case, the strengthening rock will remain with one large-scale fracture or fault that drains the system. We will discuss the implications of the findings in terms of dynamics and applications for hydrocarbon systems and mineral deposits.
Layered gabbro recovered by IODP from fast-spreading lower oceanic crust at Hess Deep, East Pacific Rise

J. Koepke ¹, K. Mengel ² and the Expedition 345 Scientists

¹Leibniz Universität Hannover, koepke@mineralogie.uni-hannover.de
²Technische Universität Clausthal, kurt.mengel@tu-clausthal.de
koepke@mineralogie.uni-hannover.de

IODP (Integrated Ocean Drilling Program) Expedition 345, Hess Deep, started at the 12.12.2012 in Puntarenas (Costa Rica) and ended at 12.02.2013 in Balboa (Panama). The principal objective for drilling at the Hess Deep Rift located in the equatorial Pacific was, to test competing hypotheses of magmatic accretion and hydrothermal processes in the lower ocean crust formed at the fast-spreading East Pacific Rise (EPR). These hypotheses make predictions that can only be tested by drilling, i.e., the presence or absence of systematic variations with depth in mineral and bulk rock compositions, presence or absence of modally layered gabbro, and the extent and nature of hydrothermal alteration and deformation.

The Hess Deep Rift is a complex region that was formed by extension as a consequence of the westward propagating Cocos-Nazca spreading center. The surface expression of rifting is first evident ~30 km from the EPR, where two 5 km wide, east-west grabens expose ~0.5 Ma crust.

The drilling was carried out in ~4850 m water depth under quite challenging borehole conditions. We recovered primitive (Mg# 73-89) plutonic lithologies including gabbro, olivine gabbro, troctolite, and orthopyroxene-bearing gabbroic rocks. The recovered rocks exhibit cumulate textures similar to those found in layered mafic intrusions and some ophiolite complexes. Details of their mineralogical and petrologic evolution, however, are novel on the ocean floor. Additionally, they were deformed primarily in a partly molten regime expressed by the abundance of magmatic foliation. After that, nor or only minor subsolidus crystal plastic deformation took place. Typical Late-stage magmatic features, like abundant crystallization of a late, evolved melt producing interstitial mineral assemblages composed of amphibole, oxides, ± apatite ± zircon, which are well-known from typical in gabbroic rocks from slow-spreading ridges (e.g. from ODP drillings at the KANE area at the Mid-Atlantic Ridge or at Atlantis bank at the Southwest Indian Ridge) were not observed.

Metamorphism at amphibolite facies is evident in tremolite-chlorite replacements of olivine + plagioclase, but at low concentrations. Metamorphism is dominated by background sub-greenschist facies alteration to prehnite + chlorite assemblages associated with cataclastic deformation, likely the result of Cocos-Nazca rifting. Penetrative amphibolite facies assemblages indicative of pervasive and intense high-temperature hydrothermal alteration of the lower crust were not observed.
Synthesis and application of trace element sulfide standard material for laser ablation inductively coupled plasma mass spectrometry

Martin Koppelberg (1), Hassan Helmy (2), Chris Ballhaus (3), Sven Sinden (4), Franz Michael Meyer (5)

1koppelberg@iml.rwth-aachen.de
2 hmhelmy@yahoo.com
3 ballhaus@uni-bonn.de
4 sindern@iml.rwth-aachen.de
5 m.meyer@rwth-aachen.de

Measuring the distribution of trace elements in sulfides is important for understanding origin and genesis of ore deposits worldwide. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is an efficient multi-element micro analytical technique to measure a wide concentration range from major to trace levels in minerals. However, for accurate results the LA-ICP-MS requires appropriate standard material. Except from a few local enrichments most sulfide trace elements are low in concentration, which also vary greatly depending on the mineralogy of the parent rock. Therefore, the use of a suitable standard is the key for all analysis with LA-ICP-MS.

Important for the choice of an appropriate standard is a great match of element composition and concentration between the sample and standard. The sample and standard matrix should have the same physical properties. The greater the conformity of the standard-matrix, the less is the difference in sensitivity. The difference in sensitivity describes the counting rate in the MS per concentration unit in the sample or standard (Heinrich et al. 2003). Isobaric interferences can occur during measurements in sulfides, which are different from interferences in conventional standards with an oxide matrix like, for example, NIST standards (Danyushevsky et al., 2011).

In this study we prepared a standard material for trace elements with an iron sulfide matrix. The method is based on the synthesis of sulfide standards for LA-ICP-MS for determination of platinum group elements (Wohlgemuth Ueberwasser et al. 2007). In a first step, we prepared two standards with five elements, to avoid interferences and formation of unwanted mineral phases. Added Elements were Cu, In, Te, Ge, Tl in the first and Ni, Pb, Cd, As, Sb in the second standard, each with a content of 100ppm. Evaluation of homogeneity was carried out by EMPA for major elements and by LA-ICP-MS for the trace elements.

The poster presentation will illustrate the preparation steps, evaluation and applications for analyzing trace elements in sulfides of the new iron sulfide LA-ICP-MS standard material.


Critical evaluation of garnet discrimination diagrams using mineral chemical data of garnets derived from various host rocks

Krippner, A. ¹, Meinhold, G. ¹, Morton, A.C. ²,³, von Eynatten, H. ¹

¹ Geowissenschaftliches Zentrum der Universität Göttingen, Abteilung Sedimentologie/ Umweltgeologie, Goldschmidtstraße 3, 37077 Göttingen (Email: anne.krippner@geo.uni-goettingen.de)

² CASP, University of Cambridge, West Building, 181a Huntingdon Road, Cambridge, CB3 0DH, United Kingdom

³ HM Research Associates, 2 Clive Road, Balsall Common, West Midlands CV7 7DW, United Kingdom

For more than 25 years, the mineral chemistry of heavy minerals has been widely used to identify and characterize sediment source areas. Especially the heavy mineral garnet has important implications for the identification of potential lithologies exposed in the source area and their evolution through time. It is a particular useful mineral in provenance research because of its high importance in defining metamorphic conditions. Garnet chemical composition depends on protolith bulk composition and pressure and temperature history.

Certain garnet compositions can be related to specific source rocks with high probability. Based on these findings, several garnet discrimination diagrams have been developed and applied to detrital garnet. In these binary and ternary diagrams, discrimination fields are drawn as strict boundaries by solid lines and some of them show distinct overlap. For this work, a large dataset was compiled for the geochemistry of garnet derived from various host lithologies, such as mantle rocks, metasedimentary rocks, and igneous rocks, in order to test the applicability of the various discrimination schemes.

The present study underlines the potential for source rock discrimination based on garnet chemistry, but existing discrimination diagrams are partly imprecise and should be improved. Different parageneses may contain similar garnets. Many garnets plot outside of their suggested discrimination fields. A multivariate statistical analysis of their reliability is still missing. It seems more appropriate to use confidence intervals and probability density distributions instead of intuitive discrimination fields with strict boundaries.
Hydrochemistry and biofilm calcification of the tufa-forming karstwater stream "Kuharsch", a "Steinerne Rinne" near Krautheim, Baden-Württemberg

Kugel, M.¹, Reimer, A.² & Arp, G.³

Universität Göttingen, Geowissenschaftliches Zentrum, Goldschmidtstr. 3, 37077 Göttingen

¹martin.kugel@gmx.net
²areimer@gwdg.de
³garp@gwdg.de

The "Krautheimer Kuharsch" is one of several enigmatic self-built tufa canals in southern Germany. Contrary to common tufa-forming streams with dams and cascades, calcification of biofilms and mosses in these streams leads to vertically accreted canal-like tufa build-ups up to 100 m length and 5 m height (Voigtländer 1966, Baier 2002). While most of the tufa canals are linked to karstic waters of the Upper Jurassic limestone plateau of the Franconian-Swabian Alb, the Krautheimer Kuharsch is the only known tufa canal in the crop-out of the Middle Triassic Muschelkalk Group. In general, moss tufa formation results from CO₂ degassing, while cyanobacterial tufa stromatolites reflect photosynthesis-induced biofilm calcification (Arp et al. 2010). The aim of the study is to find out similarities and differences in hydrochemistry and biofilm calcification in comparison to other tufa canals and tufa-forming streams. It is hypothesized that one crucial factor in the formation of self-built tufa canals is an exceptional low concentration of precipitation inhibiting ions and a correspondingly extraordinary high rate in precipitation.


Analysis of the environmental changes from the Upper Triassic to the Lower Jurassic (T/J Boundary Event) in the NE Paris Basin

Natascha Kuhlmann\(^1\)*, Jean Thein\(^1\), Jens Fiebig\(^2\), Thorsten Nagel\(^1\)

nkulmann@uni-bonn.de
jthein@uni-bonn.de
Jens.Fiebig@em.uni-frankfurt.de
tnagel@uni-bonn.de

The Triassic/Jurassic boundary is characterized by one of the “BIG FIVE”, global mass extinctions. The discussion about the causes for this event is still in progress. Two main possibilities are actually taken into consideration: on the one hand large flood basalt eruptions in the Central Atlantic (Central Atlantic Magma Province: CAMP) related CO\(_2\)-emissions and dramatic eustatic sealevel-changes, on the other cosmic impacts and their consequences. The main focus of this research work lies on the sediments of the transition zone between Rhaetium (Upper Triassic) to Hettangium (Lowest Jurassic) in the NE Paris Basin. It investigates the regional paleoenvironmental and paleoecological conditions and their rapid changes in the continent and the shallow marine environment in Lorraine, Luxembourg and Germany during the Triassic/Jurassic transition period especially the events at the boundary. The location of the Trier/Luxemburg Embayment has not yet been analyzed in detail in respect to this mass extinction until now.

The embayment is a north-eastern narrow gulf like structure in the southern prolongation of the so called Eifel North-South Depression which periodically linked the Paris Basin to the Paleo-North Sea Basin during Mesozoic and Cenozoic time. Different drill cores over all the area provide excellent data for analyzing the Triassic/Jurassic transition series in Luxemburg, France and Germany. They were described according to geological and sedimentological aspects and were sampled in close intervals. These drill cores have been analyzed with combined geochemical, mineralogical and sedimentological methods. The most complete drill core (Boust/ northern Lorraine) is presented here. It shows a complete sediment sequence from the lower Hettangium to the upper Norium.

The stratigraphical pattern of the geochemical major elements as well as of the trace elements show a sharp cut at the Triassic/Jurassic boundary and between Rhaetium and Norium. They allow a clear stratigraphic subdivision. The geochemical trends on the one hand reflect the mineralogical composition of the sediments. Trace elements and their ratios as well as important proxies on the other hand allow the reconstruction of the paleoenvironment situation (salinity, redox-milieu) of the sedimentation area.

The \(\delta^{13}\)C\(_{org}\) profile shows a prominent negative excursion at the T/J boundary and allows comparing the Boust-section to other localities in Europe and over the world. The worldwide isotope anomaly observed makes probable a global cause for the catastrophic changes at the T/J boundary.

Thin possible tuff-like layers have been observed in the section Junglinster (Luxemburg). Electron-microprobe analyses detected several platinum-group element nuggets, which are presumed to be of cosmic source or of terrestrial origin (eruption of mantle material).

Most of the data presented here are result of the PhD thesis of the first author, which is supported by FNR (Fonds National de la Recherche Luxembourg)

\(^1\)Steinmann-Institute for Geology, Mineralogy and Paleotology, Rheinische Friedrich-Wilhelms-University Bonn, Nussallee 8, D-53115 Bonn, Germany *email: nkulmann@uni-bonn.de

\(^2\)Institute of Geosciences, Goethe University Frankfurt, Altenhöferallee 1, D-60438 Frankfurt am Main, German
Integrated fracture and fluid dynamics models of carbonates encased in salt

Peter A. Kukla, Janos L. Urai, Lars Reuning, Frank Strozyk, Stephan Becker

Energy and Mineral Resources Group, RWTH Aachen University, D-52056 Aachen, Germany
Email: peter.kukla@emr.rwth-aachen.de

In the literature, salt structures and their evaporite rheologies are represented in two strikingly different ways. Studies with the focus on hydrocarbon exploration and production use 3D seismic and well data concentrating on the sub-or suprasalt sediments hence treating the evaporites as homogeneous bodies. In contrast, studies of the internal structure of salt show the extremely complex internal geometry with much less attention to the structure of the surrounding sediments. Most current numerical and analogue models of salt tectonics also tend to assume relatively homogeneous rheological models, and consequently produce relatively simple internal structures.

Giant evaporite basins such as the South Oman Salt Basin and the Permian (Zechstein) Salt Basin in Europe frequently display a complex geodynamic evolution characterized by several phases of halokinesis and associated sedimentation. Many such evaporite deposits contain brittle-ductile claystone, carbonate and/or anhydrite layers enclosed in salt. The carbonates underwent a complex diagenetic evolution from the shallow to the deep burial realm. Differential loading of clastics onto the mobile rock salt caused the growth of salt diapirs which resulted in strong fragmentation and faulting of the carbonate intervals into isolated ‘stringers’. These carbonate ‘stringers’ represent in Oman a unique intra-salt, predominantly self-charging, petroleum system, which has been successfully explored in recent years. In the European Zechstein basin, “dolomite rafts” are equally well known and pose frequent operational challenges. In both cases little is known about their fluid evolution and deformation history.

Studies based on 3D seismic, combined with well data and core analysis of the diagenetic evolution, show highly complex structures caused by both brittle and ductile deformation, which is in good agreement with observations in salt mines and analogue models. Results from finite element and discrete element models however help to constrain the effect of salt tectonics on fracture formation and the fluid evolution within the stringers through time. Successful salt basin evaluation therefore combines seismic, structural and sedimentary studies with the analysis of rheological properties and geomechanic and numerical modelling.
Anthropogenic Rare Earth Elements as Environmental Tracers for Wastewater-derived Substances in Drinking Water

Serkan Kulaksız1, Michael Bau2

1s.kulaksiz@jacobs-university.de
2m.bau@jacobs-university.de

Rare earth elements (REE) are a group of coherent elements that are useful as tracers in geochemical studies. Their similar ionic radii and trivalent state ensures normalized REE concentrations plot smoothly on semi-logarithmic plots. These smooth plots are observed in data from pristine aqueous environments. However, samples from contaminated environments exhibit unusual REE plots with individual REE concentrations up to several orders of magnitude higher than neighboring REE (background levels). Since the first study documenting the presence of anthropogenic gadolinium (Gd) in rivers in Berlin (Bau and Dulski, 1996), numerous studies have reported the presence of anthropogenic Gd worldwide in areas with high population density and advanced health-care systems. Anthropogenic Gd originates from the application of Gd-based contrast agents (Gd-CA) in magnetic resonance imaging (MRI). Patients are administered Gd-CA intravenously and excreted via the kidneys. These contrast agents are highly stable Gd chelates, which cannot be removed in wastewater treatment plants (WWTP), but are transported into surface waters with the clearwater effluent from WWTPs. The growing body of literature on Gd-CA reveals the sources, transport and pathways of Gd-CA in aqueous environments between WWTP, surface water, groundwater and tap water. These findings have been bolstered by recent studies showing anthropogenic Gd in tap water (e.g. Kulaksız and Bau, 2011) and even in samples from the southern North Sea, introduced via rivers that receive WWTP effluent (Kulaksız and Bau, 2007).

Data from tap water in western districts of Berlin carry significant anthropogenic Gd anomalies while those from the eastern districts do not. This discrepancy is caused by (artificial) bank infiltration employed in the western districts of Berlin, but also employed in other parts of the world, such as cities located along the Rhine River. The Rhine River is known to carry a Gd anomaly since 1996. With the addition of recently discovered anthropogenic La and anthropogenic Sm in the Rhine River, the role of anthropogenic REE as tracers should be highlighted, especially in relation to the drinking water quality of cities along the river. While the absolute concentrations of these elements are too low (both in surface waters and tap water) to be a health threat, their presence in tap (drinking) water causes concern for consumers as it indicates the presence of wastewater-derived substances. Hence, the presence of truly dissolved Gd-CA in drinking water can be used as a tracer for other compounds with similar behavior, that also originate from WWTP effluents (e.g. pharmaceuticals, endocrine-disruptors, etc.).

Drinking water will likely be in high demand as a commodity in the future, and bank infiltration and groundwater recharge is expected to gain importance in the management of freshwater resources. The use of anthropogenic REE as tracers in determining water quality in the form of a primary screening should be exploited.
The oxidation of the ocean-atmosphere system represents one of the most profound environmental changes in Earth’s history. It is generally accepted that atmospheric oxygen levels significantly rose during the Great Oxidation Event (GOE) between 2.4 and 2.3 Ga. However, the evolution of the atmospheric redox-state immediately before the GOE still remains heavily debated. Some redox-sensitive elements like Mo indicate an increasing redox-potential some 100 Ma before the GOE. Mo-isotopes represent a well suited proxy for redox reconstructions as fractionations are strongly dependent on the environmental redox-state. For example, in oxygenated water columns Mo is extremely soluble in its highest oxidation state as molybdate (MoO$_4$) building up an oceanic Mo reservoir. Adsorption of this molydate onto Fe- and Mn-oxyhydroxides is slow and causes large Mo-isotope fractionations with the lighter isotopes preferentially being incorporated in the hydroxide phase. By contrast, in a continuously anoxic environment such as the early Archean oceans Mo remains in its reduced form so that the original Mo-isotopic composition of crustal material remains unchanged. Thus, first variations in the Mo-isotopic composition in Archean sediments might indicate first changes in the environmental redox-state.

We present Mo-isotopes from 2.63 to 2.45 Ga black shales and iron formations of the Pilbara craton, Australia, which immediately precede the GOE. Mo-isotope signals in shales as well as in iron formations display a continuous increase in $\delta^{98}$Mo. This trend points to mobilization of molybdenum as MoO$_4$ and increasing redox-potentials already before the GOE. Moreover, a similar increase was observed in contemporaneous black shales and carbonates from the Kapvaal craton, South Africa. The contemporaneous increase in $\delta^{98}$Mo on two different cratons and in different sedimentary settings along with a continuous increase in $\delta^{98}$Mo without any scatter indicates the build-up of a sizeable and uniform seawater Mo-reservoir long before the GOE.
Using apatite to probe halogens during fluid-rock interaction

Christof Kusebauch¹, Timm John¹, Martin Whitehouse², Ane Engvik³

¹ Institute for Mineralogy, Uni Muenster, Germany; c.kusebauch@uni-muenster.de
² Swedish Museum of Natural History, Stockholm, Sweden
³ Norwegian Geological Survey, Trondheim, Norway

Apatite is a typical accessory mineral in many geological settings and is stable over a wide range of pressure and temperature. Natural apatite usually occurs as a solid solution of three end members, i.e. fluor-, hydroxy- and chlorapatite and therefore reflects the F-Cl-OH activity conditions of its formation. Apatite crystallized during fluid-rock interaction can be used as a fluid probe for halogens as it reflects not only F and Cl, but Br and I concentration in the fluid. Also apatite is rather sensitive to changes in fluid composition, undergoing dissolution-precipitation reactions leading to formation of an apatite with a changed composition. This facilitates constraints on the number of fluid events and the characteristics of their potential sources.

Here, we present a combined experimental and field related study to investigate the relationship between halogen chemistry of fluids and apatite during fluid-mineral interaction. Experiments were conducted in a cold seal pressure vessel apparatus at 0.2 GPa, different temperatures (400-700°C) and varying halogen (F, Cl, Br, I) concentrations of the experimental fluid. Synthetic Cl-Apatite was used as starting material. Due to interaction with hydrothermal fluid, this Cl-Apatite is replaced to OH- or F-rich apatite with changed halogen concentrations. Natural apatite from an alteration sequence from a regional-scale metasomatic event (Bamble Sector, SE Norway) formed at the same pressure and temperature condition as used in experiments shows the same replacement process (Cl-apatite to OH- / F-Apatite). Therefore, experimentally derived partition data can be used to back calculate fluid composition at the different alteration stages from coexisting apatite.

Halogens in apatite, measured in-situ by ion microprobe, show marked diversity for both settings (experiment and nature). Experiments show that Br and I are strongly incompatible in apatite and occur with highest concentrations in the starting apatite. During replacement Br and I are lost to the fluid and newly formed apatite has lower concentrations compared to starting apatite. In contrast, F is known to be highly compatible in apatite and our experiments show that F is completely consumed from the fluid and incorporated into replacing apatite.

Natural apatite from Bamble undergoing similar replacement processes show the same halogen trends as found in experiments. Whereas Br concentrations are highest in pristine apatite (100-500 ppm), found in the least altered rock, and lowest in highly replaced samples (10-20 ppm), F shows the opposite behavior, low values (40-100 ppm) in pristine apatite and high concentrations (2000-12000 ppm) in highly replaced samples. The observed halogen concentrations can be explained by interaction of apatite with an evolving metasomatic fluid, which is losing F (to newly formed apatites) and gaining Br (from precursor apatite) during ongoing alteration.
Partial melting and UHP metamorphic rocks exhumation:
from field evidence to multi-scale numerical modelling

Labrousse L. (1,2), Ganzhorn A.C. (1,2,3,4,5), Duretz T. (6), Prouteau G. (3,4,5), Arbaret L. (3,4,5), Gerya T. (7), Bons P.D. (8)

1 UPMC Univ Paris 06, UMR 7193, ISTeP, F-75005 PARIS.
2 CNRS, UMR 7193, ISTeP, F-75005, PARIS.
3 Université d’Orléans, UMR 7327, ISTO, F-45071 ORLEANS.
4 CNRS/INSU, UMR 7327, ISTO, F-45071 ORLEANS.
5 BRGM, ISTO, UMR 7327, F-45071 ORLEANS.
6 Minéralogie et géochimie, UNIL, S-1015, LAUSANNE.
7 Geophysical Fluid Dynamics, ETH-Z ZS-8006 ZÜRICH,
8 Department of Geosciences, Eberhard Karls University Tübingen, Germany

Partial melting reactions constitute a first order weakening process in the continental crust involved in collision zones. It can act as a possible decoupling mechanism within the lithosphere and therefore influence the dynamics of continental subduction-collision. The Western Gneiss Region, Norwegian Caledonides, exhibits a close relationship between eclogites occurrences and partial melting textures in the surrounding gneiss. This fact implies that partial melting is associated with part of the exhumation of High Pressure (HP) rocks.

Several metamorphic reactions produce silicate melts at different PT conditions, depending mainly on the availability of aqueous fluids. Even if most of the partial melting textures observed in hot orogens relate to water-absent dehydration melting, evidences of water-present partial melting of gneiss and eclogites at HP in the Western Gneiss Region suggest that water-present melting reactions may play a role in fostering HP metamorphic rocks exhumation. Another question arising from experimental rheological studies relies in quantifying the amount of liquid phase necessary to trigger strength drops of migmatites (i.e. the Rheologically Critical Melt Percentage, RCMP). Proposed values span from very low percentages close to 1% up to 20-30%, when migmatites turn to diatexites.

Combined efforts in numerical modelling from grain scale to lithospheric scale processes have been performed in this study to assess the consequences of partial melting reactions and chiefly their weakening effect.

A series of two-dimensional simple shear numerical experiments on two phase linear viscous material was performed at the crystaline aggregate scale. Melt proportion, wetting angle of melt and grain boundary migration velocity were systematically varied to test the effect of those parameters on the bulk flow behaviour of simplified migmatite. Weakening effect and textures highly depend on wetting angle when grain boundary migration is active. Strain partitioning between solid phase and melt also varies.

We also designed lithospheric scale numerical experiments to compare the effects of water-present or dehydration partial melting reactions on continental collision systems. The two-dimensional thermo-mechanical experiments explore the extent of melt-weakening by allowing a wide range viscosity variations (9 orders of magnitude). The model set-up is representative of the Scandian collision and its sensitivity to the initial Moho temperature, the value of RCMP, and the buoyancy of the extracted melts, was investigated.
Verification of the Persian Gulf Sea level changes in Holocene through sedimentary core obtained from sea floor of Bandar-Abbas neighboring areas

Razyeh Lak
Geological Survey of Iran

E-mail address: Lak_ir@yahoo.com or r_lak@gsi.ir

Abstract

The Persian Gulf is a sedimentary epicontinental and marginal basin located in a dry climate. The climate, morphology, hydrology, current, waves and tide specifications determine its sediments’ types. To study the paleoceanography of the Persian Gulf, a core having the length of 10m from shallow water close to the coastal areas of Bandar-Abbas in form of an undisturbed sample was prepared. After cutting the sample, macroscopic verifications, photography, and description of cores, 65 subsamples were prepared and granulometry and ICP analyses implemented. Meanwhile, 9 samples from facies variation locations were selected for dating purposes. Then, these samples were washed and foraminifers separated by C\textsuperscript{14} AMS instrument. After that, the ages of foraminifers were clarified, and results were calibrated. These results indicated that elements having clastic source, such as silicon, iron and magnesium exhibit different variations from calcium with biologic and intra-basinal source. Sedimentary environment verifications indicate calcium increment values in marine and lagoonal environment, but clastic sediments increase in intertidal, riverine and coastal regions. Therefore, when seawater level is high, the calcium value increases, but silicon, iron and aluminum decrease. In the conditions of seawater low level, the situation is vice versa. Meanwhile, two important stages of transgression occurred between 9300 to 7900 and 6800 to 3700 years ago. Dating results indicate that the average rate of sedimentation has been 0.96 mm per year (0.96m/ka) in the studied region.

Keywords: Holocene, Sea level change, Persian Gulf, Cores,
Reductive dechlorination of CCl₄ by Goethite-Fe(II) in the presence of organic matter

C. Laskov¹, L. Phuong, M. Gehring, S. Spahr, S.B. Haderlein

¹ Center for Applied Geosciences, University of Tübingen, Hölderlinstr. 12, 72074 Tübingen, Germany, christine.laskov@uni-tuebingen.de

Redox reactions at mineral surfaces play an important role in anoxic groundwater systems. Ferrous iron associated with iron minerals forms highly reactive surface coatings catalysing many redox reactions such as the reductive transformation or organic contaminants and governs the redox speciation of natural organic matter. Sorption of organic matter may interfere with the formation of reactive Fe(II) surface sites. Redox-active OM may although act as a mediator facilitating the electron-transfer across the mineral surface. Aim of this study was to investigate the effect of redox inert and redox active organic matter on reductive dechlorination of CCl₄ by Geothite-Fe(II) systems.

The presence of redox inert organic sorbates such as MOPS or HEPES resulted in a decrease (up to 3-fold) of CCl₄ transformation as well as in a 1.5-fold increase of aqueous ferrous iron. The decreased surface reactivity thus may be caused by competitive sorption of the organic sorbates, probably limiting the formation of highly reactive Fe(II) surface sites [1].

The addition of the redox active quinone AQDS resulted in a decrease (up to 2-fold) of CCl₄ transformation, despite the fact that AQDS does not sorb to the mineral surface. Yet, AQDS got reduced itself by the GT-Fe(II) mineral surface resulting in an oxidation of surface active ferrous iron. This concurrent oxidant effect was further investigated by addition of electrochemically pre-reduced AQDS_red. While with pre-reduced AQDS no retardation of the CCl₄ reduction was observed anymore, the yield of the main product chloroform remained much lower in comparison the a Goethite-Fe(II) system devoid of organic matter.

The presence of strongly sorbing humic acid (Aldrich-HA) had contrasting effects depending on the concentration. At low concentrations (1-10 mg DOC/L) no effect or even slight acceleration on the CCl₄ transformation rate has been observed, while at high concentrations (100 mgDOC/L) a strong inhibition (up to 5-fold) was determined. With increasing DOC also the yield of chloroform decreased. Determination of the redox status and speciation of humic acids in such ferrous iron mineral systems are currently under investigation.

This study shows that redox active organic matter affects both, the rates and mechanisms of electron transfer at iron minerals towards organic contaminants. The net effect of sorbed OM on reactions rates is highly concentration dependent, presumably due to varying contributions of complex formation, electron transfer or shielding. Yet, at typically grounditions (low DOM) no significant inhibition of contaminant degradation is expected.

2-dimensional ($\delta^{13}C/\delta^{37}Cl$) compound specific isotope analysis of chlorinated ethenes: a powerful tool to assess microbial reductive dechlorination

C. Laskov, K. Ebert, D. Buchner, S.B. Haderlein

Center for Applied Geosciences, University of Tübingen, Hölderlinstr. 12, 72074 Tübingen, Germany, christine.laskov@uni-tuebingen.de

Compound specific isotope analysis (CSIA) offers a versatile tool to track the fate of organic contaminants with regard to source allocation, assessment of natural attenuation as well as transformation pathways. For chlorinated ethenes the analysis $\delta^{37}Cl$-isotope signatures is - in addition to the commonly applied $\delta^{13}C$ analysis - of particular interest but has been previously hampered by analytical constraints. Sakaguchi-Söder et al. (2007) [1] introduced a straightforward online method to measure compound-specific $\delta^{37}Cl$ isotopes of chlorinated ethenes with a standard GC-qMS. This method was validated for trichloroethene (TCE) within the framework of an interlaboratory study [2], which also serves as a benchmark to obtain SMOC referenced $^{37}Cl$ signatures. Yet, only few chlorine isotope fractionation factors for microbial reductive dechlorination have been reported so far [3, 4]. Aim of this study was therefore to obtain SMOC referenced chlorine isotope fractionation factors during reductive dehalogenation of PCE and TCE by Desulfitobacteria as well as to investigate the influence of growth conditions.

Reductive dechlorination of PCE and TCE was determined over time in pure cultures of Desulfitobacterium hafniense strain Y51 and Desulfitobacterium sp. PCE-1. To assess the effect of growth conditions, Desulfitobacterium hafniense strain Y51 was pregrown without TCE. This non-adapted culture was then repeatedly spiked with TCE to assess the effect of enzymatic adaptation to TCE respiration on $\delta^{37}Cl/\delta^{13}C$ isotope fractionation. For the one-step transformation of PCE to TCE by Desulfitobacterium sp. PCE-1, a chlorine isotope enrichment factor of $\varepsilon_{Cl} \approx -7\%o$ for PCE was determined. For the one-step transformation of TCE to cisDCE by Desulfitobacterium hafniense strain Y51, the $\delta^{37}Cl/\delta^{13}C$ isotope fractionation depends on the adaptation to TCE respiration. The non-adapted culture (1$^{st}$ TCE spike) showed a higher carbon & chlorine isotope fractionation ($\varepsilon_{C} \approx -13\%o; \varepsilon_{Cl} \approx -4.5\%o)$ as obtained for the subsequent TCE adapted degradation series ($\varepsilon_{C} \approx -8.5\%o; \varepsilon_{Cl} \approx -3\%o$). Nevertheless, the obtained dual isotope plot indicated a rather constant ratio of $\varepsilon_{Cl}/\varepsilon_{C}$ of about 3. In contrast to fractionation factors, the dual isotope evaluation seems to be robust towards masking effects accompanying microbial degradation.

These first results show the potential of a dual $\delta^{37}Cl/\delta^{13}C$- isotope approach to further elucidate the transformation pathways of chlorinated ethenes and to improve the interpretation of in situ biodegradation in the field.

Importance of trishear deformation for mineral exploration in the southern Sudbury Basin, Canada

Iris Lenauer¹, Ulrich Riller²

¹iris.lenauer@gmail.com
²ulrich.riller@uni-hamburg.de

Understanding mechanisms of deformation that transformed the 1.85 Ga Sudbury Igneous Complex (SIC), the relic of a deformed impact melt sheet, into a fold basin, the Sudbury Basin, is paramount for Ni-, Cu- and PGE-mineral exploration. In the southern Sudbury Basin, greenschist-facies metamorphic tectonites make up the South Range Shear Zone, which accommodated northwest-directed reverse shearing and structural uplift of the southern SIC. This portion of SIC is characterized by large variations in the dip of inclined SIC-host rock contacts and foliation surface as well as layer thicknesses and observed strain gradients. By contrast, impact-induced quartz-dioritic dikes in host rocks, so-called Offset Dikes, appear to have experienced little rotation, evident by vertical ore-rich fingers within the Dikes, believed to have formed under the influence of gravity. These observations call for a deformation mechanism that can account for considerable variation in the rotational components of the southern SIC and its host rocks.

We present evidence that the orientation of layers and foliation surfaces in the southern SIC can be explained by trishear fault propagation folding. A key characteristic of trishear deformation is the transfer of localized displacement on a basal thrust fault to distributed deformation within a triangular zone, the trishear zone. Outside the trishear zone the hanging wall is translated without internal distortion. Trishear deformation of the southern SIC accounts for: angular discordances between the upper and basal contact of the SIC, local overturning of the southern SIC, steepening of planar mineral fabrics from northwest to southeast, thickness variations in the SIC layers, and the presence of the South Range Shear Zone as a zone of enhanced strain fabric intensity.

Although the SIC and its Paleoproterozoic host rocks deformed simultaneously after the impact event, a considerable strain gradient is observed between the lower and upper layers of the southern SIC. Evidently, layer thickness was affected by post-impact strain and thus, tectonic thinning. Rotation of lithological contacts is largely controlled by simple-shearing and bulk thinning. Layer rotation in the SIC is greatest within the zone of trishear deformation, causing overturned SIC-host rock contacts. Proterozoic rocks south of the SIC show lower intensity of post-impact deformation and smaller quantities of deformation than is apparent in the SIC. This can be explained by trishear deformation in which the Paleoproterozoic rocks chiefly form the hanging wall, which was translated without being affected by large strains. Depending on the location of mineral deposits relative to the South Range Shear Zone, rotation and strain vary significantly in mineral deposits. Accordingly, Offset Dike segments located at large distances to the SIC are expected to show little amounts of internal deformation and rotation. This has important consequences for assessing the geometry of sulfide-rich fingers in Offset Dikes.
The effects of impurities on CO₂ fluid properties and the consequences for storage capacity estimates and geophysical monitoring

Liebscher, A.

GFZ German Research Centre For Geosciences, Telegrafenberg, 14473 Potsdam
alieb@gfz-potsdam.de

Industrial captured CO₂ will certainly contain different types of impurities. While some of these impurities, e.g., SOₓ and NOₓ, are widely discussed due to their potential corrosive and reactive behavior, other impurities like Ar, H₂ and N₂ are often considered as less important due to their inert or at least less corrosive and reactive nature. However, typical CO₂ storage sites encounter P-T conditions between 30 to 100 °C/6 to 30 MPa. As the critical point of pure CO₂ is at 30 °C/7.4 MPa, even small amounts of impurities may significantly alter the physicochemical properties of the impure CO₂. This contribution presents calculations on the effects of different impurities on the physicochemical properties of impure CO₂ and addresses the consequences of these changes in physicochemical properties on storage capacity estimates as well as on seismic monitoring. Binary CO₂ mixtures with Ar, N₂, O₂, CO and H₂ as well as an assumed oxyfuel and pre-combustion flue gas have been analyzed. All calculations have been done with the GERG-2004 XT08 wide-range equation of state.

For all studied mixtures, even the addition of small amounts of impurities shift the critical conditions of the mixture to slightly lower temperature but notably higher pressure conditions when compared to the critical point of pure CO₂. For a given geothermal gradient and therefore given P-T conditions at a certain depth this results in notably lower densities of the mixtures compared to pure CO₂. Calculations performed for the assumed oxyfuel and pre-combustion flue gas and geothermal gradients of 25, 30 and 40 °C show that the decrease in density may amount up to about 20 to 70% in the depth interval ~ 700 to 1500 m. Capacity estimates that only refers to pure CO₂ for the volume-to-mass conversion therefore also over estimate storage capacity by up to 80% in the most worse case.

The density of the injected CO₂ is not only relevant for storage capacity estimates but also plays an important role for the interpretation of seismic data as p- and s-wave velocities are directly related to density. Calculations for homogeneous as well as patchy distribution and different CO₂ saturations indicate that the density effect on vₚ is only relevant for cold geothermal gradients and low CO₂ saturations. However, for these conditions calculated vₚ for the CO₂ mixture may be up to almost 10% lower than for pure CO₂. The use of seismic results for the estimation of CO₂ saturation may thus result in erroneously too high saturations when using data for pure CO₂ instead of CO₂ mixtures.
One of the most promising measures to mitigate CO₂ emissions to the atmosphere is carbon dioxide capture at large point sources, its transport to suitable storage sites and subsequent secure and permanent storage in deep geological formations. Although geological storage of natural gas is a widespread and well-developed technology, the potential chemical reactivity of CO₂ within the storage complex and its specific physicochemical properties make it difficult to directly transfer the knowledge gained from natural gas storage to CO₂ storage. Injection of CO₂ into deep geological formations will bring the storage systems out of reasonably well assumed thermodynamic and chemical equilibrium and may trigger complexly coupled geochemical reactions leading to dissolution of primary and precipitation of secondary minerals. The critical point of pure CO₂ is at 30 °C/7.4 MPa and therefore CO₂ storage sites, which typically encounter P-T conditions between 30 to 100 °C/6 to 30 MPa, are faced with potential two-phase CO₂ conditions and near-critical point phenomena like extreme density gradients with P and T.

The Ketzin pilot site near Potsdam is the only German CO₂ storage project. It is a pure research project with a maximum permitted total amount of injected CO₂ of 100,000 t. The injection of CO₂ started in June 2008 and is accompanied by a world-class operational and scientific interdisciplinary monitoring program. Besides the operational and scientific on-site work, the Ketzin project also involves a comprehensive experimental research program to study site-dependent but also site-independent inorganic, organic and microbiological processes related to CO₂ storage as well as the influence of CO₂ injection on petrophysical properties of the storage complex.

This contribution provides an overview of the work so far performed at the Ketzin pilot site. Time-lapse seismic and geoelectric monitoring mirrors the spatial and temporal extension and behavior of the CO₂ plume, operational P-T monitoring proves smooth and secure injection operation, extensive above-zone and surface monitoring prove lack of CO₂ leakage out of the reservoir, geological modeling with numerical simulations history match the operational observations, and spectacular camera inspections of observation wells show in-well two-phase fluid conditions with heat-pipe effects and stable inverted density profiles in the lower well parts.
Microstructure and microchemistry of Australian opals and associated minerals as indicators for nanocolloidal silica sphere formation

Moritz Liesegang¹ and Ralf Milke²

¹limo@zedat.fu-berlin.de
²milke@zedat.fu-berlin.de

Nanocolloidal amorphous silica (SiO₂ₙH₂O) is one of the most common weathering products and cementing agents on earth’s surface and subsurface. Surprisingly, there is little information about silica sphere formation in geomaterials, though this represents the fundament to understand silicification and subsequent diagenetic processes. Generations of researchers have been both fascinated and puzzled by the unique macro- to nanoscale properties of opals that created unique material science applications as photonic bandgap (PBG) crystals and new types of optical sensors.

In precious opal-A, close packed monodisperse spheres with a diameter of about 150-350 nm form a regular three-dimensional array that diffracts white light, giving the characteristic play-of-color, that is absent in common opal-A. So far, researchers attempted to link the visual appearance and trace element content to establish differences between opals of different geographic origin and color. Any systematic relation between chemical composition and silica sphere size, size distribution, and package ordering is ignored by these approaches, as well as information on solution composition to be gained from included and cogenetic minerals. We analyzed a wide range of unique samples from the Andamooka (South Australia) and Yowah (Queensland) precious opal fields at arid inland Australia. Inspired by often speculative and sometimes conflicting interpretations of opal-A genesis by the earth science and gemmological communities we performed a multi-method investigation using petrographic microscopy, XRPD, SEM, and EPMA to identify and characterize opaline silica, the mineral assemblage, and the host rock. We used a novel approach, combining opal micromorphology and microchemistry, to confine the geochemistry of the silica colloid system.

Andamooka and Yowah opal-A consists of silica spheres with an average diameter of 140-320 nm. Two groups are separated by their relative standard deviation: monodisperse spheres (rel. std. dev. <6 %) and polydisperse spheres (rel. std. dev. >10 %). Impurities of all opal-A samples are Al, Fe, Ca, Na, K, Mg and Ba, all but Al and Ca appearing in trace amounts <0.1 wt%. We have identified that monodisperse and polydisperse spheres are separated by their Na/K ratio, restricting the appearance of monodisperse spheres to values <1.3 and polydisperse spheres to values >3.0.

Opal geochemical characteristics are not sufficient to offer clues about the very restrictive chemistry of the opal-forming fluids. It is therefore essential to complement the opal geochemical fingerprint with the chemical and mineralogical properties of host rocks and associated minerals (e.g. kaolinite, alunite, K-feldspar, illite) to confine pH and salinity of the complex opal-forming solutions. The associated minerals indicate large pH variations and may serve as a tracer for the solution composition. Extensive replacement of kaolinite by alunite implies an acidic environment in which silica is solubilized and leached from the deeply weathered claystone. Opal-A and alunite can co-precipitate at pH <3.7. This pH region comprises the isoelectric point of amorphous silica. At this point, the stability of colloidal silica exhibits a local maximum.

In Australia, the major economically important opal fields display systematic geological and mineralogical similarities. We propose that the formation of stable monodisperse spheres at acidic conditions can probably be generalized to other sedimentary settings. Detailed investigations of opals and their host rocks are urgently needed to establish a mineralogic understanding of chemical re-distribution scales and mechanisms during silicate rock alteration and silica diagenesis.
Focused fluid flow zones in the Oman ophiolite (Wadi Gideah, Wadi Tayin Massif) – a key for cooling the deep crust at fast-spreading ridges

S. A. Linsler 1, T. Müller 1, S. Schuth 1, P.E. Wolff 1, J. Koepke 1, D. Garbe-Schönberg 2, H. Strauss 3

1 Leibniz Universität Hannover, slinsler@gmx.de
1 Leibniz Universität Hannover, t.mueller@mineralogie.uni-hannover.de
1 Leibniz Universität Hannover, s.schuth@mineralogie.uni-hannover.de
1 Leibniz Universität Hannover, e.wolff@mineralogie.uni-hannover.de
1 Leibniz Universität Hannover, koepke@mineralogie.uni-hannover.de
2 Christian-Albrecht Universität Kiel, dgs@qpi.uni-kiel.de
3 Wilhelms Universität Münster, hstrauss@uni-muenster.de

The Oman ophiolite potentially represents a proxy of fast-spreading oceanic crust on land. Many petrologists/geochemists built on the evidence from the Oman ophiolite a general accretion model of the deep oceanic crust at fast spreading ridges and favor that the deep plutonic crust is formed by multiple intrusions of gabbroic sills (so-called "sheeted sill model"). A strong requirement for this model is a substantial cooling of the deep oceanic crust, and many scientists believe that a seawater-derived high-temperature hydrothermal circulation system must exist. However, up to day, neither direct (field studies, petrographic investigations) nor indirect (cooling rates based on olivine speedometry) observation revealed any significant indication that such a hydrothermal cooling system exists. This is a major argument against the "sheeted sill model", which supports the other end member model for the accretion of deep fast-spreading oceanic crust, the "gabbro glacier model", where the whole deep crust is originated from the axial melt lens sandwiched between the gabbro layer and the sheeted dikes. Here, the corresponding cooling is enabled from above via the well-known hydrothermal circulation operating in the basalts/sheeted dikes.

In recent field campaigns for establishing a reference profile through typical fast-spreading oceanic crust in the Wadi Gideah (Wadi Tayin massif, Oman ophiolite), we discovered several fault zones in the deeper part of the crust, which are characterized by pervasive alteration, mainly in greenschist and sub-greenschist facies, cutting the relatively fresh layered gabbros. According to Coogan et al. (2006), we identified these zones as pathways for focused hydrothermal activity (Focused Fluid Flow Zones, FFFZ). In the centers of most FFFZ, we observed the occurrence of varitextured gabbro, which we interpreted as the result of hydrous partial melting of the layered gabbro triggered by water-rich fluids, implying that the reaction temperatures in the center of the FFFZ were well above the wet gabbro solidus, e.g., 900 to 1000 °C. This is in contrast to Coogan et al. (2006) who estimated maximum temperatures of ~ 800 °C for amphibole parageneses formed in these zones. This result and the fact that many FFFZ were observed in the gabbroic section of the Wadi Gideah imply a model that focused fluid flow could play a major role in the cooling history of the lower oceanic crust, and could thus be regarded as missing link for the confirmation of the sheeted sill model.

Planar structures (e.g. sedimentary layers, veins, dykes, cleavages, etc.) have about equal chances to be shortened or stretched, when subjected to deformation. Folds and boudinage are assumed to be the most common shortening and stretching structures, respectively. However, boudinage requires additional deformation mechanisms apart from viscous flow, like formation of fractures or strain localization. A very common, but difficult to recognize situation, is when folded layers are subjected to extension, potentially unfolding the folds back to straight layers. Open questions are whether folded layers can unfold, what determines their mechanical behaviour and how can we recognize them in the field. In order to approach these questions, we present a series of numerical simulations of the stretching of previously folded single- and multi-layers in simple shear. We investigate the parameters that affect them once they are in the extensional field. The results show that the unfolding process strongly depends on the viscosity contrast between the layer and matrix. Layers do not completely unfold when they experience softening before or during the stretching process or when other neighbour competent layers prevent them from unfolding. The foliation refraction patterns are the main indicators of unfolded folds. Additionally, intrafolial folds and cusp-like folds adjacent to straight layers as well as variations in fold amplitudes and limb lengths of irregular folds can also be used to determine whether a layer has been stretched after being compressed.
Magnesium carbonatite melt inclusions in mantle xenocrysts from the Eger Graben

Anselm Loges\textsuperscript{1},* Dina Schultze\textsuperscript{1}, Friedrich Lucassen\textsuperscript{2}

\textsuperscript{1}Technische Universität Berlin, FG Mineralogie-Petrologie, Ackerstraße 71-76, 13355 Berlin
\textsuperscript{2}Marum - Zentrum für Marine Umweltwissenschaften der Universität Bremen, Leobener Straße, 28359 Bremen

*anselm.loges@tu-berlin.de

We present geochemical and isotope data of carbonatitic melt inclusions in clinopyroxene (cpx) xenocrysts in basanite from the Spitzberg in Cotta, 20 km SE of Dresden, which forms part of a series of Tertiary basaltic-phonolitic volcanic plugs on the northern margin of the Eger Graben. The Cottaer Spitzberg is a small monogenetic volcano of basanitic composition with abundant xenocrysts and xenoliths. The CIPW-normative major mineral composition of the rocks is (in order of descending abundance) plagioclase, clinopyroxene, Fe-Ti oxides, olivine, nepheline, orthoclase and Apatite; normative orthopyroxene (opx) is absent. However, opx is present in harzburgitic mantle xenoliths and is heavily altered or completely replaced by cpx and magnetite where it is in contact with the matrix. Green-core clinopyroxenes occur as cm-sized xenocrysts showing titanium augite overgrowth. These cpx cores show inclusions of apatite Ti-magnetite and three types of melt in textural equilibrium: silicate melt, sulfide melt and carbonatitic melt. The latter shows magnesitic to ferro-magnesitic composition (up to 40 mol\% siderite component; calcite component \(<6\) mol\%). Additionally, the same carbonatitic melt is found outside the xenocrysts in the matrix where it is also associated with sulfides. Based on petrographic observation and loss on ignition data, the magnesite content of the whole rock is estimated to be 3-5 wt.\%. The silicate melt inclusions in the cpx have up to 6 wt.\% K\textsubscript{2}O, accounting for the normative orthoclase.

The abundant carbonate, silicate and sulfide melt inclusions in the cpx cores suggest fast cpx growth at the time of melt unmixing. Using the Ca-Mg distribution between carbonate and pyroxene as a barometer, we can conclude that this must have occurred at depths greater than 100 km. These observations allow us to conclude that unmixing of carbonatitic and sulfidic melt from a parental silicate melt in the mantle caused cpx and apatite supersaturation and consequently rapid formation and growth of these minerals. The fact that all involved phases are preserved as inclusions in cpx provides a rare opportunity to probe the chemistry and isotopic composition of the carbonate melt captured in the process of unmixing the mantle.
Application of a Difference Electron Nanoscope (DEN): Correlation between 3D Magnetical Structures of Synthetic Fayalite with Synchrotron and Neutron Diffraction and Mössbauer Spectroscopy

W. Lottermoser¹, K. Steiner², G. Scharfetter³, S.-U. Weber⁴, M. Grodzicki¹, A. Kirfel⁵, G. Amthauer¹

¹werner.lottermoser@sbg.ac.at, michael.grodzicki@sbg.ac.at, georg.amthauer@sbg.ac.at
²konrad.steiner@sbg.ac.at
³gerhard.scharfetter@sbg.ac.at
⁴svenulf.weber@alumni.uni-kiel.de
⁵kirfel@uni-bonn.de

Affiliation: ¹University of Salzburg, Dep. of Materials Engineering and Physics, Salzburg, Austria; ²HBLA Ursprung, Salzburg, Austria; ³University of Salzburg, Dep. of Computer Sciences, Salzburg, Austria; ⁴Technical University of Braunschweig, Dep. of Physical and Theoretical Chemistry, Braunschweig, Germany; ⁵University of Bonn, Inst. of Mineralogy and Petrology, Bonn, Germany

The evaluation of a 3-dimensional orientation of magnetic moments in solids is still a challenging problem in modern physics and crystallography. Common methods to arrive at this goal are neutron diffraction (in particular with polarized n.), magnetometry and Single Crystal Mössbauer Spectroscopy (SCMBS). However, each of these methods have their limitations, viz. antiphase domains, magnetical impurities, the confinement to special nuclides a.s.o.. X-ray and synchrotron diffraction may provide valuable information on crystallographic structures, but the separation of the magnetically effective electrons (in our case: 3d) is hardly possible with the latter experiments.

However, we are in the favourite situation that in the case of synthetic fayalite we dispose of data sets of most of the methods mentioned above and can try to combine the collected physical informations of each one. By the recently presented Difference Electron Nanoscope (DEN) we dispose of a powerful tool to display the 3-dimensional distribution of very accurately determined difference electrons from synchrotron diffraction measurements and to correlate them to the size and direction of the electric field gradient (efg) of Mössbauer spectroscopy and DFT calculations. This had been demonstrated successfully elsewhere [1]. Since Mössbauer spectroscopy is also capable of providing informations on the size and direction of the internal magnetic field H(0) with respect to the efg, we can now correlate the difference electron distribution mentioned above with H(0) and the magnetic moments’ orientation from neutron diffraction [2]. On the DEN images amazing details are visible, viz. difference electrons around special oxygens that have been identified as most probably bearing superexchange coupling.


The Argentine continental margin is a typical example of a rifted volcanic margin with large extrusions of magmatic material which form the seaward dipping reflector sequences (Hinz et al., 1999). Another example of a volcanic margin is the North Atlantic between Greenland and Norway. The study area is located south of the RioGrande Ridge and north of the Falkland-Agulhas Plateau Fracture Zone (Figure 1). Regarding hydrocarbon exploration the Argentine margin is virtually unexplored with few wells on the shelf and it is not included in the USGS World Petroleum Assessment 2000. The study area is situated between the Pelotas Basin and the Falkland Plateau assessment unit of the USGS (Klett et al., 2000) and covers an area of approximately 670,000 km2. This part of the Argentine margin was chosen to assess its hydrocarbon potential. Based on 2-D seismic reflection and refraction data a structural model was built comprising 13 horizons from the Moho to the sea floor. On the continental side the model includes rift-graben sediments with Lower Cretaceous sediments (Neocomian black shales) as possible source rocks and on the oceanic side Aptian-Albian black shales are assumed as main source rocks. The wells Puelche, Ranquel, Estrella, Cruz del Sur, Corona Australis, Pejerre are located within the study area in water depth of less than 150 m. They are all situated in the Colorado Basin. Deep water wells do not exist in the study area. The petroleum system model is supplemented with data from analog basins like the Orange Basin from the conjugated African margin.

References


Pleistocene-Holocene Karstification of Barbados
and its implications for the Devonian Grosmont reservoir, Canada

Hans G. Machel
hans.machel@ualberta.ca

About 80% of the surface of Barbados is made up of Quaternary carbonates with ages approximately 800,000 years to recent. These carbonates are extensively overprinted by epigene (top-down) karst processes. Epigene karst features include various types of caves, solution valleys, and sinkholes. Flank margin caves are the most common cave type. Sinkhole density is high, with an average of 5 sinkholes per square km. However, some areas have a much higher density while others are almost devoid of sinkholes. Sinkholes range in diameter from about 10m to 120m and are up to about 15m deep. Another striking morphological karst feature is a network of valleys, locally referred to as gullies. Their origin is problematic and much debated. Most gullies have caves along at least a part of their paths, commonly decorated with flowstone or other speleothems.

Despite the vast differences in age and size, a number of lessons learnt from karst in Barbados can be applied to karst in the Devonian Grosmont reservoir in Alberta, which is the largest heavy oil/bitumen reservoir in the world, with an estimated 400-500 billion barrels of initial oil in place. For example, numerous sinkholes identified in seismic images can be interpreted as epigene karst features that developed rapidly on one or several former land surfaces. Drainage patterns akin to the gullies of Barbados can be expected in the Grosmont as well, but not as deep or as densely spaced, and with different orientations. The Grosmont may contain a few stream caves and many more flank margin caves, while the latter should not be as frequent as in Barbados but may be considerably larger.

Integrating these aspects with the known geologic history of the Grosmont platform, it appears that the Grosmont platform was karstified in at least two major epigene episodes. The first episode was a ‘warm epigene karstification’ during the Jurassic – Cretaceous, for which Barbados provides a useful analog. The second episode was/is a ‘cold epigene karstification’ that started sometime in the Cenozoic and is continuing to this day. The present repertoire of karst features probably is a composite of these two epigene karstification episodes. In addition, circumstantial evidence suggests that epigene karst gives way to a deep hypogene (bottom-up) karst in the downdip part of the platform. The latter likely has different characteristics, i.e., most notably a maze system of passages rather than a stream system overlayed by sinkholes. At present the hypogene karst system in the Grosmont is virtually unexplored.

Left: Large flank margin cave cut open by fresh water erosion. Jack-in-the-Box gully, Barbados. Person for scale.

Right: Schematic cross section through the Devonian Grosmont reservoir, Alberta, Canada. Red arrows and circle point to potential ‘sweet spots’ due to enhanced evaporite and carbonate dissolution.
Mollusc shells are composite biomaterials which consist of an outer part where calcite fibers are embedded into an organic matrix and an inner part (Nacre) which is composed of aragonite tablets also embedded into an organic matrix. We studied the shell of Mythilus edulis by high-resolution electron back-scatter diffraction (EBSD).

Calcite fibers in the outer part of the shell exhibit a single-crystal like texture with the c-axis oriented roughly perpendicular to the fiber axis and also to the curvature of the shell. The fibers are misoriented mainly around the c-axis exhibiting a gaussian misorientation angle distribution of 15° FWHM.

Nacre tablets are highly c-axis oriented, i.e. the aragonite c-axis is roughly perpendicular to the curvature of the shell. The co-orientation of nanocrystals within the aragonite tablets could be resolved and quantified by applying new developments in high-resolution EBSD which allow for a step resolution of 125 nm. A mosaic structure with 2° FWHM misorientation distribution is revealed within the nacre tablets, and this mosaic structure spans across tablet boundaries to form composite crystals comprised of up to 20 stacked co-oriented tablets. Several of such adjacent composite crystals form larger composite-crystal stacks which exhibit small-angle misorientations (< 25°) typically around the aragonite a-axis between the individual tablet stacks. The composite crystal stacks themselves are typically misoriented by a rotation larger than 25° around the aragonite c-axis. Here {110} twin boundaries are frequent as the probability distribution of mesoscale grain boundary misorientations has a dominant peak near 64°. We attribute the formation of the mesoscale composite crystals to growth by accretion of amorphous calcium carbonate particles followed by semicoherent homoepitaxial crystallization. The crystallization percolates between the tablets through mineral bridges across matrix membranes to form the stacked-tablet composite crystals. We attribute the low-angle misorientations (mainly rotations around the a-axis) within and between the tablet stacks to the disturbance of coherent crystal growth by the 3D network of organic matrix within and the membranes between the tablets. Each composite crystal stack, composed of several tablet stacks, nucleates independently, i.e. no mineral bridge exists between two adjacent composite crystal stacks.
Speciation of arsenic and zinc in the oxidation zone of a Zn-Pb deposit
Olkusz, Poland

Juraj Majzlan¹, Irena Jerzykowska², Marek Michalik²

¹ Inst. of Geosciences, Friedrich-Schiller Univ., Carl-Zeiss Promenade 10, D-07749 Jena (email Juraj.Majzlan@uni-jena.de)
² Institute of Geological Sciences, Jagiellonian University, PL-30063 Krakow, Poland

Oxidation zones of ore deposits offer valuable insights into the long-term fate of many metals and metalloids. They are a window through which we can peek into the future and examine the fate of metal-rich waste forms over long-term periods. In this contribution, we have examined the oxidation zone of Mississippi-valley type Zn-Pb deposits near Olkusz in southern Poland. The ores are hosted by Devonian to Triassic carbonate sediments and their primary mineralogy is relatively simple, including pyrite, marcasite, sphalerite, galena, and barite. Weathering converted the primary minerals into a number of secondary ones, notably goethite, smithsonite, hemimorphite, and a number of rarer species (Cabala 2001).

Bulk powder X-ray diffraction (XRD) and Mössbauer spectroscopy indicate that goethite is the major iron oxide in the studied material. Smithsonite and hemimorphite were also detected in powder XRD data, in addition to a sheet silicate from the smectite group. Detailed investigation of the material with micro-XRD confirmed goethite as the major phase and the only iron oxide. Because the studied material originated from a geologically old environment, we assume that ferrihydrite is not present.

Chemical composition of the goethite was studied by electron microprobe (EMP) analyses. The composition is relatively uniform; the average content of As is (all data in wt%) 0.42 %, Al 1.30 %, Si 4.38 %, Pb 1.17 %, Zn 5.91 %, and Fe 68.18 %. Goethite forms pseudomorphs after the primary iron disulfides (pyrite or marcasite), occasionally with minute relics of the disulfides, or botryoidal and zonal aggregates with slight chemical variations between the growth zones. The smectite phases are very zinc-rich and belong to sauconite.

X-ray absorption spectroscopy (XAS) was used to determine speciation of As and Zn in these minerals. For goethite, the As-Fe and Zn-Fe distances appear shorter than in freshly made goethite suspensions with adsorbed As and Zn. We are still entertaining the possibility that some of the arsenate tetrahedra share an edge with the Fe octahedra. For the smectite, very strong signal in the second shell indicates a large number of Zn-Zn neighbors in the octahedral sheets. The XAS data are being further reduced and the results will be presented.

Hajigak Iron deposit: A Giant Hydrothermal System in the Central Afghanistan Iron Belt

HASAN A. MALISTANI¹,²*, JEAN THEIN¹, DITER GARBE-SCHÖNBERG³

¹ Steinmann-Institut für Geologie, Mineralogie und Paläontologie, University Of Bonn, Nussallee 8, 53115 Bonn, Germany
² Geology Department, University of Bamyan, Bamyan, Afghanistan (*correspondence: hmalistani@gmail.com)
³ CAU Kiel, Institut für Geowissenschaften, 24098 Kiel

Hajigak iron ore deposit is situated in Central Afghanistan, in the high West Hindukush. It is the largest iron ore reserve in Central Afghanistan Iron Belt (CAIB). Former studies demonstrated the mineral potential of the region and for the main Hajigak deposit resources of 1.8 billion tons @ 62 wt % Fe have been estimated. The Hajigak iron orebodies (from west to the east: Sya-Dara, VII, I-II-III, IX, XII, and Khesh) of the CAIB are distributed along with the southern flank of the Kuhi-Baba fold and structurally controlled by the Herat-Panjsher Fault System (HPF). These large to medium size and other numerous smaller orebodies occur in a North-East to South-West directed belt, stuck between Precambrian and lower Paleozoic meta-sedimentary and meta-volcanic rocks of Kalu group and Hajigak Formation. High-grade iron mineralization (>60 wt% Fe) is made up of mainly hard magnetite-hematite-goethite ore. The main host rocks to iron mineralization are all greenschist facies metamorphosed. The host rocks are defined by hydrothermally altered volcano-sedimentary units mainly composed by quartz-sericite or chlorite schists and carbonates. Varying degrees of hydrothermal alteration have affected on the primary pyrite-magnetite and carbonates to form high grade iron ores, from hypogene alteration zone, representing an early alteration stage, to the late supergene alteration zone, synchronous with the iron ore forming events. Some jaspilites from the IX, XII and SD deposits have low ΣREE content but most of high-grade hard ores from I-II-III, XII, VII and SD deposits have relatively high ΣREE contents, mostly of light REE, and exhibit large positive europium anomalies (Eu/Eu*>2), which is typical of Precambrian BIF hosted Fe deposits and younger hydrothermal plumes. The REE pattern of Khesh Fe ore deposit is defined by elevated LREE and absence of the positive Eu anomaly.

The mineralogical, geochemical and stable isotopic data from host rocks and the high-grade iron ores suggest a hydrothermal origin for the iron ore of the belt. This include multiple hydrothermal interaction with an early stage, relatively reduced hypogene fluid, which leached silica, carbonate and apatite and formed magnetite (± hematite), which evolved to more oxidizing conditions, with the advance of martmentization, increase in the REE content and goethite formation in veins and open spaces, from interaction with supergene fluids.
Dissolution, Brittle Failure and Precipitation in a Small Scale Shear Zone

C. Mantey & B. Stöckhert

Microstructures in a millimeter thick shear zone crosscutting the foliation of banded HT-LP metamorphic quartz-mica rock of the Uppermost Tectonic Unit on Crete (Greece) are investigated. Total displacement is documented by offset of layers, while the non-planar character of the shear zone resulted in alternating domains of negative and positive dilatation. At releasing bends, i.e. domains of positive dilatation (veinlets), fibrous quartz grains with an orientation oblique to the shear zone developed by successive crack formation and healing. At restraining bends, i.e. domains of negative dilatation, dissolution of material is documented by stylolites. The orientation of quartz c-axes of host rock grains and fibres in the shear zone were analyzed by EBSD and trails of fluid inclusions were inspected in high resolution BSE-images.

Numerous microcracks in fibrous quartz veinlets, decorated by tiny fluid-inclusions, are oriented normal to the fibre long axis and oblique to shear zone. Orientation of microcracks and columnar stylolites consistently reflect uniform orientation of the maximum principle stress direction for the entire period of progressive displacement along the shear zone. Comparison between offset host rock layers and orientation of quartz fibres precludes displacement control and indicates that fibre growth was governed by successive cracking and healing, with orientation controlled by stress (Cox S.F. & Etheridge M.A., 1983, Tectonophysics, 92: 147-170). Here, fibre growth reflects incremental strain during non-coaxial deformation. Though the fibres are approximately straight, their c-axis orientation systematically changes. At both vein margins it corresponds to previously developed pronounced crystallographic preferred orientation in pure quartz layers of the host rock, while towards the vein center c-axes tend to be parallel to fibre long axes. Reorientation by up to 90° over 0,5mm being continuous along the fibre, this microfabric suggests that (a) microcracks during progressive dilatation systematically formed near the center of the vein, and (b) that each crack and heal event involved a slight crystallographic re-orientation, which was directly or indirectly (via crack orientation) controlled by stress, cumulating in systematic change of crystallographic orientation along straight fibres. Dissolution along the stylolitic seams is expected to cause contemporaneous loading of the quartz fibres, eventually leading to stress release by cracking, followed by healing. On microscale, progressive displacement along the shear zone is controlled by periodic stress-redistribution between adjacent sites of positive and negative dilatation. Local dissolution and precipitation processes are envisaged as non-steady state, with a periodicity controlled by elastic distortion and brittle failure of the quartz fibres, while on larger scale displacement along the shear zone may have been approximately continuous.
Weathering of cobalt arsenides: natural assemblages and calculated stability relations among secondary Ca-Mg-Co arsenates and carbonates

Gregor Markl¹, Michael Marks¹, Insa Derrey¹,², Jan-Erik Gühring¹

¹Fachbereich Geowissenschaften, Universität Tübingen, Wilhelmstr. 56, D-72074 Tübingen, Germany; corresponding author: markl@uni-tuebingen.de
²present address: Institut für Mineralogie, Leibniz Universität Hannover, Callinstr. 3, D-30167 Hannover, Germany

The supergene alteration of cobalt arsenides produces a variety of characteristic mineral assemblages including erythrite, pharmacolite and other Ca±Mg±Co-bearing arsenates, which upon precipitation remove Co and As from natural waters. Their paragenetic relationships and stability conditions have not been investigated in detail. We present a detailed study on these assemblages, their successions and coexisting fluid compositions from the mining area of Wittichen, SW Germany, where primary skutterudite and safflorite in granite-hosted barite-calcite veins are oxidized. Water analyses from the old mines, semi-quantitative stability diagrams and quantitative reaction path modeling are used to constrain their conditions of formation.

Cobalt- and arsenate-bearing solutions invariably precipitate erythrite first and hence buffer Co concentrations to very low values. Both during safflorite dissolution and erythrite precipitation, the fluid's Co/As ratio decreases rapidly. Therefore, spherocobaltite (Co carbonate) is unstable in the presence of arsenate ions under most conditions.

The formation of various mineral assemblages precipitating after or simultaneously with erythrite strongly depends on Ca²⁺ and Mg²⁺ activities and pH. Small changes in one of these parameters lead to different mineral assemblages. These small changes are partly governed by fluid-host rock or fluid-vein mineral reactions and partly by the precipitation of the secondary arsenate minerals themselves. This complex interdependence produces the rich variety of mineral assemblages observed, which effectively serves as a very sensitive monitor of fluid compositions. Furthermore, the assemblages themselves are able to buffer the Ca-Mg-Co-As concentrations in the fluid to some extent and effectively immobilize both As and Co in close proximity to the ore deposit.
Ferropericlase (Mg,Fe)O is thought to be the second most abundant mineral phase in Earth’s lower mantle. Due to its strong elastic anisotropy and potentially weak rheological behavior it may play a key role in controlling rheology of the lower mantle and in generating seismic anisotropy (e.g. McNamara et al. 2002; Marquardt et al. 2009). At pressures between approximately 40 GPa and 70 GPa at 300 K, the ferrous iron in ferropericlase undergoes a spin crossover from high-spin to low-spin state (Badro et al. 2003). Our understanding of the impact of the spin crossover on strength and texture development in ferropericlase is incomplete. The only published deformation study on (Mg,Fe)O through the spin transition (Lin et al. 2009) pressure region has very limited pressure resolution. However, the results of the previous study indicate a decrease of ferropericlase strength throughout the spin crossover region and in the low-spin state.

Here, we present new results from synchrotron radial x-ray diffraction measurements on (Mg$_{0.9}$Fe$_{0.1}$)O and (Mg$_{0.8}$Fe$_{0.2}$)O carried out at the Advanced Light Source (Lawrence Berkeley National Laboratory) throughout the entire spin crossover pressure range. In our experiments, pressure was remotely increased using a gas membrane system, which allows for obtaining a very fine pressure resolution. In contrast to the previous report of Lin et al., our data do not show any decrease of average differential strains (and thus strength) in ferropericlase across the spin crossover. In contrast, our experiments suggest that the strength of ferropericlase increases when iron changes from high to low-spin state and remains large in low-spin state.

We will discuss the findings on the strength of ferropericlase in light of their implications for lower mantle rheology. Furthermore, we will present our analysis of texture development in high- and low-spin ferropericlase, which can be related to seismic anisotropy observations in the lowermost mantle.

μCT 3D-quantification and visualization of porosity and permeability networks of Muschelkalk (Middle Triassic, central Europe) limestones

Nikolas Martin¹, Christoph Heubeck², Bernhard Illerhaus³

¹nikolas.martin@gmx.net, ²cheubeck@zedat.fu-berlin.de, ³bernhard.illerhaus@bam.de

Middle East Mesozoic carbonates deposited in ramp settings hold approx. 50% of the world’s remaining recoverable reserves of conventional petroleum. The responsible and efficient exploitation of these reservoirs require detailed field management based on a thorough understanding of reservoir quality, including the high-resolution 3D distribution of porosity and permeability as a function of depositional facies and diagenetic history. Comparative assessment of well-exposed carbonate ramps can contribute to this understanding at scales ranging from km-scale lateral variability of flow-relevant parameters to mm-scale facies-dependent geometry of pore spaces. In this pilot study, we here report on preliminary findings of micro-computer tomography (μCT) 3D-studies of four limestones, sampled from the epicontinental, shallow marine, storm-dominated Muschelkalk carbonate ramp of central Europe (Middle Triassic, 243 Ma to 235 Ma). This unit has been widely used in the literature as an analog to Middle East carbonate ramps.

The samples show a wide variety of pore systematics (fracture, oomoldic, intergranular, biomoldic). To examine 3D rock fabric and 3D porosity, μCT was run at the BAM Bundesanstalt für Materialforschung und -prüfung on micro-drilled cylinders 5 mm and 2 mm in diameter (which had been cut at the Geoforschungszentrum Potsdam, GFZ), using a 225 kV μCT device with a 2048 x 2048 pixel flat-panel detector system and x-ray intensities of 7 W and 14 W, resulting in voxel sizes of 2.2 µm and 9.2 µm and in focal points of ~7 µm and ~14 µm, respectively. Visualization using VGStudio MAX showed intricate and complex natural pore network geometries ranging from 0.1% to ~25% of both fabric-selective (grain size, grain type, sorting) and fabric-insensitive (carbonate mineralogy, fracturing, compaction and pressure solution) type. Thin sections cut in three orthogonal planes allowed the description of macroscopic textures and quantification of porosity on thin section-scale through image analysis, and allowed upscaling relationships between μCT and thin-section datasets to be derived.
Decompression experiments with a H$_2$O-bearing phonolitic melt were performed at a super-liquidus $T$ of 1323 K in an internally heated argon pressure vessel, applying continuous decompression (CD) as well as stepwise decompression (SD) techniques. The hydrous melt was decompressed from 200 MPa at true and interpolated decompression rates (DRs) of 0.0028-4.8 MPa·s$^{-1}$ to investigate the effect of decompression method on melt degassing. After rapid quench, the vesiculated glass products were compared in terms of bubble number density (BND), bubble size distribution and residual H$_2$O content. At decompression rates of $>0.17$ MPa·s$^{-1}$ the decompression method does not influence the degassing behavior. SD and CD result in high BNDs of $10^4$-$10^5$ mm$^{-3}$. On the contrary, SD run products display up to 3 orders of magnitude higher BNDs and smaller bubble diameters than products of CD experiments at low decompression rates of $\leq 0.024$ MPa·s$^{-1}$. In general, decompression induces a super-saturation with H$_2$O in the melt. At a certain $\Delta P$ bubbles will nucleate homogeneously within the melt and grow by H$_2$O diffusion into the bubbles to readjust equilibrium. The extent of super-saturation is mainly controlled by the decompression rate, because the diffusional transport of H$_2$O is limited within a certain time. At low CD rates only few bubbles nucleate in the melt, because the decompression period provides sufficient time for H$_2$O diffusion into existing bubbles. Therefore, bubble growth is the predominant degassing process. CD samples quenched at different target $P$ at 0.024 MPa·s$^{-1}$ trace an equilibrium degassing path in terms of residual H$_2$O content in the glass. In contrast, SD results in instantaneous super-saturation with H$_2$O due to rapid $P$ drop, which can only be reduced by a massive nucleation event. The differences between the decompression techniques decrease with increasing nominal decompression rate. The residual H$_2$O contents in the glass (measured by micro-FTIR) also seem to increase with decompression rate, but high BNDs with bubble interspaces on a micrometer scale complicate measurements. Micro-FTIR reflection measurements are expected to bypass this problem. Nevertheless, the experiments revealed that SD techniques are not suitable to investigate the dynamic processes during continuous magma ascent at low nominal decompression rates. Further experiments with CD will provide new insights into the dynamic processes within ascending magmas.
The combustion of solid biomass to produce electrical power and heat has become an important factor in the aim to substitute fossil and nuclear fuels by renewable energy sources. Solid biomass fuels are mostly obtained from waste products from forestry (mainly wood) and agriculture (mainly straw), and thus do not have the problems associated with liquid biofuels, which due to rapid increase in demand lead to recognizable intrusion into acreages by energy crops. Nevertheless, the use of energy crops for solid biomass combustion, such as Miscanthus grass, has increased in the last decade.

Solid biomass contains various inorganic components in different amounts and speciation, depending on, e.g., plant type, soil, and harvest season. They remain as ashes after combustion, as they are non-combustible. One portion mostly stays at the combustion grate as bottom ash; the other is carried out of the boiler as fly ash with the flue gas. In modern combustion devices, various filter techniques (e.g. cyclones, electrostatic precipitators) remove a significant amount of this fly ash from the flue gas, with the remainder released into the atmosphere. The quantities, physical properties, and chemical composition of these fractions strongly depend on the combustion parameters, such as burning temperature, combustion scale, fuel type, which also determines the amount of unburned carbon left after the combustion process. Incomplete combustion often leads to the formation of soot and organic compounds such as dioxins or tar, which both can be hazardous for living organisms. The variety of possible particle types, which are generated during the combustion of biomass, is pronounced, as is the diversity of inorganic phases, which form from inorganic components.

Bottom ashes (in large-scale combustion devices fly ashes as well) usually are treated as waste products. Bottom ashes are considered to be unproblematic and sometimes are used as fertilizer additives, because they also contain valuable nutrients and can act as a pollutant absorber, i.e. for heavy metals. Fly ashes, however, may be enriched in heavy metals and therefore have to be disposed as problematic waste. The suitability of bottom ashes for utilization heavily depends on the fuel type and quality. Characterization of a wide range of biomass ash types can help to assess the risk or potential, especially when it is crucial to return ashes from biomass combustion to the soil to avoid depletion of nutrients.

In this study, various bottom ashes from eight different wood types have been investigated in regard to their mineral composition by using X-Ray Diffraction Analysis and Rietveld-Refinement. From these data, the nutrient-supplying substances were assessed. Furthermore, heavy metal contents were determined by using Atomic Absorption Spectroscopy, to assess the maximum ratio of these ashes when used as fertilizer additives.
Formation of channel-flow systems by dehydration reactions - a thermodynamic study of phase relations in various lithologies

Hans-Joachim Massonne, Institut für Mineralogie und Kristallchemie, Universität Stuttgart

The study is based on numerous P-T pseudosections which were calculated for various rocks of major crustal lithologies (sediments, felsic to mafic igneous rocks) and different P-T regimes (low to ultrahigh pressure, very low- to high-grade). For these calculations in the system K₂O-Na₂O-CaO-MgO-FeO-Al₂O₃-SiO₂-H₂O (±TiO₂, ±MnO, ±O₂, ±CO₂) the PERPLE_X software package (Connolly 2005), thermodynamic data by Holland & Powell (1998 and updates), including those for solid-solution series compatible to this data set, and a haplogranitic melt model (White et al. 2001) were used. The contouring of the obtained P-T pseudosections by isopleths for bulk H₂O contents in the minerals demonstrates that dehydration during prograde metamorphism can result in the release of large quantities of water over a narrow temperature interval. This release results in the formation of weak zones in crust and mantle and, thus, could give rise to the formation of channel flows. This hypothesis is strengthened by the coincidence of P-T regimes, for which massive water release is observed in the PERPLE_X calculations, with those assigned to channel-flow systems based on numerical modeling and deduction from natural geotectonic environments.

The subduction of oceanic crust, for example, results in massive dehydration of its sedimentary cover starting at about 250°C (e.g. Massonne 2009). This process generates a channel-flow system that helps to build up accretionary wedges at active continental margins. During further subduction of the oceanic crust garnet formation in the temperature interval 450-550°C also causes the release of large quantities of water resulting in an upwards-directed channel flow along the interface of subducted crust and overlying mantle. In a very similar manner this process acts during continent-continent collision when (meta)sediments on top of the lower continental plate, which is thrust under the upper plate, dehydrate to form garnet at high-pressure conditions. The resulting channel flow along the interface of both plates is, however, subhorizontal. During the further underthrusting of the lower continental plate partial melts form at higher temperatures (≥600°C) by mica+amphibole-dehydration melting. This process causes the generation of another subhorizontal channel-flow system, probably also near the interface of the colliding plates, and might be the reason that the rigid portions of both plates move in opposite direction to form extended areas of thickened continental crust. At the lower boundary of the lower continental plate dehydration, albeit of minor extent, should take place to produce a weak zone at the mantle boundary by serpentinization. This continuously produced weak zone at the front of the proceeding plate allows the penetration of the buoyant rigid continental plate into the mantle lithosphere during the underthrusting event of the continent-continent collision. This process, related to colliding oceanic plates, could have also taken place in Archaean times when subduction of oceanic crust was prevented by lacking eclogitization of this crust in the still hot Earth. This kind of collision gave rise to melting of the basic material and, thus, to the formation of continental crust.
Shear zones may reach down to mantle depths as continuation of seismically active fault zones, as for example in the tectonic environment of subduction zones and fracture zones. The macro-scale time-dependent rheology of such shear zones is controlled by nano- to micro-scale deformation and recrystallization processes in the effected upper mantle rocks (i.e., peridotites). What is the characteristic rock record, what are the micro-scale processes and what are the characteristic time scales for damage healing? These questions are addressed by a comparison of microstructures from naturally and experimentally deformed peridotites at characteristic stress histories, i.e. a high stress and strain rate event followed by stress relaxation at approximately constant pressure-temperature conditions. Shear-zone peridotites from the Ivrea zone in the Southern Alps are chosen as an ideal natural model case to study the material behavior of peridotites at transient high-stress, high strain-rate deformation. Because the presence of pseudotachylytes in peridotites from the Balmuccia complex in the Ivrea zone gives independent evidence of earthquake-related deformation at upper mantle depth. The natural microstructures are compared to those from experimentally deformed natural olivine-rich peridotites. The experiments comprise sequences of deformation (at 300 or 600 °C) and annealing at varying temperature (700 to 1100 °C), time (up to 144 hours) and stress (up to 1.5 GPa). They are carried out in a Griggs-type apparatus and are designed to simulate the natural stress history in upper mantle rocks in the uppermost plastosphere.

The natural and experimentally deformed peridotites provide a spectrum of characteristic microstructures that are indicative of systematic stress and strain rate variations: (1) deformed porphyroclasts with pronounced undulatory extinction, deformation lamellae, kink bands and healed microcracks, and (2) localized fine-grained zones of isometric grains, with weak, unsystematic texture patterns, occurring characteristically in intragranular zones (former microcracks or highly damaged zones) of porphyroclasts and surrounding them. These heterogeneous microstructures with characteristic variation in grain sizes and intragranular deformation features are an indication of an initial stage of low-temperature plasticity with microcracking at high stresses and high strain rates overprinted by recovery and recrystallization at relaxing stresses. Extrapolation of the experiments to natural conditions suggests that the observed characteristic microstructure may develop within as little as tens of years and less than ten thousands of years. These deformation and recrystallization microstructures have a great diagnostic potential for past seismic activity because they are expected to be stable over geological time scales, since driving forces for further modification are not sufficient to erase the characteristic heterogeneities during further low stress histories.

Microfabric evolution in peridotites during transient high-stress deformation and subsequent recovery and recrystallization – nature and experiment

Matysiak, A.M.\textsuperscript{1}, Trepmann, C.A.\textsuperscript{2}, Renner, J.\textsuperscript{3}, Druiventak, A.\textsuperscript{4}

\textsuperscript{1}agnes.matysiak@lmu.de, \textsuperscript{2}claudia.trepmann@lmu.de, \textsuperscript{3}joerg.renner@rub.de, \textsuperscript{4}anthony.druiventak@rub.de
Geology of North Gondwana from a central North African perspective

Guido Meinhold

Geowissenschaftliches Zentrum der Universität Göttingen, Abteilung Sedimentologie/Umweltgeologie, Goldschmidtstraße 3, 37077 Göttingen, Germany; guido.meinhold@geo.uni-goettingen.de

The Precambrian basement of central North Africa is largely covered by Palaeozoic and younger sedimentary rocks. The Palaeozoic rocks are well preserved in the intracratonic Kufra and Murzuq basins where they can be studied in outcrops along the margins of the basins. The Palaeozoic sedimentary succession of both basins contains substantial thicknesses of clastic, marine and non-marine sediments. The precise stratigraphic age of most of these sediments is poorly known. The region has been the focus of great interest for hydrocarbon exploration in recent years since the discovery of large oil fields in the Murzuq Basin, SW Libya. The Murzuq Basin is an important petroleum province with proven major petroleum reservoirs in Cambrian, Ordovician and Devonian sandstones. On the contrary, no hydrocarbon discoveries have been made in the Kufra Basin. Perhaps the most critical exploration uncertainty in these basins is the existence of an effective source rock, i.e. lower Silurian (Rhuddanian) organic rich shales of the Tanezzuft Formation. These shales have charged very prolific petroleum systems in western Libya and eastern Algeria. However, these have not, so far, been encountered in the Kufra Basin either in outcrop or the subsurface. The organic rich shales of the lower Silurian Tanezzuft Formation were preferentially deposited above a glacially sculpted topography after the late Ordovician (Hirnantian) glaciation (e.g., Lüning et al., 2000, Earth-Sci. Rev., 44, 121-200). The large hydrocarbon reserves in Palaeozoic strata of the Murzuq Basin makes it attractive to international oil and gas companies to explore the region in more detail, providing the impetus for field-based research in southern Libya. The centre of the Murzuq Basin has been extensively studied in recent years by seismic and borehole data. However, the margins of this basin, especially the eastern margin, needed studies focused on understanding the provenance and depositional history of the sedimentary succession. This is also needed for the Kufra Basin where oil and gas exploration is so far limited to seismic and six exploration wells. In this presentation, the geological evolution of central North Africa will be summarized and illustrated by outcrop and analytical data. These data are expected to lead to new stratigraphic concepts at the margins of the Kufra and Murzuq basins. They allow the first investigation of potential source rock intervals within the lower Silurian succession along the eastern margins of these basins. Furthermore, understanding the age and origin of the sedimentary strata is important for reconstructions of palaeosource areas and sediment transport and may give novel approaches to test current palaeotectonic models, with important implications for our understanding of the evolution of the North Gondwana margin during the Palaeozoic (e.g., Meinhold et al., 2013, Gond. Res., 23, 661-665).
Sedimentary provenance analysis for palaeotectonic reconstructions and exploration of natural resources

Guido Meinhold

Geowissenschaftliches Zentrum der Universität Göttingen, Abteilung Sedimentologie/Umweltgeologie, Goldschmidtstraße 3, 37077 Göttingen, Germany; guido.meinhold@geo.uni-goettingen.de

Sediments are an important archive for unravelling the Earth’s history. They can provide, for example, information about ancient climates, the evolution of fauna and flora, and environmental changes. Moreover, they are often the only record of ancient plate tectonic processes. This is especially the case if one considers the formation of siliciclastic sediments. A key for deciphering information from the siliciclastic sedimentary record are the detrital components of which these deposits are composed. Quartz, feldspar, lithic fragments and phyllosilicates are often the dominant components. Heavy minerals are commonly minor components and make up to one percent or less of the total detrital material. Sedimentary provenance analysis is a powerful method for deciphering information from the detrital record. It has undergone a renaissance in recent years with the application of advanced techniques for in situ analysis of mineral grains. One of the key techniques nowadays routinely used is detrital mineral U-Pb geochronology. This technique is important not only for sedimentary provenance analysis but also for stratigraphic work in fossil-free sedimentary successions. It allows estimating the maximum age of a sedimentary succession, based on the youngest detrital age component, if no biostratigraphic data are available. The Palaeozoic succession of the Saharan Platform is one example where a multi-method provenance approach has successfully been applied. It comprises voluminous amounts of sandstone, and biostratigraphic age control is lacking in many cases. Having provenance information from these deposits is of economic interest because some of the Palaeozoic sandstones are important reservoir rocks hosting large oil and gas reserves which make them attractive to the hydrocarbon industry. In this talk, basic concepts of sedimentary provenance analysis and methods are presented and their application is exemplarily shown on a number of case studies.
Impact of formation conditions on the reactivity of ferrihydrite

Robert Mikutta∗, Anja Freund1, Dennis Lorenz1, Georg Guggenberger1

Institut für Bodenkunde, Leibnitz Universität Hannover

*mikutta@ifbk.uni-hannover.de

In acidic terrestrial and hydromorphic soil environments, ferrihydrite represents an important poorly crystalline hydrous Fe(III) oxide involved in controlling the mobility of organic matter (OM) as well as of other oxyanions. Ferrihydrite precipitated in presence of OM and other solution components such as aluminum (Al) may possess an altered structural composition and, hence, may exhibit a different biogeochemical reactivity compared to pure ferrihydrite. The major objective of this study was to determine the impact of (i) dissolved OM (DOM) and (ii) aluminum on the surface properties of ferrihydrite and to relate this (iii) to sorption properties as a parameter describing the solid-phase reactivity. Ferrihydrite was precipitated in the presence of two different DOM solutions (aromatic versus sugar enriched) and Al by alkaline titration at different molar metal:carbon ratios (0.1 und 1.0) and molar Al:Fe ratios (0.01, 0.1, 0.2). The ferrihydrite phases were characterized for their Fe, Al, and C/N contents as well as their specific surface areas and porosities (by N2 adsorption), and surface charge properties. The reactivity was tested in 168-h adsorption experiments with 100 µM arsenate, followed by a desorption cycle. The exchange of sorbed organic C (OC) with sorbing arsenate was determined in the 0.45-µm filtered supernatants. The modeled adsorption rates, the total amount adsorbed and desorbed arsenate as well as desorbed OC was correlated with structural ferrihydrite properties, thus, supporting the view that the soil solution composition is crucial for modifying the structure and reactivity of poorly crystalline hydrous Fe(III) oxides.
Aided by a team of collaborators (see below) I performed a multi-method investigation of spectacular iridescent glass bottles, most of them being former beer containers, that were dug up in the search of precious opal in central Australia, and that both document the former activity of opal researchers as well as the creative force of weathering directed to anthropogeneous materials.

The most conspicuous property of these beer bottles is their iridescence that largely resembles the play of colour in precious opal found in the same area, and that has made people to believe that the growth of precious opal within the mudstone country rocks is still going on. The weathering layers in fact consist of an opal-like, amorphous, silica-rich substance. However, different from precious opal, it does not constitute a highly ordered framework of equally-sized silica spheres, mimicking the structure of atomic crystals, but it is made of spherical particles in the 10-nm size range that arrange themselves into dense and porous layers, with a very constant periodicity. These layers thus form a Bragg reflector whose optical properties can be modeled with the Bragg equation modified by the refractive index of opal.

Since the 1970s the formation of silica layers on dissolving silicates is explained by a leached layer mechanism, where a diffusion-controlled alkali-depletion front is followed by a dissolution front in steady state. This mechanism is physically impossible. The absence of chemical gradients both within the surface layers as well as in the weathering glass clearly indicate an interface-coupled dissolution-precipitation mechanism.

This mechanism is also responsible for the self-organisation of the amorphous material into regularly spaced layers. Dissolution-precipitation via a nm-sized surface fluid film implies that the precipitating impure silica is saturated with water, and then increasingly dehydrates when silanol groups polymerise into the silica network, releasing water, and reducing the volume of the solid material. If the volume reduction happens at very constant conditions (buried in the ground) it will evolve a constant sequence of dense and porous layers of amorphous silica particles controlled by their attractive forces.

The spacing of the dense layers is in the 100-150 nm range and much closer than previously assumed, before FIB-SEM preparation and imaging. From Bragg relations it follows that the colors visible to the human eye are dominantly 2nd order reflections, where the more intense 1st order reflections are only visible by organisms sensitive to UV light, like insects. It is long established that beetles are attracted by electromagnetic energy ranging from blue (by human perception) into UV. The impact of thrown away beer bottles on the mating behavior of beetles in the Australian Outback has produced prizewinning research before.

I propose that beetles do not only react to the surface structure and absorption colour of weathered brown glass bottles, but also to their strong Bragg reflectance in the UV range. Interference between animal behaviour and mineral surface properties is a completely new field that deserves some interest.


** Awarded with the Ig-Noble price for Biology in 2011.**

Acknowledgements: Thanks to Konrad Hammerschmidt, Richard Wirth, Nicholas Norberg, and Gregor Neusser.
Barium (Ba) is delivered to marine sediments mainly by detrital plagioclase and authigenic barite. The latter is formed in ocean surface water by bio-induced processes, probably triggered by the release of Ba during the decay of phytoplankton biomass resulting in barite precipitation [1]. Due to the link between biological productivity and barite formation, Ba concentration in marine sediments is used as a proxy for paleoproductivity. The reliability of this proxy, however, is challenged by potential desorption of Ba from particles in the water column, detrital input, and especially Ba mobility in anoxic sediments. Better constraints on the marine Ba cycle and on effects of Ba remobilisation in marine sediments are sought to be obtained by investigating Ba isotope variations.

Experimental studies on Ba isotope fractionation have so far focused on precipitation of Ba-carbonates and -sulphates [2,3] and on adsorption of Ba onto Mn-oxides and clay minerals [4]. In order to estimate isotope fractionation during transport of aqueous Ba, as it occurs in anoxic marine sediments, we investigated Ba isotope fractionation during diffusion of dissolved Ba$^{2+}$ ions through a silica hydrogel. Initially, diffused Ba was found to be fractionated by as much as -2.2 ‰ in $\delta^{137/134}$Ba relative to the BaCl$_2$ stock solution. With continuing duration of the experiments, the $\delta^{137/134}$Ba values increased rapidly to about -0.6 ‰ after 27 days. We hypothesise that initial kinetic isotope fractionation caused by Ba diffusion switched to a later control via adsorption of Ba onto the silica hydrogel. Our experiments show firstly that fractionation of Ba isotopes of more than 2 ‰ in $\delta^{137/134}$Ba (~0.7 ‰/amu) are possible under experimental conditions and that the light Ba isotopes are favoured substantially during Ba diffusion through an aqueous medium.

The global lithological map database GLiM: large scale representation of small scale variability

Nils Moosdorf¹, Jens Hartmann¹

¹ University of Hamburg, KlimaCampus, Bundesstraße 55, 20146 Hamburg, Germany (nils_sci@moosdorf.de)

Lithology describes the geochemical, mineralogical, and physical properties of rocks. It plays a key role in many processes at the Earth surface, whose understanding at the global scale requires a high resolution. The new high resolution global lithological map database (GLiM: Hartmann & Moosdorf, 2012) was assembled from more than 75 existing regional geological maps, and translated into lithological information with the help of regional literature. The GLiM represents the rock types of the Earth surface at an “average scale” of 1:3,750,000. The lithological classification consists of three levels. The first level contains 16 lithological classes comparable to previously applied definitions in global lithological maps (Dürr et al., 2005). The additional two levels describe more specific rock attributes in a total of 26 attributes.

The high resolution of the GLiM allows observation of regional lithological distributions which often vary from the global average. The GLiM enables analysis of regional variability of Earth surface processes at global scales. It is currently used to quantify global scale permeability (Gleeson et al., 2011), or strontium isotope ratios (which can be used for provenance studies: Bataille et. al., 2012). While the GLiM features an unmatched spatial and thematic resolution at global scale, it faces consistency issues because of its multiple sources, which may be resolved in following versions.

A gridded version of the GLiM is available at the PANGEA Database (http://dx.doi.org/10.1594/PANGAEA.788537). For other versions, please contact the authors.

Cited references:


Chemical rock weathering in glaciated areas is involved in several feedback loops in the earth system. The fluxes and geochemical characteristics of glacial weathering have been assessed at many single locations, but only a few studies have compared multiple sites to draw broader conclusions.

We present a new database containing data of nearly 100 glaciated catchments, published in more than 45 sources. This database allows analyzing general patterns associated with the effect of glaciers on chemical weathering.

A first analysis of the database shows that cation concentrations decrease with increasing glacial cover. The mean cation concentrations are below the global average of rivers, but cation denudation rates are above global averages because of the high runoff from the catchments. An important coupling in the earth system, that of chemical weathering with climate via CO₂ consumption, depends on the acids involved in the rock weathering. Our study indicates that particularly for high weathering intensity of carbonate rocks, the dominating acid involved is sulfuric acid from oxidized pyrite. This would render chemical rock weathering under glaciers a CO₂ source to the atmosphere, rather than a CO₂ sink.

In contrast to chemical weathering in temperate catchments, the controls prominent in these regions, namely runoff and lithology, are of minor importance in the assessed glaciated catchments. Their influence seems overprinted by the extent of glacial cover, which reduces chemical weathering rates.

The database will be analyzed in depth to identify relations between ion concentrations, weathering rates, stoichiometry and seasonality with potential influencing factors (e.g. dominating lithology). In addition, the importance of chemical weathering under glaciers at global scale will be assessed by extrapolation to current or past glaciated areas.
Infrared spectroscopy allows determining directly the mineralogical compositions of planetary surfaces via remote sensing. For the interpretation of the remote sensing data, laboratory spectra of analogous materials are necessary for comparison.

IRIS (InfraRed for Interplanetary Studies) at the Institut für Planetologie/WWU Münster is a laboratory focused on building a database of mid-infrared spectra for the interpretation of expected data from BepiColombo, Europe’s first mission to Mercury, anticipated to be launched in 2016 and arriving in 2022. On board is a mid-infrared spectrometer (MERTIS-Mercury Radiometer and Thermal Infrared Spectrometer). This instrument allows mapping spectral features in the 7-14 µm range, with a spatial resolution of ~500 m [1].

The main focus of our MERTIS related studies is to assess the effects of surface processing on the material properties. The surface of Mercury is exposed to radiation, heat, and particles, as well as impacts of large bodies and micrometeorites. This affects the structure and thus spectral properties of the mineral phases on the surface. Any infrared study of this material will have to take these effects into account for the interpretation of the MERTIS data [2].

To achieve this, we will use both natural rock samples (e.g. lunar samples), but also analogue materials (e.g., synthetic regoliths). A further focus will be space weathering by analyzing samples that underwent artificial space weathering in laboratory [3].

Here we present first results for the ungrouped achondrite Northwest Africa (NWA) 7325, which was found 2012 in Western Sahara. First analyses revealed a unique sample with high plagioclase and Cr-diopside abundances, and minor occurrences of olivine [4, 5]. Zoned and lath-like plagioclase in veins within pyroxene and areas around mafic silicates indicate a period of rapid cooling and crystallization in the evolution of the rock [4]. The Al/Si and Mg/Si ratios as well as especially the very low Fe content are similar to the surface properties of Mercury. Thus NWA 7325 is speculated to be the first sample from this planet [5]. Here, we present first mid-infrared and Raman data from a sub-sample of NWA7325. Besides further characterization of the mineralogical composition of the meteorite, the (infrared) spectral information will also be useful to compare it with available data from Mercury based on ground based observations (e.g., [6]) or the BepiColombo mission.

Palynomorph- based Paleoenvironmental and Paleoecological implications of upper part of the Chamanbid Formation at the type section, Koheh-Dagh, NE Iran

Moshayedi Maryam

M. Sc., School of Geology, Faculty of Science, University of Tehran, Tehran, Iran

Author e-mail: mmoshayedi@alumni.ut.ac.ir

Palynomorphs and organic matter contents retrieved from thirty four rock samples collected from the uppermost beds of surface section of the Chamanbid Formation at its type section are used to investigate spore-plant relationships and determination of Paleoenvironmental changes. The type section is located about 60 km southwest of Bojnourd, NE Iran. This rock unit consists of Calcareous Shale and Limestone and conformably overlies the Bashkalateh Shale and with a sharp lithological break underlies the Mozdoran Formation. Diverse and well preserved palynomorphs dominated by terrestrial palynomorphs including 39 species of spores (of 28 genera) and 13 pollen species (assigned to 11 genera) are identified. Other palynomorphs, in descending order of abundance are dinoflagellates, fungal spores, foraminiferal test linings, SOM and wood debris which statically studied. The miospores are assigned to Filicopsida, Lycopsida, Ginkgoopsida, Coniferopsida, and Bryopsida. Notable abundance, in the Chamanbid palynofloras of fern spores viz.: Klukisporites, Cicatricosisporites, Cyathidites is interpreted to imply that the host strata accumulated under moist warm climate during the Tithonian. This can be seemingly confirmed with reference to co-occurrence of dinoflagellates such as Systematophora areolata, Tehamadinium spp, Cribroperidinium spp. and Kallosphaeridium spp. and fungal spores. Marked relative abundance of Corollina upward in the section studied seems to indicate progressive dominance of dry warm climate towards the Late Jurassic time. Abundance of non-mature bladed form large brown wood debris, bright SOM, foraminiferal test linings and few numbers of proximate dinocysts indicate that the upper part of the formation deposited in a lagoon that witnessed intermittent marine incursions.

Keywords: Palynomorph, Paleoecology, Paleoenvironment, Koheh- Dagh, Chamanbid
Safe geological CO$_2$-storage in depleted hydrocarbon reservoirs and deep saline aquifers requires fundamental knowledge of the petrophysical, mineralogical and geochemical properties of reservoir and cap rocks. Potential changes of physical rock properties depend on chemical reactions with scCO$_2$ and H$_2$CO$_3$ and affect the integrity of the reservoir. The project COBRA (CO$_2$ Borehole Research Apparatus), funded by the German BMBF (Federal Ministry of Education and Research), deals with all these aspects in full-scale technical experiments prior to field application. The primary aim of the project is to use a full-scale borehole simulator (80bar, 100°C) to evaluate water-rock interaction processes and identify potential leakage pathways within well installations. For this purpose innovative monitoring techniques will be adapted (e.g. Time Domain Reflectometry, TDR) in order to document water-rock interaction in real time during the experiment. The major feature of this project is the full-scale size of this borehole simulator, where rock samples react with CO2-rich fluids. Extraction of fluids is possible during the experiment. Prior to this, small-scale experiments were conducted with three potential storage and cap rocks to provide basis data for the full scale and long-time tests. Investigated rock specimens are Triassic sandstones (reservoir rocks, e.g. from Middle Buntsandstein and Upper Keuper), and a Jurassic mudstone (cap rock, Opalinus Clay) from South-West Germany. The rock samples with a volume of 1 cm$^3$ were displaced in a small autoclave to react with brine (75g/l NaCl) and scCO$_2$ for two weeks at 60°C and 80bar. The mineralogical and geochemical investigations comprise the identification of element and mineral composition by X-ray diffractometry, (micro) X-ray fluorescence, and thin section analysis. The red Middle Buntsandstein sandstone specimens show a mineral composition of quartz, feldspars, ankerite and hematite and clay minerals and a chemical composition of 94.5% SiO$_2$, 2.5% Al$_2$O$_3$, 1.7% K$_2$O and 0.5% Fe$_2$O$_3$. Sandstone from the Upper Keuper is composed of 89.7 % SiO$_2$, 5.9% Al$_2$O$_3$, and 1.8 % CaO, 0.15% Na$_2$O, 0.34% K$_2$O, 0.45 MgO, resulting in a mineral composition of quartz, dolomite, calcite, mica and clay minerals. The mudstone consists of 58.7% SiO$_2$, 23.1% Al$_2$O$_3$, 4.5% Fe$_2$O$_3$, and 4.3% CaO, and 3.2% K$_2$O, and 2.1% MgO, 0.35% Na$_2$O, 0.21% P$_2$O$_5$, and 1.1% TiO2 and has a mineral composition of quartz, dolomite, calcite, mica, pyrite, amphibole and clays. The composition of the resulting fluid is analysed by ion chromatography and ICP-OES in order to document processes of water-rock interaction. Results will be interpreted with regard to alteration processes affecting the storage integrity of the reservoir rocks.
Melt/rock interaction in the deep crust of fast-spreading ridges: evidence from the Wadi Gideah in the Oman Ophiolite.

T. MÜLLER¹, J. KOEPEKE¹, D. GARBE-SCHÖNBERG², P.E. WOLFF¹, H. STRAUS³

¹Institut für Mineralogie, Leibniz Universität Hannover, Germany (t.mueller@mineralogie.uni-hannover.de)
²Institut für Geowissenschaften, Christian-Albrechts-Universität zu Kiel, Germany (dgs@gpi.uni-kiel.de)
³Institut für Geologie und Paläontologie, Westfälische Wilhelms-Universität Münster, Germany (hstrauss@uni-muenster.de)

We undertook three detailed field campaigns in the Wadi Gideah, which is located in the Wadi-Tayin Massif in the southern part of Oman Ophiolite, sampling a complete section through oceanic crust. The southern massifs of the Oman Ophiolite are regarded as the best area for studying primary “normal” fast-spreading ridge processes. We follow the concept of performing all analytical investigations, like analyses of major- and trace elements and isotopes, on the same sample to create data sets as coherent as possible.

Here we present our data obtained so far focusing on first geochemical and petrological logs of the Wadi-Gideah section. The main interest of the project is to focus on mineral chemical- as well as bulk major/trace element compositional evolution with profile depth.

With the structural data obtained during the field campaigns we reconstructed the layered stratigraphy of a virtually undeformed oceanic crust with a thickness of approximately 6 km. We identified pillow lavas (600 m), sheeted dikes (1300 m), varitextured gabbros (400 m), foliated gabbros (1600 m) and layered gabbros (2200 m) as main lithologies from top to bottom (estimated thickness in parenthesis), resting upon a very thin MOHO transition zone (<50 m) on the mantle sequence.

First results based on electron microprobe analyses of the constituent mineral phases of the gabbroic section reveal compositions of XMg (Mg/(Mg+Fe)) of olivine molar from 0.76 to 0.82, XMg in clinopyroxene from 0.82 to 0.91 and An% in plagioclase from 79 to 85 mol% for the layered gabbro sequence. Foliated gabbros display more scattering in the mineral data, and show slightly more evolved compositions of XMg in olivine from 0.65 to 0.74, XMg in clinopyroxene from 0.74 to 0.87 and An% in plagioclase from 62-82 mol%. Compositions of varitextured gabbros are more evolved as shown by An% plagioclase varying from 60 to 85 mol%. These general trends in mineral chemistry are also observed for bulk rock major and trace element data. While layered gabbro cumulates show only minor variability for most elements over the entire thickness, systematic trends in La/Sm, La/Yb, Zr/Hf, Nb/Ta, Cr/Zr etc. can be observed in the transition from foliated gabbros and varitextured gabbros towards sheeted dikes and basalts. In addition to the bulk rock data, trace element data for the different minerals will also be obtained. The acquisition of isotopic data (Sr, Hf, Nd, S) is in progress.

The combined petrological and geochemical data, together with structural data for the gabbro section to be obtained with EBSD technique, will provide a coherent data base for testing existing conceptual models for the accretion of fast-spreading oceanic crust. Far reaching goals include to elaborate a complete mass balance and to establish the hydrothermal alteration cycles for deep fast-spread oceanic crust.
The silicate Earth’s Nb/Ta paradox: terrestrial versus extraterrestrial origin

C. MÜNKER1, R.O.C. FONSECA2, T. SCHULZ3, M. PATYNIAK1

1 Institut für Geologie und Mineralogie, Universität zu Köln, Germany, c.muenker@uni-koeln.de
2 Steinmann Institut, Universität Bonn, Germany
3 Dept. für Lithosphärenforschung, Universität Wien, Austria

When compared to chondrites, the silicate Earth exhibits a marked Nb deficit relative to its geochemical twin Ta [1]. This observation is surprising, as both elements are considered lithophile. Therefore, this feature is commonly referred to as “terrestrial Nb paradox”. Many explanations for this paradox that favour the presence of hidden silicate reservoirs, but these models cannot explain the observation that the Early Archean silicate Earth was already depleted in Nb, as evident from Nb/Ta in early Archean basalts and komatiites. Moreover, several hidden reservoir models [e.g., 2] hing on Nb/Ta measurements in rocks that only comprise volumetrically insignificant portions of the Earth’s silicate rock record. This would so far leave core formation at high pressures in a reduced early Earth as the only fully viable explanation for the terrestrial Nb paradox [3].

To assess the possibility if compositional variations on small planetesimal precursors of the Earth can also account for the Nb deficit, we investigated in a combined geochemical and experimental approach the role of low pressure metal segregation. We performed high precision measurements of HFSE concentrations employing isotope dilution and ion exchange separation on representative groups of iron meteorites, their sulfide inclusions and achondrites. By employing such a protocol molecular interferences on many HFSE, in particular for iron meteorites and sulfides rich in transition metals, can be avoided. Our results indicate that reduced achondrites exhibit strongly subchondritic Nb/Ta (as low as 1), whereas more oxidised achondrites (e.g., eucrites) exhibit near chondritic Nb/Ta. As expected, iron meteorites exhibit extremely low Nb-Ta concentrations (<1 ppb), whereas Nb can be strongly enriched relative to other HFSEs in sulfides (to ppm levels).

To simulate metal-sulfide segregation on small planetesimals further, we also performed experiments at ~1300°C and 10 kbar using a piston cylinder apparatus. Measured sulfide-silicate partition coefficients for Nb are ca. 2 orders of magnitude higher than for Ta. At fO2 lower than IW-3, Nb becomes chalcophile while Ta remains lithophile, and the silicate melt is thus depleted in Nb, as found in our study for more reduced achondrites.

Collectively, our results reveal that Nb may already be sequestered into planetesimal cores at low pressures and low fO2, provided that immiscible sulfide and metal liquids were segregated. Therefore, the silicate Earth’s Nb deficit may be be inherited from differentiated planetesimals that did not fully equilibrate with the proto-Earth upon their accretion. The silicate Earth’s missing Nb may therefore be hosted by the terrestrial core, and the Nb deficit in the silicate Earth may provide a measure of incomplete core-mantle equilibration during the early history of the Earth.

Zinc Mineralisation at Undur (Mongolia): future prospects

Munkhtsetseg Tumur and Ralf Milke

Freie Universität Berlin, AB Mineralogie-Petrologie, Malteserstr. 74-100, 12249 Berlin

1 bilegmaa04@yahoo.de

Mongolia is one of the major countries providing metal ore deposits for the 21st century. Exploration activities were strong until 1990 in collaboration with the Sowjet Union and the GDR. During the last decade the developments on the metal markets have sparked a second run on Mongolia's ore ressources, now lead by international mining trusts. We present results on ore petrography from the hydrothermal Zn-mineralisation Undur in eastern Mongolia that was explored by five drill-holes in 2008.

The sulphide ores are bound to quartz veins hosted by permian volcano-sedimentary rocks that are altered by silicification and pyritisation around the mineralised zones. Two such focus areas have been identified in close vicinity, and the most promising Northern zone, around 600 x 400 m in size, was the target of drilling.

The dominant sulphide minerals are sphalerite and pyrite. Pyrrhotite is omnipresent as small precipitates unmixed from sphalerite. Arsenopyrite occurs widespread but always as a minor ore component. Galena is restricted to a few investigated samples. Other minor sulphide minerals are marcasite and chalcopyrite. Intense search after other sulphide phases in the available samples by ore microscopy and electron microscopy revealed no additional species. The reaction of ore-forming fluids with the country rock has lead to abundant crystallisation of chamosite that frequently occurs in the quartz veins and trapped into the sulphides. Late pore fillings consist of spherulitically crystallised siderite with patchy Ca-Mg-Fe zoning. Mutual replacement textures between sulphide minerals indicate complex non-equilibrium reaction processes following primary crystallisation. Especially pyrite occurs in several generations, including brecciated early pyrite, massive pyrite, replacement pyrite after arsenopyrite and marcasite, and late-stage fracture fillings.

The presence of chamosite is in line with assumed ore formation temperatures below 300°C based on fluid inclusion investigations. The original Fe-concentration in sphalerite was reconstructed by combining electron microprobe data with re-integration of unmixed pyrrhotite by image processing. The high original Fe content near 20 mol% FeS component indicates crystallisation at a very shallow near-surface level.

The most important trace elements in the sulphides are Ag in Galena of about 5000 wt-ppm, and Ga in Sphalerite of about 2000 ppm, where especially the latter could become important for economical use.

The location of the potential ore deposit Undur close to the Main Mongolian Lineament speaks for a tectonically controlled mineralisation process. The relation between alpinotype tectonics in the central Asian orogen, jurassic and cretaceous magmatism in the region, and hydrothermal ore deposit formation is a matter of debate, with large implications for further exploration activities.
Evaporitic sulfate concretions, Moodies Group (~3.2 Ga, Barberton Greenstone Belt, South Africa)

SAMI NABHAN¹, CHRISTOPH HEUBECK², MARTIN HOMANN³

¹sami.nabhan@fu-berlin.de
²christoph.heubeck@fu-berlin.de
³martin.homann@fu-berlin.de

Quartz-rich sandstones of fluvial to supratidal facies in the Archean Moodies Group (~3223 Ma, Barberton Greenstone Belt, South Africa) include several regionally traceable beds with common to abundant nodular concretions of chert and megaquartz pseudomorphs after gypsum and barite crystal shapes. Electron microprobe analyses confirm this assessment by showing remnants (<20 µm) of these minerals and of carbonates within the concretions but not in the host rock. In addition petrographic thin sections show characteristic mottled extinction of poikilotopic gypsum cement, now silicified.

Concretions reach up to 8 cm in diameter, are stratiform and commonly associated with aqueously reworked fine-grained tuffaceous sediment of originally rhyodacitic composition. Detailed geological mapping indicates a braided fluvio-deltaic setting, transitional to sandy supratidal flats which were colonized by microbial mats and occasionally underwent desiccation; the setting is clearly nonmarine. Gypsum pseudomorphs commonly grew inward into concentric hollow or fluid-filled cavities, suggesting mantling of an unknown precursor mineral by gypsum, followed by its dissolution; some gypsum crystals also grew displacively outward. Nodule growth apparently took place under early diagenetic conditions in unconsolidated sediment in the vadose zone, dominated by frequent capillary fluctuations of groundwater brines under mildly evaporative conditions. Partially reworked rhyodacitic tuffs may have delivered alkali cations such as Ca, Na, Ba, and K while carbonates were supplied by atmospheric silicate weathering of mafic to ultramafic volcanic rocks. The provenance of sulphate ions is unknown but may have included microbial and/or abiotic disproportionation of volcanic S or SO2.

Nodular concretions of the Moodies Group may represent the oldest terrigenous evaporites known to date. Their chemical and isotopic composition constrains the occurrence of sulfate in the atmosphere and hydrosphere of the Early Earth, its interaction with the emerging biosphere, Archean weathering, possibly local climatic conditions, and vadose-zone hydrodynamics of the world’s oldest well-preserved siliciclastic shoreline system.
Molybdenum (Mo) isotopes are increasingly widely applied in the Earth Sciences, primarily to investigate the oxygenation of Earth’s ocean and atmosphere. The respective models rely on the understanding of the recent Oceanic Mo isotope cycle. Early studies indicated homogeneous ocean water ($\delta^{98}$Mo = 2.3‰, relative to our standard that is 0.25‰ below NIST SRM 3134), a continental input of $\delta^{98}$Mo c. 0.0‰ and Mo sedimentation split into an anoxic sink ($\delta^{98}$Mo similar to ocean water) and an oxic sink ($\delta^{98}$Mo = -0.7‰). While first order models based on these parameters improved our understanding of the oxygenation history of the atmosphere and hydrosphere, more recent studies show that matters are significantly more complex.

Published open ocean water samples (n > 180) from different oceans and depth confirm that open ocean water is homogeneous in $\delta^{98}$Mo, averaging 2.34‰ (± 0.1‰; 2 SD). Sedimentary Mo is always lower in $\delta^{98}$Mo than dissolved Mo in the overlying water column. Fe-Mn crusts and pelagic sediments show a $\delta^{98}$Mo of around -0.7‰, i.e. an offset to ocean water of c -3.0‰. This offset is related to equilibrium fractionation between dissolved tetrahydral- and adsorbed octahydral Mo oxyanions. Suboxic to anoxic sediments from continental margin settings, another potentially important sink, show variable $\delta^{98}$Mo values between oxic and euxinic sediments. Mo deposited under strong euxinic conditions shows $\delta^{98}$Mo as heavy as that of ocean water i.e. the main Mo source, due to quasi complete Mo scavenging. In the recent ocean this is only observed in the Black Sea below 400m depth. The residual Mo depleted bottom water of the Black Sea shows $\delta^{98}$Mo significantly above open ocean water (≤ 2.9 ‰). Such high $\delta^{98}$Mo are found not only in the waters of restricted basins but also in shallow shelf environments (Wadden Sea) where Mo scavenging outruns remixing. These anomalies reflect preferential scavenging of light Mo isotopes under anoxic conditions, or via association to organic matter. The early estimates on the continental runoff assumed $\delta^{98}$Mo values coincident with silicate rocks and molydenites (-0.1 to +0.3‰). More recent molybdenite compilations show a very broad range of $\delta^{98}$Mo (-0.4 to +2.3‰) averaging 0.4 ‰. Dissolved river load is similarly variable (0.14 to 2.4‰), but the resulting volume normalized average tends to be enriched in heavy Mo isotopes. Proposed causes for the latter observation are soil retention of light Mo isotopes, incongruent weathering of igneous bedrock or weathering of exposed marine sediments.

While the global continental run off can be modelled reasonably well with a $\delta^{98}$Mo of ≤0.4 ‰, large variations in the data sets hinder a conclusion on whether there is an offset between continental crust and dissolved river load on a global scale. A permanent bias would however require a continuous net volume increase of a hidden reservoir with low $\delta^{98}$Mo. Further, given the processes involved, it appears adventurous to assume a constant $\delta^{98}$Mo for the continental run off over geological times.

To sum up: recent studies show that there is neither a perfect archive nor a perfect measure of the continental run off in terms of $\delta^{98}$Mo. To improve global mass balance models and paleocean reconstructions, significantly larger data sets are needed to separate local from global effects. Further, studies that lead to a better understanding of the processes involved will not only reduce uncertainties in global models, but also allow to extend the use of Mo isotopes to a much larger number of applications in geo(bio)chemistry.
Microtaphofacies: Applying the concept to Cenozoic carbonates

James H. Nebelsick

nebelsick@uni-tuebingen.de

Microtaphofacies encompasses the taphonomic analysis of indurated limestones using methods applied during the study of carbonate microfacies. It differs from the taphonomic analysis of three dimensional components with respect to the dimension involved (2 D), the level of observation (down to µm scale), descriptive possibilities, quantification techniques and application to different rock units. Indurated limestones, as such, offer restricted possibilities for taphonomic analysis as fossil components cannot easily be isolated and observed as such. Taphonomic terminology is also derived largely from investigations on three dimensional objects in Recent environments. Carbonate environments are thus underrepresented in taphonomic analysis despite the fact that such an approach is inherent in the microfacies analysis. The preservation of constituent components, resultant grain sizes and carbonate fabrics are all directly associated with taphonomic processes and lead to limestone classification as well as interpretation of depositional environments.

Potential advantages of applying taphonomic analysis to carbonates in thin section include the possibility of recognizing complex interaction and sequential succession of processes including abrasion, fragmentation, encrustation and bioerosion. It is also possible to assess most constituent components of the limestones regardless of their state of preservation. Microfacies techniques allow for application of rigorous statistical techniques including multivariate analysis of quantified taphonomic data. Standard sampling methods allow both vertical and horizontal changes to be followed. Early diagenetic features such as dissolution of aragonite can also be followed. The high resolution interpretation of ecological parameters is also enabled by the direct correlation of component diversity, taphonomic features, and sedimentary environments.
Organic rich marls of the so called “Bächentaler Bitumenmergel” which are cropping out in an open pit mine in the Karwendel area of Northern Tyrol were investigated regarding their source rock potential, their organic geochemical characteristics and their isotopic composition. The black marls of the investigated succession were deposited during the Lower Toarcian oceanic anoxic event (OAE) in the deeper parts of a local half-graben structure. The formation of the basin was most probably triggered by extensional tectonics.

The sampled section has a total thickness of 36 m. The succession starts in the Pliensbachian with hemipelagic to pelagic wackestones to packstones followed by a carbonate breccia at the top. A thin clayey, weathered layer of vulcanoclastic origin represents a transitional horizon and the beginning of the Lower Toarcian black shale sedimentation. The bituminous, fine grained mudstones and marls of the “Bächentaler Bitumenmergel” were deposited during the whole Lower Toarcian with a total thickness of about 25 m. The top of the succession is characterized by an Upper Toarcian alternating sequence of bioturbated limestones and grey marls, both free of organic matter.

The black marls of the investigated succession can be grouped into three units regarding the gained results. The lower part of the succession, 6 m in thickness, shows TOC values below 3 % and hydrogen indices (HI) up to 600 mg HC/g TOC. Carbon isotopes of the marls vary between boundary values of -2 and -13 per mill delta $^{13}$C PDB. The middle part with a thickness of about 10 m is characterized by generally higher TOC contents of up to 13 %. The HI and carbon isotope values vary between 600 and 700 mg HC/g TOC and -2 to -4 per mill delta $^{13}$C PDB, respectively. This unit ends abruptly at a layer of carbonate debrite. The third part of the black marl interval is characterized by more or less constant TOC values of about 2 % and strong negative excursions of HI and carbon isotope values. The T$_{\text{max}}$ data for all samples vary between 416 and 425 °C indicating low maturity of the entire succession.

Due to our results the investigated black marls of Bächental represent high quality, oil-prone source rocks. The depositional environment of the basin was characterized by suboxic to anoxic conditions for the lower part of the black marls followed by an abrupt change to strongly anaerobic conditions with salinity stratification of the water column in the middle part. The layer of debrite obviously disturbed the anoxia and triggered a shift to less reducing conditions for the upper part of the black marl development.
Formation Mechanisms of Sulfate and Sulfide Scalings in the Geothermal Power Plant of Soultz-sous-Forêts: Insights from Sulfur Isotope Analyses

Fabian Nitschke(1), Julia Scheiber(2), Thomas Neumann(3), Utz Kramar(4)

1 fabian.nitschke@kit.edu
2 scheiber@soults.net
3 neumann@kit.edu
4 utz.kramar@kit.edu

Abstract

Scaling formation in surface installations of geothermal power plants can substantially affect power production by impairing the heat transfer and reducing pipe diameters. In addition, the mineral deposits can incorporate natural occurring radioactive nuclides in the crystal lattice during precipitation and have to be regarded as a potential hazard to health and environment. A profound understanding of formation mechanisms should facilitate the prevention of scaling. Therefore, fluid samples and scalings from the geothermal power plant at Soultz-sous-Forêts were investigated in detail. Fluid shows a total salinity (TDS) of 92 g/l and can be classified to a Na-(Ca)-Cl-type. Considerations of the saturation state reveal a slight oversaturation with respect to celestine, whereas barite is just below saturation. X-Ray diffraction measurements together with scanning electron microscopic observation reveal that the scalings consist of barite-celestine solid solution (Ba-Sr-sulfates) interlayered with very fine layers of galena (Pb-sulfide). The mineralogical composition could be confirmed by X-ray fluorescence analysis showing a bulk composition of Ba (31.7 – 34.6 mass-%), Sr (10.8 – 12.1 mass-%), Pb (6.2– 12.4 mass-%) and S (13.1 – 14.5 mass-%) for the sulfates, and Pb (66.6 mass-%) and S (11.7 mass-%) for the sulfidic part of the scalings. Other metals/metalloids like Sb (5.6 mass-%), Cu (4.2 mass-%), As (2.3 mass-%) and Fe (2.0 mass-%) are present in minor amounts in the sulfides. Sulfur isotope studies show strong fractionation between the sulfate (δ^{34}S = +15‰) and sulfide (δ^{34}S = -12‰) phases. This indicates that bacterial sulfate reduction occur temporarily initiating sulfide precipitation from sulfate-rich fluids. The layered structure of the scalings can be correlated well with the operation state of the plant. Accordingly, sulfate layers precipitate under regular operation conditions, whereas sulfides formed during shut off times in stagnant waters.
The impact of volcanic ash in jet turbine engines

Marcus Nowak1, Christopher Giehl1, Holger Marxer1, Richard Brooker1,2

1Department of Geosciences, Univ. Tübingen, Germany; 2Department of Earth Sciences, Univ. Bristol, UK

The grounding of commercial aircraft throughout Europe due to the long lasting Eyjafjallajökull volcanic eruption in Iceland April 2010 and in South America due to the Puyehue volcano in the Chilean Andes in June 2011 has focused public attention on the potential dangers of flying jet engines through volcanic ash clouds. A severe problem is the melting of volcanic ash in the combustion chamber to form a built up of silicate material on hot turbine parts behind the combustor. This restricts flow through the turbine and ultimately causes the engine to stall.

In this study we highlight the importance of the volcanic ash composition in this process. We have simulated the melting on a range of typical volcanic compositions in a combustion flame and deposition on Nickel Super Alloy (NSA), a material commonly used for turbine hot section vanes and blades. We investigate the ‘wetting’ of the surface with melt and the adhesion properties of the deposit when cooled, as well as the importance of melting rate of material inside the combustion flame. For testing the effect of volcanic ash on turbine blades we have set up a simplified turbine hot section test system using an acetylene-oxygen combustor with a normal to mildly oxidizing flame. The maximum $T$ is about 3300°C in the flame core of 5 to 10 mm length just after the nozzle. The $T$ of the acetylene-oxygen flame jet decrease 2000°C/10 mm in the high-$T$ flame core region and about 100 to 50°C/10 mm in the jet of the acetylene flame. An Al$_2$O$_3$ tube was used for the volcanic ash delivery (<125 µm for most powders) 1 to 2 cm after the tip of the high-$T$ flame core. The particle mean velocity is about 15 m/s for particles in the 50-160 µm size range. The $T$ of particles is a complex function of particle size, flame-heat-transfer coefficient (heat conduction and heat capacity), particle travelling speed, and flame $T$ distribution in the direction of flame movement. We estimated the travel time for ash particles in the 80 mm long flame with a travel way of about 50 mm and an exhaust flame speed of 15 m/s to be 6 ms comparable to the residence time of ash particles in the combustor and hot turbine section of modern jet engines. As target we used a NSA turbine blade and NSA sheets 0.5 mm thickness, 6 cm length and 1 cm width. A microscope with video DV camera was used to monitor the interaction between the blades and the volcanic ash heated and transported with the acetylene flame.

First results show that the conditions that lead to the initial deposition of melt on the turbine vanes and blades are important as this allows a subsequent rapid accumulation of more material until a catastrophic build up and clogging of vane and blade air film cooling systems occurs. The nature of this initial coating also dictates the ease of removal by ‘in flight cooling’ that involves closing down the engines, allowing the melt to form glass and then relying on thermal shock to dislodge the material from the turbine vanes. We demonstrate that the range of volcanic ash compositions commonly found in nature have different properties that effect both these processes. It remains unclear which compositions and procedures (if any) are used by the aero industry, but previous standard tests (Arizona Road Dust Test) may not be realistic and may not accurately address the true extent of the risks involved.
Cyclic ductile and brittle deformation related to coseismic thrust fault propagation – structural record at the base of a basement nappe (Preveli, Crete)

Jens-Alexander Nüchter¹, Sara Wassmann², and Bernhard Stöckhert³

¹jens.nuechter@rub.de
²sara.wassmann@rub.de
³bernhard.stoeckhert@rub.de

The structural record at the base of a basement nappe (Preveli nappe, Crete, Greece) thrust upon sedimentary rocks is investigated, aimed on understanding mechanisms which result in decoupling of the thrust sheet from its original substratum. We identify several superimposed deformation stages, each with peculiar characteristics in structural style and indications of episodic deformation at initially high differential stress. The final stage involves formation of a matrix supported breccia transected by pseudotachylites, comprising the lowermost 30 m of the nappe. Brecciation and pseudotachylite formation occurred in a single event and structures were not modified afterwards. Complete solidification of breccia and composition of phengite crystallized during devitrification of pseudotachylites place the sequence of events into the middle crust. We propose a model relating episodic deformation and cyclic stress history to propagation of a thrust fault in a limited number of seismic events. Terminal brecciation and frictional fusion record passage of the fault front beneath the site of observation and decoupling the thrust sheet. Absence of discernible further deformation is consistent with negligible basal friction during transport as a nappe. Brecciation and pseudotachylite formation mark the switch from a history of repeated coseismic loading and postseismic stress relaxation in the plastosphere, driven by seismic events on the approaching thrust fault, to passive transport with deformation localized in a weak thrust plane. For a sequence of superimposed ductile to brittle structures, our model provides an alternative to progressive cooling and exhumation concomitant with deformation over millions of years.
Subduction processes in Anatolia – occurrence, timing and consequences for plate dynamics

Oberhänsli, R.¹, Candan, O.², Koralay, E.³, Çetinkaplan, M.², Pourteau, A.¹, Bousquet, R.³

¹roob@geo.uni-potsdam.de; Amaury@geo.uni-potsdam.de;²osman.candan@deu.edu.tr; ersin.koralay@deu.edu.tr; mete.cetinkaplan@deu.edu.tr;³bousquet@min.kiel.de

To decipher the palaeogeography of the Neotethys Ocean in Anatolia, we investigate metamorphic rocks from high-pressure (HP), low-temperature (LT) belts formed during the closure of several oceanic branches, building up the present Anatolia continental micro-plate. During the last 15 years, we documented widespread occurrences of HP-LT metasedimentary and metavolcanic rocks throughout Anatolia. Two coherent HP-LT metamorphic belt, the Tavşanlı Zone and the Ören-Afyon-Bolkardağ Zone, can be followed north of their non-metamorphosed equivalent (the Tauride Carbonate Platform) from the Aegean coast and NW Anatolia to southern Central Anatolia. Timing and P–T conditions we determined for the HP metamorphism of the Ören-Afyon-Bolkardağ Zone (70–65 Ma; 1.0 GPa/330 °C) contrast those published for the overlying Tavşanlı Zone (88-78 Ma; 2.4 GPa/500 °C). These belts trace the suture of a Neotethys oceanic branch connecting the Vardar suture in the Hellenides to the Inner Tauride suture along the southern border of the Central Anatolian Crystalline Complex. The eastward continuation of these belts remains enigmatic. The southern flank of the Tauride Carbonate Platform is outlined by another HP-LT metamorphic belt, in the Alanya and Bitlis regions. In the Bitlis Massif (SE Anatolia), we recently found eclogites (1.9-2.4 GPa/480-540°C) in a calc-arenitic meta-sedimentary sequence within the Barrovian-type metamorphic basement. Peak metamorphism was dated to 84.4–82.4 Ma (U/Pb on zircon). On the other hand, we previously reported carpholite-bearing metasedimentary rocks forming the low-grade cover of the Bitlis massif that recorded 0.8–1.2 GPa/340-400°C at 79–74 Ma (Ar/Ar on white mica). These differences in timing and P–T conditions between the eclogitic and the blueschist-facies units indicate that different metamorphic peak conditions were reached at different times and rapid exhumation from approx. 65 to 35 km depth in a single subduction zone. Syn-decompression HT overprint of the eclogites can be related to asthenospheric flow provoked by subducting slab break off. The Bitlis HP rocks sample a subduction zone that separated the Bitlis–Pütüre (~Bistun?) continental block from the South-Armenian block, further north. The most likely lateral continuation of this HP belt is found to the west, in the Alanya Nappes, south of the Taurides, where eclogites and blueschists yielded metamorphic ages around 80 Ma. The evolution of the Alanya–Bitlis HP belt clearly contrasts with that of the northerly Tavşanlı and Ören-Afyon belts, testifying an additional, more southerly, subduction zone, and thus an additional oceanic branch. South of, the Bitlis complex, post-Eocene blueschists witness the separation of the Bitlis–Pütüre block from the Arabian plate, and southward migration of the subduction zone between Late Cretaceous and Oligocene. Our investigations throughout Anatolia lead to conclude that, during Late Cretaceous, continuous convergence between Africa and Eurasia engendered the simultaneous consumption of several, separated branches of the Neotethys Ocean and amalgamation of different terranes. This complex geodynamic setting and its time frame are coupled to processes in the over-riding lithosphere, such as hydration, back-arc extension, and asthenospheric flow, which were thought crucial for the rise of the Eastern Anatolial Plateau. Based on thermodynamic modelling, we show that low densities (required for plateau rise) and reduced seismic velocities inferred from geophysical observations, interpreted as complete replacement of lithospheric- by asthenospheric mantle, can be explained by partial hydration of the lithospheric mantle wedge during protracted subduction.
Detailed facies and sequence analysis of carbonate platforms based on ditch cuttings – a case study from Oman

Michael Obermaier 1, 2; Daniel Bendias 1; Thomas Aigner 1

1: University of Tübingen, Sedimentary Geology Research Group, 72076 Tübingen, Germany
daniel.bendias@uni-tuebingen.de, t.aigner@uni-tuebingen.de

2: current address -Shell Projects and Technology, 2288GS Rijswijk, Netherlands
michael.obermaier@shell.com

While seismics allow to interpret large-scale depositional geometries, well logs can give valuable information about subsurface rock properties and fluid content. However, to fully understand a geological system it is inevitable to investigate real rocks from the subsurface. Since cores are often limited to reservoir intervals, detailed geological knowledge (lithofacies types, depositional environments) about entire formations are scarce and can make predictions about lateral and vertical facies changes difficult. The systematic analysis of cuttings from non-cored intervals with good sample recovery (2-3 meters) can give more detailed insights into subsurface facies and depositional environments.

In this case study, cuttings from the Sudair and Jilh Formations in the subsurface of Oman were investigated. These two formations were deposited in a flat epeiric carbonate ramp setting and comprise mainly carbonates (dolomite) with subordinate shale, anhydrite and fine sandstone units. Facies analyses in outcrop analogs indicate an inner ramp position with depositional environments ranging from a coastal marsh to a distal high-energy shoal setting. Foreshoal or offshoal facies were not detected.

The semi-quantitative analysis of carbonate and siliciclastic cuttings reveal, besides lithology, also information about carbonate texture, components, pore type and pore fill. The combination of lithology, Dunham texture and carbonate components (ooids vs. peloids vs. bioclasts), supported by sedimentary features such as rootlets provide information on subsurface depositional environments. To determine the depositional environments, background knowledge about the geological setting is essential. Synthetic cuttings were generated by crushing outcrop samples of time-equivalent strata and comparing them to real subsurface cuttings. A general facies atlas based on cuttings could be established and the respective depositional environments could be interpreted.

Vertical changes in cuttings (lithology, texture, components) were used for sequence stratigraphic interpretations. The resulting multi-fold cyclicity (> 10s of meters) builds the basis for regional scale correlations and highlights thickness and facies changes. In combination with certain well logs (Por, SH, SW) a link between facies and reservoir properties can be established.

The authors would like to gratefully thank Petroleum Development Oman (PDO) for project sponsoring and together with the Ministry of Oil and Gas of the Sultanate of Oman for permission to publish this paper. Special thanks go to Suleiman Al-Farqani (PDO) for his introduction into cuttings analyses. We are also thankful to Shuram Oil and Gas (Muscat, Oman) for providing fieldwork logistics. Advanced Logic Technology (ALT, Luxembourg) is thanked for access to the WellCAD software.
Estimating magma residence times by diffusion modeling of Fe-Mg chemical and isotopic zoning in natural olivines

M. Oeser1,*, S. Weyer2,*, R. Dohmen3,*, I. Horn4,*, S. Schuth5,*

1 m.oeser@mineralogie.uni-hannover.de
2 s.weyer@mineralogie.uni-hannover.de
3 ralf.dohmen@rub.de
4 horn@mineralogie.uni-hannover.de
5 s.schuth@mineralogie.uni-hannover.de

* Leibniz Universität Hannover, Institut für Mineralogie, Callinstr. 3, D-30167 Hannover
# Ruhr-Universität Bochum, Institut für Geologie, Mineralogie und Geophysik, Universitätsstr. 150, D-44780 Bochum

Recent studies have shown that chemical diffusion at magmatic temperatures generates Fe and Mg isotope fractionation in olivine that exceeds potential equilibrium isotope fractionation by an order of magnitude [1,2]. Accordingly, diffusion-generated Fe-Mg chemical zoning in olivine should be coupled with Fe-Mg isotopic zoning. In this case, magma residence times of crystals can be derived by adequate modeling of both, chemical and isotopic zoning.

We investigated this approach on olivine grains in basaltic rocks from the Massif Central volcanic region (France). Large, chemically zoned olivines were analyzed by femtosecond laser ablation MC-ICP-MS. With this technique an external precision of ±0.10‰ (2 SD, based on replicate analyses of glass standards) can routinely be achieved for both $\delta^{56}$Fe and $\delta^{26}$Mg.

Several olivines show significant Fe-Mg isotopic zoning (of up to 1.5‰ for $\delta^{56}$Fe and up to 0.8‰ for $\delta^{26}$Mg) that is coupled with the chemical zoning expressed as Mg#. Furthermore, the Fe-Mg isotopic zoning profiles are inverse, resulting in a negative correlation between $\delta^{26}$Mg and $\delta^{56}$Fe. This strongly indicates that the observed zoning was generated by diffusion of Fe into and Mg out of the olivine during magma evolution (e.g. [3]). Consequently, the clearly diffusion-generated chemical and isotopic zoning in such olivine crystals can be used to estimate the duration of chemical diffusion between crystal and melt. This duration can reflect the residence time of crystals in a magma chamber before an eruption [4]. Simplified and independent modeling of Fe- and Mg-chemical and isotopic zoning of the investigated olivines points to magma residence times between 0.5 and 10 years, which is similar to the short timescales determined by diffusion modeling of chemical gradients in olivines hosted in basaltic lava flows from Mt. Etna [5].

A major focus of our project is to apply our developed technique to olivine crystals in MORBs to improve our knowledge on magma evolution at mid-ocean ridge settings. Olivines from the Mid-Atlantic Ridge (DSDP holes 332A and 396B) and the Costa Rica Rift (ODP hole 896A) show both normal zoning and reverse zoning of forsterite (up to 4 mole percent). Fe-Mg isotopic profiles will be determined to prove whether the chemical zoning was generated by diffusion and thus provides information on magma residence times of these olivines. Furthermore, some of the MORB samples contain glassy parts with unzoned olivine phenocrysts. This may provide an opportunity to determine potential equilibrium isotope fractionation between melt and olivine, as we can analyze the Fe-Mg isotopic composition of both glass and olivine in situ.

References:
Petrological and geochemical investigations of Late Intermediate Period ceramics, southern Peru (Poster presentation)

Daniela B. Oestreich¹, Ulrich A. Glasmacher², Markus Reindel³, Heike Otten⁴

¹Daniela.Oestreich@geow.uni-heidelberg.de
²Ulrich.A.Glasmacher@geow.uni-heidelberg.de
³Markus.Reindel@dainst.de
⁴Heike.Otten@dainst.de

The Late Intermediate Period (A.D. 1000-1400; Unkel, 2006) is the last period in the low lands of southern Peru before the Inca people migrated from the High Andes into this region. The people of the Late Intermediate Period manufactured ceramics that are different in shape, decoration, and engobe between northern and southern Peru. In the low lands of southern Peru, the Chillo excavation site revealed a large number of ceramic artifacts and sherds. Those ceramic artifacts and sherds were classified by Otten (2009). In addition to describing the decoration a division into fine and coarse ceramic and four subgroups was done. Criteria for the subgroups were color, hardness and temper (texture, grain size and distribution) of the ceramics. Based on the characterization of Otten (2009) 47 ceramic artifacts and sherds were sampled to represent all types of ceramic artifacts. XRD, thin sections, ICP-ES and ICP-MS analytical techniques were applied to reveal the mineral and chemical composition. Furthermore, the mineral composition of the engobe was determined by using Raman spectroscopy. As one of the research questions was to determine the source areas for the clay and temper adobe of pre-Paracas, Paracas, Nasca, and recent time, brick samples of recent time, clay mortar from Chillo houses, Quincha fired and unfired clay, and geological clay deposits of various formation times were included in the analytical research. The red/purple engobe are hematite, black are carbon and jacobsite, white are anhydrite, and yellow are a mixture of different pigments. The main mineral phases are quartz, plagioclase (albite, anorthite), hematite, mica (muscovite), talc and frequently amphibole (actinolite) and goethite. Regarding the chemical composition, the ceramics could well be correlated. Except two ceramics (2501-215, 2501-218) which have shown some differences in major and trace element distribution and also higher concentrations in rare earth element distribution (Fig. 1).

Figure 1: Major, trace and rare earth element distribution of the Chillo ceramics.

According to the results a local clay horizon could be excluded as a potential raw material source. However the results of the other samples suggested a common or similar origin of raw materials. Notes on imported raw materials have not been established.
In anoxic aquifers, the iron redox system often plays a major role in biogeochemical electron transfer processes as well as in transformation processes of pollutants. To date, little is known about the potential role of natural organic matter on redox processes under iron reducing conditions. To address this question, we studied redox speciation of model quinones upon interaction with iron minerals.

Specifically, we investigated in detail the electron transfer process between surface-bound Fe(II) at goethite and AQDS (anthraquinone-2,6-disulfonate) in equilibrium conditions. Several pH conditions were evaluated: 6, 7 and 8, as well as the presence of phosphate. Also, the reversibility of the redox reaction as well as the electron balance were addressed, using spectroscopic techniques to determine the redox speciation of the AQDS.

Results show that a fast, reversible electron transfer reaction occurs at neutral and basic pH values, but no reaction takes place at pH 6. In the case of an electron transfer reaction, a close electron balance is achieved, although a fraction of Fe(II) cannot be recovered with traditional acidic extraction techniques.

Also, knowing the redox speciation of the AQDS, it is possible to calculate a Nernst potential for the system at equilibrium, thus reporting an estimation of the redox potential of the Fe(II)-goethite system.
δ44/40 Ca as tracer of changes in the Cenozoic calcium isotope budget

St. Pabich¹, N. Gussone¹, K. Rabe¹ and B.M.A. Teichert²

¹WWU Münster, Institut für Mineralogie, Germany, stephanie.pabich@uni-muenster.de, ²WWU Münster, Institut für Geologie und Paläontologie, Germany

To gain a better understanding of earth’s climate changes, the reconstruction and understanding of the oceanic chemical and isotopic evolution over geologic time is one of the main aims in earth science. In this context, Ca as one of the major elements in the ocean is especially important because its variation in concentration is controlled by different factors including the CO₂ concentration of the atmosphere, continental weathering and Ca carbonate sedimentation. Imbalances in input and output of Ca to the ocean will cause a shift in the Ca isotopic composition of the ocean (cf. Zhu and MacDougall 1998, Skulan et al. 1997). Therefore, the Ca isotope ratio of paleo-seawater that is recorded in biminerals like foraminiferas tests is an ideal tool to study changes in the Ca budget of the ocean.

The PEAT program (IODP Exp. 320 and 321) recovered a unique, well-preserved sediment record (Pälike et al. 2010, Lyle et al. 2010), providing an excellent archive of the Cenozoic, an era known for its times of extreme and rapid climate variability, expressed in e.g. temperature changes and rapidly shifting carbonate compensation depth (CCD) (Zachos et al. 2001, Pälike et al. 2012).

Here, we use this record to establish a reliable δ44/40 Ca paleo-seawater record for the Late Paleogene between 45 Ma and 23 Ma and model changes in the Ca budget through time. To achieve this aim, we selected the most appropriate available micro fossils as archives for the Ca isotope composition of the paleo-ocean. Based on occurrence, isotope fractionation behaviour and preservation, we chose the benthic foraminifers Nuttalides spp., Gyroidinoides spp. (G. soldanii and G. neosoldanii) and Cibicidoides spp. (C. subhaidingerii, C. mundulus and C. grimsdalei) from the size-fraction >63μm for δ44/40 Ca measurements. Foraminifer tests were hand-picked under the binocular and cleaned following the method described in Gussone and Filipsson (2010). An aliquot of each sample was mixed with a 44Ca/40Ca double-spike to correct isotope fractionation during measurements (Gussone et al. 2011) prior to the isotope analysis by thermal ionisation mass spectrometry.

Our results suggest considerable differences in the Ca isotope record of benthic foraminifers during the Eocene and the Oligocene. Throughout the Eocene, the δ44/40 Ca values show little variation with relatively constant values and no significant fluctuations during phases of large short term CCD fluctuations, revealed by rapid changes in the carbonate content of the sediments and the occurrence of several carbonate accumulation events (CAE). In contrast to the Eocene, the Oligocene is characterised by sediments with uniformly high carbonate content and a long term trend with increasing δ44/40 Ca towards the late Oligocene.

Past seawater δ44/40 Ca values were calculated from the benthic foraminifer record applying the calibration for Gyroidinoides spp. (1000lnα = -1.25 %) from Gussone and Filipsson (2010). The Ca budget during the Eocene is relatively constant, indicating that the short term CCD fluctuations are too small to alter the isotopic Ca budget. The Oligocene on the other hand, is characterized by a general increase in δ44/40Ca_seawater values. Together with the continuously deep CCD, this is consistent with a massive long-term (> 1 Ma) Ca carbonate deposition and decreasing Ca concentration in the ocean water. Combined with Neogene data from Heuser et al. (2005) and Sime et al. (2007) the data suggest an increase in δ44/40Ca_seawater values during the Oligocene with a maximum at the end of the Paleogene.

Quantitative models of the Ca input to output ratio and changing the fractionation between seawater and the oceanic Ca sink suggest an increase in CaCO₃ sedimentation during the Oligocene and a decrease in Ca concentration of the ocean associated with a depletion of light Ca isotopes.

Zr-in-rutile thermometer at UHT-conditions from paragneisses in the Mafic Complex of the Ivrea Zone, Northern Italy

Jonas Pape¹, Klaus Mezger²

University of Bern, Institute of Geological Sciences, Bern, Switzerland
¹jonas.pape@students.unibe.ch, ²klaus.mezger@geo.unibe.ch

Rutile is a common accessory mineral in a wide variety of metamorphic rocks. Several studies have shown that the incorporation of Zr into rutile grown in equilibrium with quartz and zircon is temperature dependent and this forms the basis of the single-mineral Zr-in-rutile geothermometer (e.g. Zack et al., 2004, Watson et al., 2006). Experimental data for Zr diffusion in natural and synthetic rutile suggest that Zr volume diffusion is very slow (Cherniak et al., 2007) and thus rutile may preserve high-T information.

However, many studies have shown that the Zr contents of rutile grains vary from a few hundred to several thousand ppm within a single sample, which results in enormous temperature spreads. It is not clear whether or not rutile grains preserve primary Zr concentrations or whether the Zr concentrations are modified during post-peak metamorphic stages due to resetting by diffusion.

This study focuses on the behavior of incorporation and resetting of Zr in rutile at UHT-conditions and during post-peak metamorphic cooling. Samples were taken from the Mafic Complex of the Ivrea Zone, which contains paragneiss septae. These septae are considered to be derived from the lowermost part of the Kinzigite Formation, which was affected by a multi-stage intrusion of gabbroic rocks building up the Mafic Complex. Therefore, these paragneisses are expected to have been exposed to temperatures up to 1250 °C.

Individual rutile grains show homogenous distribution of Zr, however, the Zr contents between rutile grains can range from ~200 to ~7700 ppm within single samples. This concentration spread results in temperatures from ~600 to ~1000 °C. Some rutile grains show homogeneous lamellar exsolution of zircon or baddeleyite with crystallographic control. Zirconium contents of zircon-lamellae were re-integrated to obtain the bulk Zr contents of host grains prior to exsolution. This results in equilibration temperatures of 1000 to 1150 °C.

The data of this study suggest that even peak metamorphic temperatures up to 1150 °C are preserved by the Zr-in-rutile thermometer. Exsolution and diffusion are important mechanisms that cause resetting of Zr in rutile during cooling, but exsolution of Zr-bearing phases is only observed in rutiles that contained originally more than ~9600 ppm of Zr. This exsolution does not lead to net Zr loss from the rutile grains. Thus, the Zr-in-rutile thermometer seems to be very robust and suitable to record UHT conditions. The different Zr-contents observed in rutile grains from the same sample record prograde rutile growth.

References:
Ultra-high temperature metamorphism in H.U. Sverdrupfjella, Western Dronning Maud Land, East Antarctica

Jim Pauly\(^1,a\), Horst R. Marschall\(^2\), Klaus Mezger\(^1,b\)

\(^1\)University of Bern, Institute of Geological Sciences, Bern, Switzerland
\(^a\)jim.pauly@students.unibe.ch; \(^b\)klaus.mezger@geo.unibe.ch

\(^2\)Woods Hole Oceanographic Institution, Department of Geology and Geophysics, Woods Hole, MA 02543, USA
hmarschall@whoi.edu

The central location during the amalgamation of both supercontinents Rodinia and Gondwana makes Dronning Maud Land in East Antarctica a key area for understanding the formation history and paleogeography of Rodinia and Gondwana. The high grade Maud Belt extends over a length of \(\sim 1500\) km and borders the geologically separated Archean Grunehogna Craton. The Maud Belt in Western Dronning Maud Land (WDMl) is characterized by high-grade metamorphic rocks. It comprises meta-igneous and meta-sedimentary rocks metamorphosed at amphibolite- to granulite-facies grade during the Mesoproterozoic (1080–1030 Ma) ‘Grenville’ orogeny related to the assembly of the Rodinia supercontinent (e.g. Arndt \textit{et al.}, 1991) as well as parts that were reactivated in a second orogenic event during late Neoproterozoic-early Phanerozoic (600–480 Ma), the ‘Pan-African’ orogeny, leading to the assembly of Gondwana (e.g. Groenewald \textit{et al.}, 1995; Board \textit{et al.}, 2005). The role of the high-grade rocks in WDMl is still in discussion. A Grenville-age orogenic origin of the Maud Belt in western DML and a pure thermal Pan-African overprint was proposed by Groenewald \textit{et al.} (1995) whereas other authors assume tectono-thermal overprinting during Pan-African times (e.g. Jacobs \textit{et al.}, 2003; Board \textit{et al.}, 2005).

We present first evidence for ultra-high temperature-high pressure metamorphism during the Pan-African orogeny in H.U. Sverdrupfjella, WDML. Two key samples, a garnet bearing felsic gneiss and a coarse-grained banded amphibolite, were studied in detail to reconstruct the \(P-T-t\) history. In addition to petrographic and conventional geothermobarometric methods, trace elements in rutile and zircon as well as thermodynamic calculations were used to constrain the metamorphic evolution. Peak temperatures in excess of 900 \(^\circ\)C and pressures of 2 GPa are preserved. Secondary garnet formation and breakdown products define the retrograde path. Two generations of rutile can be distinguished by trace element abundances. Rutile formed at peak and near peak metamorphic conditions preserves ultra-high temperatures based on the \(Zr\)-in-rutile thermometer. The second generation of rutile indicates a prograde origin and records lower than peak temperatures. Zircon was dated by secondary ion mass spectrometry and Ti concentrations were determined in order to calculate temperatures by Ti-in-Zircon thermometry. The combined information supports a Pan-African age for the ultra-high temperature-high pressure metamorphism and provides clear evidence for a proper orogeny in Western Dronning Maud Land at that time.


Discovery of the $^{184}$Os-$^{180}$W decay system: Effects of secondary neutron capture and nucleosynthetic heterogeneity

Stefan T. M. Peters$^{1,2,*}$ Carsten Münker$^{1,2}$ Harry Becker$^3$ Toni Schulz$^3$

$^1$Institut für Geologie und Mineralogie, Universität zu Köln, Germany

$^2$Steinmann-Institut, Universität Bonn, Germany

$^3$Institut für Geologische Wissenschaften, Freie Universität Berlin, Germany

$^4$Department of Lithospheric Research, Universität Wien, Austria

*Correspondence: stefan.peters@uni-koeln.de

The abundance of $^{180}$W, one of the rarest stable nuclides, in some meteorites is different than in terrestrial materials. We have previously shown that this isotopic heterogeneity reflects alpha decay of $^{184}$Os (Peters et al., LPSC 2013, abstract #2074; Goldschmidt 2013, abstract #4635). In addition to in situ radiogenic production, secondary neutron capture and nucleosynthetic s-process heterogeneity may have minor effects on the abundance of $^{180}$W in meteorites (Schulz et al., 2012; Cook et al., 2013). This may cause scatter on the $^{184}$Os-$^{180}$W isochron that we have previously presented for iron meteorites and chondrites, thus affecting the calculated half life for $^{184}$Os. We therefore explored these effects for our existing dataset.

Meteorites from the IVB group, as well as the anomalous IVB iron Chinga, are reported to display minor s-process deficits (Qin et al. (2008), Kruijer et al. (2012a)). This may affect $\varepsilon^{180}$W via the mass bias correction. Using the theoretical model for stellar nucleosynthesis by Arlandini et al. (1999), we consequently estimate that $\varepsilon^{180}$W requires a downward correction of $0.23 \pm 0.03 \varepsilon$-units for the IVB irons, and $0.35 \pm 0.17 \varepsilon$-units for Chinga. The effects caused by secondary neutron capture on $^{180}$W are expected to be similar to those for $^{182}$W, which namely has a similar neutron capture cross section. Cosmic ray exposure ages for most of our samples are $\leq 100$ Myrs. At this level cosmogenic effects on $^{182}$W are generally less than 10 ppm (e.g., Kruijer et al. (2012a)) and are therefore most likely similarly low for $^{180}$W. Reported cosmic ray exposure ages are larger for three meteorites that were investigated, namely $390 \pm 50$, $775 \pm 70$ and $940 \pm 90$ Myrs for Weaver Mountains, Cape of Good Hope, and Bendego, respectively. For these meteorites, we approximated the magnitude of cosmogenic effects by the difference between the measured $\varepsilon^{182}$W and the pre-exposure value for the meteorite group that is based on the empirical model for neutron capture effects on W and Pt isotopes by Kruijer et al. (2012b). Following this approach, upward corrections of $0.10 \pm 0.15$ and $0.25 \pm 0.16$, and $0.64 \pm 0.10 \varepsilon$-units would be required, respectively. When the corrected $\varepsilon^{180}$W values are used to recalculate the slope of the combined $^{184}$Os-$^{180}$W isochron for iron meteorites and chondrites, a slightly shallower slope is obtained ($m = 0.000279 \pm 0.000067$, MSWD = 1.4) than for the uncorrected data ($0.000295 \pm 0.000060$). This slope corresponds to a decay constant $\lambda^{184}$Os($\alpha$) = $6.11 \pm 1.46 \times 10^{-14}$ a$^{-1}$ that is identical within uncertainty to the slope based on the uncorrected data ($\lambda^{184}$Os($\alpha$) = $6.46 \pm 1.34 \times 10^{-14}$ a$^{-1}$).

We prefer, however, the value for the slope based on the uncorrected data, because the applied corrections increase the uncertainty for individual data due to error propagation. Moreover, these corrections are within the limits of analytical uncertainty and are model depended.
Pharmacosiderite is a hydrous iron arsenate which was first described 1813 by HAUSMANN and occurs predominantly in oxidizing zones of ore deposits. The pharmacosiderite group includes natural minerals and synthetic materials with similar crystal structure and properties. The first investigation of the crystal structure of pharmacosiderite by ZEMANN (1947) described the pharmacosiderite as a cubic mineral with zeolite-like framework and a nominal chemical formula $\text{AFe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 6-8\text{H}_2\text{O}$, where $\text{A} = \text{K, Na, Ba, H}_3\text{O}^+$. For the investigation of the crystal structure of pharmacosiderite, we selected natural large crystals from five different localities. The chemical and physical properties have been determined by optical microscopy, SEM, EMP and XRD. (1) The sample PS-LT comes from Nevada (USA) and consists of translucent brownish green, euhedral cubes associated with barite and goethite. This pharmacosiderite is cubic ($P\overline{4}3m$) with a lattice parameter of $a=7.9707\ \text{Å}$, and the $A$ site is dominated by Ba. (2) Green transparent, euhedral crystals of PS-CW with edge lengths of maximum 0.2 mm originate from an abandoned mine in Cornwall/England. The space group was determined as $P4_3m$ with $a=7.9758\ \text{Å}$, the $A$ site is dominated by K. (3) The sample NA-PS from an abandoned mine in Nevada (USA) shows green euhedral cubes with an edge length to 0.2 mm. The space group is $P\overline{4}3m$ with $a=7.9749\ \text{Å}$ and the $A$ site is dominated by Ba, with a minor proportion of Na. (4) The sample CU-PS comes from an arsenic-rich layer of a mine in Nevada (USA). The intensive green, transparent crystals form euhedral cubes with edge length up to 0.6 mm. The space group was determined to $P\overline{4}3m$ with $a=7.9997\ \text{Å}$, the $A$ site is dominated by K. (5) Two bariopharmacosiderite (BA-PS_I and BA-PS_II) from a mine in Germany show greenish brown crystals with cubic morphology. The space group was determined on three crystals as $P4$ or $P\overline{4}3m$ with $a=7.9916\ \text{Å}$ and $c=8.0007\ \text{Å}$. Two arsenic-rich soil samples were collected in Switzerland. The soil has developed from limestone hosting an iron ore deposit which was probably locally mined and smelted in medieval times (TRUNINGER, 1922). Samples were taken in depths of 1-10 cm (S1, topsoil) and 60-70 cm (S2, subsoil with visible ore fragments). Bulk analyses (by XRF) show that S1 contains 926 mg As/kg and S2 4020 mg As/kg. Interestingly, the sample S2 also contains a high amount of thallium (~1260 mg Tl/kg). Only in S2, pharmacosiderite, molybdenite and yet unknown phases with Mn, Fe and Cu could be detected. From preliminary EMP results of the pharmacosiderites, we received the empirical chemical formula $(\text{Ba}_{0.95}\text{K}_{0.03}\text{Na}_{0.01})\text{Fe}_4[(\text{As}_{0.83}\text{P}_{0.17})\text{O}_4]_3(\text{OH})_4 \cdot n\text{H}_2\text{O}$. In the near future, we will refine the structural models for all single crystals. Another part of our investigation is the question if Tl enters the $A$ site of pharmacosiderite in the contaminated soils.

Outcrop to micro-scale heterogeneities of a large carbonate sand shoal complex (Middle Triassic, South Germany)

Petrovic, A. and Aigner, T.

1 alexander.petrovic@uni-tuebingen.de
2 t.aigner@uni-tuebingen.de

Modern carbonate shoal bodies are characterized by a complex anatomy. The large to small scale internal heterogeneities and geometries are mainly controlled by variations of water energy as well as factors such as storm intensity, sediment supply and sea-level changes. In contrast, the fossil records of carbonate shoals have usually a homogeneous appearance in outcrop scale, caused mainly by stratigraphic averaging.

The Quaderkalk-Formation in the Upper Muschelkalk in South Germany represents a large scale carbonate shoal system with a maximum cover of more than 3000 km², deposited along an epicontinental, very gently inclined carbonate ramp in the regressive part of a 3rd order sequence. Skeletal and oolitic dominated carbonates build up a complex system of four chronologically separated geobodies with prominent geometries. This study is focused on the largest geobody of the Quaderkalk-Formation. In order to characterise the heterogeneities of this body, 1D sedimentological analysis with the study of hundreds of thin slices, a high resolution 1D sequence analysis, outcrop wall panels and 2D correlations were carried out.

The results portray a very heterogeneous carbonate shoal-complex from outcrop to micro scale, which is strongly controlled by the paleo-morphological (paleohigh), water energy, and sea-level changes. Additionally, the entire shoal complex can be subdivided in different energy-areas characterized by grain size, components and their position on the shoal-complex.
Basaltic magma degassing: an experimental perspective

Michel Pichavant and Nolwenn Le Gall

ISTO, Orléans, France

pichavan@cnrs-orleans.fr

Magma degassing is responsible for the transfer of volatiles from deep interiors toward planetary atmospheres. At a more local scale, gas emissions are manifestations of magmatic flows towards the Earth’s surface. Measurement of gas compositions and fluxes is one of the main tools for monitoring active volcanoes. Degassing is a direct consequence of magma ascent since volatile solubilities decrease with pressure. Therefore, upon decompression, volatiles must exsolve from the melt. Currently, degassing processes are studied with different approaches including analytical (gas compositions, volatiles in glass inclusions), experimental (volatile solubilities and speciations) and theoretical (melt-fluid saturation thermodynamic models).

Basaltic magmas are now recognized to be major carriers for volatiles such as H$_2$O and CO$_2$. Because of their relatively high temperatures and low viscosities, basaltic magma degassing is commonly viewed as a near-equilibrium process. There are however several observations that do not fit into a simple, unique, equilibrium degassing model for basaltic magmas. To test mechanisms of basaltic magma degassing, continuous decompressions of volatile-bearing (2.7-3.8 wt% H$_2$O, 600-1300 ppm CO$_2$) Stromboli melts have been performed from 250-200 to 50-25 MPa at 1180-1140°C. Ascent rates were varied from 0.25 to ~ 1.5 m/s. Glasses after decompression show a wide range of textures, from totally bubble-free to bubble-rich, the latter with bubble number densities from $10^4$ to $10^6$/cm$^3$, similar to Stromboli pumices. Vesicularities range from 0 to ~ 20 vol%. Final melt H$_2$O concentrations are homogeneous and always close to solubilities. In contrast, the rate of vesiculation controls the final melt CO$_2$ concentration. High vesicularity charges have glass CO$_2$ concentrations that follow theoretical equilibrium degassing paths whereas glasses from low vesicularity charges show marked deviations from equilibrium, with CO$_2$ concentrations up to one order of magnitude higher than solubilities. FTIR profiles and maps reveal glass CO$_2$ concentration gradients near the gas-melt interface. Our results stress the importance of bubble nucleation and growth, and of volatile diffusivities, for basaltic melt degassing. Two characteristic distances, the gas interface distance (distance either between bubbles or to gas-melt interfaces) and the volatile diffusion distance control the degassing process. Melts containing numerous and large bubbles have gas interface distances shorter than volatile diffusion distances, and degassing proceeds by equilibrium partitioning of CO$_2$ and H$_2$O between melt and gas bubbles. For melts where either bubble nucleation is inhibited or bubble growth is limited, gas interface distances are longer than volatile diffusion distances. Degassing proceeds by diffusive volatile transfer at the gas-melt interface and is kinetically limited by the diffusivities of volatiles in the melt.

Our experiments show that CO$_2$-oversaturated melts can be generated as a result of magma decompression. They provide a new explanation for the occurrence of CO$_2$-rich natural basaltic glasses and open new perspectives for understanding explosive basaltic volcanism. They also stress the need for systematic experimental studies of (1) bubble nucleation and (2) volatile diffusion in basaltic melts and (3) degassing, vesiculation and fragmentation of CO$_2$-oversaturated melts. Disequilibrium degassing can occur for temperatures, decompressions, ascent rates and melt compositions typical of basaltic systems, and interpretation of gas data at basaltic volcanoes should integrate this possibility.
Adsorption experiments with ferrihydrite and organic model substances

Lydia Pohl¹, Julia Neidhardt², Karin Eusterhues², Kai Uwe Totsche³

¹lydia.pohl@uni-jena.de
²julia.neidhardt@gmx.de
³karin.eusterhues@uni-jena.de
⁴kai.totsche@uni-jena.de

Ferrihydrite can bind high amounts of soil organic matter and may play an important role in its long-term stabilization. In adsorption and coprecipitation experiments with natural organic matter (litter extracts and lignin) we observed that the polysaccharides of the litter extract and the aromatic compounds of the lignin were preferentially bound to ferrihydrite. This polysaccharide fractionation was additionally accompanied with a fractionation of the individual sugar monomers, where mannose and glucose were enriched in the mineral-associated OM, especially during coprecipitation. To better understand the behavior of polysaccharides and aromatic compounds, adsorption experiments were also done with glucose, galactose, glucuronic acid, vanillin and vanillic acid.

Experiments with synthetic sugar monomers resulted in relatively low maximum loadings of ~15 and ~25 mg C g⁻¹ for glucose and galactose, whereas glucuronic acid produced a maximum loading of 72 mg C g⁻¹. The adsorption of vanillin and vanillic acid led to loadings of ~18 and ~160 mg C g⁻¹.

We conclude that the observed preferential association of polysaccharides from natural OM with ferrihydrite is not caused by direct interaction of the neutral polysaccharides’ hydroxyls. Instead of that, we assume that (i) the dominant adsorption mechanism is inner sphere or outer-sphere complexation of carboxyls on the ferrihydrite surface and (ii) the enrichment of glucose and mannose in the ferrihydrite-associated OM may be explained by a preferential association of these monomers with carboxyl-rich compounds.
Infrared Spectroscopic High Pressure Experiments on Leucite: Detection of Three Phase Transitions up to 19 GPa at Ambient Temperature

Julia Pohlenz1, Ulrich Schade2, Monika Koch-Müller3

1pohlenz@gfz-potsdam.de

2ulrich.schade@helmholtz-berlin.de

3monika.koch-mueller@gfz-potsdam.de

The important zeolite group member leucite is commonly known to show an exceptional complex behaviour in respect to its temperature induced phase transitions. However, its pressure dependent phase transitions are not well investigated to this date. To address this issue, a natural tetragonal leucite (K$_{0.93}$Na$_{0.10}$Al$_{0.98}$Fe$_{0.01}$Si$_2$O$_6$) was studied with in-situ mid- and far-infrared (IR) spectroscopy. The pressure was induced by a diamond anvil cell (DAC). To visualise lattice vibrations, two series of measurements in the far IR region between 20 and 700 cm$^{-1}$ were conducted at the synchrotron source BESSY II of the Helmholtz-Zentrum Berlin für Materialien und Energie (HZB). In these series, pressures up to 12 GPa and 17 GPa could be obtained. One mid IR-study between 500 and 1600 cm$^{-1}$ to cover intratetrahedral vibrations was performed at GFZ Potsdam reaching up to 19 GPa. Pressure dependent changes in the collected IR spectra were detected via shifts of band energies, band energy offset rates or via variations in the full width at half maximum (FWHM) of bands using an autocorrelation function. Our data suggest a total of three phase transitions in the given pressure range. A first order transition (tetragonal to triclinic, I$4_1$/a $\rightarrow$ P-1) is found around 2.4 GPa, already identified by Goryainov et al. (2000) and Gatta et al. (2008) from Raman and X-ray studies, respectively. The remaining two transitions have been observed for the first time and suggest a high order transition around 6 GPa as well as a second order transition around 10 GPa. The obtained spectra provide a means of detailed determination of spectral features and their corresponding structural vibrations and thus a deeper insight into effective phase transformation mechanisms.


Selenium incorporation in pyrite and hematite

Sebastian Potsch¹, Nicolas Börsig², Thomas Neumann³

¹Sebastian.Potsch@kit.edu
²Nicolas.Boersig@kit.edu
³Thomas.Neumann@kit.edu

The radionuclide $^{79}$Se plays an important role for the safe disposal of high-level nuclear waste (HLW). Due to its long lifetime and high mobility, the behavior of selenium to migrate into the biosphere is of great interest. In aqueous solutions the geochemical properties of Se strongly depends on its speciation. Under oxidizing conditions, Se exists as selenate (Se$^{VI}$) or selenite (Se$^{IV}$) and has a high mobility. In contrast, under reducing conditions, Se is sparingly soluble as elemental selenium (Se$^{0}$) and selenide (Se$^{II}$). In the near field of an HLW disposal site, the interaction of dissolved Se species with mineral phases is the main reason for a Se immobilization. In this work the retention of Se by pyrite and hematite is investigated.

The stability of synthesized selenium doted pyrites will be investigated under oxidized conditions. Pyrite was chosen, because it is the most common sulfide mineral in the Earth’s crust and it is a constituent in HLW-concerning geological formations (e.g. Opalinus Clay). Natural pyrites can also incorporate many elements up to several wt.% and it is a sorption sink for different radionuclides in deep geological disposals. First precipitation experiments exhibit synthesized products with a pyrite structure and a selenium content at least of 1 wt.% with a selenium uptake up to 99 % from the solution of coprecipitation experiments. Furthermore the structure of Se doted pyrite will be studied by XAS and its stability will be investigated by electrochemical studies and XPS due the surface controlled oxidation.

Hematite occurs in host rocks and barrier materials of HLW repositories and can also be a corrosion product of the steel canisters that contain the nuclear waste. In contrast to the reversible adsorption of charged Se species on the surface of hematite, incorporation processes may represent a possibility for a permanent immobilization of Se. To investigate the Se sorption by hematite during the mineral formation, a method for the synthesis of hematite by Schwertmann & Cornell (2000) was adjusted to meet natural conditions. In order to reach a transferability of the synthesis conditions to the expected hydrochemical conditions of an HLW disposal site, the synthesis took place in solution at moderate temperatures of 50°C and under a neutral to slightly alkaline pH. In the presence of Se, the formation of hematite decreases the amount of Se in solution due to both adsorption and incorporation processes. The percentage of Se retention by incorporation was determined by comparing with results of adsorption studies of Se on hematite under the same hydrochemical conditions.
Prograde and retrograde evolution of carpholite-bearing assemblages — An example from the Afyon Zone, W Anatolia

Amaury Pourteau¹, Roland Oberhänsli², Romain Bousquet³, Pierre Lanari⁴, Olivier Vidal⁵, Osman Candan⁶

¹pourteau@geo.uni-potsdam.de, ²roob@geo.uni-potsdam.de, ³bousquet@min.uni-kiel.de, ⁴pierre.lanari@geo.unibe.ch, ⁵olivier.vidal@ujf-grenoble.fr, ⁶osman.candan@deu.edu.tr

Fe-Mg-carpholite (or ‘carpholite’) is the index mineral for high-\(P/T\), subduction-related metamorphism of Al-rich, Ca- and Na-poor meta-sedimentary rocks. During prograde subduction-related metamorphism, carpholite forms after chlorite (mostly stable at \(LP\)) and before chloritoid (mostly stable at \(MT\)). In a simplified FMASH chemical system, uni-variant \(P-T\) fields are separated by di-variant fields, in which two ferro-magnesian phases coexist. Along the prograde path, ferro-magnesian phases become progressively richer in Mg. In the extended KFMASH, the only K-bearing phase is phengitic white mica, which becomes richer in Al-celadonite with increasing pressure, and in pyrophyllite with increasing temperature. In past years, the sensitivity of phengite, as well as chlorite, to \(P-T\) changes has been used for accurate thermobarometry. In Western–Central Anatolia, a late Cretaceous, low-grade HP belt (the Afyon Zone) encompasses a wide diversity of carpholite-bearing rocks, from (a) well-preserved carpholite–chloritoid assemblages, recording prograde metamorphic stages, to (b) highly-retrogressed rocks containing white mica–chlorite ± chloritoid replacing carpholite.

(a) We investigated carpholite–chloritoid relationship in quartz veins, quartz-bearing and -free phyllites from the Afyon Zone. Our study reveals textural, and chemical features related to the progressive replacement of carpholite by chloritoid during prograde metamorphism. Thermodynamic equilibrium among texturally-ambiguous carpholite–chloritoid pairs can be tested by comparing calculated values of Mg–Fe distribution coefficient (\(K_D\)) to those obtained from evident textures (from our samples and the literature). Thermodynamic modelling based on Gibbs free-energy minimisation (i) allows interpreting our observations in terms of \(P-T\) changes, (ii) illustrates the change of the effective bulk composition due to the fractionation of chloritoid progressively grown after carpholite, and (iii) suggests the potential use of \(K_D\)(Car/Ctd) as a geo-thermometer.

(b) In addition, retrograde assemblages were investigated using WDS spot analyses and EDS element maps quantified with XMapTools© for phengite and/or chlorite thermobarometry. \(P-T\) estimation was combined to \(^{40}\)Ar–\(^{39}\)Ar geochronology carried out on white mica to determine the precise timing of accurate metamorphic stages.

Our study on the prograde and retrograde petrographic record of low-grade HP metamorphism highlights that complete \(P-T-t\) paths can be obtained for meta-pelitic rocks to better constrain the burial and exhumation of continental units in ancient subduction zones.
The dynamic magmatic processes prior to the 39 ka Campanian Ignimbrite (CI) eruptions at Campi Flegrei (CF), occurring during magma ascent, cannot be observed directly in nature. Nevertheless, these processes may lead to potentially catastrophic eruptions threaten millions of people in and around Naples (Italy). Therefore, experimental simulations of CI magma ascent are necessary and will give detailed insight to the mechanisms of CF super eruptions.

A pressure decrease during magma ascent accompanied with fluid oversaturation in the melt initiates bubble nucleation, growth, coalescence and segregation, and possible partial crystallization, which lead to a substantial density decrease and a change in viscosity. These processes may act as driving forces for increased ascent rates and may lead to catastrophic eruption styles.

Discrepancies of previous studies demonstrate that the P-T-t conditions and volatile contents (H\textsubscript{2}O, CO\textsubscript{2}, Cl) of the primitive melt prior to the eruption, generating the CF volcanic products are not well constrained. This study is focused on the conduction of continuous decompression experiments \cite{1} using a trachytic CI composition \cite{2} to gain insight into the dynamic degassing processes. First isothermal decompression experiments, above the liquidus at 1050 °C, are performed using a starting pressure of 200 MPa and H\textsubscript{2}O content of 5 wt% and a continuous decompression to 100, 75 and 50 MPa with different decompression rates. Changes in decompression rate and type of starting material lead to significantly different degassing behavior of the melt. Fast decompression rates lead to massive volatile oversaturation, thus bubble nucleation is the predominant mechanism. In contrast, bubble growth is the preferred mechanism at slow decompression rates to reequilibrate the system. Additionally, different types of sample material are used. The degassing behavior of massive glass cylinders compared to glass powder with different grain size fractions is investigated.

In ongoing experiments, additional volatiles (CO\textsubscript{2}, Cl) will be added to simulate conditions closer to the CF volcanic system. To investigate heterogeneous bubble nucleation caused by decompression induced crystallization processes, experiments will be performed at lower temperatures below the liquidus.

Microdigitate Fe/Mn oxidic microbialites from the Äspö tunnel (Sweden) -
A modern example of the microbial subterranean fossil Frutexites

Quéric NV, Heim C, Ionescu D, Schäfer N, Zippel B, Kappler A, Byrne JM, Rodríguez-Martínez M, Reitner J

Enter The Äspö Hard Rock Laboratory (HRL) offers a unique window into the subterranean terrestrial biosphere, where the growth of mainly chemolithoautotrophic microbial consortia at the rock-water interfaces strongly depends on the flow, oxygen content and the chemical composition of the discharging subterranean fluids. Net-like mineralizing microbial mats are covering surfaces under fluid dropping systems in which the dysoxic brackish water gets partly oxygenated. These microbial systems are organized in a distinct, rough lamination of mineralized layers bordering divergently branched microcolumns. Mainly composed of iron hydroxides and iron and manganese oxides, they strongly remind of fossil Frutexites structures: submillimeter-sized, Fe-Mn-rich microbial fossils, where the microstructure preservation is strongly controlled by its mineral aggregate character. Dating back to the Precambrian, these marine and terrestrial microbial fabrics were similarly related to hidden and cryptic environments. Fluorescence in situ Hybridization on thin sections displays distinct areas of densely packed bacteria and archaea in the interstitial regions of these dendritically organized iron minerals. They are shown to harbor a particular, diverse microbial community as indicated by 454 pyrosequencing and Denaturing Gradient Gel Electrophoresis on the base of the 16S rRNA gene. This microbe-mineral complex is mainly a microaerophilic conglomerate of originally marine, terrestrial and groundwater bacteria involved in a coupled iron and manganese redox cycling. Harbouring a remarkable ferromanganese oxidizing community, these mineralized coatings may have an important detoxifying effect by lowering the concentration of toxic metals dissolved in the Äspö HRL rock-pervading fluids.
Carbonate and zeolite from the Louisville Seamount chain as indicators of changing fluid-rock interaction

S. Rausch1, W. Bach2, A. Klügel3

1srausch@uni-bremen.de
2wbach@uni-bremen.de
3akluegel@uni-bremen.de

Intense circulation of seawater through the oceanic crust changes physical properties of the rocks and is the most important mechanism of chemical exchange between lithosphere and hydrosphere. Upon ageing, the oceanic crust accumulates carbonates, which precipitate from circulating seawater in veins, vesicles, and breccia cement. Seamounts emerge above the abyssal plains and therefore are less covered with sediments, which allows for prolonged seawater circulation. To examine the importance of seamounts for seawater-crust chemical exchange and CO2 uptake, we studied IODP samples from the Louisville seamount chain (Expedition 330), which is located on the Pacific plate north east of New Zealand. Void-filling carbonates (calcite, aragonite, siderite and Fe-/Mn-rich calcite) and minor zeolites from four seamounts aged between 50 and 74.2 Ma have been examined. The formation temperature, calculated from oxygen isotopic ratios, lies in the range of 2.2 to 18.4 °C. A slight downhole increase in temperature is observed in holes U1372A (74.2 Ma) and U1376A (64.1 Ma). Samples from U1374A (70.7 Ma) show temperatures from 3.0 to 9.7 °C with no systematic downhole trend. Carbonate-cemented volcanic breccias of holes U1372A and U1374A have Sr isotopic values that indicate precipitation shortly (a few million years) after seamount formation. In contrast, samples from younger seamounts (U1376A and U1377A, B; 50.0 Ma) show evidence for precipitation from seawater-derived fluids that had exchanged Sr with the basement. Highly variable extents of fluid-basement interaction are also shown by the REE+Y concentrations of carbonates. The oldest seamounts (U1372A, U1374A) are characterized by negative Ce-anomalies and positive Y-anomalies, pointing to precipitation from pristine seawater. In contrast, the two younger seamounts (U1376A and U1377A, B) show REE patterns that lack these seawater signatures and show subtle positive Eu anomalies, indicative of enhanced exchange with basement. The magnitude and direction of elemental exchange seems to be strongly controlled by temperature. The isothermal gradient displayed by carbonates from Hole 1374A may suggest recharge of cold seawater deep into the basement, making the seamount a possible paleo-seawater-recharge site in the upper 350 mbsf. From 350 to 522 mbsf in Hole U1374A, carbonates give way to low-temperature zeolites (gmelinite, tetranatrolite, phillipsite) and thaumasite as void-filling material, in lithologies with higher abundance of intrusive sheets and hyaloclastites. These minerals are interpreted to form at temperature below 100 °C. A relatively rapid precipitation of carbonate in the seamount basement at Hole U1374A may have sealed the upper volcanic basement (upper 300 mbsf) and may have facilitated a closed-system circulation of slightly warmer fluids. In contrast, linear downhole decrease in δ18O observed in carbonates from U1372A and U1376A suggest roughly steady-state thermal gradients of 50°C/km, corresponding to a conductive heat flow of around 150 mW/m². Ongoing work is devoted to assigning compositional trajectories to these depth-temperature relations, hoping to establish common ratios for the flux of heat and elements in carbonates and zeolites. If successful, this approach would provide novel insights into the role of seamounts in ocean-crust exchange budgets.
Imaging active faults

Klaus Reicherter¹, Thomas Wiatr, Christoph Grützner, Jochen Hürtgen, Andreas Rudersdorf, Jack Mason
¹k.reicherter@nug.rwth-aachen.de

all at: RWTH Aachen University, Inst. of Neotectonics and Natural Hazards, Lochnerstr. 4-20, 52056 Aachen, Germany,
www.paleoseismicity.org

Identifying active faults by geophysical and remote sensing methods is the essential topic of our review presentation. Many efforts have been achieved in the last years to image active faulting prior to cost-intensive trenching or drilling. The term “active fault” is somewhat critical as defined by the USGS, it states that a fault has moved one or more times in the past 10,000 years, which is by far too short to cover seismic cycles entirely. So, many faults in intra-plate setting have earthquake recurrence periods on the order of several thousands to ten of thousands years, especially when considering stresses induced by loading/deloading, e.g. from ice sheets during the Quaternary. Also, the USGS definition does by no means fit the requirements of critical facilities, where is seismic safety of 1,000,000 years should be guaranteed. So, we feel more comfortable with the definition that faults that moved during the last 120,000 years (i.e. approx. one glacial cycle), and are likely to generate earthquake(s) again.

Active faults can be identified by several methods in the landscape, basically tectonic morphology and field mapping are very helpful tools, if based on remote sensing. The technical advances over the last decades allow high resolution imaging of fault areas with both airborne and ground-based LiDAR. Airborne LiDAR helps to identifying geomorphic indication of fault activity, like deflected drainages, fault scarps, hanging valleys, landslides and rock falls, by removing the vegetation cover or man-made structures. Applications of terrestrial LiDAR on active faults are still rare, however, reflection intensity patterns or high-resolution images of fault planes (free faces) are promising. Small but very detailed digital elevation models show corrugations and kinematic indicators on the faults plane. The roughness of the fault plane is in general directly a function of fault-slip rate and erosion rate.

Apart from footwall observations of faults, the hanging wall of normal faults (and vice versa the footwall of a thrust fault) functions as a sediment archive storing fault-related and fault-quiescence deposits. To image the architecture of the hanging wall frequently ground-penetrating radar is applied, as well as electric tomography and seismic reflection – all depending on the resolution desired. Other methods comprise geodetic ones like GPS-methods, DiNSAR and traditional leveling data, which also are dependent on spatial and time resolution. If active faults are surveyed in offshore areas, classical seismic reflection and hydroacoustic methods are usually applied.

The evaluation and detection of seismically active structures (i.e. faults and folds) is still of immense societal importance, as all last major earthquakes, like the Tohoku-oki in 2011, the Christchurch series in 2010/11 and the Port-au-Prince/Haiti earthquake in 2010, occurred unexpected and in areas, where traces of such powerful prior earthquakes have not been detected by geoscientists before.
Melt interfaces during magma mixing: an experimental approach

C. Renggli¹, S. Wiesmaier², C.P. De Campos³, W. Ertel-Ingrisch⁴, D.B. Dingwell⁵

¹christian.renggli@gmx.ch
²sebastian.wiesmaier@min.uni-muenchen.de
³decampos@lmu.de
⁴ertel-ingrisch@lmu.de
⁵dingwell@lmu.de

In recent years an increasing number of experimental studies on magma mixing, with the main focus on the mixing dynamics, have been performed (e.g. De Campos et al. 2011, Perugini et al. 2013). Here we propose two new experimental lines to test the role of the interface between miscible magmas during the mixing process. Both experiments are performed at high T, atmospheric pressure and stable liquid conditions.

In the first experiment a platinum sphere falls across the interface of two contrasting melt layers (ryholite and basalt). We hope to gather information on the behavior of the rhyolite dragged into the basalt (chemical and physical interactions). Furthermore, the results might be a first step to include particles in high T magma mixing experiments.

In the second experiment a flat bottomed bob is slowly introduced to the melt-melt interface. Being attached to a gravimetric balance system, the interfacial tension can be determined in-situ following Veksler et al. (2010). A time series of experiments should show the change of the interfacial tension as the diffusional gradient between the two melts develops.


Perugini et al., 2013, Chem. Geol. 335: 8-23.


Dept. for Earth and Environmental Sciences LMU München

Theresienstr. 41/III, 80333 München
Facies distribution and clinoform geometries in Messinian reef slopes
(Cariatiz reef, Almería, SE Spain)

Reolid, J. 1, Betzler, C. 2, Braga, J.C. 3 & Martín, J.M. 4

1jesus.reolid@uni-hamburg.de; Institut für Geologie, Universität Hamburg
2christian.betzler@uni-hamburg.de; Institut für Geologie, Universität Hamburg
3jbraga@ugr.es; Departamento de Estratigrafía y Paleontología, Universidad de Granada
4jmmartin@ugr.es; Departamento de Estratigrafía y Paleontología, Universidad de Granada

Slopes of Neogene coral reef platforms have been intensely studied and several models were developed to describe facies distribution within individual clinoform growth packages. These models usually postulate a systematic downslope facies trend encompassing coral framework, coral breccia, slope calcirudite, slope calcarenite and basinal sediments. Facies boundaries are usually gradual. It is well known that such facies distribution and clinoforms geometries can change in time. Here, however, we will also show that clinoforms of a carbonate platform which have the same geometry can show different facies tracts. The study area is located in the Cariatiz carbonate platform at the northern margin of the Sorbas Basin in the Betic Cordillera (Southeast Spain). The following facies occur in the carbonate platform slope deposits: (1) Talus slope facies adjacent to the reef framework consist of framework debris, a breccia with small framework debris in a Halimeda rudstone matrix, and serpulid patches. (2) Middle slope facies consist of Halimeda rudstone and bivalve-rich bioclastic packstone where Halimeda is absent. (3) Distal slope facies dominated by basinal sediments, marls and diatomites, and locally grainstone-packstone with siliciclastic grains. Fan-delta conglomerates occur intercalated in the reef deposits. In the reef progradation, it is possible to recognize two clinoform types with almost the same geometry but with different facies tracts. Clinoform type I contains every facies from the classical slope model. In clinoform type II, most of the classical facies are absent. At the toe of slope of this clinoform-type, there is a sharp contact from framework debris to distal slope facies. These data show that clinoform geometry and facies distribution are not necessary related. Facies distribution in clinoforms appears to be linked to different accommodation regimes, with an higher facies diversity in slope deposits formed during sea-level highstands.
Radial fibrous dolomite (RFD) – a new cement type found in Upper Carboniferous swamp deposits (Ruhr Area/NW Germany)

D.K. Richter¹*, F. Heinrich, A. Geske¹, R.D. Neuser¹, H. Gies¹, A. Immenhauser¹

¹Ruhr-University Bochum, Institute for Geology, Mineralogy and Geophysics, Universitätsstraße 150, 44801 Bochum, Germany

*detlev.richter@rub.de

Radial fibrous calcites (initially described by BATHURST in 1959; RFC according to KENDALL 1985) are common inorganic carbonate cements in marine carbonate sequences of Paleozoic and Mesozoic age (TUCKER&WRIGHT 1990). More recently, however, this fabric was also described from stalagmites formed in dolomite caves and in biogenic endoskeletons (belemnite guards; RICHTER et al. 2011). Despite its widespread occurrence throughout much of Earth’s history, the origin and the controlling mechanisms of the c-axis anomalies that characterize this fabric are unknown.

Here, for the first time, we present radial fibrous dolomites (RFD). This cement type is rather common in concretionary carbonates (so called within swamp deposits (“Torfdolomit”) in Upper Carboniferous sequences of the Ruhr Area of NW Germany. Excellent preservation of plant structures within these dolomites is indicative for an early diagenetic origin of this fabric that is usually found beneath marine ingressive intervals ($\delta^{13}$C_V-PDB isotope values as low as -22‰ evidence the strong influence of organic carbon mainly from plant debris).

The swamp dolomites are nonstoichiometric ($d_{104}=2.887-2.931$ Å), rich in Fe (up to 4.6%) and Mn (up to 7.3%) and display a low ordering degree ($I_{015}/I_{110}=0.03-0.39$). Cathodoluminescence (CL) spectra show bright peaks between 630 and 640nm. This observation is unusual for dolomites (650nm for dolomites with red CL and 580nm for dolomites with yellow CL — GILLHAUS et al. 2010).

The convergent orientation of the c-axis, within two dimensional images of fibrous dolomitic fans, is documented by Electron Backscatter Diffraction (EBSD). The genesis of these fibrous, radial dolomite fabrics in continental deposits is poorly understood.


Tectonically induced crater floor modification at Sudbury: importance for the identification of Cu-Ni sulfide exploration targets

Ulrich Riller\textsuperscript{1}, Martin Clark\textsuperscript{2}, Iris Lenauer\textsuperscript{3}, Tasca Santimano\textsuperscript{4}

\textsuperscript{1}ulrich.riller@uni-hamburg.de
\textsuperscript{2}mdc003@gmail.com
\textsuperscript{3}iris.lenauer@gmail.com
\textsuperscript{4}tsanti@gfz-potsdam.de

Understanding post-impact shape change of the 1.85 Ga Sudbury Igneous Complex (SIC), the relic of a deformed impact melt sheet, and its host rocks, is paramount for Ni-, Cu- and PGE-mineral exploration. Respective mineral deposits related to the SIC are found: at its base, notably in the so-called Sublayer; in its immediate periphery; and in the physically connected so-called Offset Dikes. Non-cylindrical folding and northwest-directed reverse faulting of the SIC are commonly accepted as the main deformation processes that generated this fold basin, known as the Sudbury Basin. In detail, however, individual segments of the Basin, notably the North Range, the South Range and the East Range, and their respective host rocks deformed by different mechanisms, which have important ramifications for mineral deposit exploration.

The North Range was affected mostly by discontinuous deformation and solid-body tilting and, thus, offers insight into the final crater floor geometry, i.e., after thermal erosion of target rock. Analysis of high-resolution topographic data suggests that the topography of the final crater floor is characterized by amplitudes of up to 400 m over wave lengths of hundreds of meters to a few kilometers, and amplitudes of up to 1500 m over a wave length of about 25 km. Crater floor depressions are spatially associated with a thickened Quartz Gabbro–Norite layer and Sublayer hosting economically important sulfide mineral deposits. This relationship points to a viable exploration strategy.

In terms of first-order structure, the East Range is made up by two synclines, the NE-lobe and the SE-lobe, and an anticline in between. Spatial analysis of pre-SIC mafic dykes in host rocks lead to the identification of a major anticline. This anticline is characterized by abrupt plan-view thickness variations in the lower SIC and the presence of curved faults displaying significant strike separations and repetition of SIC contacts. Ore bodies in the East Range are, thus, expected to be thickened in fold hinge zones but displaced on curvi-planar fault surfaces.

Deformation in the South Range involved simultaneous shearing on the South Range Shear Zone and variable tilting of the SIC and adjacent target rocks, which can be explained by trishear deformation. This deformation mechanism can account for large rotation magnitudes of, and strain intensities in, the SIC as well as rather low rotation magnitudes and strains in adjacent host rocks. Thus, trishear deformation has important consequences for the downward projection of sulfide-rich zones in Offset Dikes. During trishear deformation the plan-view geometry of the SIC likely changed from convex outward to concave inward. This shape change imparted local contact-parallel shortening that caused corrugation of SIC contacts and thickness variations of individual SIC layers. Knowledge of such variations is most important for estimating the sulfide content at the base of the SIC.
Mineralogy and Geochemistry of Mississippian and Lower Pennsylvanian Black Shales at the Northern Margin of the Variscan Mountain Belt (Germany and Belgium)

Daniel Rippen¹, Anna K. Uffmann¹, Ralf Littke¹

¹ RWTH Aachen University, EMR - Energy & Mineral Resources Group, Aachen, Institute of Geology and Geochemistry of Petroleum and Coal, Lochnerstr. 4-20, D-52056 Aachen, daniel.rippen@emr.rwth-aachen.de

Ongoing exploration on unconventional gas resources in Central Europe led to a focus of interest on Paleozoic black shale formations. The work presented here comprises diverse assessment-critical data of potentially economic black shale formations of the Carboniferous, including mineralogy, geochemical data, petrophysical data and geological parameters such as burial and thermal history. The sampled and investigated Paleozoic black shales are highly to overmature mature in terms of oil generation, although some gas generation potential remains. Especially the shales of the uppermost Mississippian “Hangende Alaunschiefer” (Upper Alum Shale) in the western areas of Germany and its Belgian equivalent (Chokier Formation) have high contents of organic carbon, are tens of meters thick and reached the gas window. Adjacent carbonates are often stained black and are rich in solid bitumen, indicating a former oil impregnation of these reservoirs. Furthermore, the geochemical and petrophysical properties of the Upper Alum Shale and Chokier Formation black shales are similar to those of already producing shale gas plays like the Barnett shale in the USA. These shale sequences are enriched in silica, needed for enhanced fraccability performance at production stage. Although most of the hydrocarbon potential for the Mississippian shales is exhausted, a high retention potential of thermally generated gas is favored by thick overlying sequences of greywackes and shales in most of the investigated areas. Based on these observations, the Upper Alum Shale and the Chokier formation can be regarded as potential gas shale targets. Any exploration will have to take place north of the outcrop areas, because present-day Mississippian strata are completely eroded south of the studied outcrops. Most other Mississippian and Pennsylvanian black shales are relatively thin and are therefore not considered as primary targets for shale gas plays.
Response of *Globigerina bulloides* and *Globigerina falconensis* to paleomonsoon events in the Northwestern Arabian Sea during the last 18 kyr

Fiona Rochholz¹, Samereh Abdolalipour, Hartmut Schulz

¹Fiona.Rochholz@student.uni-tuebingen

Paleobiology, AG Micropaleontology, Tübingen, Hölderlinstr. 12, 72074 Tübingen

Paleomonsoonal reconstructions provide detailed information about climate changes and therefore help to get a better understanding of the monsoonal system evolution and its influence on climate in the following decades. The focus of the Bachelor study is on the relative (percentages) and absolute (specimens per g dry sediment) abundances of the two planktic foraminiferal species *Globigerina bulloides* and *Globigerina falconensis*, in order to test, if these species can be used as indices of the paleomonsoonal intensities. For instance, the more frequent, larger species *Globigerina bulloides* is established as faunal proxy to record the summer upwelling in the areas of the western parts of the Arabian Sea, whereas the smaller *Globigerina falconensis* might represent the intensity of the winter hydrographic situation, which is characterized by deep mixing of surface and nutrient-charged subsurface waters. Here, we present our preliminary data from a long sediment core MD00-2354 located at the northern Owen Ridge in the northwest Arabian Sea (21°02.55′N, 61°28.51′E, 2740 m water depth) on two different size fractions 355-250 µm and 250-150 µm. We expect that the potential changes not only in numbers but also in size might provide further information on the monsoon history since the last glacial maximum, i.e. of the past ~ 18,000 years. Altogether we analyzed a total of 100 samples, taken at 2.5 cm intervals which corresponds to an average resolution of (18,000/100=) 180 years.

The census of species demonstrates a general increase in the amount of both species after the cold period of Heinrich Event 1 (H1 Chrononzone, ~18-15 kyr BP), with several faunal events of strong increase or decrease in relative abundances. Although *G. bulloides* appears to be more frequent than *G. falconensis*, but both species illustrate increasing trends after 15 kyr to 2.6 kyr BP. Strong minima in *G. bulloides* are observed at around 8 kyr, 5.6 kyr and 3.4 kyr BP. *G. falconensis* increases in relative abundance in the monsoonal periods, when *G. bulloides* reaches its minimum values, nevertheless the maximum values of both species are observed in the time period after 9 kyr BP. Some counts done at the beginning of this work were checked again; however, the recounts confirmed a strong decrease in the frequencies of both species between 2.6 and 0 kyr BP from over 25 % (*G. bulloides*) and 10 % (*G. falconensis*) to ~ 1 % in all fractions, respectively. Whether this abrupt drop in relative abundances is a result of monsoon-involved changes in Arabian Sea climate or of bioturbation is yet to be discussed and needs further research.
The GFZ Potsdam 1280-HR SIMS Instrument – Design Overview

1Rocholl, Alexander, Helmholtz-Zentrum Potsdam, Alexander.Rocholl@gfz-potsdam.de
2Wiedenbeck, Michael, Helmholtz-Zentrum Potsdam, Michael.Wiedenbeck@gfz-potsdam.de
3Couffignal, Frédéric, Helmholtz-Zentrum Potsdam, couffig@gfz-potsdam.de
4Glynn, Sarah, Helmholtz-Zentrum Potsdam, sarahglynn22@gmail.com
5Kidane, Abiel, Helmholtz-Zentrum Potsdam, at.kidane@gmail.com

The Deutsches GeoForschungsZentrum Potsdam / Helmholtz Zentrum Potsdam is currently installing a CAMECA 1280-HR SIMS instrument. Data production for the geochemical user community will begin in autumn of 2013. The new ion microprobe laboratory will function as an open user facility, in accordance with the Helmholtz Society’s support of the global scientific community through providing access to top-end infrastructure. The 1280-HR instrument will be integrated into the Helmholtz SIMS network; the activities in the Potsdam laboratory will be closely coordinated with new SIMS infrastructure currently being installed in both Dresden (accelerator SIMS) and Leipzig (NanoSIMS 50L). While the 1280-HR is intended mainly for geoscience studies, the facility will also support a limited number of well defined material science investigations, as well as serving as a platform for instrument development work. This abstract provides a brief overview of the new facility’s design and operational goals.

The state-of-the-art, ultra-high sensitivity and large geometry instrument currently being installed consists of the basic 1280-HR design, including the five trolley multi-collection system along with a Resistive Anode Encoder. The system is thus optimized for both low-uncertainty isotopic ratio determinations (e.g., \(\delta^{13}C\), \(\delta^{18}O\) and \(\delta^{34}S\)) as well as quantification and distribution mapping of low concentration elements in minerals, glasses or biological materials. The possibility of very high mass resolution of \(M/dM \geq 25,000\) allows the separation of isobaric masses, such as \(^{40}Ca\) and \(^{40}K\). The sample loading system consists of the standard 2-position carousel; a high capacity 500 l/s turbo pump with vibration damping provides improved vacuum in the sample source chamber. The most significant design modification unique to the Potsdam instrument is the addition of 5 flanges in the coupling and projection sections of the machine, including one intended for the integration of a total ion current measuring capability. Factory testing has shown a repeatability for \(\delta^{18}O\) determination (n= 10) of \(\pm 0.25 \%\) (1sd) on a quartz disk, with further improvements in analytical uncertainty expected once the instrument enters routine service. Envisioned key analytical topics include H, B, C, O, S and Pb isotopic studies, geochronology applications and the quantification of volatile elements in geological materials.
The stability of Fe-Ni carbides in the Earth’s mantle: evidence for a low Fe–Ni–C melt fraction in the deep mantle

A. Rohrbach1,2, S. Ghosh2, M.W. Schmidt2, C.H. Wijbrans1, S. Klemme1

1 Institut für Mineralogie, Westfälische Wilhelms–Universität Münster, Germany; arno.rohrbach@uni-muenster.de, ineke.wijbrans@uni-muenster.de, stephan.klemme@uni-muenster.de

2 Institut für Geochemie und Petrologie, ETH Zürich, Switzerland; sujoy.ghosh@erdw.ethz.ch, max.schmidt@erdw.ethz.ch

The deep Earth mantle contains significant amounts of carbon [1] and oxygen fugacity is sufficiently low [2-5] to contain diamond, metal (with varying Fe-Ni ratios) and carbides as reduced carbon bearing phases [6-8]. The Fe–C redox couple determines the nature of the reduced phases; their stability however ultimately depends on the presence of Ni. We have experimentally investigated the Fe–Ni–C subsolidus ternary at 10 GPa, and secondly determined eutectic melting temperatures in this system.

On the iron rich side we observe two stoichiometric carbides, (Fe,Ni)3C and (Fe,Ni)7C3. The solubility of nickel in these carbides is limited to XNi = 0.24 in (Fe,Ni)3C and XNi = 0.11 in (Fe,Ni)7C3. No carbides are stable on the nickel rich side of the ternary (XNi > 0.52) where Fe–Ni metal coexists with diamond. As a consequence, we obtain two fields where 3 phases coexist: (1) (Fe,Ni)3C coexists with (Fe,Ni)7C3 and diamond (2) Fe–Ni metal is in equilibrium with (Fe,Ni)3C and diamond.

Because Ni is more noble than Fe, it partitions strongly into the reduced phases such that at low metal fractions the metal phase reaches XNi > 0.5 (at a bulk Ni-content of 1800 ppm for the mantle). Thermodynamic calculations suggest that the mantle contains ~0.1 wt.% Fe,Ni metal at ~300 km depth. Adopting bulk C contents of 50 to 500 ppm in the mantle [1] would result in the phase association (Fe,Ni)3C + metal + diamond at 10 GPa. In the uppermost lower mantle, about 1 wt.% metal [2] is expected in a C-free mantle; this would dissolve ca. 100 ppm C, any further C would then lead to (Fe,Ni)3C carbide saturation.

An unexpected finding of this study is that eutectic temperatures in the Fe–Ni–C system are ~1210 °C at the Fe–C side, decreasing to 1125 °C at an XNi of 0.5 in the reduced phase. Hence we postulate that most of the deep reducing mantle will contain a small Fe–Ni–C melt fraction. Only those mantle regions where C-contents are less than what can be dissolved in the metal (50 ppm at 400 km depth, ~100 ppm at 700 km depth) would not contain such a melt phase.

References

Impact of deep convective storms on stable isotopes in precipitation, climate and paleo-altimetry records in NW-Argentina

Alexander Rohrmann1, Manfred R. Strecker1, Bodo Bookhagen2, Andreas Mulch3,4, Dirk Sachse1, Heiko Pingel1, Carolina Montero5

1Institut für Erd- und Umweltwissenschaften, University of Potsdam, 14476 Potsdam, Germany
2Department of Geography, University of California, Santa Barbara, CA, USA
3Biodiversity and Climate Research Centre (BiK-F) & Senckenberg, 60325 Frankfurt am Main, Germany
4Institute of Geosciences, Goethe University Frankfurt, 60438 Frankfurt am Main, Germany
5Instituto de Bio y Geociencias del NOA (IBIGEO), Universidad Nacional de Salta, CONICET, 4400 Salta, Argentina

The use of water stable isotopes (oxygen and hydrogen) have become common practice in studying the complex processes between atmosphere, topography and biosphere. Yet, despite its importance for identifying signals of elevation and/or climate change in stable isotope records a thorough understanding of atmospheric and topographic conditions influencing stable isotope fractionation is still lacking, especially within high-elevation orogens and orogenic plateaus. We report on stable isotope compositions of >200 stream-water samples along 3 E-W transects from the South Central Andes in Argentina between 22 and 28° S lat and ~64 to 68.5° W long, from the Andean foreland in the E, the Eastern Cordillera and across the Altiplano-Puna plateau in the W.

δ18O values from stream waters range from -0.6 to -11.5 ‰ along transect 1 (22 to 24° S), -4.3 to -11.4 ‰ for transect 2 (between 24 to 26° S), and -2.3 to -6.9 ‰ for transect 3 (26 to 28° S). We observe a negative correlation between δ18O and changes in elevation (lapse rate) for transect 1 of ~1.9 ‰ km⁻¹ (R²= 0.7). Along transect 2 the lapse rate reduces to 0.9 ‰ km⁻¹ (R²= 0.43), and there is no clear relationship for transect 3 with 0.2 ‰ km⁻¹ (R²= 0.17). There exists a large deviation from the empirical relationship between oxygen (δ18O) and hydrogen (δD) isotopes in meteoric water (2.8 ‰ km⁻¹), as well as Rayleigh fractionation, for transects 2 and 3.

Variations in storminess as a result of variable upper level (500 mbar) air-flow over the Andes control the isotopic composition of precipitation. As a result there exists a two to three-fold longitudinal N-S gradient with respect to the degree of isotopic fractionation, which is at odds with the generally applied isotope temperature fractionation, but correlates well with the occurrence of deep convective rain-storm events. The strong convection and higher storminess south of 24° S is exemplified by remotely sensed daily rainfall (TRMM 90th/50th percentile ratio) and NCEP/NCAR reanalysis climate data from 1979 to 2012. Our findings have fundamental implications for interpreting stable isotope records as proxies for elevation and the evolution of topography due to protracted tectonism, because the impact of deep convection in reducing the amount of stable isotope fractionation in precipitation -and not topography or climate- has not been considered in previous paleo-altimetry and tectonic studies.
Unraveling the role of faults in the evolution of orogenic belts- Insights from convergent analogue sand wedges

Tasca Santimano¹, Matthias Rosenau², Onno Oncken³

¹tsanti@gfz-potsdam.de
²rosen@gfz-potsdam.de
³oncken@gfz-potsdam.de

In an orogenic belt, the primary geometry of the wedge is affected by first order structures i.e. fault planes along which deformation occurs. Moreover, wedge growth and fault activity are related to the principles of the Critical Taper Theory (Davis et al, 1983). The Critical Taper Theory states that a sand wedge evolves towards a critical state characterized by a stable geometry and no internal deformation. In a sub- or supra-critical state, the wedges have an instable geometry and internal deformation occurs in order to adjust its geometry accordingly to reach the critical taper. This adjustment to reach criticality is made by creating new faults especially if new material is added to the wedge, or reactivating old faults in order to change the length or height of the wedge respectively. Spatially, the wedge can be characterized into three zones based on fault activity and geometry of the wedge (Lohrmann et al, 2003). To observe the temporal evolution of the faults, a series of simple analogue experiments were performed where sand wedges are created. In the experiments one parameter-basal frictional coefficient is varied from <0.4 to >0.6. The growth of the sand wedge and formation of the fault planes is recorded using Particle Image Velocimetry (PIV). Analysis of the PIV data consists of quantifying the fault spacing and lifetime of a fault i.e. first order deformation and reactivation of older faults i.e. second order deformation, in relation to the geometry of the wedge. Our experiments show that the magnitude of fault spacing follows a periodic pattern over time. Fault dip is consistent for all the faults. Second order deformation or fault reactivation is mainly observed in wedges with the lowest basal friction and presumably controlled by fault weakness (faults planes filled with low friction material from the basal detachment) and favorable stress conditions (shallow dipping maximum principal stress axis). Fault reactivation seems to allow the wedge to adjust its geometry more sporadically. The magnitude of displacement in the vertical and horizontal component, of a reactivated fault is controlled by the critical taper. Specifically, for weak wedges the rate of displacement over time is constant in the vertical component but increases in horizontal component. In addition, fault reactivation is not a continuous event but occurs episodically with increased frequency towards the end of an accretion cycle. These preliminary observations in the sand box experiments may shed light on the deformation in fault networks or the evolutionary stage of a natural orogenic belt.

References


Lohrmann, J., Kokowski, N., Adam, J., Oncken, O., 2003: The impact of analogue material properties on the geometry, kinematics and dynamics of convergent sand wedges. Journal of Structural Geology 25, 1691-1711
The Ongole domain in the SW part of the Eastern Ghats Belt represents a late Palaeoproterozoic granulite terrain and is mainly composed of a suite of charnockites and enderbites within which metapelitic granulites and basic granulites occur as enclaves. The magmatic formation history and the timing of the metamorphism are still under discussion. In this study, major and trace element geochemistry of the magmatic rocks suggests that the intrusions took place in a magmatic arc setting. The metapelitic granulites are Fe-Al rich hercynite-quartz bearing rocks showing reaction textures indicating two separate metamorphic events. The initial MP-HT event (spinel-quartz, >900°C at 6-6.5kbar) was followed by a MT-HP event (kyanite rim around spinel, grossular-rich Grt2, ~700°C at 9kbar).

Zircons from charnockites show oscillatory-zoned magmatic cores with broad metamorphic rims. LA-ICPMS dating revealed concordant magmatic intrusion ages between 1760 – 1720 Ma and a concordant metamorphic age between 1620 – 1600 Ma. In addition, magmatic cores as well as metamorphic rims in zircon from an intrusive enderbite show concordant ages of ~1600 Ma, indicating syn-metamorphic intrusion. Zircons from metapelites show unzoned to oscillatory-zoned inherited cores surrounded by narrow to broad rims. The inherited cores show a range of Palaeoproterozoic ages (1900-1700 Ma) while the rims show concordant ages between 1620 – 1600 Ma, complying with the metamorphic age from charnockites. In contrast, texturally controlled in situ EMP monazite dating of two chemically distinct monazite generations in metapelites revealed two metamorphic events separated by 50-80 Ma. Small, rounded to subrounded, unzoned monazite grains that are armored within porphyroblastic garnet show older ages of ~1620 Ma. These grains have higher proportions of Y+HREE and lower ThO₂ than the larger, patchy zoned matrix monazite grains with younger ages (~1540 Ma), only occasionally preserving older cores. The older monazite grew prior to Grt1, while younger monazite grains in the matrix and inclusions in Grt2 that are depleted in Y+HREE indicate that monazite crystallized together or subsequent to garnet.

Monazite in charnockites is strongly zoned with highly variable ThO₂ contents (7-28wt%). Some matrix grains are irregular in shape with highly corroded margins due to dissolution and precipitation processes. They hardly preserve any signature of the older (~1620 Ma) metamorphism.

The second generation of monazite crystallization is characterized by the incorporation of high ThO₂ contents by coupled dissolution-precipitation processes at high temperature conditions. This resulted in a chemical variation mainly controlled by huttonitic substitution, which is in contrast to high-Th monazite of other areas. It seems that during the second metamorphic monazite crystallization event, the monazite grains of the Ongole granulites were partially reset due to dissolution-precipitation processes. Due to this behavior, the monazite grains preserved complex metamorphic histories that are not recorded in the coexisting zircon grains, highlighting the fact that both zircon and monazite dating complement each other for better understanding and interpretation of a complex polymetamorphic terrain.

In summary, the Ongole domain mainly formed by magmatic intrusions from 1750-1700 Ma (formerly thought to be also a metamorphic event) and experienced its first UHT metamorphism at ~1600 Ma that was accompanied by syn-metamorphic intrusions. This was followed by a crustal thickening event 50-80 Ma later at ~1540 Ma.
Facies and depositional environments identified in Barremian limestones from the northwestern part of Pădurea Craiului Mountains (Romania)

Săsăran, E. 1, Bucur, I.I. 1, Pleș, G. 1

1Department of Geology, Faculty of Biology and Geology, Babes-Bolyai University, M. Kogalniceanu 1, 400084, Cluj-Napoca, Romania (emanoil.sasaran@ubbcluj.ro, ioan.bucur@ubbcluj.ro, george.ples@ubbcluj.ro)

The Barremian limestones from Pădurea Craiului Mountains, known in the old literature as „Lower pachyodont limestones” belong to the Coposeni Member of the Blid Formation. These carbonate deposits were analysed in two areas, the Șerbota Hill and Osoiu Hill. The limestones from Șerbota Hill are well stratified, represented by centimetric or decimetric beds, limited by subaerial exposure surfaces. The most frequent facies are „muddy”, other facies as bioclastic peloidal packstone/grainstone occur subordinately. The „muddy” facies is represented by mudstone/wackestone with charophytes, ostracods and gastropods, wackestone with small foraminifers and dasycladalean algae, peloidal wackestone with riviulariacean-type cyanobacteria, packstone with charophytes and bioturbated packstone with dasycladalean algae. The most important strucures evidencing the subaerial exposure of these deposits are the pseudo-microcarst and the microcarst surfaces, pedogenetic cracks, nodules, root traces and horizontal, planar and circumgranular cracks. Based on the facies analysis and the sedimentary structures we identified subtidal, normal-marine or restrictive, brackish/lacustrine and palustrine environments. In some cases the subtidal limestones are subaerial exposed, in other cases the depositional environments have a cyclic distribution. Based on the biotic component we recognized three evolutive stages: 1) marine, shallow-water subtidal; 2) brackish/lacustrine and 3) palustrine. The marine fauna and flora are well represented by dasycladaleans algae, foraminifers, rudist fragments and riviulariacean-type cyanobacteria. The marine stage was shifted to a more brackish/lacustrine one, with charophytes, ostracods, gastropods and small bivalvs with thin tests. The products of the vadose diageneisy are represented by stalactitic and meniscus type cements. The freatic diagenesis is evidenced by intense dissolution of the bioclasts and by the scalenoedric „dog-tooth” cement types. In the last stage, the lacustrine deposits are subaerial exposed and the limestones undergo pedogenetic processes. The limestones from Osoiu Hill crop out in a 90 m thick section, and are very good stratified. The main microfacies are represented by peloidal-oncoidal-fenestral grainstone, peloidal-fenestral packstone and fenestral wackestone/mudstone. Besides, we also identified mudstone/wackestone with ostracods and gastropods, ooidal-pisoidal grainstone/packstone, algal-microbial mats and unfossiliferous dolomitized, breccified mudstone/wackestone. Based on the identified facies and carbonate microfacies, we consider that these limestones were formed in the intertidal and supratidal domains. The facies associations and depositional environments, indicate that the limestones from Serbota Hill were accumulated on a depressionary area on the Barremian carbonate platform, and the Osoiu Hill limestones were formed on a more flat area, a little higher then the previous one. It is possible that the distribution of the carbonate environments from the Barremian platform in Padurea Craiului was controled by the irregular topography inherited after the Tithonian-Berrriasian exondation event.

Acknowledgments: This work is a contribution to the research project financed through COB Romania-Austria, 554/2012 grant.
The partitioning of P, Sc, Co and Zn between and within the minerals of Upper Mantle Peridotites

Tobias Schaefer¹ Lena Schaefer² Rainer Altherr³ Thomas Ludwig⁴

¹tobias.schaefer@geow.uni-heidelberg.de
²lena.schaefer@geow.uni-heidelberg.de
³rainer.altherr@geow.uni-heidelberg.de
⁴thomas.ludwig@geow.uni-heidelberg.de

The intracrystalline distribution and intercrystalline partitioning of the trace elements P, Sc, Co and Zn in peridotites was investigated using secondary ion mass spectrometry (SIMS). Major elements were analysed by electron probe microanalyses (EPMA). The samples are spinel and garnet peridotites of both orogenic and xenolithic origin from various locations like the Alps, Norway, the French Massif Central, and Saudi Arabia. To pay attention to possible chemical zoning of the minerals, we took profiles across entire grains with a solution of one measuring point every 5-20µm for EPMA and 50-60µm for SIMS. These profiles show that even in grains with chemical homogeneity over wide areas, close to the rims, most of the minerals show indeed chemical zoning to varying degrees, at least in some elements with low diffusion rates. These zonings would have been missed if only a few measurements would have been taken from the core.

Our results for P clearly show that its diffusion is very slow. Even in well-equilibrated samples with almost no chemical zoning, P is not sufficiently equilibrated. Either there are zonations or there are different concentrations in different olivine and/or pyroxene grains. It is well possible that the partitioning of P is almost independent of the temperature. Completed with data from literature (Witt-Eickschen & O’Neill 2005), our results show that P cannot be used for geothermobarometry. An interesting behaviour of P is that some of the intracrystalline heterogeneities, like distinct displacements or small-scale peaks in the concentration-profiles, seem to fall together with microtectonical elements like kink bands.

The partitioning of Sc and Co between orthopyroxene and clinopyroxene had previously been identified by Seitz et al. (1999) as temperature dependent and therefore can be used as geothermometers. Our data support this conclusion, while pointing out to pay attention to the different diffusion rates of the elements used for thermometry. In the case of Sc, Co and Zn, these differences could also be advantageous for the geothermometry of peridotites, which suffered an event of heating or cooling. Our samples sometimes show well equilibrated, completely flat concentration profiles for the fast diffusing Co and Zn, but zoned profiles for the slower Sc. If the concentrations of Sc in the cores are still flat, representing an older equilibration, it could be used to calculate the temperature before the event. Additionally Co and Zn represent the temperature of the last event itself.

Variation in plagioclase chemical and isotopic composition in the UCZ of the Eastern Bushveld Complex, South Africa

M. Schannor1*, L. Hecht2, I. Veksler3, T.D. Manyeruke4

1Institut für Geologische Wissenschaften FU Berlin, Germany (correspondence: *mathias.schannor@fu-berlin.de)
2Museum für Naturkunde (MfN) Berlin, Germany
3GFZ German Research Centre for Geosciences, Potsdam, Germany
4NKWE Platinum (Pty) Ltd., South Africa

The layering of the Bushveld complex and especially the petrogenesis of chromitite layers remains a matter of debate until today. This study presents new electron microprobe and Sr isotope data of cumulus and intercumulus plagioclase in the Upper Critical Zone (UCZ) of the Eastern Bushveld Complex in the stratigraphic interval between the UG2 chromitite and the Merensky Reef (MR). Transitions of lithologies were investigated with special attention paid to massive chromitite layers and thin chromite seams.

The composition of cumulus plagioclase ranges from An60 to An77 and shows no long-range differentiation trend in the UG2-MR interval. The intercumulus plagioclase composition ranges from An13 to An83. The lowest values represent plagioclase of the UG2 pegmatoidal footwall pyroxenite and the highest occur within the Bastard unit norite. Cumulus plagioclase in anorthosites are enriched in FeO and An component relative to that in norites and pyroxenites. Fe and An content of intercumulus plagioclase seem to be depleted relative to cumulus plagioclase.

An unusual feature is the distribution of potassium in interstitial plagioclase, cementing chromitite layers. In contrast to the adjacent silicate host rocks K is clearly depleted in chromitite hosted plagioclase regardless whether it is a massive chromitite layer or a thin chromite seam.

One explanation for this anomalous depletion of K could be the electrochemical migration of alkali metals in conductive intercumulus melt along gradients of redox potentials from chromitite layers to the underlying silicate rocks [1]. Sodium as a major component of plagioclase is buffered by plagioclase-liquid equilibrium in the mush and is therefore similar abundant in all layers.

Initial Sr isotopes of interstitial plagioclase in chromitite layers tend to be more radiogenic as in the neighbouring silicate rocks ([2],[3]) indicating a new influx of magma penetrating the residual magma and interacting with the overlying felsitic roof rock to form chromitites. These chromitites then move to the floor of the chamber entraining a small amount of magma within the slurry, which crystallises interstitial silicates with higher values for Sr isotopes.

This process could take place before the electrochemical migration of alkalis sets in.

A methodological approach of geochemical fingerprinting of in situ gold samples from various South African gold provinces

M. Schannor12* L. Hecht21 C. Gauert3

1 Institut für Geologische Wissenschaften FU Berlin, Germany (correspondence: *mathias.schannor@fu-berlin.de)
2 Museum für Naturkunde (MfN) Berlin, Germany
3 Dept. of Geology, University of the Free State, Bloemfontein, South Africa

Previous studies on electron microprobe analysis concerning the chemical composition of Gold mostly report results for Au, Ag and Hg (e.g. [1],[2]).

The main reasons for obtaining insufficient results for other elements are:

(1) Gold as major matrix element produces lots of X-Ray lines for each analyzing crystal overlapping with the other elements’ peaks. In the majority of cases an interference correction as introduced in [3] is difficult since there is a lack of well-established Gold standards containing various trace metals. (2) The detection limits (DL) for trace elements in Gold lie above the actual concentrations of these elements.

This study presents a procedure of analyzing the composition of gold producing sufficient low detection limits for some trace elements.

Low DLs are achieved by increasing the beam voltage and current to the feasible maximum and by increasing the counting time [4]. In general this is well applicable to gold samples without risking any beam damage since the high thermal conductivity of gold induces a transfer of the energy into the sample. A problem, however, occurs when the measurement time is too long. Due to an overcharging of the spectrometers reduced counting rates cause false results. Therefore a cumulative measuring mode has been applied dividing the counting time into shorter intervals (20s). Already 12 accumulations decrease the DL by a factor of approximately 3.5. Best results are found for 50 accumulations regarding the heavily increasing counting times per spot.

To test the method gold grains of various formations of different ages in South Africa and a certified secondary Au standard have been measured and compared to measurements with laser ablation ICP-MS and µ-SR-XRF of the same grains. Results for Au, Ag, Cu, Ni, Ti and Fe are in good agreement within given errors with the secondary Au standard and show as well conformity comparing the different applied methods.

LA-ICP-MS is more sensitive due to DLs and covers a broader range of elements whereas EMP yields a better reproducibility and is capable of analyzing smaller grains. Mercury and sulphur could only be determined by EMP.

The information obtained from this study emphasizes the problem of comparing analytical results that were obtained by different micro-analytical techniques and constitutes an important step to fingerprinting of economically important gold ores.

Anatolia’s high-pressure Rosetta marbles – multiple pseudomorphism

Franziska Scheffler¹, Roland Oberhänsli², Amaury Pourteau³, Matteo Di Lucia⁴

¹franziska.scheffler@geo.uni-potsdam.de
²roob@geo.uni-potsdam.de
³pourteau@geo.uni-potsdam.de
⁴dilucia@geo.uni-potsdam.de

Rosetta marbles comprise morphological diverse, radiating, rosette-like structures made of decimeter- to meter-scale calcitic rods of a high-pressure metamorphosed carbonate platform of Anatolia. Although these structures are locally large in diameter and spectacular in appearance, they were not investigated in detail so far.

The Anatolian microplate is characterized by several subduction-related, HP–LT metamorphic belts. These belts represent parts of the northern Anatolide–Tauride microcontinent that were buried and exhumed during the closure of a Neotethyan oceanic branch in late Cretaceous-early Palaeocene. This platform consists of a complete section of a passive continental margin covered by rift-related Triassic to upper Cretaceous pelagic sediments, which are composed of silty to pure marbles intercalated with meta-cherts.

Rosetta structures are restricted to the almost-pure marble horizons of the sequence and develop in three dimensions within single beds. Each calcitic rod is made of smaller calcitic fibers, showing parallel orientation oblique to the rod axis and strontium content abnormally-high (up to 3500 ppm) for calcite, but typical for aragonite. The fibers are in turn overprinted by even smaller and un-oriented calcite crystals.

The fibrous habit of calcite and its high Sr content indicate that they represent pseudomorphs after aragonite, formed during subduction-related metamorphism. Additional pieces of evidence for HP–LT metamorphism are aragonite inclusions in quartz (Raman spectroscopy) and widespread HP–LT index mineral assemblages in adjacent layers of metamorphosed Triassic clastic sediments. Locally, well-preserved rosetta structures display selenite-like calcite rods (e.g. swallowtail or palmate structures), strikingly resemble typical selenite morphologies, indicating they might represent pseudomorphs after gypsum mega-crystals. Radiolarian remnants in meta-chert and imprints of rosetta structures as bottom-marks of meta-chert beds suggest gypsum formation in a restricted, deep-marine environment in sulphur-oversaturated brines. Complete extraction of sulphur to form the calcite rods implies a dramatic change of the geochemical environment prior to burial in the subduction zone. During rock exhumation, the aragonite fibers were retransformed to calcite.

A detailed stratigraphic, petrographic and chemical inspection of Anatolia’s rosetta marbles allows us to distinguish syn-sedimentary from metamorphic crystal growth processes. We foresee that further investigations of these primary textures and pseudomorphs will allow a more detailed characterization of the northern margin of this Neotethyan domain.
Magnetic polarity stratigraphy in fluvial systems:
an example from the Upper Rhine Graben, Germany

Stephanie Scheidt¹, Ulrich Hambach ², Christian Rolf³

¹Stephanie.Scheidt@liag-hannover.de
²Ulrich.Hambach@uni-bayreuth.de
³Christian.Rolf@liag-hannover.de

Magnetic polarity stratigraphy is an indispensable technique for dating and correlation of rock sequences in Earth Sciences. Although, in principle, the method can be applied to any rock, magmatites and fine grained sediments yield generally best results. Geologically young and still water saturated fluvial sediments, however, are a special challenge for palaeomagnetic investigations. Low content of magnetisable minerals and various synsedimentary and post depositional processes result in inconclusive and scattered data sets. Hence, palaeomagnetic techniques are yet seldom applied in stratigraphic studies of those fluvial archives.

Here, we take a step forward and present the first results from a thorough magnetostratigraphic study on four drilling cores from the northern Upper Rhine Graben representing three depositional zones of the Heidelberg Basin. The silts, sands and gravels are delivered mainly by the river Rhine and secondarily by the river Neckar.

The components of natural remanent magnetisation (NRM) were separated by alternating field (AF) demagnetisation and thermal demagnetisation. The characteristic remanent magnetisation (ChRM) was isolated by principle component analysis (PCA). Further magneto-mineralogical investigations were performed. The results allow an unambiguous correlation among the wells. Hence, magnetostratigraphy sets out to provide an independent time frame for Pliocene and Pleistocene fluvial sediments where other approaches beside biostratigraphic age control does not come to result.

We discuss our data with respect to previous performed stratigraphic investigations such as pollen based biostratigraphy (Knipping 2008, Heumann per. comm.), lithostratigraphic correlation (Ellwanger et al. 2008), heavy mineral analyses (Hagedorn & Boenigk 2008) and sliding window spectral analyses of γ-ray logs (Hunze et al. 2012).

References


Linked uplift of the Central and Eastern Anatolian plateaus

Taylor F. Schildgen¹, Domenico Cosentino², Cengiz Yıldırım³, and Manfred R. Strecker⁴

¹tschild@uni-potsdam.de
²cosentin@uniroma3.it
³cengizyildirim0@gmail.com
⁴Manfred.Strecker@geo.uni-potsdam.de

Assessing geodynamic mechanisms of topographic growth and plateau development requires integrated observations of surface deformation, crustal-scale faulting, and geophysical characteristics of the crust, lithosphere, and mantle. Over the past 10 years, a wealth of geophysical data has provided new insights into the crust, lithosphere, and mantle beneath Eastern Anatolia, and in the past several years, geophysical surveys have also extended into Central Anatolia. Our new data on the uplift history of the Central Anatolian plateau margins together with kinematic analysis of the structures that were active during uplift reveal that the northern and southern margins of the Central Anatolian plateau were uplifted through fundamentally different mechanisms. Also, uplift in Central Anatolia occurred several million years later than in Eastern Anatolia. Considering the geophysical constraints on the modern geometry of the Tethyan slab, we propose that lithospheric delamination and slab break-off occurred first beneath Eastern Anatolia, and then propagated westward toward Central Anatolia. In Central Anatolia, uplift along the southern plateau margin seems predominantly related to slab break-off and slab tearing. In contrast, uplift of the northern plateau margin appears to result from crustal shortening along the restraining bend of the North Anatolian Fault. These uplift mechanisms may be linked, as mantle upwelling and westward mantle flow are predicted to occur after slab break-off, and both processes may have helped to form the North Anatolian Fault through accelerated westward escape of the Anatolian microplate.
Sn- and SnO₂-based nanoparticle films as anode material in Li-ion batteries

Sabine Schlabach¹, Goran Kilibarda¹,², Volker Winkler¹,², Michael Bruns¹, Dorothée Vinga Szabó¹

¹Karlsruhe Institute of Technology, Institute for Applied Materials, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen. sabine.schlabach@kit.edu
²University of Freiburg, Department of Microsystems Engineering, Georges-Köhler-Allee 102, 79110 Freiburg.

Improving long-term stability of electrode materials in Li-ion batteries requires a detailed understanding of interplay between synthesis parameters, resulting structure and morphology, chemical composition and application relevant properties of participating materials.

A microwave plasma process is used to synthesize Sn- and SnO₂-based nanoparticles with primary particle size below 10 nm and coeval narrow particle size distribution. The particles are deposited in-situ on preheated Ni substrates, forming highly porous nanoparticle films of approximately 100 nm to 2 µm thickness without conventional slurry formation or further treatment. These films are assembled in Swagelok half-cells together with Lithium foil as counter electrode, a Whatman glass fiber separator and soaked with electrolyte (1 M LiPF₆ in EC:DMC (50:50)).

Depending on the synthesis setup and applied parameters, the decomposition of the metal organic precursor, Sn(C₄H₉)₄, results in various material combinations, yielding different structures, morphologies and electrochemical properties. To understand the interplay mentioned above, the nanoparticles and the nanoparticle films are characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). The electrochemical behavior of Swagelok half-cells is tested by combining cyclic voltammetry (CV), long-term battery cycling and electrochemical impedance spectroscopy (EIS).

Complementary investigations show, that the in-situ deposited nanoparticle films possess almost tree-like structure, however, there is slight difference for the two material classes. The primary particles of the SnO₂-based materials are faceted and reveal tetragonal cassiterite structure. For the Sn-based materials the particles are spheres showing tetragonal structure of metallic Sn. Carbon is amorphous; and in some cases, onion-like structure is observed.

The cycling behavior of the investigated materials shows some characteristic features: large difference between discharging and charging capacity for the first cycles, pronounced negative slope for the first cycles, corresponding to huge degradation of specific capacity and a shallower slope after achieving coulombic efficiency close to 100%. The whole reaction of the cycle can be described as partially reversible. Using XPS, formation of a “solid electrolyte interphase” (SEI) is emerging for the first time by crossing a potential of 1 V. This interphase is dominated by lithium carbonate but also consists of a complex mixture of different lithium compounds and other decomposition products of the electrolyte. A matrix of hydrocarbons and the addition of vinyl carbonate to the electrolyte improve the cyclic performance. Besides the SEI-formation destruction and cracking of the nanoparticle film contributes to the degradation of the anode material. A significant improvement of the long-term stability could be obtained with Sn-C composite material.
Sandstone reservoirs occur in the lowermost part within the mixed carbonate-siliciclastics of the Mafraq Formation. The geometry and internal architecture, as well as the depositional environment of sand-bodies were studied in outcrop analogs in the central Oman Mountains.

1D sedimentological analyses in outcrops were used to create a sequence stratigraphic framework, 2D correlations and 2D wall panels. The thicknesses of sand-bodies range up to twelve meters. Their lateral extent can be mainly estimated as more than 4 to 5 kilometers. The sandstones show channel- and sheet-geometries (figure 1).

Depositional environments of the sand-bodies change from proximal tidal channels and channels of an estuarine system to more and more distal deposits of the intertidal to the subtidal zone. The sandstones of the estuarine channels possess a rather high reservoir volume.

![Figure 1: Schematic diagram of geometries, orders of magnitude of thickness and lateral extent of the sand-bodies.](image)
Effects of water and pressure on F and Cl diffusion in phonolite melt

Burkhard C. Schmidt¹; Michaela Freese² and Anna Böhm³

Experimentelle und Angewandte Mineralogie, GZG, Georg-August Universität Göttingen, Goldschmidtstr. 1, D-37077 Göttingen, Germany

¹ burkhard.schmidt@geo.uni-goettingen.de
² monika.michaela@arcor.de
³ present address: Institut für Energie- und Klimaforschung - IEK-2, Forschungszentrum Jülich, 52425 Jülich, Germany. a.boehm@fz-juelich.de

The diffusion of fluorine and chlorine in a Na-rich phonolitic melt of Montaña Blanca, Tenerife, was investigated experimentally between 850 and 1200 °C, at 1 and 2 kbar for anhydrous conditions and for water contents of about 2, 4 and 6 wt%. Diffusion couple experiments were performed in rapid quench cold-seal pressure vessels and in an internally heated pressure vessel. Experimental durations were 1 - 48. After the experiments, concentration profiles along the direction of diffusion were measured by electron microprobe and the diffusion coefficients were determined from the diffusion profiles by assuming concentration independent diffusion.

Fluorine and chlorine diffusion increases with increasing temperature and shows Arrhenian behaviour. The temperature dependence is stronger for chlorine diffusion than for chlorine diffusion. In the investigated range of water concentration, the activation energy remains roughly constant for both halogens with 90 ± 10 kJ/mol for F and 135 ± 20 kJ/mol for Cl. Water increases the diffusivity of both halogens. However, the effect of H₂O is stronger for Cl than for F. Compared to dry conditions, 6 wt% water leads to an increase in fluorine diffusivity of about 1.5 log units and of about 2 log units for chlorine diffusivity.

The effect of pressure on F-diffusion was investigated for dry conditions at 1000 °C in the range of 1 to 5 kbar. The results show that there is a small, but systematic increase in log D from about -11.94 m²/s at 1 kbar to -11.8 m²/s at 5 kbar. Further experiments are in progress to study the pressure effect for Cl diffusion.
The Evolution and Provenance of the Western Branch of the East African Rift System (Albertine Rift, Uganda)

Sandra Schneider¹, Dennis Brüsch², Jens Hornung³ & Matthias Hinderer⁴

¹schneider@geo.tu-darmstadt.de
²bruesch@geo.tu-darmstadt.de
³hornung@geo.tu-darmstadt.de
⁴hinderer@geo.tu-darmstadt.de

The 500 km long Albertine Rift, which forms the northernmost part of the western branch of the East African Rift System (EARS), is characterized by a succession of mainly N-S trending individual asymmetrical tectonic basins that are bordered at both sides by steep faulted escarpments that rise up thousands of meters adjacent to the rift floor. These include the > 5000 m a.s.l. high Rwenzori Mountains, which represent a horst block of old crustal rocks that is situated in the middle of the graben and displays the highest non-volcanic mountain range in Africa. Initiated in the middle Miocene, erosion of the thermally induced uplifted rift flanks led to the accumulation of up to 4 km thick syn-rift sediments into the graben that mainly comprise lacustrine, deltaic and fluvial siliciclastica from clay to coarse gravel with sporadically occurring ferruginous and calcareous intercalations. Outcrops of Miocene to Pleistocene synrift sediments are exposed in two areas on the Ugandan side of Lake Albert: 1) Kisegi-Nyabusosi and 2) Kaiso-Nkondo. During several field campaigns within the years 2006-2012, logging of siliciclastic outcrops revealed almost complete sedimentary successions for both study areas with thicknesses of ~340 m (Kisegi-Nyabusosi) and ~250 m (Kaiso-Nkondo). Based on detailed sediment sampling, this study aims to reconstruct the provenance of the rift sediments, which has not been studied in this part of the western rift branch, before. Our work is based on bulk rock geochemistry, light and heavy mineral analyses as well as Pb-U ages of detrital zircons which we compare to data obtained from potential source rocks, regoliths and modern river sediments that have been studied, contemporaneously. The major purpose of our study is: 1) to identify, characterize and separate potential source rocks/areas and to ascertain the time of their sediment supply, 2) to reconstruct the palaeogeographic and tectonic evolution of the sediment supply paths and depocenters, which includes the coupling and exhumation history of different tectonic blocks, with special focus on the uplift of the Rwenzori Mountains and 3) to describe and compare the spatial (Kisegi-Nyabusosi vs. Kaiso-Nkondo) and temporal (Miocene to Pleistocene) evolution of the rift sediments.
Weathering Controls on the Composition of Modern River Sediments in a Tropical Environment – a case study from the Western Branch of the East African Rift System (Albertine Rift, Uganda)

Sandra Schneider¹, Dennis Brüsch², Jens Hornung³ & Matthias Hinderer⁴

¹schneider@geo.tu-darmstadt.de
²bruesch@geo.tu-darmstadt.de
³hornung@geo.tu-darmstadt.de
⁴hinderer@geo.tu-darmstadt.de

The Albertine Rift (AR) is an active rift setting within a tropical environment that provides a perfect natural laboratory for studying all processes that influence the composition of siliciclastic rocks. In vicinity to the Equator the climate is warm and humid with seasonal monsoon-like rainfalls and high precipitation rates that are among the highest on earth. Sediments produced in this area are not only controlled by many different rock suites, but also by intense chemical weathering that has the ability to modify and even mask the original tectonic imprint. Besides extreme climate, the AR also represents a tectonically active rift setting, where thermal-induced rift-flank uplift provides differences in topographies, including the low-relief rift plateau as well as the high-relief Rwenzori Mountains. Exposed basement rocks comprehend the Archean Gneiss-Granulite-Complex, Palaeoproterozoic metamorphic rocks in mobile belts and rift-related Cenozoic intrusive magmatic provinces. Here, first-cycle sediments of all bedrock types (metamorphic, magmatic and sedimentary) can be studied.

Based on light and heavy mineral analysis as well as bulk rock geochemistry, this study presents detailed petrographic and geochemical data on the composition of 31 modern river sediments that drain the rift flanks, including the >5000 m high Rwenzori Mountains, towards the AR in western Uganda. Sampling sites cover active beds of first order rivers, but also lower order tributaries. The main purpose of our work is 1) to quantify the effects of chemical weathering on the sediment composition 2) to determine the factors that control the rate of weathering and 3) to ascertain the extent to which the original tectonic signature can be preserved even under intense chemical alteration in a tropical environment.

During this study we learned that the most crucial factor concerning weathering intensity is time and therefore the duration to what a sediment is exposed to alteration processes. Prolonged time is provided in low-relief regions, like the rift shoulder and adjacent plateaus, where tectonic quiescence leads to low erosion and transportation rates and minerals are longer stored in soils or overbank deposits. Strong chemical weathering is indicated by mature sediments that are enriched in quartz and are poor in feldspar and rock fragments and that show a distinct loss in mobile elements. In the high-relief Rwenzori Mountains, immaturity of produced sediments is demonstrated by a high content of instable minerals together with values of soluble elements that are close to the composition of the UCC. Here, high erosion rates, fast transportation and deficiency of intermittent storage lead to limitation of chemical weathering processes.
Radioactive Waste Disposal in Switzerland: the Geoscience Perspective

Michael Schnellmann & Andreas Gautschi

1Nationale Genossenschaft für die Lagerung radioaktiver Abfälle Nagra, Switzerland, michael.schnellmann@nagra.ch

In Switzerland, the Nuclear Energy Law requires the disposal of all radioactive waste in deep geological repositories. The procedure for selecting sites is defined in the Sectoral Plan for Deep Geological Repositories (SFOE 2008) and foresees site selection in three stages: Stage 1 consists of a systematic search approach starting with evaluation of the general tectonic situation, followed by host rock selection and a detailed search for adequate local host rock configurations. Regional fault zones are avoided and the envisaged repository depth for high-level waste is 450-900 m, with upper and lower limits constrained by the expected future erosion and the technical feasibility, respectively. Stage 1 has been concluded with the proposal of four different sedimentary host rocks for the low- and intermediate-level waste repository; for the high-level waste repository the Opalinus Clay formation in Northern Switzerland has been selected (Nagra 2008). The ongoing Stage 2 aims at narrowing down potential siting regions considering existing and new field data (e.g. 300 km of new regional 2D reflection seismic data). During Stage 3 the remaining sites will be investigated in detail (deep boreholes, 3D seismics) resulting in the final site selection and the General License applications.

Opalinus Clay is a 80 – 130 m thick marine claystone formation of Jurassic age (Aalenian). An extensive site and host rock investigation program has been carried out during the past 30 years comprising extensive seismic surveys, a series of deep boreholes within and around the potential siting regions, experiments in the International Mont Terri Underground Rock Laboratory and compilations of data from Opalinus Clay in third-party drillholes, outcrops and tunnels. Thanks to the wealth of existing information and experience and the comparably uniform lithology of the Opalinus Clay, process understanding gathered at these locations can be transferred to the potential siting regions, if the local conditions (e.g. host rock overburden, stress field) are considered. However, during the stepwise site investigation and selection approach, local site investigation programs will become successively more important.

Most relevant properties of Opalinus Clay for long-term safety are summarized as follows:
- diffusion is the dominant transport mechanism, with advection playing a secondary role
- faults do not represent preferential flow-paths due to an efficient self-sealing mechanism
- stable, reducing geochemical conditions and favourable sorption properties are present
- the self-sealing capacity of the Opalinus Clay minimizes the effects of perturbations caused by the repository (excavation damaged zone)

These conclusions are supported by multiple lines of evidence showing consistency among hydraulic properties (tests and observations at various scales), pore water geochemistry, laboratory- and in-situ diffusion experiments and natural tracer profiles across the Opalinus Clay.

References:
Cr isotopic variations in Neoarchean to Paleoproterozoic sediments as tracer for the evolution of free atmospheric oxygen

Ronny Schoenberg¹, Ilka C. Kleinhanns², Sümeyya Eroglu³ and Florian Kurzweil⁴

¹schoenberg@ifg.uni-tuebingen.de
²kleinhanns@ifg.uni-tuebingen.de
³suemeyya.eroglu@uni-tuebingen.de
⁴flokurzweil@hotmail.de

Stable Cr isotopic variations in sedimentary archives bear great potential to reveal significant redox-changes in the atmosphere and oceans throughout Earth’s history [1,2]. Thereby, small variations in δ⁵³/⁵²Cr values of up to 2.75 billion year old banded iron formations (BIFs) have been interpreted as the initiation of oxidative weathering on the continents, facilitated by small levels of oxygen in Earth’s atmosphere [1]. This is more than 300 million years before the generally accepted first appearance of free atmospheric oxygen at the 2.4 Ga Great Oxidation Event (GOE), as indicated by the disappearance of mass-independent fractionation of sulfur isotopes (MIF-S). Others [3], however, doubted this interpretation and suggested that the observed Cr isotope variations in Neoarchean BIFs are caused by non-redox isotopic effects during precipitation of chromium from deep-water hydrothermal sources. Another interesting observation in the study of [1] is that 2.4 – 1.85 billion year old BIFs lack any anomalous δ⁵³/⁵²Cr values, which lead these authors to speculate that atmospheric oxygen might have disappeared again directly after the GOE and re-emerged some 500 million years later.

In this study we determined the stable Cr isotopic compositions of well-preserved Neoarchean to Paleoproterozoic chemical sediments from near-surface depositional environments, in order to address these problems. Our first few data of carbonates from the 2.55-2.48 Ga old Malmani Subgroup of the Transvaal Basin in South Africa have so far not revealed any Cr isotopic compositions that point towards oxidative continental weathering at that time. However, much more work is needed to confirm this preliminary statement. Large Cr isotopic variations with δ⁵³/⁵²Cr values between +1.4‰ and -1.2‰ in 2.06 Ga old lacustrine carbonates, marine stromatolites and jasperites from the Pechenga Greenstone Belt and 2.0 Ga old organic-rich siliceous deposits from the Onega Basin, both situated in the NW Fennoscandian Shield, reveal significant redox-cycling of chromium on the continental surface during that time. These results clearly dismiss the hypothesis of [1] that free atmospheric oxygen disappeared again after the GOE and only reappeared 1.85 billion years ago.

Characterization of natural oxygen carriers for chemical looping combustion

Alexander Schopf¹, Florian Mayer² & Hans-Joachim Massonne³

¹ alexander.schopf@mineralogie.uni-stuttgart.de
² florian.mayer@ifk.uni-stuttgart.de
³ h-j.massonne@mineralogie.uni-stuttgart.de

Chemical looping combustion (CLC) is a new technology to burn solid, liquid and gaseous fuels in power plants. This technique allows the gathering of pure carbon dioxide in the exhaust gas for carbon capture and storage. Further benefits are the overall loss of efficiency below one percent and no production of nitrogen oxides NOx. CLC uses a dual fluidized bed system. To transfer the oxygen from the air reactor to the fuel reactor solid oxygen carriers (OC) are required. The OC emits its oxygen in the fuel reactor to burn the fuel. Transported back to the air reactor the OC is oxidized by air.

The main target of the study is the search for environmentally friendly natural OCs that have a good abrasion resistance, a high reactivity with the combustion gases (CO, H₂ and CH₄), a high oxygen capacity, and a good price-performance ratio. In addition, these OCs should be stable up to at least 1000°C and last for as many oxidation-reduction-loops as possible. Commercially available OCs such as various Fe- and Mn-oxides were studied by thermal gravimetric analysis (TGA) to simulate the conditions in a CLC power plant, such as different gas mixtures and temperature ranges. The OCs are conditioned before testing (crushed and/or sieved to provide particle sizes between 125 and 250 μm) to ensure comparable test conditions. Before and after the treatment in the TGA the OCs are analyzed with different mineralogical methods using a polarizing microscope, a C-H-analyzer, an X-ray powder diffractometer, an ICP-OES, an X-ray fluorescence spectrometer, and an electron microprobe including an energy-dispersive system. After testing the aptitude of potential OCs in the TGA, large-scale experiments were achieved in the electrically heated 10 kWth bubbling fluidized bed reactor at the Institute of Combustion and Power Plant Technology at Universität Stuttgart.

So far, ilmenite sands were used as OCs. In this project different iron oxides, chromite and pyrolusite were tested. Ilmenite and MIOX® ME 400 from the Kärntner Montanindustrie (Austria) have already demonstrated their suitability as OCs in the pilot plant at the IFK. MIOX® ME 400 consists basically of hematite with a tabular crystal habit; the ilmenite is granular. Both substances endure more than 12 oxidation-reduction-loops. More samples will be tested in the TGA and the pilot plant in the future.
ThinSectionManager -

An Integrated Software Solution for Archiving and Analyzing Thin Section Data

M. Schuh ¹; D. Bendias ²; T. Aigner ³

¹M.schuh@neckargeo.net; ²Daniel.bendias@uni-tuebingen.de; ³T.aigner@uni-tuebingen.de

The ThinSectionManager software application combines a robust, spatially aware database engine and a flexible file storage system with a convenient graphical user interface to systematically store and access thin section data.

Being based exclusively on open source software components and by relying on open or well documented data formats, ThinSectionManager aims to provide a sustainable, long-term software solution for the management of thin sections as digital assets, and to avoid the sometimes severe business consequences of vendor lock-in and employee turnover.

Within the application, thin sections are hierarchically grouped into projects and individual spatial locations. Individual thin sections can then be described directly in the program in a very systematic way. At first, overview and detailed images as well as master data like measured depth, name and location are recorded for each thin section. The ThinSectionManager provides the means to gather a wide variety of additional data for each individual thin section, based e.g. on lithological, sedimentary, petrophysical and diagenetic parameters and pre-defined classifications (e.g. grainsize, sorting, Dunham classification etc.). In addition, ThinSectionManager offers user-definable catalogues for the more flexibly describable or project specific parameters related to thin sections, such as facies associations, clastic components or specific names of microfossils.

In order to access, search and filter all available thin section data within a project, ThinSectionManager offers a convenient point-and-click interface to construct queries of arbitrary complexity over the entire range of available parameters. These queries can then be saved and restored in order to provide reproducible search results, and return a matching subset of the bulk data (e.g. all oolitic grainstones showing porosity in a specific stratigraphic interval). Finally, printable reports of the queried data, based on pre-defined or user-definable layouts, can be created, as ThinSectionManager offers export functionality to an enterprise-grade open source reporting solution (Jasper).

As a result the ThinSectionManager provides an easy to use software to input, manage, examine and reutilize thin section data.
Kyanite bearing corundum-muscovite (ruby-fuchsite) rocks from Mysuru (province of Karnataka, India) were recently described by Raith and Schuhmacher (2012). In the frame of an experimental investigation on fluid-induced mineral reactions with reaction coronas and their natural analogues, we investigated a new sample of this rock. It shows an almost completely monomineralic corona of kyanite (Ky) grown around corundum (Crn) grains, with minor amounts of muscovite. Such Ky-reaction coronas are rather rare in natural rocks. The rubies vary in size from 100 microns up to 1 cm and constitute less than 10 vol% of the rock. The thickness of the Ky-corona is between 10 and 100 μm and largely independent of the host mineral’s diameter. Both mineral phases are homogeneous regarding their chemical composition. Kyanite crystals do not show epitactic growth patterns with the host. The valley-and-hill shape of Ky-Crn phase boundary is typical for fluid-dominated dissolution-reprecipitation processes along fluid pathways in the Ky rim such as grain boundaries and cleavage planes (Lucassen et al. 2012). Besides lamellar twinning Crn contains up to three differently oriented sets of plane structures crosscutting the grain. These planes are composed of an Al-phase with an Al₂O₃ content of 83 wt% and no other significant oxides (determined by electron microprobe), only trace amounts of SiO₂. This phase is probably an Al-hydroxide (diaspore or boehmite) as described previously. This phase was also observed at the grain boundaries Crn-Ky and along Ky-Ky grain boundaries inside the corona as fine ~ 1μm thick layers. In contrast to the layers within the host mineral these boundary layers contain measurable amounts of SiO₂ increasing with distance to the Crn grain. The layers in and around the rubies form a network, connecting host and corona minerals probably representing fluid pathways. These would probably play an important role for the interface-controlled dissolution-precipitation reaction of corundum with an aqueous silica bearing species as proposed by Raith and Schuhmacher (2012).
Experimental investigation of a fluid induced mineral reaction: Corundum $\rightarrow$ aluminosilicate

Dina Schultz1, Gerhard Franz2, Richard Wirth3, Jörg Nissen4

1d.schultz@campus.tu-berlin.de

2 gerhard.franz@tu-berlin.de

3 richard.wirth@gfz-potsdam.de

4 joerg.nissen@tu-berlin.de

We investigated the transformation of corundum ($\alpha$-$\text{Al}_2\text{O}_3$) into aluminium silicate phases in the presence of silica bearing fluids. The pressure-temperature range was set between 5-10 kbar and 500°-800°C in hydrothermal and piston cylinder experiments. Starting material was preferably inclusion-free natural corundum (‘leucosapphire’) and synthetic undoped corundum in single crystals of ~1 mm$^3$ size, together with powdered SiO$_2$ (tridymite, quartz) in either pure water or 25% HCl, additionally in experiments with water variable concentrations of NaCl and KCl were added to increase Al solubility. Aim of the study was to reproduce naturally occurring reaction coronas of kyanite around corundum.

However, we observed that the formation of aluminium silicate phases at the corundum surface seems to be limited not only by the sluggish nucleation rate of the Al$_2$SiO$_5$ polymorphs, but also by the corundum grain’s microstructure. In a first step a silica-enriched propagation front is visible penetrating into the grain from the surface towards grain centre. SiO$_2$ contents of up to 1 wt% are incompatible within the corundum structure, which leads in a second step to the formation of nanometer-thick silica-concentrated lamella. These Al-Si-bearing lamellae show strict epitactic intergrowth with the host grain as they are all parallel to the corundum basal plane (0001). Near to the propagation front these lamellae are randomly distributed, while with distance to this front the lamellae are concentrated or accumulated along μm-thick symmetric planes crosscutting the corundum grain parallel to (0001). Similar structures have been discussed in previous reports and been described as exsolutions and glide planes. Transmission electron microscopic investigations identified the silica rich lamellae structurally as pyrophyllite.

Given the fact that pyrophyllite is thermodynamically unstable at these experimental conditions floats the option that we observe a metastable nucleation and growth of nanosized pyrophyllite before formation of aluminiumsilicate.
Quantification of ionic diffusion in sodalites by micro-Raman spectroscopy

A. Schulz\(^1\), C. H. Rüscher\(^2\), L. Schomborg\(^3\), J. C. Buhl\(^4\)

\(^1\)alexander.schulz@pci.uni-hannover.de
\(^2\)c.ruescher@mineralogie.uni-hannover.de
\(^3\)l.schomborg@mineralogie.uni-hannover.de
\(^4\)j.buhl@mineralogie.uni-hannover.de

Quantification of ionic diffusion in sodalites is important for the understanding of ionic-exchange and sorption and desorption of fluids (H\(_2\), O\(_2\), H\(_2\)O, CO\(_2\)) in such porous systems. In this respect it is surprising that only few publications in this direction are available. E.g., Sippel [1] and Levi et al. [2] used at that time very sophisticated radiogenic methods for significant Na-self diffusion for NaCl-sodalite crystals at temperatures between 500 and 700°C. Barrer and Saxon-Napier [3] claimed the effect of some very high proton diffusion in basic hydro sodalite below 100°C using dielectric measurement technique. The effect of reversibel ion-exchange in sodalites, e.g. as used for the preparation of solid solutions Na\(_x\)(Li, K, Rb, Ag)\(_{8}\)(Al\(_6\)Si\(_6\)O\(_{24}\))Cl\(_2\), has been known for a long time, too [4]. Thus it could be interesting to re-investigate ionic diffusion in sodalites in a more systematic way. There could also be growing interest to get deeper insight in the reactivity of embedded anion group like B(OH)\(_4\)\(^-\) and BH\(_4\)\(^-\) in the sodalite cage [5]. Here the first one could be seen as the end-member of the second one via a stepwise reaction with water for hydrogen release: Some insight about this, about the exchange of Na\(^+\) and K\(^+\) ions and also about the stepwise dehydration of Na\(_8\)(Al\(_8\)Si\(_6\)O\(_{24}\))(B(OH)\(_4\))\(_2\) sodalite could be achieved in temperature dependent infrared (TIR) absorption experiments [6]. Another approach is now possible with the use of micro-Raman spectroscopy on crystals of sufficient size and quality. We may show that this method enables depth profile analysis with spatial resolution in the order of 1 \(\mu\)m and sufficient good relative intensity and spectral resolution to estimate diffusion coefficients for OH\(^-\) and H\(^+\) for Na\(_8\)(Al\(_8\)Si\(_6\)O\(_{24}\))(B(OH)\(_4\)) in dehydration and H\(^+\)/D\(^+\)-exchange experiments, respectively. The data are compared to Na-self diffusion coefficients and data estimated using Na/K exchange experiments of Na\(_8\)(Al\(_8\)Si\(_6\)O\(_{24}\))Cl\(_2\) and also with respect to H/OH-exchange in Na\(_8\)(Al\(_8\)Si\(_6\)O\(_{24}\))(BH\(_4\))\(_2\). It may be noted that the method (micro-Raman spectroscopy) could complement micro-IR-imaging on fluid sorption and desorption in nanoporous systems [7] providing an improved spatial resolution.

Evidence for subduction of Eurasian continental lithosphere under the Pamir

B. Schurr1, C. Sippl2, F. Schneider3, S. Kufner4, X. Yuan5, J. Mechie6, L. Ratschbacher7 and the TIPAGE team

1schurr@gfz-potsdam.de
2sippl@gfz-potsdam.de
3felix@gfz-potsdam.de
4kufner@gfz-potsdam.de
5yuan@gfz-potsdam.de
6jimmy@gfz-potsdam.de
7lothar@geo.tu-freiberg.de

Subduction of lithosphere is one way that shortening during continental collision may be accommodated. Although continental crust generally resists submergence due to its buoyancy, it may be pulled down intact by a leading oceanic plate during the last stage of the Wilson cycle or, alternatively, the lighter crust may be scraped off partly or entirely to allow the remnant lithosphere to sink into the mantle. The Pamir north of the western Himalayan syntaxis is arguably the best place to study this process, as an active Wadati-Benioff zone attests to subduction and mantle xenoliths to deep burial of Eurasian crust. This is remarkable as, to the best of our knowledge, no oceanic plate is involved here. The intermediate depth earthquakes are an oddity too, because everywhere else on Earth deep seismicity (depth > 100 km) is exclusively occurring in active or closed oceanic subduction zones. However, it is these earthquakes that allow us to image deformation and structure at depths, where we are blind in other orogens. We use seismological data from several temporal deployments between 2008 and 2012 and a suite of passive seismic methods, i.e. high resolution earthquake locations, source mechanisms, tomography and receiver functions, to understand the processes acting at this unique setting. The relocated seismicity clearly defines two distinct planes below Pamir and Hindu Kush separated by a gap where strike and dip directions change abruptly. The Pamir seismic zone forms a thin (~10 km width), curvilinear arc that strikes east-west and dips south at its eastern end and then progressively turns by 90° to reach a due eastward dip at its southwestern termination. Receiver functions (RF) reveal that the earthquakes are occurring inside a thin low velocity zone (LVZ), which can be tracked to at least 150 km depth. We interpret this as subducted lower crust that is eclogitized along its descent. Local earthquake tomography images an arcuate high velocity region underlying the seismogenic plane, most probably representing cold Eurasian mantle lithosphere. On top of the LVZ imaged by RFs and just above the onset of deep seismicity, very low seismic velocities attest to probably middle crustal material that has been pulled down to depths locally exceeding 90 km before it is detached from the lower crust. We show that beneath the Pamir a big chunk of crust is pulled down by cold mantle lithosphere to depths between 80-100 km, where lower crust and mantle detach to continue subduction, and from where on earthquakes commence inside the lower crust probably due to metamorphic reactions.
A new approach combining diffusion chronometry and thermal modeling of parent body metamorphism to identify pre-accretion features

Schwinger, S.¹, Dohmen, R.² and Schertl, H.-P.³

¹Sabrina.Schwinger@rub.de  ²Ralf.Dohmen@rub.de  ³Hans-Peter.Schertl@rub.de

Carbonaceous chondrites are a unique archive of the early history for the solar system since their bulk chemistry is primitive. These meteorites are affected by different degrees of metamorphism on their parent body. It is one of the most important challenges to distinguish if certain element and isotope signatures found in minerals or mineral aggregates were formed before or after accretion into the parent body. We developed a strategy to distinguish between these two cases and applied it to the CO3 chondrite Kainsaz.

We analyzed the chemical zoning in isolated refractory forsterites as well as chromites and fayalitic olivines in type II chondrules of Kainsaz using the electron microprobe and simulated the profiles found in olivine using compositionally dependent diffusion coefficients according to [1], [2], and [3]. The quality of the fits and the consistency between different elements (Fe-Mg, Mn, and Ca) strongly indicates that the zoning was formed by solid-state diffusion. Since diffusion in olivine is strongly temperature dependent, the chemical zoning provides only an integrated information of the thermal history. We modeled the measured profiles using the integrated diffusion coefficient over time as fitting parameter. This approach allows us to quantify the magnitude of the compositional change of the initial profiles by diffusion processes, which is directly related to the thermal history of the mineral.

In addition we applied various spinel-olivine thermometers [e.g., 4, 5] for chromites associated with olivine in Type II chondrules and found consistently very high temperatures (1300-1600°C). In combination with our diffusion modeling we can conclude a rapid cooling (on the orders of 100 °C/hours) from these high temperatures, which is consistent with the chondrule texture. Thus, the zonings observed have to represent pristine features formed prior to the final accretion into the parent body and did not re-equilibrate during thermal metamorphism on the parent body. We can further conclude that the formation of Fa-rich olivines in the solar nebula at high temperatures requires non-canonical redox conditions (significantly above IW-6).

Our approach also allows us to constrain the later thermal history of the parent body. Peak temperatures for parent body metamorphism of Kainsaz were estimated to be about 480°C by Raman spectroscopy of carbonaceous matter [6]. Assuming these peak temperatures, the mean cooling rate on the parent body must have been at least about 100°C/Ma to preserve the pristine zoning in the olivine crystals. Numerical modeling of the thermal histories in different burial depths in parent bodies of different sizes revealed that thermal histories with peak temperatures of 480°C and fast enough cooling rates can be only realized in bodies with a radius smaller than about 20-30km.

Application of image logs for geomechanical characterization of the Malm Aquifer in the Bavarian Molasse Basin

Robin Seithel¹, Ulrich Steiner², Prof. Dr. Thomas Kohl³, Dr. Birgit Müller⁴

¹Robin.Seithel@student.kit.edu
²Steiner@erdwerk.com
³Thomas.Kohl@kit.edu
⁴Birgit.Mueller@kit.edu

Herein we present the first results of a local stress field study around strongly deviated geothermal wellbores in the Molasse basin and its potential hydraulic impact. So far, wellbore logs have been analyzed in order to identify fracture planes, facies and karstification within the reservoir. These results in combination with well tests and temperature logs can serve for an estimation of the hydraulic parameters. Almost every geothermal well in the eastern Molasse basin is strongly deviated. Usually the principal stresses around the borehole are inclined to the wellbore axis and failure phenomena such as breakouts (BOs) and drilling induced fractures (DITFs) are not directly aligned with the stress field. From BO and DITF the stress field in the periphery of the wellbore could be characterized in terms of stress orientations and relative stress magnitudes. These dictate the angles of BO and DITF along the wellbore walls. The observed BO and DITF data combined with modeling results enables us to estimate the orientation and magnitude of the local stress field. The study site consists of three wells, two of them being parallel to the nearly consistent N-S regional stress field and one perpendicular to it. The latter has a better hydraulic connection to the reservoir and thus a higher productivity. In the first two wells the observed BOs and DITFs are in good agreement with the regional stress field. Because of the orientation of the third well we assume a different BO and DITF pattern. However, no significant changes could be discerned, a local perturbation of the regional stress field is therefore hypothesized. These stress changes may result from local structures which account for the improved hydraulic conditions. A slip- and dilation- tendency analysis can improve the understanding of wellbore and reservoir connectivity and its hydraulic impact.
The influence of H₂O and pressure on phase relations in peralkaline iron-rich melts: an experimental study

NICKI CAROLINE SIERSCH¹, CHRISTOPHER GIEHL*¹, MICHAEL MARKS¹ AND MARCUS NOWAK¹
¹Fachbereich Geowissenschaften, Eberhard Karls Universität Tübingen, Germany
*correspondence: christopher.giehl@uni-tuebingen.de

Previous phase equilibrium experiments investigated the phase relations of a peralkaline phonolitic dyke rock, which is a potential parental melt composition of the Ilímaussaq plutonic complex/South Greenland (Marks & Markl 2003, Giehl et al. 2013). In these experiments, all major mineral phases of the dyke rock except iron-rich amphibole were reproduced at 100 MPa, low fO₂ and nominally dry conditions. In this study, we present phase equilibrium experiments investigating the effect of H₂O melt concentration and P on phase relations and liquid lines of descent. Besides higher H₂O content, increasing P is expected to stabilize amphibole (Harms et al. 2004).

Starting glasses were pre-hydrated with 2.7 and 4.7 wt% H₂O at 100 MPa and 850 °C in gold capsules for H₂O-bearing experiments. Run products were analyzed with Karl-Fischer titration, infrared spectroscopy and electron microprobe analysis (EMPA). Phase equilibrium experiments were performed in hydrothermal rapid-quench cold seal pressure vessels at 750 to 700 °C and low fO₂ adjusted with graphite-lined gold capsules. Nominally dry glass powder was used for experiments at 150 MPa and prehydrated glasses were used for experiments at 100 MPa. Mineral phases and coexisting glasses were analyzed with EMPA.

The observed mineral phases are clinopyroxene (Cpx), aenigmatite (Ae, Na₃Fe₅TiSi₉O₂₀), eudialyte (Eud, Na₄Ca₂(Fe,Mn)ZrSi₈O₂₂(Cl,OH)₂), alkali feldspar (Afs), nepheline (Nph) and sodalite (Sdl, Na₈Al₆Si₆O₂₄Cl₂) coexisting with residual melt (Fig. 1). The comparison with previous results shows that the abundances of Afs, Nph and Sdl decrease with increasing H₂O melt concentration and mineral phase sizes of Afs and Ae increase (up to 160 µm). Close to H₂O-saturation Nph and Sdl are unstable. For nominally dry conditions phase stabilities at 150 MPa are identical compared to 100 MPa experiments. Neither higher H₂O melt concentration nor increased P stabilized amphibole. However, mineral phase compositions of coexisting Cpx, Ae and Eud provide new data to calibrate a possible geothermometer based on Mn partitioning between these mineral phases.

Fig. 1: Experimental products at 100 MPa, 700 °C, hydrated starting glass (backscattered electron image): clinopyroxene (Cpx), aenigmatite (Ae), eudialyte (Eud), alkali feldspar (Afs) and residual glass (Gl).

This is the abstract submission template. Please use this file to fill out and upload your abstract(s). Ensure that it fits into one column and one page.

Mechanisms of minor and trace element incorporation in sphalerite from the district of Aachen/Kelmis (Germany, Belgium)

S. Sindern¹, H. Bostelmann², F.M. Meyer³, A. Hellmann⁴, L. Gronen⁵, S. Bohle⁶,

¹sindern@rwth-aachen.de
²heike.bostelmann@rwth-aachen.de
³m.meyer@rwth-aachen.de
⁴andre.hellmann@rwth-aachen.de

The sphalerite structure allows incorporation of numerous elements, such as Ag, Cu, Tl, Cd, Co, Fe, Mn, Mo, Ni, Pb, As, Ga, In, Sb, Te, Ge, Sn. The abundance of elements that are in solid solution in the sphalerite lattice is controlled by coupled substitution. Other elements may be hosted in (micro-) inclusions of other minerals. Some of the elements accumulated in sphalerite are critical for technological processes (e.g. Ge, In, Te). Sphalerite, as well as its processing products, can thus play an important role as a source for these critical elements. In this study LA-ICP-MS, electron-microprobe and high-resolution electron FEG-SEM analyses are applied to investigate minor and trace element variations in sphalerite from the Pb-Zn occurrences of Diepenlinchen, Albertsgrube, Hastenrath, Thermae, Bleiberg and Altenberg in the German and Belgian district of Aachen and Kelmis. The data are compared with literature data as well as new analyses from a wide range of sphalerite deposits and occurrences such as Bad Grund, Breitenbrunn, Lüderich, Meggen, Sofia Jacoba, Werlau, Wildberg (Germany), El Aguilar (Argentina), Hollersbach, Lafatsch (Austria), Maarmorilik (Greenland), Gorno (Italy), Trepca (Kosovo), Carhuacayan, Casapalca, Cerro de Pasco, Huanzala (Peru), Mezica (Slovenia), Santander (Spain), Ammeberg, Dannemora, Falun, Garpenberg, Loka Brunn, Sala, Stollberg, Vattholma (Sweden), Capnic, Herja, Rodna, Tibles (Romania), Nenthead (UK), Elmwood, Joplin (USA). In the German and Belgian district of Aachen and Kelmis sphalerite formed in post-variscan carbonate-sulfide veins that are hosted by Upper Devonian to Upper Carboniferous shales and carbonates. The mineral is characterised by collomorphous textures with alternating bands varying in colour between dark brown and light brown/yellow (“Schalenblende”). Most element concentrations are found to be in the same range of values of other occurrences world-wide. Only Tl shows exceptionally high values. The incorporation of trace elements in sphalerite from Aachen and Kelmis is distinct for particular elements and thus controlled by distinct mechanisms. While Ag is mainly incorporated in inclusions, other elements like Sb and Tl are in solid solution in the sphalerite lattice due to coupled substitution with Zn. The abundance of minor and trace elements in collomorphous sphalerite is highly variable, even on a deposit scale. Regional, structural or lithologic control on element distribution cannot be observed. Rather, local fluid-mineral equilibrium, sulphide mineral abundances, and the availability of elements appear to ASCERTAIN the main control on sphalerite trace metal compositions.
Organic Facies Variability in Posidonia Black Shale from Luxembourg: Implications for Depositional Environment and Thermal Maturity

Jinli Song¹, Philipp Weniger¹, Ralf Littke¹

¹Institute of Geology and Geochemistry of Petroleum and Coal, Energy and Minerals Resources Group (EMR), RWTH Aachen University, Lochnerstr. 4-20, 52056 Aachen, Germany

Posidonia Shale (Lias ε, Lower Toarcian) samples were obtained from a well in southern Luxembourg (Esch-sur-Alzette). Elemental compositions and organic facies were studied along the cores, and accordingly the thermal maturity and depositional environment were evaluated. The organic matter content is high with an average of 7.2 %, ranging between up to 13.5 % (60.8 % in one exceptional sample) and 2.8 %. The average vitrinite reflectance value is about 0.55 %, indicating an early stage of oil generation. Peak oil generation has definitely not been reached. Several biomarker based maturity parameters support the low thermal maturity including OEP values, low ratios of C₂₇ diasteranes / (diasteranes + regular steranes) and C₂₉₅ α,1₄α,1₇α(H)-steranes 20S/(20S+20R).

Rock-Eval data and microscopy observations reveal that the organic matter is composed of hydrogen-rich type II kerogen derived from abundant alginite. Small algal bodies derived from nanoplankton predominate, but large telealginite (Tasmanales) also occurs. Fish bones and pyrite are also abundant characterizing a marine depositional environment where strong sulphate reduction occurred. Short-chain n-alkanes predominating over long-chain n-alkanes, as well as a low terrigenous/aquatic ratio (TAR) indicates a low input of terrigenous organic matter. Sterane distribution indicates an origin from a marine carbonate depositional environment which corresponds to the general marlstone lithology. Additionally, C₃₀-2₄-propyl-1₄α(H), 1₇α(H)-cholestane (20R) was also detected, supporting the marine origin.

The depositional environment is dominated by anoxic conditions but with several more oxic interruptions. Relatively high concentration of gammacerane but also with certain variations with depth combined with low Pr/Ph ratios could probably indicate higher salinity in the paleoenvironment during deposition of the Posidonia Shale in Luxembourg. The highest C₂₇/C₂₉ ratio due to more algal input might indicate a maximum flooding zone beneath the bottom of the altered falciferum zone of the Lower Toarcian. This interpretation would fit well to the global sea level curve and indicate the most productive section for the Posidonia Shale.
Experimental investigation on the Formation of Molten Volcanic ash: Implications for Volcanic ash Harzards to Aircraft Safety

Wenjia Song,1* Kai-Uwe Hess,2 Donald Bruce Dingwell,3 Corrado Cimarelli4

1song.wenjia@min.uni-muenchen.de
2hess@lmu.de
3dingwell@lmu.de
4cimarelli@min.uni-muenchen.de

*Corresponding author

Volcanic ash is one of the major hazards caused by volcanic eruption. Particularly the threat to aviation from airborne volcanic ash have been widely recognized and documented. In the past 12 years, more than 60 modern jet airplanes, mostly jumbo jets, have been damaged by drifting clouds of volcanic ash that have contaminated air routes and airport facilities. Seven of these encounters are known to have caused in flight loss of engine power to jumbo jets carrying a total of more than 2000 passengers. In all instances, the primary causes of engine thrust loss are that the volcanic ash particles have lower melting point about 1100 °C; than the temperatures in the combustion chamber of a jet engine, in excess of 1600 °C and when the molten volcanic ash particles leave this hottest section of the engine, the resolidfied molten volcanic ash particles will be accumulated on the turbine nozzle guide vanes, which reduced the effective flow of air through the engine causing finally failure of engine operation. Thus, it is essential to investigate the melting process and subsequent deposition behavior of volcanic ash under gas turbine conditions. Although few research studies that investigated the deposition behavior of volcanic ash at the high temperature could be found in public domain, to the best our knowledge, no work addresses the formation of molten volcanic ash.

In this work, volcanic ash produced by Santiaguito volcano in Guatemala in November 8, 2012 was selected for study because of their recent activity and potential hazard to aircraft safety. We used the method of accessing the behavior of deposit-forming impurities in high temperature boiler plants on the basis of observations of the change in shape and size of a cylindrical coal ash to study the sintering and fusion phenomena as well as determine the volcanic ash melting behavior by using characteristic temperatures by means of heating microscope instrument and different thermal analysis methods to investigate the sintering process of volcanic ash under the different heating rate. As the volcanic ash injected into combustion chamber of a jet engine will be suddenly exposed to high temperature zone heated, in order to simulate this process, the volcanic ashes were placed directly in the furnace and exposed to different high temperatures from 1200-1500 °C to investigate the evolution of sintering characteristics, viscosity, porosity, bubble and mineral transformation with time during the melting process under different temperatures.
Diagenesis of Buntsandstein Geothermal Reservoirs, Upper Rhine Graben, Germany

D. Soyk¹, M. Fensterer², J. Bauer³, T. Bechstädt⁴

¹dominik.soyk@geow.uni-heidelberg.de, Universität Heidelberg; ²Geozentrum Nordbayern; ³Universität Göttingen; ⁴Uniwersytet Jagielloński

The Upper Rhine Graben (URG) in South West Germany is an area with a particularly high geothermal potential. Present mean geothermal gradients are higher than 40 °C/km and can even exceed 60 °C/km locally. Despite a long lasting exploration and production (E&P) history for hydrocarbons still little is known about reservoir properties for deep (>1000m) geothermal energy. Permo-Triassic sediments represent these deep geothermal targets in the URG and its surroundings. In the research project “AuGE – Outcrop Analysis in Geothermal Exploration” Rotliegend, Buntsandstein and Muschelkalk outcrop analogues are studied at and close to the graben shoulders and compared with selected drill core samples from vintage E&P wells in the graben centre. Studies include investigation of petrophysics, faults and fractures, diagenesis and thermohydraulic reservoir modelling. Here, the diagenesis of Buntsandstein reservoirs is presented.

Geothermal reservoirs are most commonly fractured reservoirs so in this study focus was both on faults and fractures and whole rock reservoir properties. Besides primary rock composition (i.e. facies) diagenesis is the main controlling factor for formation, preservation and/or destruction of matrix porosity and permeability by compaction, cementation and leaching. Permeability of a fracture network is also highly dependent on the diagenetic history as well as on other factors such as changes in stress field over time and response of the rock to these changes. Cements precipitated during or after (brittle) deformation can either prop open or seal fractures. Changing whole rock mechanic properties during time by cementation can leave fractures to remain open. Since main targets in geothermal exploration are usually large fault zones, hydrothermal alteration of reservoir rocks in large fault zones is another focus in this research project.

In summary prediction and modelling of subsurface reservoir properties are not reliable without consideration of diagenesis. Here an integrated approach to the characterisation of geothermal reservoir quality with focus on diagenesis is presented.
Relic super-Si garnet from the Almklovdalen peridotite, Norway

Dirk Spengler¹, Herman L.M. van Roermund², Franziska Scheffler³ & Roland Oberhänsli⁴

¹spengler@geo.uni-potsdam.de
²H.L.M.vanRoermund@uu.nl
³Franziska.Scheffler@geo.uni-potsdam.de
⁴Roland.Oberhaensli@geo.uni-potsdam.de

We report the first finding of garnet megacrysts enclosed in orogenic peridotite from the western part of the Western Gneiss Region, Norway (Brueckner et al., 2010). Garnetite from the active Gusdal quarry at Almklovdalen contains flattened grains of purple, slightly birefringent garnet several cm in size in association with partially elongated olivine and orthopyroxene grains that have bimodal size distribution. Most olivine and orthopyroxene grains are several mm in size and occur as small clusters or aligned apparently in between single garnet grains. The minor grain fraction is several 100 µm in size and occurs as inclusion within cores of the largest garnets. In addition, large garnet cores have rod shape inclusions that are 40-60 µm in width, up to 600 µm in length and morphologically oriented in four directions, apparently following <111> of garnet. Single rods are composed of either orthopyroxene or clinopyroxene or both. Though, areas that contain rod shape inclusions are scarce and spatially distal to mm-size olivine and orthopyroxene. The primary mineral phases are partially to completely replaced by secondary minerals. These include kelyphite + orthopyroxene reaction rims at former olivine-garnet interfaces and amphibole, orthopyroxene and chlorite replacing garnet along rims and cracks and replacing inclusions in garnet.

Except for the outermost 100 µm rims, garnet has no compositional gradient which suggests chemical equilibration. The average composition is pyropic (78 mol.%) and low in CaO (4.02 wt.%) and Cr2O3 (1.00 wt.%) contents. Mm-size orthopyroxene has “W”-shape Al2O3 concentration gradient with a plateau of 0.79 wt.% in the crystal core and the lowest concentration of 0.71 wt.% in the mantle area (c 300-500 µm distal to the rims). Iterative use of the Al-in-orthopyroxene/garnet barometer and Ca-in-orthopyroxene thermometer calibrations of Brey & Köhler (1990) to core compositions suggest 2.94 GPa/726 °C. Thus, garnetite equilibrated just below the diamond stability field (Day, 2012) at a cratonic geotherm with 38 mW/m² surface heat flow (Hasterok & Chapman, 2011). Al concentration gradients across orthopyroxene mantle and rim areas are qualitatively consistent with diffusion profiles expected during a prograde and subsequent retrograde metamorphic evolution in a subduction zone.

Microstructure, chemistry and equilibration conditions of minerals of Almklovdalen garnetite essentially resemble those of Otrøy Archaean garnetite (Van Roermund et al., 2001; Spengler et al., 2006). It follows that the mantle fragments at both areas are not only derived from the same interval of c 90-110 km depth of the hanging wall lithosphere of Laurentia during the Caledonian orogeny (Brueckner, 1998). Both peridotites also contain garnet that have super-Si garnet precursors, which seem to have a shared history since the Archaean.

Kupferschiefer Cu-Ag-Au-deposit Spremberg, Germany: Sulfur isotope study indicates hydrothermal origin of copper sulfides.

Volker Spieth¹, J.-C. Kopp², H.-J. Massonne³

¹vs.globalmetal@gmail.com
²juergen.birgit.kopp@t-online.de
³h-j.massonne@mineralogie.uni-stuttgart.de

The Kupferschiefer deposits in Central Europe were an important Cu-resource for many centuries. Today, the deposits are only mined in Poland. With the development of the Kupferschiefer Cu-Ag-Au deposit at Spremberg new material from drill cores is available for scientific study. In order to better understand the genetic relationship of the deposit we analyzed concentrates of sulfide minerals such as chalcocite, chalcopyrite, bornite and pyrite in the stable isotope laboratory in the Institut für Geowissenschaften at Universität Tübingen. The sulfur isotopic composition of 55 micro specimens, separated from sulfide-rich layers and veins, were measured from the Spremberg deposit and from the Cu-deposits in Lubin and Rudna, Poland, and Wettelrode, Mansfeld district, Germany, for comparative reasons. The results of these measurements allow the interpretation of the geochemical environment during deposition. For instance, a biogenic sulfate environment during metal deposition leads to strongly negative δ³⁴S sulfur values.

For the Spremberg samples, the measurements gave two groups of different sulfur isotopic results for the geometallic setting of the evolving epigenetic copper enrichment, beginning in the underlaying Rotliegend sandstone extending through the various Kupferschiefer layers into the overlaying Zechstein limestone. This is evidenced by sulfur isotopic measurements of 23 samples ranging from δ³⁴Sulfur values of -25 ‰ to -46 ‰ for one group. These moderate to extreme negative sulfur isotopic values of the rich epigenetic linear and disseminated copper mineralization have been documented and interpreted in the Polish mining districts as ascending metal brines mixing with brines of cooler sulfate-rich formation waters, complementing the diagenetic processes of the black shale metallurgy. This study used 15 comparative original samples from Lubin and Wettelrode that gave δ³⁴Sulfur values in the range of -25 ‰ to -36 ‰, therefore confirming the two brine mixing fluids model of previous research.

Copper sulfide veinlets in the Spremberg Cu-Ag-Au deposit crosscutting the Kupferschiefer strata show the second group of sulfur isotopic values and are indicative of a hydrothermal origin of the metal brines. These veinlets represent in their sulfur isotopic composition the main stage of the non-ferrous metal mineralization event and demonstrate a fracture-hosted hydrothermal genesis. For the Spremberg Cu-Ag-Au-deposit, distinct and separate δ³⁴Sulfur values in the range of -10 ‰ to -17 ‰ with an average of -14 ‰ show the pure hydrothermal aspect of this metallic mineralization – in total agreement with the Rudna hydrothermal event that has been measured with δ³⁴Sulfur values of -10 ‰ to -12 ‰.

Microscopy, microprobe analysis and Micro Raman Spectroscopy carried out at the Institut für Mineralogie und Kristallchemie at Universität Stuttgart, as well as geological observations at the deposit sites are concurring with the sulfur isotopic results. The Cu-Ag-Au rich part of the Spremberg Kupferschiefer deposit exhibits a multistage sequence of mineralization influenced by hydrothermal, ascending metal brines.
The challenge to distinguish submarine mass failure deposits from tsunami backwash deposits - an example from Hornitos, Northern Chile

Michaela Spiske1*, Heinrich Bahlburg1, Robert Weiss2
1Westfälische Wilhelms-Universität, Institut für Geologie und Paläontologie, Corrensstrasse 24, 48149 Münster, Germany; *spiske@uni-muenster.de
2 Virginia Polytechnic Institute and State University, 4044 Derring Hall, Blacksburg, VA 24061, U.S.A.

Sedimentary features of onshore tsunami deposits were studied in great detail within the last decade. While the characteristics of such onshore deposits are well documented, the associated marine tsunami effects, such as sediment dispersion, re-deposition, and sediment bypassing during runup and backwash are scarcely reported. The knowledge of the appearance of submarine tsunami features is important, not only to understand the hydrodynamic processes involved, but also because pre-Quaternary sediments tend to be of marine origin when extending the geological record farther into the past. In this study we challenge the former interpretation of a backwash tsunami origin of a Pliocene coarse clast unit at Hornitos that was previously linked to the Eltanin impact tsunami. The respective unit contains several tens of meters long rock slabs and components from both the shallow marine basin and onshore environments, such as alluvial fans, beaches, cliffs and the local basement rocks. It is intercalated into breccia layers of smaller scale that represent the likewise energetic background sedimentation. The unit was most likely emplaced by a high-density flow with possible hydroplaning at its base and front. This is underlined by soft-sediment deformation and sand dykes. The comparison to recent submarine tsunami sediments shows that there are hardly any similarities, most notably because the unit at Hornitos was deposited en masse without any obvious trends. Our re-interpretation considers the local synsedimentary tectonic background and a comparison to recent submarine tsunami sediments caused by tsunamis with similar onshore wave heights. We show that a relation to the Eltanin impact can be excluded because enhanced models that include a shoaling effect as soon as the tsunami approaches shallow shelf regions prove that such an impact did not entail large onshore wave heights at Hornitos. Additionally, the biostratigraphic age of the La Portada formation is not overlapping with the age of the Eltanin impact. Instead, we argue for an earthquake-triggered debris flow origin of the unit. Its emplacement occurred a phase of increased uplift during the Pliocene that entailed the oversteepening of the coastal scarp. Contemporaneous increase in the frequency of seismic events caused slope failures and cliff collapses. Hence, the megabreccia unit at Hornitos represents an extraordinary event that is intercalated into mass wasting deposits of smaller scale, but is not linked to a tsunami.
OH-defects in detrital quartz grains as tool for provenance analysis

Roland Stalder¹, Rolf Dieter Neuser²

¹ Universität Innsbruck, Austria, roland.stalder@uibk.ac.at
² Ruhr-Universität Bochum, Germany, rolf.neuser@rub.de

OH-defects of 95 detrital quartz grains from 4 localities in North-west Germany were studied by Infrared (IR) microscopy. By applying novel analytical strategies, the water contribution of fluid and mineral inclusions was minimised and the amount of water incorporated as OH-point defects was quantified. The defect water concentration in all studied quartz grains ranges between 0 and 50 wt ppm H₂O with a mean value around 10 wt ppm. Grains from the investigated sandstones (Carboniferous and Triassic) exhibit in average nearly three times higher defect water concentrations (18 wt ppm) than grains from North Sea beach sands (6.5 wt ppm). This difference may reflect the different source regions of the respective quartz grains, namely predominant provenance from Central Europe and predominant provenance from the Baltic Shield, respectively.

IR spectra of the detrital quartz grains were compared to reference spectra from samples of known localities and rock types in order to identify potential sources from which the quartz grains were sampled. Most detrital quartz grains exhibit IR signatures typical for granites (showing an Al-specific band at 3378 cm⁻¹) and regional metamorphic rocks, but also absorption bands typical for pegmatites and hydrothermal quartz (showing a Li-specific band at 3480 cm⁻¹) are observed. In contrast, IR signatures typical for high-pressure origin (i.e., hydrogarnet substitution with an absorption band at 3585 cm⁻¹) and for tourmaline-bearing rocks (showing a B-specific band at 3595 cm⁻¹) are subordinate to insignificant. From some grains also cathodoluminescence (CL) spectra were recorded and compared to the results from IR spectroscopy. No correlation between water content and CL colour was revealed, especially when a change in CL colour during excitation is not strong, underlining the potential of IR spectroscopy to add new aspects for the characterisation of quartz grains of unknown origin.
Playing against nature: cost effective hazard mitigation in the presence of deep uncertainties

Seth Stein¹

¹Earth and Planetary Sciences, Northwestern University, USA  seth@earth.northwestern.edu

In trying to mitigate natural hazards, society plays a high-stakes game against nature. Often nature surprises us, when an earthquake, hurricane, or flood is bigger or has greater effects than expected from detailed natural hazard assessments. In other cases, nature outsmarts us, doing great damage despite expensive mitigation measures. Society faces the challenge of finding a level of hazard mitigation that minimizes total cost to society. That cost is the sum of mitigation costs, such as earthquake resistant construction, plus the expected loss for future earthquakes assuming a given level of mitigation. The expected loss is the sum of losses in various expected events times the assumed probability of each event. Less mitigation decreases construction costs but increases the expected loss and thus total cost. More mitigation gives less expected loss but higher total cost. Our ability to find this optimal level of mitigation that balances resources used for hazard mitigation with other societal needs (schools, hospitals, etc.), thus depends on our ability to estimate the probabilities of future events and their effects, and the uncertainties in these estimates. These uncertainties are "deep uncertainties" that arise when the probabilities of outcomes are poorly known, unknown, or unknowable. This occurs when we have multiple possible models with poorly known parameters, because we inadequately understand the system or it has inherently unpredictable elements. In such situations, past events may give little insight into future ones. The challenge is illustrated by the 2011 Tohoku, 2008 Wenchuan, and 2010 Haiti earthquakes that occurred in areas predicted by earthquake hazard maps to have significantly lower hazard than nearby supposedly high-risk areas which have been essentially quiescent. Given the limited seismic record available and limited understanding of earthquake mechanics, hazard maps often depend heavily on poorly constrained parameters and the mapmakers' preconceptions. When these prove incorrect, maps do poorly. Thus we need to better understand uncertainties, communicate them to users, and make sensible policy given them.
Synthesis and Crystal Chemistry in the system Ca$_3$(Fe,Mn,Ti)$_3$O$_8$-$d$ and Ca(Fe,Mn,Ti)O$_3$-$d$

Stöber S. 1 & Pöllmann H. 2

1 stefan.stoeber@geo.uni-halle.de
2 herbert.poellmann@geo.uni-halle.de

With the improvement of iron rich CAC cement properties due to intergrinding and sintering of Mn - secondary raw materials and cement raw meal, perovskite phases contain significant concentrations of Mn$^{3+}$/Mn$^{4+}$ ions, dependent on the oxygen fugacity ($f_{O_2}$). Brownmillerite phases, structurally described as oxygen deficient perovskites, can compensate certain amounts of Mn$^{4+}$ due to incorporation of additional oxygen, but will become unstable and dissolve into Alumina rich Iron – Manganese - brownmillerites Ca$_2$(Al,Mn,Fe)$_2$O$_5$-$d$ and perovskites Ca(Mn,Ti,Fe)O$_3$-$d$. Beside the typical layer sequence of tetrahedra (t) - octahedra (o) in brownmillerite type structure, different stacking sequences can be stabilized due to the variation of $f_{O_2}$. These structures are built up of different sequences like “oo” or “too”. In order to investigate these phases, samples with the chemical compositions CaFeO$_3$-$d$ - CaMnO$_3$-$d$ - CaTiO$_3$ were synthesized either as powders by sol - gel methods or as single crystals. The crystal structures were refined using neutron diffraction techniques at the BENSC E6 of the Helmholtz - Centre Berlin for Materials and Energy, the manganese valences were determined by iodometric titration. The valence state of iron was determined by Mössbauer - spectroscopy. The phases with the chemical composition Ca(Fe,Mn,Ti)O$_3$-$d$ with ABO$_3$-$d$ type structure crystallize predominately in space group Pnma. With the incorporation of trivalent iron the space group changed to I4/mcm and finally into Pm-3m. The phase transition is also dependent on the temperature level, which was proofed by high temperature XRD. Phase with the chemical composition Ca$_3$(Fe,Mn,Ti)$_3$O$_8$-$d$ ($n = 3$ A$_3$B$_3$O$_8$-$d$) were only synthesized purely in a narrow range as long as enough iron filled the tetrahedrally coordinated sites in the crystal structure.
The braided river dominated Horingbaai Fan-delta, NW Namibia: Dating of Skeleton Coast fan progradation using marine terrace stratigraphy

Harald Stollhofen¹, Ian G. Stanistreet², Christoph von Hagke³, Anna Nguno⁴

¹harald.stollhofen@fau.de
²istantreet@btconnect.com
³vonhagke@caltech.edu
⁴anguno@mme.gov.na

Drainage pattern and the degree of interaction with the marine system characterizes the 10 x 13 km Horingbaai Fan as a braided river dominated fan-delta, issuing outboard of the coastal escarpment of NW Namibia. Both catchment and coastal depositional setting classify as arid to hyper-arid. Upper and Middle fan segments are dominated by a braided river system, only in the Upper Fan are fluvial sediments interleaved with hyperconcentrated flow deposits. In terms of its gradient (0.01) the Horingbaai Fan-delta is rather steep compared to other braided river dominated fans and classifies close to the modal range for debris flow dominated fans. The gradient of the Horingbaai fan-delta and of several other Skeleton Coast fan systems populate a "depositional slope gap" postulated by earlier authors within a gradient range of 0.009-0.026.

The Lower Fan-delta has been repeatedly inundated by the marine system, as is the case with the submarine portion of the fan presently. Plio-Pleistocene sea level highstands have left marine terraces on the fan surface which provide an opportunity to date the clastic, unfossiliferous fan sediments. The bulk of Horingbaai Fan-delta progradation took place between the formation of a widespread erosional surface incising Middle to earliest Late Pliocene Karpfenkliff and Kamberg Formations but prior to the emplacement of the warm-water fauna bearing Late Pliocene "Oyster Terrace" (∼2.4-2.2 Ma), an equivalent of the +30 mP (marine terrace package) in coastal southwest Africa. A younger phase of fan-delta progradation, postdating "Oyster Terrace" formation is overall weaker and more irregular, accompanied by mostly cold-water fauna bearing Middle Pleistocene, Upper Pleistocene and Holocene marine terraces deposited during interglacial highstands.

Horingbaai Fan-delta progradation is contemporaneous to a Late Pliocene period of uplift and climate change. The latter is viewed contemporary with the intensification of Northern hemisphere glaciations and subsequent strong glacial-interglacial variations in concert with sealevel fluctuations and wet/dry alternations.
Automated Mineralogy by Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMSCAN) is widely applied in the fields of economic geology and mining as a tool for rapid data generation. The fast determination of material properties and parameters, such as modal mineralogy, grain size distribution and mineral liberation, is essential for the characterization of ores and optimization of mineral processing. While the EPMA is an invaluable tool for especially WD point analysis, the QEMSCAN can produce large images with a high BSE resolution, combined with semi quantitative EDX-spectra mappings, which conceal the range of a whole sample. An adjustable Species Identification Protocol (SIP) allocates the EDX-spectra to mineral phases. This makes a more detailed image analysis easier and faster, compared to conventional techniques.

We use a QEMSCAN 650F for the investigation of different mineralogical and metallurgical questions. Red mud is being produced as waste in the course of alumina extraction from bauxite ore. In addition to low grain sizes, it is a very complicated material due to mineral reactions and “caking”, resulting from hydrometallurgical leaching processes and calcination. Although waste material, red mud may have potential for immobilizing pollutants such as arsenates and phosphates in natural soils and waters [1]. In order to account for the heterogeneity, it is very important to identify all involved and newly formed minerals during the immobilization in order to verify/identify, to which phases arsenates and phosphates are bound [1]. The mineral phases can ideally complete be identified, characterized and quantified by QEMSCAN analysis. The measurement and calculation of grain size, distribution and liberation of each mineral is generally useful for improving the extraction of aluminium from aluminium hydroxide minerals and additional valuable constituents. This can also lead to a minimization of the red mud as waste material and therefore a reduction of disposal costs.

Additionally, intermetallic compounds have been investigated. By producing micro chemical mappings, several laves phase exsolutions with differing Nb concentrations were identified. As opposed to single point analysis, the texture and chemical relationship of the whole sample were investigated within one measurement. The acquired images and data has been used for the characterization and statistically reliable quantification of laves phases and their chemical relationship to neighboring phases. Together with conventional analytical methods, QEMSCAN analysis can be used for a more intense material characterization of larger sample areas.

The Archean-Proterozoic transition witnessed substantial changes in the redox state of Earth’s atmosphere-ocean system. The first significant rise in atmospheric oxygen referred to as the Great Oxidation Event occurred some 2.4 Ga ago. It has been constrained by the disappearance of mass-independently fractionated sulfur isotopes (MIF-S), and respective isotope records have been generated from key sedimentary successions worldwide. This isotopic signature is thought to record the photochemical processing of volcanogenic sulfur dioxide in a low-oxygen atmosphere, but additional atmospheric gases play an important role as well. The threshold level of atmospheric oxygen abundance proposed for the formation and preservation of MIF-S is $10^{-5}$ PAL (present day atmospheric level).

Lately, a number of studies employing a multitude of redox-sensitive elements and their abundances and stable isotopic compositions call for a much more differentiated evolution of Earth’s redox state. More detailed assessments appear possible in terms of the atmospheric oxygen level and its temporal evolution, but also in respect to the spatial arrangement of oxic versus anoxic (or even euxinic) water column conditions.
Dating crustal thickening of the crystalline core of the Himalaya in Himachal Pradesh, NW India

Konstanze Stübner¹, Djordje Grujic², Randall Parrish³

¹Geodynamics, University Tübingen, Germany, konstanze.stuebner@uni-tuebingen.de
²Department of Earth Sciences, Dalhousie University, Halifax, Canada, djordje.grujic@dal.ca
³NERC Isotope Geosciences Laboratory, Keyworth, UK, rrp@bgs.ac.uk

The exhumation of the crystalline core of the Himalaya (GHC) has been the focus of many studies. In contrast, the early Himalayan evolution of crustal shortening and thickening following collision at ~55 Ma has been studied in less detail. This is in part due to the fact that early Miocene high-temperature conditions with widespread migmatization and leucogranite emplacement has overprinted and largely erased the prograde history of the GHC.

The lower-grade metamorphic conditions of the GHC in the western compared to central and eastern Himalaya make this an ideal area to study the ‘Eohimalayan’ evolution. We present new zircon and monazite U/Th–Pb geochronologic data from central Himachal Pradesh, NW India, which documents the pre-Himalayan and early Himalayan metamorphic history of the Indian passive margin: (1) Voluminous and widespread granite emplacement in the Early Ordovician caused contact metamorphism of the sedimentary host rock, the Late Proterozoic to Cambrian Haimanta Group. (2) Crustal thickening in the Eocene/Oligocene led to prograde Barrovian metamorphism, which peaked in partial melting at 41 Ma and at 37 Ma. (3) High-grade metamorphic conditions persisted throughout the Oligocene. (4) Rapid cooling of the GHC started at ~21 Ma and is attributed to tectonic exhumation.

Our data provides the first age constraints on partial melting in central Himachal Pradesh. Compared to the eastern Himalaya, partial melting in the NW Himalaya occurred 15–20 m.yr. earlier, and the onset of extrusion of the GHC occurred 8–10 m.yr. earlier, thus signifying considerable variation of the early tectonic evolution along the Himalaya.
At the Precambrian-Cambrian boundary about 550 Million years ago the Earth experienced processes never witnessed in its history before. Together with the amazing development of first metazoan life forms came major changes in the chemistry of ocean and atmosphere, and in the plate tectonic configuration. One more piece in this still unsolved puzzle of the Pc-C boundary is a widespread deposition of sediments rich in calcium phosphate minerals and the occurrence of massive chert rocks, which consist almost exclusively of SiO₂ in the form of microcrystalline quartz.

This is exactly what we observe in a sedimentary basin in the Karatau mountains, Kazakhstan: a massive chert unit in between large deposits of carbonate and phosphate sediments at the Pc-C boundary. The most straightforward key to decipher this archive of siliceous rocks seems to be Si isotope data: δ²⁸Si values should reflect isotope fractionation effects due to precipitation or silicification processes as well as a source signal, indicating the reservoir the Si was derived from. Analyses were carried out on chert material selected from three stratigraphic profiles after dissolution of the bulk rock samples. Since the process of silicification takes place on the level of sediment grains and pore space, we also investigated Si isotopes and Al content in situ on the microscale. For this we used state-of-the-art UV-femtosecond laser ablation MC-ICP-MS technique on a polished thin section of chert with suspicious banding (‘zebra chert’).

Our bulk rock data show higher isotope variability (-1.76 ‰ < δ³⁰Si < +1.97 ‰) in pure cherts than in the silicified phosphatic rocks (-0.23 ‰ < δ³⁰Si < +1.42 ‰). Additionally, we observe a positive correlation of a higher Si isotope ratio with Al, K and Ti content. On the microscale, things look different: Al content and Si isotope ratios correlate negatively. Furthermore, in the thin section we could distinguish between different generations of quartz (chalcedony with wrinkle banding extinction, botryoidal chalcedony, cryptocrystalline quartz, microquartz, and fracture filling megaquartz) associated with differing Si isotope ratios.

As the elements Al, K and Ti in bulk rock samples are likely derived from a clay mineral component, the heavy Si isotope signature might be associated with deposition near a continental riverine source, as is observed today in dissolved riverine Si. The high variability in the pure silicate rocks might be achieved by varying evaporation rates in a silica-saturated Precambrian ocean. On the microscale, the Al containing components might serve as nuclei. This way a much faster precipitation of Si is possible, inducing a stronger kinetic fractionation effect of Si isotopes.
Towards Archaean sequence stratigraphy: Delta architecture bridges shallow- and deep-water facies (Moodies Group, Barberton Greenstone Belt, South Africa, ~3.22 Ga)

Laura Stutenbecker¹, Christoph Heubeck², Martin Homann³ and Sami Nabhan⁴

¹laura.stutenbecker@fu-berlin.de
²christoph.heubeck@fu-berlin.de
³martin.homann@fu-berlin.de
⁴sami.nabhan@fu-berlin.de

The Moodies Group (~3.22 Ga), uppermost unit of the Barberton Greenstone Belt, South Africa, consists of ~3.7 km thick sandstones and siltstones with subordinate conglomerates, BIFs and volcanics, preserved in several complex, tightly folded, doubly plunging and overturned synclines tens of km in strike length. They are separated from each other by isoclinal and faulted antiforms. Bedding is subvertical throughout. The lack of detailed mapping, structural complexity and uneven exposure has to-date prevented a basinwide correlation between extensive fine-grained rhythmic siltstones, thought to be the result of prodelta sedimentation, and stratigraphically equivalent sandstones, thought to be of fluvial and coastal-plain facies, approximately midway in the Moodies Group. This affects negatively our ability to model basin evolution and reconstruct tectonic settings.

A potential key locality in addressing this problem exists in the eastern Saddleback Syncline within unit MdS1 where an up to 200 m thick, well exposed, resistant weathering cherty litharenite unit (the incorrectly named “Lomati Quartzite”) with abundant shallow-water sedimentary structures gradually wedges out northeastward over ~4 km along strike to grade into the >1 km thick but poorly exposed fine-grained sandstones and siltstones of the Moodies prodelta facies. 12 stratigraphic measured sections across this complex, spaced a few hundred m apart, allow differentiating 13 mappable units which are arranged in an overall progradational architecture. Preliminary findings include: (1) abundant tidal sedimentary structures in sandstones, cut by broad and shallow channels, provide clear evidence of a tide-dominated delta architecture; (2) pebbly sandstones, possibly of a coastal plain facies, occupy proximal and basal units only; (3) three prominent and laterally extensive mud-cracked shale units (regressive surfaces) serve as stratigraphic markers; (4) a rhyodacitic tuff unit, as yet undated, may provide a chronostratigraphic calibration and (5) horizontally-stratified sandstones with abundant microbial mats in the middle of the unit represent a tidal-flat facies. Continuing investigations aim at constraining tidal range and assessing the consequences of intensive chemical weathering, high subsidence rates, and the complete lack of vegetation for Archean delta dynamics.
Die Konstruktion hochauflösender numerischer Gesteinsmodelle zur Simulation von Mehrphasenfluss in Karbonaten

M. Bartenbach*, T. Aigner**, M. Baumhoer*, M.P. Suess*** (*Statoil ASA, **Eberhard Karls Universität Tübingen, ***Wintershall Holding GmbH)

Biologically-mediated Precambrian ocean and atmosphere oxidation was controlled by marine Fe(II) concentrations

Elizabeth D. Swanner¹ and Andreas Kappler²

¹elizabeth.swanner@ifg.uni-tuebingen.de
²andreas.kappler@uni-tuebingen.de

The evolution of oxygenic photosynthesis by cyanobacteria unambiguously initiated redox changes in the Earth system by introducing molecular oxygen (O₂) into the atmosphere and oceans beginning in the late Archean. The effect of oxygenic photosynthesis on Earth’s redox state has been considered in terms of the overall oxygen build-up after accounting for sinks in organic carbon and dissolved, gaseous and mineral-derived electron donors (Fe²⁺, CH₄, pyrite) (reviewed in 1). Our approach alternates how oxygen production by marine cyanobacteria is affected by the anoxic, circumneutral, Fe(II)-rich conditions that characterized Precambrian seawater.

Experiments with the marine cyanobacterium Synechococcus PCC 7002 demonstrate that the 0.5mM Fe(II) present in Precambrian seawater inhibits growth and curtails oxygen production by this strain. We also observed depressed rates of Fe(II) oxidation in photosynthesizing cultures, probably due to Fe(III) reduction with photochemically or biological generated reactive oxygen species (ROS). This finding suggests that Fe(II) could persist in the Precambrian photic zone, and was a negative feedback on biologically-mediated oxidation.

Evidence for transient oxidation events up to several hundred million years before the Great Oxidation Event (GOE) between 2.45 to 2.3 Ga (reviewed in 1) suggest that cyanobacteria evolved early but oxygen production was suppressed. Episodic mantle plume events, especially common during early atmospheric oxidation at the Archean-Proterozoic boundary, are associated with increased periods of iron formation deposition due to enhanced hydrothermal Fe(II) delivery to seawater (reviewed in 2). This expression of mantle heat loss may have controlled the biological oxidation of surface environments, because rates of oxygen production by cyanobacteria are depressed in the presence of Fe(II). We propose that oceanic Fe(II) concentrations link Earth’s secular to surface redox evolution via the regulation of oxygenic photosynthesis. We will discuss the implications of this idea for the tempo of oxidation, the oxidative balance between oxygen and existing reductive sinks, and the spatial and temporal heterogeneities in the Precambrian marine sedimentary record.


Fluid-rock interaction along a HP/LT vein system on New Caledonia

Stephan Taetz¹, Timm John¹, Michael Bröcker¹

¹Institut für Mineralogie, Westfälische Wilhelms-Universität, Münster, Germany. stephan.taetz@uni-muenster.de

Large amounts of fluids are released at high-pressure conditions from subducting slabs due to breakdown of hydrous minerals. Channelized flow of these fluids induces the formation of high-pressure vein systems within the slab allowing high fluid fluxes over larger distances. Fluid-rock interaction along the flow structures can lead to significant mobilization and transport of trace elements. Detailed investigation of vein-forming processes and the interaction of the internal or external fluid with the wall-rock can help understanding the fluid flow and transport of trace elements in and out of subducting slabs. Furthermore this has implications on the chemical signature of the resulting arc magmas. A well-preserved example of such a vein system can be found in the Pouébo Eclogite Mélange (PEM) in the NE part of New Caledonia.

The PEM consists of exhumed fragments of a high-pressure/low-temperature metamorphic belt. Seafloor-altered, fractionated MORB source material was subducted during the Eocene and reached eclogite-facies peak metamorphic conditions at c. 44 Ma [1, 2]. Published and new EMP data indicates P–T conditions of c. 1.9 GPa and 500-600 °C by Cpx-Grt-Phg thermobarometry [1, 3, 4]. The sampled vein-wall-rock association can be differentiated into three distinct zones: (a) Metre-long, cm-thick high-pressure veins with a coarse-grained, inclusion-free Grt-Qtz-Phg assemblage, minor Ap, Rt and accessory Omp. (b) Fine-grained, 3-5 cm thick omphacite-rich metasomatic reaction selvages surrounding the veins, gradually passing into 3) an unaltered fine-grained, Gln-rich host rock with coarse tabular Omp, Ep and mostly isolated, inclusion-rich Grt porphyroblasts.

The differences between these zones are obvious from texture and mineral assemblage. Mineral chemical data show that the individual mineral phases display very similar compositions throughout a profile from vein to host rock. Trace element data of these phases however show systematic distributional differences within the individual grains. For instance, Grt grains from vein, selvage and host rock show several features in their REE zoning patterns indicative of multiple stages of mineral growth. These growth episodes are most likely induced by the breakdown of hydrous minerals (e.g. Ep, Amp) and resulting fluid-mediated mobilization and redistribution of trace elements. Further major and trace element analysis of bulk rocks and on mineral scale will allow to carry out mass balance calculations that should enable us to determine fluid fluxes. Such data will also help solving the question whether or not elements had been transported locally or over larger distances.

References:
Provenance of Pliocene and Pleistocene Rhine sediments: evidence from detrital zircon thermochronology

Michael Tatzel¹, Hilmar v. Eynatten², István Dunkl³

¹ mtatzel@googlemail.com
² hilmar.von.eynatten@geo.uni-goettingen.de
³ istvan.dunkl@geo.uni-goettingen.de

Pliocene to Pleistocene Rhine sediments have revealed a distinct provenance boundary as evidenced by heavy mineral assemblages. The shift from predominantly stable heavy mineral assemblages (zircon, tourmaline, rutile) to predominantly metamorphic assemblages (garnet, epidote, green hornblende) has been ascribed to the extension of the Rhine’s drainage basin from the Black Forest and Vosges (including their Permo-Mesozoic cover) to the Alpine Molasse basin and the Central Alps (e.g. Boenigk, 1983). This shift, assigned to the uppermost Pliocene, should be accompanied by distinctly younger (i.e. Late Cretaceous to Neogene) detrital mineral cooling ages in Pleistocene Rhine sediment.

We have tested this hypothesis using detrital zircon (U-Th)/He dating (ZHe), complemented by detrital zircon fission track (ZFT) analysis. ZHe age distributions of two Pliocene and two Pleistocene samples from a drillhole at Ludwigshafen (northern Upper Rhine Graben) and the open cast mine Hambach (Lower Rhine Embayment) are based on 91 ZHe-ages. In the northern Upper Rhine Graben a clear change is observed from predominantly Permo-Triassic and Variscan age components in the Pliocene sample to the predominance of Alpine cooling ages in the Pleistocene sample. For the latter, more than two-thirds of the zircon grains exhibit Late Eocene to Late Miocene ZHe ages, accompanied by a significant change in the heavy mineral assemblage towards predominance of garnet and epidote-group minerals. ZFT data confirm this scenario, though ages are slightly higher given the higher closure temperature of the ZFT thermochronometer.

Pliocene and Pleistocene samples from the Lower Rhine Embayment strongly contrast in heavy mineral composition (like for Upper Rhine Graben samples), but show largely similar ZHe age distributions that are dominated by Permo-Triassic and Variscan age groups. This observation is interpreted to reflect admixture of sediment with low heavy mineral concentration but zircon-dominated heavy mineral assemblage in the Pleistocene, derived from local drainages of the Rhenish Massif. Emerging contribution of Alpine-derived sediment, however, is reflected by Eocene to Miocene single-grain ages in the ZHe and ZFT age spectra of the Lower Rhine Embayment samples.

The halogen (F, Cl, Br) content of continental granitoid plutonic rocks and the contribution of their volatile-bearing phases

H. Teiber\textsuperscript{1}, M.A.W. Marks\textsuperscript{1}, T. Wenzel\textsuperscript{1}, W. Siebel\textsuperscript{1}, R. Altherr\textsuperscript{2}, G. Markl\textsuperscript{1}

\textsuperscript{1}Universität Tübingen, Mathematisch-Naturwissenschaftliche Fakultät, FB Geowissenschaften, Wilhelmstrasse 56, D-72074 Tübingen, Germany
(*correspondence: holger.teiber@uni-tuebingen.de)

\textsuperscript{2}Ruprecht-Karls-Universität Heidelberg, Institut für Geowissenschaften, Im Neuenheimer Feld 234-236, D-69120 Heidelberg, Germany

In our study we investigated the halogen contents (F, Cl, Br) of various granitoid rocks, as well as the halogen contents of their volatile-bearing phases. The various rock samples were taken from the western Bohemian Massif (post collisional to the Variscan orogeny) and from the central Aegean (Tertiary back-arc extension), representing two different tectonic settings. In general, the rocks can be subdivided in three different volatile-bearing silicate mineral assemblages: (1) hornblende + biotite, (2) only biotite and (3) biotite + muscovite. Accessory apatite is present in all samples, whereas tiny fluorite and rare titanite were observed in some samples.

The extraction of the halogens (F, Cl, Br) from the whole-rock powders was performed by Pyrohydrolysis. The trapped halogens were subsequently analyzed by Ion Chromatography. The F and Cl contents of the primary volatile-bearing silicate minerals and apatite were quantified by Electron Microprobe Analysis. Br contents of available mineral separates were analyzed by Total Reflection X-ray Fluorescence.

The F content of all investigated whole-rocks is in the range of 500-3000 \(\mu\text{g/g}\) and 50-900 \(\mu\text{g/g}\) for Cl, respectively. In several samples, F and Cl contents of the whole-rocks roughly correlate with the halogen contents of micas and apatite. Br in the whole-rock powders is always <1 \(\mu\text{g/g}\). Quantifiable Br contents were only found in a few Aegean hornblende and apatite separates with concentrations of around 2 \(\mu\text{g/g}\).

For many samples the calculations of the halogen budget, based on the modal amounts of major primary halogen-bearing minerals and their respective halogen contents, reveal strong misfits compared to the whole-rock concentrations. This indicates that appreciable amounts of F and Cl are not incorporated in these primary minerals. Indeed, detailed X-ray mapping and short-term leaching experiments (2 minutes) confirm that significant amounts of F and Cl are present (1) in tiny secondary mineral phases, (2) in fluid inclusions and are (3) potentially located along grain boundaries. Tiny fluorite was observed in most samples showing strong F misfit and is therefore mainly responsible for the missing F. However, all these observations cannot be accounted for budget calculations based on modal amounts of the various minerals.

In summary, our study shows that significant amounts of halogens in whole-rocks might be of secondary origin. For this reason, great care has to be taken when using the halogen contents of whole-rocks for petrogenetic models.
High-tech metals as emerging contaminants: Strong increase of anthropogenic gadolinium in tap water of Berlin between 2009 and 2012

N. Tepe¹, M. Romero² and M. Bau³

¹n.tepe@jacobs-university.de
²m.romero@jacobs-university.de
³m.bau@jacobs-university.de

With the continuous development of new technologies and new substances, high-tech metals have become emerging contaminants of natural system. We focus on the appearance, distribution and behaviour of anthropogenic rare earth elements (REE) in tap water in the City of Berlin, Germany. First reported in German rivers in 1996, microcontamination of surface waters with anthropogenic gadolinium has become a typical feature in industrialized countries with highly developed health care system. Anthropogenic Gd is derived from Gd-based contrast agents used in magnetic resonance imaging (MRI). These water-soluble and highly stable agents are injected into the bloodstream of patients and are released from the body within 24 to 48 hours. Due to their high stabilities, the anthropogenic Gd cannot be removed from waste water by commonly used waste water treatment technologies and, hence, they are transferred to surface and ground waters, and eventually into tap water. This anthropogenic Gd, therefore, is a tracer for the presence of waste water-derived dissolved substances which in contrast to anthropogenic Gd, may have a high (eco-)toxicity.

Published results of a first systematic study of REE in tap water from several districts in Berlin had been based on samples taken in 2009. Shale-normalized REE patterns in tap water from the western districts of Berlin showed large anthropogenic positive Gd anomalies, whereas the eastern districts did not show anomalous Gd enrichment. Considering that anthropogenic Gd levels in the Havel River have increased substantially over the past two decades and that migration times from the river to the groundwater wells fall in the range of months to years, it was predicted that the contamination of Berlin tap water with anthropogenic Gd would increase in the near future. To verify this prediction, we engaged in an update of the monitoring study of 2009 and here report the results for tap water sampled in December 2012. Between 2009 and 2012 anthropogenic Gd increased significantly. In the western districts the smallest increase can be observed in Zehlendorf (increase by a factor of 1.5), while the maximum increase is observed at Jungfernheide (increase by a factor of 11.5). Similar to 2009, highest contamination levels persist in the districts Mitte, Reinickendorf and Charlottenburg-Wilmersdorf.

Hence, tap water in eastern Berlin is unlikely to be affected by waste water-derived contaminants, such as pharmaceuticals and personal care products, whereas the situation in the central districts of Berlin needs to be monitored in more detail. The strong increase of anthropogenic Gd in tap water between 2009 and 2009 demonstrates the increasing impact of high-tech metals on the environment and is further evidence that high-tech metals are emerging contaminants.
Rare earth elements, Zr, Nb, Hf, and Th in glacial meltwater rivers and the impact of estuarine mixing on their input into the ocean

N. Tepe\textsuperscript{1} and M. Bau\textsuperscript{2}

\textsuperscript{1}n.tepe@jacobs-university.de
\textsuperscript{2}m.bau@jacobs-university.de

Retreating glaciers are one of the consequences of global climate change, and glacial meltwater rivers connect the melting temperate glaciers and polar inland glaciers to the ocean. However, the distribution of dissolved rare earth elements (REE) and high field strength elements, such as Zr, Nb, Hf, and Th, in glacial meltwater rivers in Iceland is also affected by volcanic eruptions (e.g., the Eyjafjallajökull in 2010), due to the input of colloids and nanoparticles from volcanic ashes which might change the chemical composition of the water.

Water samples from glacial meltwater rivers and volcanic ashes from southern Iceland were sampled in 2010 to characterize the geochemistry of glacial meltwaters, to investigate the impact of colloids and nanoparticles from mafic volcanic ashes on water chemistry, and to characterize their behaviour during mixing with seawater. The REE, Zr, Nb, Hf and Th show high particle-reactivities and low solubilities, and in surface waters, therefore, are not truly dissolved, but associated with particles. Comparison of the trace element distribution of river particulates (i.e. >0.45 µm filter residues) and volcanic ash to that of the respective glacial meltwater (i.e. <0.45 µm filtrates) reveals very close similarities, indicating that REE and HFSE bound to colloids and nanoparticles dominate the dissolved REE and HFSE distribution in glacial meltwater rivers in southern Iceland.

Laboratory mixing experiments were performed with particle-rich glacial meltwater from the Markarfljót River and a seawater endmember to investigate the effect of estuarine mixing on REE and Y input from glacial meltwaters into the ocean. The results suggest that admixture of minute amounts of seawater (leading to a salinity of only 3.4) already has a tremendous impact on the signature of the REE and Y input via the Markarfljót River. Besides significant lowering the REE concentrations (presumably due to aggregation of colloids and nanoparticles), the REE input develops all the features typical of the REE and Y distribution in seawater, i.e., depletion of light REE relative to heavy REE, negative Ce and positive Y anomalies, as the amount of admixed seawater (hence salinity) increases. After the initial drop, the REE and Y concentrations tend to increase again upon addition of increasing amounts of seawater (i.e. as salinity increases), probably due to REE and Y desorption from or incongruent dissolution of aggregated former colloids and nanoparticles.

Our results suggest that the REE and Y input into the ocean is characterized by a specific REE distribution pattern regardless of the lithology in the catchment, i.e. run-off from mafic and intermediate/felsic landmasses produce similar REE and Y input into the ocean.
Trace element study on rutile from a chromite-bearing norite of the Bushveld Complex (South Africa), new insights for magma fractionation

Tobias Terhaar¹, Armin Zeh²

¹tobias.terhaar@web.de
²a.zeh@em.uni-frankfurt.de

This study presents results of a detailed textural and micro-chemical study on rutile from a chromite-bearing pegmatoidal norite. This norite occurs below the UG2 chromitite layer of the Critical Zone in the western part of the Bushveld Complex. In the investigated sample rutile crystallized successively in four distinct textural positions. The rutile generation Rt1 occurs as randomly oriented crystals in chromite, and Rt2 is found in melt inclusions in chromite together with baddeleyite + srilankite + silicate minerals. Generation Rt3 forms mostly euhedral, rarely acicular crystals intergrown with matrix silicates, while Rt4 is closely intergrown with zircon.

The rutile grains reveal large variation in composition, which obviously results from successive rutile growth during the entire magma crystallisation history. This is reflected in trace element analyses with LA-SF-ICP-MS, revealing an enormous and systematic increase of Nb (2.7 to 11113 ppm), Ta (0.209 to 439 ppm), Hf (4.29 to 120 ppm), U (0.037 to 23.0 ppm) and W (0.3 to 475 ppm) from Rt1 to Rt4. The chromium and vanadium content remains nearly constant from Rt1 to Rt3 (Cr ~ 4000 ppm, V ~ 900 ppm), but increases enormously to 8000-12000 ppm for Cr and 1700 ppm for V, respectively, in rutile Rt4. The lack of any chemical zoning in nearly all rutile grains, despite the enormous compositional intergrain variations, indicates that new rutile formed successively during magma fractionation, and that the primary rutile composition has not been changed by subsequent diffusion, despite the high magma crystallisation temperatures of >800-1100°C. This is clearly reflected in mostly identical core – rim analyses, and the lack of any diffusion profiles checked by BSE imaging and EPMA. All rutiles show variable Zr/Hf with a maximum at 20±4, and a bimodal Nb/Ta distribution with maxima at 10 and 21.

Zr-in-rutile and Ti-in-zircon thermometry (Ferry & Watson, 2007) indicate that rutile Rt4 and associated zircon crystallized at about 850°C. For rutile Rt1 to Rt3 much lower temperatures between 500 to 750°C have been calculated. These temperatures, however, do not reflect the conditions during rutile growth, but result from low zirconium and silica activities during Rt1 to Rt3 crystallisation, which occurred prior to zircon and/or quartz-saturation. Very high temperatures of 1010°C of some Rt4a rutile grains perhaps result from rutile crystallisation in highly fractionate, but silica undersaturated melt drops. These results indicate that the interpretation of crystallisation temperatures of detrital rutile grains, used in provenance studies, has to be done carefully.

The Rodder Maar (Eastern Eifel/Germany) proved to be a meteorite impact crater

Jean Thein*¹ and Natascha Kuhlmann¹

The Rodder Maar is a nearly ellipsoidal crater lake, with a maximum diameter of 360 m. It is situated in the north of Brohl Valley, near the Village of Rodder and lies at the northern rim of the Pleistocene volcanic province of the Laacher See in the Eastern Eifel, about 15 km west of the Rhine Valley. In the immediate vicinity the Pleistocene phonolitic dome of Olbrück Castle and the Oligocene Steinberg (Königssee) basalt volcano are found. For a long time, the Rodder Maar therefore was interpreted to be of phreatomagmatic volcanic origin. Since 20 years the formation of the craterlike feature is discussed controversially. A volcanic origin must probably be excluded as no volcanic rocks erupted from the crater have been identified in the lake or around it.

Therefore the idea was born that the Rodder Maar could be the crater of a large meteorite impact.

The crater lies in siliciclastic rocks of lower Devonian age, mainly slates and sandstones, foliated and folded during the Variscan Orogeny. During the orogeny frequent quartz veins have been formed, which reach up to several meters of thickness. The basement rocks have been weathered intensively during upper Mesozoic and lower Cenozoic, with the formation of a kaolinitic weathering crust with frequent crusts of goethite and hematite, found all around the crater on the surface. Loess and a thin, cm thick blanket of volcanic ash covers the area around the Rodder Maar. It originates from eruptions of neighboring volcanoes.

A geomagnetic survey effectuated by Meyer W. et al. (Bonn University) revealed no magnetic anomaly as it should be supposed to exist in a volcanic maar structure. Negendank et al. (Centre of Geoscience Research Potsdam) drilled in the center of the crater and found about 14 m of loess with breccia of devonian rocks in the lower part of the section. No traces of meteoritic material, volcanics or impactites had been detected however. The Rodder Maar shows no typical rim, as observed at impact or volcanic craters. This may be due to young erosion processes (Eifel river valleys are formed by younger Pleistocene erosion). Small scale morphologic structures are hidden by dense forest and a young loess cover.

During the last years the authors collected numerous rock samples from the northern and northeastern areas of the crater. Many samples are heavily fractured, especially the quartzitic Devonian sandstones and the iron rich quartz veins. No breccia are however observed in the southern and western surroundings of the crater.

Preliminary chemical analyses have detected no traces of meteoritic material. Microscopic thin section analyses of the breccia however revealed that some of the larger quartz grains show obvious deformation structures similar to shocked rocks at other small impact craters. Very dense subparallel fracture systems are observed in which the single crystal lamellae display highly undulatory extinction in different optical directions under crossed nicols. This strongly brittle crystal lattice can hardly be explained by tectonic stress and is not observed in the surrounding Rhenish Slate Mountains. Some grains show faint planar deformation features (PDF). The dimension of the crater and so the impact energy is however too small to develop clear PDF’s as observed in larger impact structures.

The actual data strongly support the hypothesis that Rodder Maar is a young impact structure. It is the third proved impact crater in Germany!

Current geophysical, geochemical and mineralogical research leaded by Bonn University, as well as a planned drill core up to the basement of the structure are supposed to finally confirm the impact.

¹ Steinmann-Institute for Geology, Mineralogy and Paleontology, Rheinische Friedrich-Wilhelms-University Bonn, Nussallee 8, D- 53115 Bonn, Germany. *email: jthein@uni-bonn.de
Evolution of overprinted HP metamorphic rocks from the Rhodope: can zircon provide additional information?

Thomas Theye¹ & Anthi Liati²

¹thomas.theye@mineralogie.uni-stuttgart.de
²anthi.liati@empa.ch

The petrology of a migmatized garnet gneiss from eastern Rhodope, close to Kimi area, was studied here with the aim of evaluating records of high-P metamorphic event(s) and comparing the results with those obtained from hosted zircon. The Rhodope zone is an Alpine polymetamorphic nappe stack recording a series of metamorphic events of HP, UHP and, in parts, HT conditions (see [1] for a review and references). In the studied tectonic unit, HP metamorphic events occurred at c. 150 Ma, c. 120 Ma and c. 74 Ma ([1, 2]). The time of UHP metamorphism remains speculative. U-Pb SHRIMP-dating of zircon from the gneiss studied here revealed two metamorphic events: at c. 150 and c. 74 Ma, both interpreted to reflect HP conditions, based on REE patterns and type of metamorphic rims of zircon; [1]).

The migmatised host rock of zircon contains quartz + plagioclase + K-feldspar + phengite as main constituents. In addition, minor biotite, garnet, and allanite (partly replaced by monazite) are present. Phengite is well aligned and defines a metamorphic foliation. Garnet occurs either as small (< 0.3 mm), essentially euhedral crystals, or as cm sized skeletal aggregates. Microprobe analyses of garnet reveal that, from core to (inner) rim, Mg decreases and Ca increases, at a fairly constant Mn level. An outer rim of garnet exhibiting some resorption is characterized by a drop of Mg and Ca and an increase in Mn. White K-mica composition is in the range of 3.10 to 3.23 Si per formula unit. The lower Si values are measured in phengite rim zones. Single zircon crystals contain tiny inclusions of quartz, biotite and phengite. In the inner, 150 Ma old, metamorphic domain, Si contents of phengite reach values as high as 3.33 Si p.f.u. In the outer, 74 Ma old, metamorphic rim, Si of phengite is max. 3.17.

The pseudosections resulting by use of PERPLE_X modeling [3] display a large PT stability field of Qtz + Plag + Kfs + Phg + Bt + Grt with H₂O or melt. Ca and Mg isopleths for Gt indicate about 10 kbar/700°C for the core, whereas (inner) rims grew during cooling down to 9 kbar/640°C. A subsequent pressure release to 6 kbar and 580°C is indicated by Grt outer rims. Si isopleths for phengite well coincide with the derived conditions. The same calculations tentatively applied to Si richer phengite included in the 150 Ma old zircon domain result in c. 15 kbar (at 700°C). However, HP conditions are indicated also by the REE pattern of the 74 Ma old outer rim of zircon that contains muscovite with low Si content.

Conclusively, the P-T path segment reconstructed for the gneiss is subsequent to the 150 Ma metamorphic peak and records the late history of the 74 Ma event documented in zircon.

CT imaging of rock salt: 3D multi-scale analyses of the structural inventory

Nicolas Thiemeyer¹, Maximilian Pusch², Jörg Hammer², Gernold Zulauf¹

¹Institute of Geoscience, Goethe University Frankfurt am Main, Altenhöferallee 1, 60438 Frankfurt am Main (n.thiemeyer@em.uni-frankfurt.de; g.zulauf@em.uni-frankfurt.de)

²Federal Institute for Geosciences and Natural Resources (BGR), GeoZentrum Hannover, Stilleweg 2, D-30655 Hannover (maximilian.pusch@bgr.de; joerg.hammer@bgr.de)

Non-destructive CT imaging is an established technique in geosciences (see Mees et al. 2003 and references therein). However, CT studies of rock salt are rare (e.g. Zulauf et al. 2009, 2012, Burliga & Czechowski 2010, Mertineit et al. 2012). We present scientific approaches and possibilities of CT investigations on rock salt using a Phoenix nanotom s (GE Sensing and Inspection Technologies) at the Goethe University of Frankfurt am Main. This µ-CT has a maximum resolution of less than 1 µm per voxel and allows high resolution scans amplifying and improving CT studies acquired by clinic computer tomographs. CT analyses are capable for visualisation and quantification of any detectable portion of a rock volume depending on density contrast and the designated scale. In the case of rock salt, pore space, fractures or mineral assemblages (e.g. anhydrite or celestine) can be analysed and quantified. Moreover, three-dimensional visualisations expose spatial distribution anisotropies of pore space to give important additional information to laboratory measurements or macro- and microscopic observations regarding porosity, permeability and reservoir properties. An elevated porosity (< 1.3 Vol.-%) can be observed in hydrocarbon-bearing rock salt samples from salt diapirs, implying that hydrocarbons are responsible for hampered closure of pore space during the halokinetic uprise. Generally, CT imaging supports the overall characterisation and interpretation of structural inventories of rock salt and helps to uncover the distribution of mineral phases or fluids and the deformation history of the salt rocks on multiple requested scales.


**U-Pb Dating of Silcretes in the Siebengebirge (Rhenish Massif, Germany)**

F. Tomaschek¹, A. Nemchin², R. Merle², T. Geisler¹

¹ Steinmann-Institut, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany [ftom@uni-bonn.de; tgeisler@uni-bonn.de]
² Curtin University, Department of Applied Geology, Perth, Australia [r.merle@curtin.edu.au; a.nemchin@curtin.edu.au]

Paleo-weathering processes eventually lead to characteristic products such as silcretes (“Tertiärquarzite”). High U and low Th and initial Pb concentrations often found in opaline silica potentially allows the application of U-Pb techniques for age determination by ion microprobe, which, in turn, would allow constraining the timing of silification events, i.e., dating paleo-weathering episodes. To test this possibility, we sampled opal from the Siebengebirge, Germany. The Siebengebirge is located at the northern margin of the Rhenish Massif, where fluviatile sediments of Oligocene age were buried below an extended trachyte tuff cover. This trachyte tuff represents an early stage of the Siebengebirge volcano, produced mainly at around 25 Ma. The tuff provides a chronostratigraphic reference horizon as well as a source for the mobilization of silica during weathering. Silica was found to silicify some domains within the tuff and, in particular, certain horizons within the Oligocene sediments directly below the tuff. In the published geological literature it has often been suggested that this regional silification event occurred during intense weathering more or less synchronous with the deposition of the volcanic ashes.

The investigated samples comprise silicified gravels and sands from a classic locality in the Mittelbachtal, renown for the occurrence of wood opal. Cementation of the gravels occurred during at least three successive growth stages, filling the pore space: early paracrystalline silica (opal-CT), fibrous chalcedony (quartz-moganite intergrowths), and late microcrystalline quartz. Silification of associated wood is more complex, as it seems to involve replacement reactions. Green fluorescence, observed under short UV light, indicates high U concentration and was used to select domains that are most promising for ion microprobe U-Pb analyses.

First analyses of the opal-CT and chalcedony cement using a sensitive high-resolution ion microprobe (SHRIMP) yielded a mean $^{206}$Pb/$^{238}$U age of about 13 Ma that is significantly younger than the expected age of about 25 Ma. There are several possible interpretations to account for this observation. For instance, silification at the sampled Mittelbachtal locality might be a late and local phenomenon. Alternatively, silica U-Pb ages might be younger due to ageing processes that may have caused loss of radiogenic Pb. To address this problem, we aim to analyze samples in various relations to the volcanics, and closely combine the in situ U-Pb age (SHRIMP, SIMS, LA-ICPMS) and structural information (IR, Raman spectroscopy) in our ongoing study.
The structure of a material consists of ordered atoms, ions, molecules, which determine the physical properties of a material. Depending on the orientation distribution of grains (=crystallites) in the polycrystalline material, the history of the material is only partly understandable by ex situ measurements. With help of in situ measurements, the processes taking place during texture development in dependence of the influencing factors: pressure, temperature, deformation, additives and grain sizes are studied.

Starting material was produced by cold pressing pure polycrystalline halite of different grain sizes and with different additives using a uniaxial press (100 tons). The powder was cold pressed at 200 MPa and finally heated 4-5 days at 150°C for recovery of the microstructure. The measurements were performed at the beamline BW5 in 1° steps in the omega angle range of +/-20°, while the cylindrical samples with 8 mm diameter were heated and deformed in axial compression with the tensile-compression device of Kammrath and Weiss. For heating a direct voltage and current supply on the sample is applied. The 2D images were recorded with a Perkin Elmer detector. For the grain orientation analysis, the programs FABLE [1], MAUD [2] and BEARTEX [3] were used.

In general a decrease in yield strength in the pure samples, which even decrease more with increasing temperature and grain size is observed. Under the same stress conditions the pure samples show a decrease in the Young’s modulus and the yield strength and an extended plastic regime. Silica gel additives in the halite bulk cause a lower strain accumulation, expressed through a larger Young’s modulus, a strengthening of the samples, which correlates with a decrease in plasticity. In the texture development a sustainability of the starting texture is observed, which correlates well with the mechanical behaviour. The amorphous phase likely protects the single grains from deformation, alleviating strain accumulation by introduction of defects and therefore the preservation of the grain shape.

References

Effects of vegetation cover on denudation rates in the East Africa Rift

Veronica Torres Acosta1, Taylor F. Schildgen2, Brian A. Clarke3, Dirk Scherler4, Bodo Bookhagen5, Hella Wittmann6, Friedhelm von Blanckenburg7, Manfred R. Strecker8

1 acosta@geo.uni-potsdam.de,
2 tschild@uni-potsdam.de,
3 bac43@psu.edu,
4 scherler@caltech.edu,
5 bodo@eri.ucsb.edu,
6 wittmann@gfz-potsdam.de,
7 fvb@gfz-potsdam.de,
8 Manfred.Strecker@geo.uni-potsdam.de

Increasing slope or relief in a landscape has long been known to correlate with faster erosion rates. Despite a number of studies that have attempted to clarify the additional roles of precipitation or vegetation, deciphering the complex influence of climate on erosion rates in a landscape with variable slope and relief has remained difficult.

The eastern and western branches of the East African Rift System (EARS) constitute first-order tectonic and topographic features in East Africa, which have a profound influence on the distribution and amount of rainfall, and thus the efficiency of surface processes. The Kenya Rift is an integral part of the eastern branch and is characterized by pronounced differences in morphology, rainfall, and vegetation cover. While paleoclimatic studies in this region reveal general stability of the precipitation regime and vegetation cover, short-term changes on timescales of ca. 10^4 yrs have affected the area multiple times throughout the Pleistocene.

We present 20^{10}Be-derived catchment-wide mean denudation rates from various morphotectonic sectors of the Kenya Rift. The sampling locations include steep rift escarpments, step-faulted composite escarpments, and gently inclined rift-shoulder areas. These different environments also span a rainfall gradient of 0.004 to 4 m/yr, and vegetation covers that range from very sparse to dense. For comparison, 10^{10}Be-derived denudation rates are also available from the Rwenzori mountains in the western branch of the rift system. There, rainfall is high and the vegetation cover is denser than in the studied sites in Kenya, but the range of relief and hillslope angles is similar. A first-order comparison of our new denudation rates in Kenya with the climatic and topographic characteristics of the catchments show no obvious correlations with denudation rates. However, denudation rates from different savanna environments in the eastern branch of the rift (Kenya Rift) are up to 0.13 mm/yr, while denudation rates from the densely vegetated (mostly forested) western branch (Rwenzori Mountains) are more than 50% lower when comparing areas of similar relief or hillslope angles. Generally, millennial-scale denudation rates in the East African Rift increase faster with topographic relief where vegetation cover falls below a threshold value. This pattern implies that vegetation stabilizes the soil layer and supports steeper slopes, and that minor changes in climate can substantially affect denudation rates if they cause vegetation cover to cross the threshold. Conversely, variations in climate and ensuing vegetation changes may have little discernible effect if the vegetation threshold is not crossed.
Deformation experiments are carried out on natural vein quartz in a modified Griggs-type solid medium apparatus to explore the preservation potential of microfabrics created by crystal-plastic deformation at high stress, overprinted during subsequent creep at lower stress. A corresponding stress history is expected for the upper plastosphere, where fault slip during an earthquake causes quasi-instantaneous loading to high stress, followed by stress relaxation. The question is whether evidence of crystal-plastic deformation at high stress, hence an indicator of past seismic activity, can still be identified in the microstructure after overprint by creep at lower stresses. First, quartz samples are deformed at a temperature of 400°C and constant strain rate of $10^{-4}$ s$^{-1}$ (“kick”), and then held at 900 to 1000°C at residual stress (“creep”). In quartz exclusively subject to high-stress deformation, lamellar domains of slightly differing crystallographic orientation (misorientation angle <2°) and a few tens of micrometers wide occur. In transmission electron microscope (TEM), these areas show a high density of tangled dislocations and cellular structures. After “kick and creep” experiments, pronounced short-wavelength undulatory extinction (SWUE) is observed in the polarization microscope. The wavelength of SWUE is up to 10 µm, with oscillatory misorientation of up to a few degrees, as indicated by the electron backscatter diffraction (EBSD) technique. TEM inspection reveals domains with high density of dislocations and differing diffraction contrast bound by poorly-ordered dislocation walls. Only zones with exceptional damage generated during high-stress deformation are replaced by small new grains with a diameter of about 10 to 20 µm, forming strings of recrystallized grains. For large original grains showing SWUE, the Schmid factor for basal $\langle a\rangle$ glide is found to be high. SWUE is taken to reflect high-stress crystal-plastic deformation, the modified microstructure being sufficiently stable as an indicator of past seismic activity, still discernible after subsequent creep.
Palagonitization of basalt glass in the flanks of mid-ocean ridges: implications for bioenergetics of oceanic intracrustal ecosystems  

Andreas Türke¹, Wolfgang Bach², Wolf-Achim. Kahl³, Andreas Klügel⁴

¹atuerc@uni-bremen.de  
²wbach@uni-bremen.de  
³wakahl@uni-bremen.de  
⁴akhuegel@uni-bremen.de

When basalt glass is exposed to oxygenated aqueous solutions, rims of palagonite form along fractures at the expense of glass. The flanks of mid-ocean ridges are the largest reservoir of basalt glass on Earth, and the flow of oxygenated seawater fluxed through these flanks is great (>10¹⁶ kg/yr; Fisher, 2005; Hydrogeol. J. 14, 69-97). Hence, large amounts of palagonite form in this setting, but palagonitization is kinetically sluggish at the prevailing temperatures in flanks (< 25 °C), allowing chemolithoautotrophic microbes (i.e., those that fix CO₂ by using inorganic energy sources of energy and electrons) to catalyze oxidation reactions of ferrous iron for catabolic energy gain. Tubular and granular alteration textures, present in basalt glass samples, from both modern and ancient rocks, are interpreted as trace fossils of endolithic microbes chemically ‘drilling’ into fresh glass (McLoughlin et al., 2010; Geobiology DOI: 10.1111/j.1472-4669.2010.00243.x). While the energy sources fueling this putative microbial life in basalt are unknown, it has been suggested that steady-state Fe oxidation in ridge flanks can support a microbial biomass production on the order of 10¹¹ g C per year (Bach and Edwards, 2003; GCA 67, 3871-3887). These authors suggest that most of the Fe oxidation takes place within the first 10 Myrs of ridge flank evolution, and it is uncertain which energy sources chemolithoautotrophs may use in older crust.

The North Pond Area on the western flank of the Mid-Atlantic Ridge at 23°N was drilled during Integrated Ocean Drilling Program Expedition 336 to sample 8 Myr-old ridge flank crust and instrument the drill holes with observatories for coupled hydrological, geochemical, and microbiological investigations. From these drill cores, we have analyzed fresh glass and adjacent palagonite rinds by electron microprobe and LA-ICP-MS to determine the geochemical changes involved in palagonitization. We also analysed whole rock powders to determine the overall crust-seawater exchange in a young ridge flank. Palagonite is an abundant alteration phase in the basement, along with clay minerals, Fe-oxyhydroxides, and zeolites. The palagonite appears to be highly oxidized, containing only little to none ferrous iron. Radioactive elements are enriched in the palagonite relative to the fresh glass (U>K>Th), reaching concentrations for U (and K) where radiolytic production of molecular hydrogen (H₂) may be a significant energy source (Blair et al., 2007; Astrobiology 7, 951-970).

Based on these results, we hypothesize that microbial ecosystems in ridge flank habitats undergo a transition in the principal energy carrier fueling carbon fixation from Fe oxidation in very young crust to H₂ consumption in old crust. We argue that thick rinds of palagonite in old crust protect the remaining fresh glass from alteration and thwart the oxidation of ferrous iron in the glass. These palagonite rinds have accumulated enough U and K to release nannomolal quantities of H₂ per kg rock and year. Unless the H₂ is swept away by rapid fluid flow (i.e. in young flanks), it may easily accumulate to levels high enough to support chemolithoautotrophic life. In older flanks, crustal sealing and sediment accumulation have slowed down seawater circulation such that radiolytically produced H₂ greatly increases in significance for catalytic energy supply.
Experimental melt degassing with different starting materials: glass cylinder vs. powder

S. Ulmer\textsuperscript{1}, H. Marxer\textsuperscript{2}, O. Preuß\textsuperscript{3}, M. Nowak\textsuperscript{4}

\textsuperscript{1}s.ulmer@student.uni-tuebingen.de
\textsuperscript{2}holger.marxer@uni-tuebingen.de
\textsuperscript{3}oliver.preuss@uni-tuebingen.de
\textsuperscript{4}marcus.nowak@uni-tuebingen.de

Decompression experiments for the investigation of magma degassing can be performed using glass powder or solid glass cylinders as starting material. The decompression of a hydrous melt results in H\textsubscript{2}O super-saturation, which is reduced by nucleation and growth of H\textsubscript{2}O bubbles. The use of powder as starting material may result in a memory effect within the melt, where the bubbles nucleate heterogeneously at former glass grain boundaries as nucleation sites. In order to exclude influences caused by the starting material on the degassing process of a hydrous phonolitic melt (Vesuvius AD79 composition), a set of decompression experiments was performed using a glass powder (1:1 mixture of two grain size ranges of 200-500\textmu m and <200\textmu m) as well as a glass cylinder.

The experiments were conducted in two steps. At first \(\sim 5\) wt\% H\textsubscript{2}O were dissolved in the melt. The powder experiment was equilibrated at 200 MPa and 1573 K for 24 h. The cylinder experiment was equilibrated at 200 MPa and 1323 K for 96 h. Subsequently the samples were decompressed at a super-liquidus \(T\) of 1323 K and a continuous decompression rate of 0.024 MPa\textsuperscript{-1}\textsuperscript{s} to a final \(P\) of 75 MPa. At target \(P\) the samples were rapidly quenched under isobaric conditions. Samples were analyzed in terms of BND (bubble number density), BSD (bubble size distribution) and residual H\textsubscript{2}O content. The H\textsubscript{2}O content was analyzed with the EMP and NIR. A quantitative comparison of the two experiments was difficult, because the capsule of the glass cylinder experiment was strongly deformed. Nevertheless, the samples display similar degassing behavior despite different starting materials. The bubbles are distributed homogeneously in the glass and the BNDs of both samples are below 50 mm\textsuperscript{-3}. The residual H\textsubscript{2}O contents are close to the solubility of 3 wt\% at 75 MPa and 1323 K and indicate near equilibrium degassing. These results imply that former grain boundaries disappear at equilibration at 1573 K within this phonolitic melt. It is still unknown in which way the run time affected the results, because bubble coalescence could have reduced the BND to a certain extent during decompression.

Future studies with a trachytic glass composition and different grain size ranges will be performed to investigate the effect of the starting material on degassing experiments in more detail. The target \(P\) will be increased to 100 MPa in order to reduce decompression time.
Small volume, monogenetic volcanoes dispersed within volcanic fields provide important insights into the generation and collection of magmas in the upper mantle, and the role of local/regional tectonics in those processes. Many of these insights reflect the relative simplicity of a monogenetic system, which allow researchers to “filter out” some of the complexities found in longer-lived systems such as stratovolcanoes. Low volume monogenetic fields occur in many tectonic settings, including extensional, flexure zones, and relatively neutral, and are commonly not clearly related to “standard” volcanotectonic processes such as subduction, hot spots, and rifting. These fields represent magmatic systems that are just at the threshold of being able to erupt. Why do these volcanoes form in the first place? What controls the location of a given volcano – the location of its magma source, or upper crustal structure, or both? Is there a relationship between the physical scales of the volcanoes on the surface (e.g., eruptive volume, feeder dike length) and the physical scales of their magma sources? Recent work is suggesting that the answer to the latter might be “yes” in some cases, and that mantle heterogeneity and processes that mechanically focus small volumes of melt are critically important.

From a physical volcanological perspective, monogenetic volcanoes record a rich variety of eruptive styles, but have the advantage of producing landforms and deposits that are manageable in size for field-based study. All sorts of magmatic and phreatomagmatic eruptive styles and deposits are preserved at monogenetic volcanoes, including effusive, Strombolian, violent Strombolian to sub-Plinian, Vulcanian, tephra fall, ballisticallyemplaced deposits, and pyroclastic density current deposits. Any given volcano can record multiple transitions from one style to another, and often these transitions are related to changes in the shallow plumbing of a volcano and its external environment, regardless of whether there are changes in magma composition. Improving our understanding of causes and transitions of eruptive styles at monogenetic volcanoes gives us information that can be translated to eruptive styles at larger, more hazardous systems. Monogenetic volcanic landforms similarly record the diverse nature of eruptive processes: lava shields, scoria cones, maars, tuff cones, spatter ramparts, and lava fields. Recent work highlights, for example, the point that simple geometry changes in shallow plumbing can result in transitions from relatively quiet (effusive, Strombolian) styles to hazardous violent Strombolian styles later in an eruption. Eroded volcanic fields give us direct access to their shallow plumbing systems, including diatremes. New experimental results are elucidating the way phreatomagmatic explosions produce maar craters and diatremes. Research on all of these issues adds to our fundamental understanding of magmatism and has immediate applications to hazard and risk assessments in volcanic fields.
Identification of Ca-, Mg-, and Fe-carbonates by Raman spectroscopy

M.A. van Zuilen¹, N. Rividi², B. Menez³, P. Philippot⁴

¹Institut de Physique du Globe de Paris, France, vanzuilen@ipgp.fr
²Institut de Physique du Globe de Paris, France, nicolas.rividi@flux-tendu.com
³Institut de Physique du Globe de Paris, France, menez@ipgp.fr
⁴Institut de Physique du Globe de Paris, France, philippot@ipgp.fr

In many geosciences studies there is a specific need for fast characterization of carbonate composition while avoiding complex sample preparation or sample destruction. Raman spectroscopy is a highly versatile non-destructive technique enabling in-situ characterization of minerals. It can be combined with confocal microscopy enabling high-resolution Raman mapping of entire rock thin sections, or can be integrated in portable instruments for direct field-based mineral identification. It is thus important that well-established spectral databases exist which enable unambiguous identification of a wide variety of carbonate minerals. The most common carbonates in the Ca-Mg-Fe system are the CaCO₃ polymorphs calcite, aragonite, and vaterite, as well as the solid solutions CaMg(CO₃)₂-CaFe(CO₃)₂ (dolomite-ankerite) and MgCO₃-FeCO₃ (magnesite-siderite). Although various carbonate end-members have been studied exhaustively by Raman spectroscopy, a simple protocol for rapid distinction of various carbonate solid solutions is still lacking. Here we present a detailed study of Raman shifts in various carbonate standards of known composition in the Ca-Mg-Fe system. Carbonates with rhombohedral symmetry display a Raman spectrum with six characteristic vibrational modes – four of these represent vibrations within the (CO₃)²⁻ unit and two represent external vibrations of the crystal lattice. We show that Raman band shifts of internal mode 2ν₂ (range 1725-1765 cm⁻¹), and external modes T (range 170-215 cm⁻¹) and L (range 285-330 cm⁻¹) for siderite-magnesite and ankerite-dolomite solid solutions display distinct and well defined positive correlations with Mg number (Mg/Mg+Fe+Mn+Ca). It will be shown that these carbonate solid solutions can be distinguished from other end-member carbonates such as calcite, vaterite and the orthorhombic polymorph aragonite. Finally, it is shown that detailed micron-resolution Raman hyperspectral maps can be generated of carbonate crystal-zonation.
Geochemistry and mineralogy of metallurgical slags from Thuringia

Veronika Veselská¹, Juraj Majzlan²

¹veronika.veselska@gmail.com
²juraj.majzlan@uni-jena.de

Metallurgical slags from the past copper production are witnesses of the intensive exploitation of the Kupferschiefer in the wider region of Eisenach in Thuringia. In general, metallurgical slags might contain high concentrations of copper, zinc, cobalt, nickel, and lead. The slags are of interest from two points of view. One of them is their potential to be re-used as sources of metals, perhaps those which were not targeted by the old miners. The other point is of environmental nature because despite of their mostly glassy character with a long period of weathering, the metals may be potentially released into the environment depending on their association with slags and on the geochemical conditions.

According to microscopic observations of metallurgical slags and X-ray diffraction (XRD) analyses, amorphous phases constitute the major part of the slag samples. Either they are fully vitreous with a lack of crystalline phases or they contain inclusions of pure metals or metal sulphides at the edge of pores in the glasses. The results of XRD analyses suggest that a number of Fe, Ni, Cu, Co and Pb sulphides are present; the exact nature of these is being verified by WDS analyses at the moment. Many metallic inclusions contain only metallic copper, lead, iron or their mixture. The sulphides can be considered to be the major metal carriers. The results of electron microprobe analyses indicate a high concentration of copper in all of them (72.91 wt% of Cu on average). Contents of Fe, Ni and Co reach up to 88.77, 28.02 and 8.30 wt%, respectively and vary depending on specific sulfides. Arsenic appears to be associated with sulfides enriched in Ni. However, the concentrations of Pb are very low in sulphides (0.04 wt% of Pb on average). Glasses are depleted in metals in general (<1 wt%). Their chemical composition is dominated by SiO₂, CaO and Al₂O₃ (44.69, 29.69, 11.08 wt% on average, respectively).

Keywords: Copper, Metallurgical slags, Mineralogy
Spatial heterogeneity of the neodymium isotopic composition of Mesoarchean seawater: Evidence from the Witwatersrand, Pongola and Pietersburg BIFs, South Africa

Sebastian Viehmann1, Michael Bau2, Albertus J.B. Smith3, Nicolas J. Beukes4, Elton L. Dantas5, Bernhard Bühn6

Banded Iron Formations (BIFs) are unique archives in the Precambrian rock record, because they are marine chemical sediments which directly precipitated from seawater and, therefore, provide information about ancient seawater, such as its pH and redox state. Rare earth elements and yttrium (REY) in pure Precambrian seawater precipitates have become viable tracers of ancient ocean geochemistry because of their comparability to modern seawater REY systematics and due to their resistance to overprint by post-depositional geological processes like diagenesis or metamorphism [e.g. 1,2]. Moreover, it is well-established that Sm-Nd isotopic compositions of pure marine chemical sediments give detailed insights into the sources of REY in ancient seawater [e.g. 3, 4].

In this study we present Sm-Nd isotope data for pure sample aliquots [5] of stratigraphically and geochemically well-characterised ~2.9 Ga Witwatersrand BIFs (Kapvaal Craton, Republic of South Africa). Together with the Pongola BIFs, the Witwatersrand BIFs are the oldest well-preserved Superior-type BIFs deposited on a stable craton under shallow marine conditions in the geological rock record. BIF sample powder was digested in Parr-type bombs with HF-HNO3 acid mixtures and Sm-Nd were separated by ion exchange column chemistry. Isotopic compositions and concentrations of Sm and Nd were analysed by a Finnigan Triton Plus at the University of Brasília through applying isotope dilution technique.

The availability of Mesoarchean pure chemical sediments from the stratigraphically correlatable Witwatersrand and Pongola Supergroups [6] and from the Pietersburg Greenstone Belt provide unique insights into the spatial variation of the Nd isotopic composition of Mesoarchean seawater, into the evolution of marine εNd and into the source of REY in watermasses in different compartments during several trans- and regression cycles. εNd(t) values of the lowermost pure Ijzermijn BIF (εNd2.9Ga = -4.3 to -1.9) in the Mozaman Group of the Pongola Supergroup are generally indistinguishable from intercalated shales (εNd2.9Ga = -4.7 to -2.7), suggesting a major continental REY contribution to the depositional environment of the Ijzermijn BIFs with minor influence of hydrothermal fluids with mantle-derived Nd [3]. In contrast, stratigraphically slightly younger Water Tower BIFs from the Witwatersrand Supergroup range from εNd2.9Ga = -1.9 ±0.4 to -1.2 ±0.2, indicating enhanced hydrothermal contributions to watermasses during the BIF precipitation transgression period. The overlying Contorted Bed BIF succession displays heterogeneous εNd2.9Ga = -5.9 ±0.3 to +0.8 ±0.4. The base of Contorted Bed IF represents the deepest marine conditions during a transgression period cycle [5]. As expected, the basal Contorted Bed BIF sample yields the strongest Eu anomaly (indicating the presence of hot hydrothermal fluids) and the most radiogenic εNd, also reflecting elevated contributions from mantle-like hydrothermal fluids. This value overlaps with slightly older (~2.95 Ga) and deeper marine Pietersburg BIFs (εNd2.9Ga = -0.8 to +0.9) which carry a strong hydrothermal signal [4]. The most unradiogenic εNd suggests detrital contamination during BIF deposition, accompanied by a close stratigraphic association with a shale band and slightly elevated REY and Al concentrations. The εNd2.9Ga (εNd2.9Ga = -1.3 ±0.1) from the middle Contorted Bed BIF succession overlaps with Water Tower BIFs, indicating a similar depositional environment during precipitation of Contorted Bed BIFs (excluding the base) and Water Tower BIFs with slightly enhanced mantle-like hydrothermal contributions compared to underlying Mozaman BIFs.

The spatial differences in Sm-Nd isotopic compositions of contemporaneous Mesoarchean pure BIFs strongly indicate a heterogeneous initial εNd in the Mesoarchean oceans, suggesting that similar to the modern ocean, the marine residence time of Nd was smaller than the mixing time of the Mesoarchean ocean. Therefore, samples from individual BIF are unlikely to provide information on the (redox)state of the global atmosphere-hydrosphere system.

Mineral composition control the formation of organo-mineral associations

-An artificial soil experiment using $^{15}$N and $^{13}$C labeled litter

C. Vogel$^{1}$, S. Schulz$^{2}$, K. Heister$^{3}$, F. Buegger$^{3}$, M. Schloter$^{2}$ and I. Kögel-Knabner$^{1,4}$

$^{1}$ Lehrstuhl für Bodenkunde, Department Ecology and Ecosystem Management, Center of Life and Food Sciences Weihenstephan, Technische Universität München, D-85350 Freising-Weihenstephan, Germany

$^{2}$ Research Unit of Environmental Genomics, Research Center for Environmental Health, Helmholtz Zentrum München (GmbH), D - 85764 Neuherberg, Germany

$^{3}$ Institute of Soil Ecology, Research Center for Environmental Health, Helmholtz Zentrum München (GmbH), D - 85764 Neuherberg, Germany

$^{4}$ Institute for Advanced Study, Technische Universität München, Lichtenbergstrasse 2a, D-85748 Garching, Germany

Soils are complex and dynamic systems composed of minerals, organic matter (OM) and microorganisms as solid constituents. The mineral-organic matter-microorganism interactions in soil influence the formation of organo-mineral associations as reactive interfaces. Clay minerals, iron oxides and charcoal are considered as major constituents affecting the formation of these interfaces in soil. The analyses of complex interaction between minerals, organic and microbial components in soil are hampered by the huge influence of different environmental conditions and the usually unknown initial conditions. Therefore, artificial soil systems offer a valuable approach where the formation and interactions of soil properties and processes can be studied in a well-defined system.

The aim of our study was to examine the effect of different mineral compositions and charcoal on the formation of organo-mineral associations after OM addition to an already established artificial soil system.

For this purpose, 35 g of artificial soil (< 2 mm) was mixed with 0.35 g $^{13}$C and $^{15}$N labeled litter (< 200 µm) and incubated over 63 days. The artificial soils were produced in a long-term incubation experiment over 842 days. Four different compositions (montmorillonite (MT), illite (IL), montmorillonite + charcoal (MT+CH), illite + ferrihydrite (IL+FH)) and in addition a natural topsoil (Luvisol) were used for the incubation. The experiment was performed in three independent replicates per composition under defined conditions at 14 °C and a water holding capacity of 60 %. Samples were taken directly after litter addition and then after 7, 21 and 63 days. The isotopic nitrogen and carbon composition of the bulk soil and the soil fractions were monitored using an isotope ratio mass spectrometer after a combined density and particle-size fractionation.

Our results show that $^{13}$C is mineralized relatively quickly whereas the $^{15}$N remained constant. The immediate enrichment in the small-sized fractions indicates a rapid development of newly formed interfaces. The highest $^{15}$N and $^{13}$C concentrations in organo-mineral associations after 63 days were observed in the clay-sized fraction. First results point to a different effect of the clay minerals illite and montmorillonite on the formation of organo-mineral associations.
Mineral particles clustered in submicron structures provide preferential organic matter sequestration spots

C. Vogel¹, C. W. Müller¹, C. Höschen¹, F. Buegger², K. Heister¹, S. Schulz³, M. Schloter³ and I. Kögel-Knabner¹, ⁴

¹ Lehrstuhl für Bodenkunde, Department Ecology and Ecosystem Management, Center of Life and Food Sciences Weihenstephan, Technische Universität München, D-85350 Freising-Weihenstephan, Germany
² Institute of Soil Ecology, Research Center for Environmental Health, Helmholtz Zentrum München (GmbH), D - 85764 Neuherberg, Germany
³ Research Unit of Environmental Genomics, Research Center for Environmental Health, Helmholtz Zentrum München (GmbH), D - 85764 Neuherberg, Germany
⁴ Institute for Advanced Study, Technische Universität München, Lichtenbergstrasse 2a, D-85748 Garching, Germany

The sequestration of organic matter (OM) by organo-mineral associations is widely accepted. However, in most cases, these complex structures remain a black box due to the common measurements of soil fractions as a whole. By combining nano-scale secondary ion mass spectrometry (NanoSIMS) with isotopic tracing, it is possible to study the formation and spatial heterogeneity of organo-mineral associates.

The aim of our study was to follow the formation of organo-mineral associations and the distribution of C and N over time by imaging the complex interaction between soil mineral surfaces and decomposed organic compounds.

We incubated a topsoil (sieved <2 mm, Ap from a Luvisol) with $^{15}$N and $^{13}$C labeled litter material under controlled conditions. Samples were taken 2 hours after start of incubation and after 1, 7, 21 and 42 days. Parallel to the determination of microbial biomass $^{13}$C (C$_{mic}^{13}$C), salt extractable organic carbon-$^{13}$C (SEOC-$^{13}$C) and the isotopic N and C composition of bulk soil and soil fractions (combined density and particle size fractionation) using isotope ratio mass spectrometry (IRMS), the spatial distribution of the OM was investigated by NanoSIMS analysis of the clay-sized fraction.

By quantification of exposed areas visible via NanoSIMS, we showed that only 13 to 19 % of the mineral surfaces were covered by OM, whereas most mineral surfaces did not show any OM coverage. Our study demonstrates that mineral particles in clustered structures with rough surfaces exhibit the preferential binding spots for OM. The comparison of the OM-coated areas revealed by the 2D NanoSIMS imaging and N$_2$ adsorption gives evidence that mineral particles with a high specific surface area are covered by OM in these clustered structures. Consequently, we demonstrate distinctive micro-scale spots enriched in $^{13}$C and $^{15}$N and a preferential binding to rough surfaces of mineral clusters as a highly active zone.
The "speed limit" to soil weathering – do mountains matter to CO$_2$ withdrawal?

Friedhelm von Blanckenburg$^1$, Jeannie Dixon$^2$

$^1$ GFZ Postdam, fvb@gfz-potsdam.de
$^2$ University of California Santa Barbara, jean.dixon@geog.ucsb.edu

A general assumption made by geoscientists is that the rise of mountains in the late Cenozoic has increased global rates of silicate weathering, and, as a consequence, increased the withdrawal of atmospheric CO$_2$. Cosmogenic Beryllium-10 in the mineral quartz is now the Geochemists workhorse in the determination of Earth surface rates, and allows us to challenge this hypothesis. Measured locally, such denudation rates are assumed to reflect soil formation rates; measured in river sediment, rates quantify catchment-averaged denudation; when combined with chemical loss balances, using Zr as refractory element, soil weathering rates are obtained.

We compiled global datasets of long term, soil-based denudation and weathering rates, and short term, river-based sediment and dissolved loads. We find that globally 95% of soil (here: the mobile layer at the Earth surface) formation rates and weathering fluxes in soil-mantled landscapes fall below a global maximum that we define as “speed limit”. The speed limit of soil formation obeys is 350 t km$^{-2}$ y$^{-1}$, and the associated limit to the soil weathering flux is 150 t km$^{-2}$ y$^{-1}$, corresponding to denudation and weathering rates of 150 and 60 mm ky$^{-1}$, respectively. When measured in river sediment, we find landscapes in which erosion rates exceed the soil formation speed limit. Such high erosion rates are typically found in active mountains of high relief and hillslope gradients. There, erosion is governed by mass wasting processes, and a complete soil cover is not sustainable. Yet chemical weathering rates from dissolved river loads of rapidly eroding mountain rivers suggest that these landscape also obey or fall below the limit of weathering observed for soils. This finding appears to suggest that a continuous soil cover is a prerequisite for weathering.

We conclude that the optimal conditions for CO$_2$ withdrawal are those where a large fraction of the terrestrial Earth surface is soil-covered, and is eroding near soil production speed limit. The weathering fluxes from rapidly eroding settings do not exceed the speed limit determined in upland soil mantled landscapes. Considering their small global area, such sites may not contribute substantially to global weathering budgets.

Juvenile volcanic ash is often dominantly composed of silicate glass and as such can be approximated by standard glasses with constrained physical and chemical properties that facilitate the isolation of dominant viscous deformation mechanisms. We sintered powdered standard glass (NIST 717a) and compositionally homogeneous glass spheres at 600, 650 and 675 °C under ambient pressure conditions analogous to surface ash deposition, shallow tuffisite vein formation and aircraft engines. We show that sintering of glass-rich volcanic ash is grain-size and melt viscosity controlled. We measured the dynamic change in open and closed porosity and ultrasonic wave velocity to explore the temporal evolution of pore-structure during viscous sintering. Finally, we explored the effect of sintering on the peak stress required for macroscopic failure of samples at ambient and moderate temperatures (<575 °C) and discuss the implications for shallow and surface volcanological processes. We find that the timescale over which open porosity approaches zero and strength approaches that of pore-free melt at a particular melt viscosity is dependent on the grain-contact surface area; this can be estimated from the particle shape, the packing type and the initial total porosity. This consideration permitted the development of a 1D model for the sintering timescale of volcanic ash deposits. If volcanic ash is heated to supra-magmatic temperatures (e.g., in commercial aircraft engines), it is likely that viscous neck formation between grains will be rapid if the grains are sufficiently small; which is often the case at standard cruising altitudes. Crystalline volcanic ash will typically sinter by lattice and boundary diffusion over slow timescales, however, at sub-micron grainsizes, at estimated jet-engine combustion-chamber temperatures sintering is equally fast for silicate melts and crystalline material and therefore physical state becomes irrelevant.
A record of the transition from continental extension to rift tectonics in hydrothermal vein-type mineralizations: fluid-inclusion, crush-leach and Raman data from SW Germany


1Eberhard Karls Universität Tübingen, Mathematisch-Naturwissenschaftliche Fakultät, FB Geowissenschaften, Wilhelmstrasse 56, D-72074 Tübingen, Germany
(*correspondence: benjamin.walter@uni-tuebingen.de)

2 present address: Centre for Ore Deposit Research, University of Tasmania, Hobart, Tasmania 7001, Australia

3 School of Earth Sciences, University of Leeds, LS2 9JT, UK

To get a better understanding of the formation of the worldwide occurring hydrothermal vein-type deposits in extensional settings, especially with regard to the involved fluids, a systematic study was carried out on a large number of mineralogically different deposits in the Schwarzwald mining district, SW Germany. Based on former fluid inclusion studies we know that fluid-mixing was the major ore-forming process. The majority of hydrothermal vein-type deposits in the Schwarzwald were formed during (a) Jurassic/Cretaceous and in (b) post-Cretaceous times. Whereas formation of type (a) veins relates to large-scale extensional tectonics in response to the opening of the N-Atlantic, type (b) veins are structurally related to the opening of the Upper Rhinegraben rift system. Both periods of ore precipitation differ significantly in mineralogy and geochemistry: in vein-type (a) the major gangue minerals are fluorite, barite and quartz in different modal amounts with Pb-Zn-Cu-Ag or U-Bi-Co-Ni-Ag mineralization. Type (a) veins were formed from high salinity (> 20-27 wt. % NaCl + CaCl$_2$ eq) low T (50-150 °C) brines. In contrast, type (b) preferably consists of quartz-barite-veins with Pb-Zn-Ag mineralization and carbonate-barite-veins with Cu-Ni-As mineralization. The veins of type (b) precipitated from very variable low- to highly-saline low temperature fluids (2-22 wt.% NaCl + CaCl$_2$ eq, 50-150 °C) which are partly CO$_2$-, partly sulfate-bearing. Cl/Br ratios of type (a) veins from the central part of the Schwarzwald are rather homogeneous with values of about 100 ± 20. In contrast, in the southern Schwarzwald Cl/Br ratios of 20-824 were found. Type (b) shows a broad distribution of Cl/Br ratios (30-1988) in the whole Schwarzwald.

During Jurassic and Cretaceous times, the sedimentary cover rock units unconformably overlying the basement lithologies were still tectonically undisturbed. Fluid mixing and vein formation took place along the basement-cover unconformity; in the central Schwarzwald the sedimentary aquifer comprised red bed sediments (Rotliegend and Buntsandstein) hydrologically separated from overlying Middle Triassic units by clay aquitards. These are missing in the southern Schwarzwald as is evidenced by with high Cl/Br ratios recording the involvement of halite dissolution brines probably derived from Middle Triassic evaporite units. Later, during Rhinegraben formation, basement units were juxtaposed to younger sedimentary cover rocks which resulted in tapping of fluid reservoirs that were formerly hydrologically separated by aquitards. The Sulfate- and CO$_2$-bearing fluids of differing salinities evidence this increased variability of fluid reservoirs taking part in fluid mixing and thereby vein-forming processes.

These data are interpreted to show that Jurassic/Cretaceous veins formed by binary fluid mixing, while the Paleogene to Neogene veins formed by multi-component fluid mixing.
Halogen (F, Cl, Br) systematics in alkaline-peralkaline volcanic rocks from the Upper Rhine Graben (Southwest Germany)

L. Wang1, M.A.W. Marks1, J. Keller2, U. Neumann1, G. Markl1

1 Universität Tübingen, Mathematisch-Naturwissenschaftliche Fakultät, FB Geowissenschaften, 72074 Tübingen, Germany

(*corresponding author, E-mail address: Lianxun.wang@student.uni-tuebingen.de)

2 Albert-Ludwigs-Universität Freiburg, Institut für Geowissenschaften - Mineralogie-Geochemie, 79104 Freiburg, Germany

Halogen (F, Cl and Br) abundances have been determined in a comprehensive sample set of alkaline to peralkaline volcanics, from the Kaiserstuhl, Hegau and Urach areas in southwest Germany. They range in composition from primitive mantle-derived ol-nephelinites and ol-melilitites to evolved tephrites, hauynophyres, phonolites and silico-carbonatites (bergalites).

Our results show that the primitive ol-nephelinites and ol-melilitites from all investigated localities generally have low Cl (<100 ppm) and Br (<0.3 ppm) concentrations, with relatively high and constant amounts of F (around 1100±100 ppm). This might imply a rather F-rich but Cl- and Br-poor mantle source beneath the Upper Rhine Graben.

Tephritic samples comprise tephritic glass, tephritic lava and sub-volcanic essxite, representing different crystallinity. Measurements on these samples reveal positive correlations between F and Cl and between Cl and Br, with the highest values in the glass sample (F = 1800 ppm, Cl = 6800 ppm, Br = 25 ppm) and low concentrations in tephritic lavas and essxite samples (F, Cl and Br as low as 800 ppm, 100 ppm and 0.4 ppm, respectively). This is inferred to reflect different degrees of magma degassing during late-stage crystallization and cooling. Preliminary calculation of the degassing patterns of F, Cl and Br reveals that up to 55% F and up to 98% Cl and Br escaped from the magma by degassing.

The hauynophyre group (hauyne-rich phonolite) holds the highest Cl (2900 - 7600 ppm) and Br (12 - 34 ppm) concentrations. These high values are mainly attributed to the presence of sodalite-group minerals, which incorporate significant amounts of Cl and Br largely preventing them from later degassing. The highly variable F contents (400 - 1500 ppm), however, probably reflect different degrees of degassing, similar to the tephritic samples.

Most importantly, a positive linear correlation between Cl and Br is observed for the majority of the investigated samples, independent of rock type, sample locality, degree of evolution or degassing, suggesting that Cl and Br have a very similar geochemistry. The average Cl/Br ratio of 382 ± 134 is in accordance with previous studies on mantle-derived samples (e.g., Jambon et al., 1995; Palme and O’Neill, 2003). In contrast, no clear correlation is evident between F and Cl. Overall, our results imply, that during magmatic processes (e.g., fractional crystallization, degassing), Cl and Br behave very similar, whereas F can be strongly fractionated from them.
Modern carbonate shoal bodies display both a complex geomorphology and internal architecture. Detailed analysis of a Middle Triassic (Uppermost Muschelkalk) shoal body within a single sedimentary cycle also shows internal heterogeneities in a similar scale to recent ones. This poster is a contribution to a larger project on outcrop analogue studies for subsurface carbonate reservoirs.

Within an overall regressive hemi-sequence the terminal high-frequency sedimentary cycle of the Upper Muschelkalk just below the Muschelkalk-Keuper boundary was investigated in northern Bavaria (South Germany). This cycle begins with the “Ostrakodenton”, passing into the shoal body of the "Grenzquader” unit and ends up with the “Grenzbonebed” which represent the sequence boundary.

14 sections were logged sedimentologically including gamma ray measurements and, 53 thin sections analysed in terms of microfacies. Furthermore, 2D-correlations document in detail the lateral facies changes from foreshoal over shoal to lagoon within a few kilometers across a gently inclined carbonate ramp.

On the kilometer-scale, bedding and cycle styles vary systematically across the carbonate ramp, as well as the types and distribution of porosity. On the hundreds to tens of meters scale, the overall sedimentary architecture appears more uniform. On the meters to centimeters scale, small-scale changes in sedimentary structures and textures give rise to a high degree of small-scale heterogeneities.
Dissolution precipitation creep in high P/T metamorphic rocks and the role of interphase boundaries

Sara Wassmann\textsuperscript{1}, Bernhard Stöckhert\textsuperscript{2}

\textsuperscript{1}Sara.Wassmann@rub.de
\textsuperscript{2}Bernhard.Stöckhert@rub.de

Subduction zone models invariably invoke deformation to be concentrated along the plate interface. Endothermic dehydration reactions withdraw additional heat from the subducted lithosphere, implying a cool geotherm. Localization of deformation in a region of low temperatures requires specific material properties, environmental conditions, and mechanisms controlled by temperature and stress at depth. Such information cannot be obtained by geophysical observations with the appropriate resolution, but the record of high pressure metamorphic rocks exhumed from subduction zones provides details on P-T-history, deformation mechanisms, and stress state, albeit not readily correlated with the former dynamic situation on larger scale. We investigated rocks exhumed in a subduction zone setting with polarizing microscope and SEM. Microfabrics suggest dissolution precipitation creep to be the predominant deformation mechanism in high P/T metamorphic rocks, which - if representative for subduction zones in general - poses constraints on conditions, rheology, and flow patterns. Our key observations and conclusions are: (1) Deformation is typically highly inhomogeneous and localized into shear zones; (2) stresses are generally too low to drive crystal plastic deformation; (3) dissolution generally proceeds along interphase boundaries; (4) an aqueous fluid at quasi-lithostatic pressure is available throughout, allowing tensile fracturing and crack healing or sealing; (5) low stress combined with high strain rates required for localized deformation at typical subduction rates implies low viscosity; (6) contribution of shear heating to the thermal budget of subduction zones should be moderate.
X-ray diffraction, magnetization, and $^{57}$Fe Mössbauer spectroscopic characterization of natural single-crystals of chrysoberyl

S.-U. Weber¹, F.J. Litterst², U. Menzel², W. Lottermoser³, G. Amthauer⁴

¹Abteilung Festkörperchemie, Institut für physikalische und theoretische Chemie, TU Braunschweig, Braunschweig, e-mail: su.weber@tu-braunschweig.de
²Institut für Physik der kondensierten Materalie, TU Braunschweig, Braunschweig, e-mail: j.litterst@tu-braunschweig.de
³Fachbereich Materialforschung und Physik, Paris-Lodron-Universität Salzburg, A-5020 Salzburg, e-mail: werner.Lottermoser@sbg.ac.at
⁴Fachbereich Materialforschung und Physik, Paris-Lodron-Universität Salzburg, A-5020 Salzburg, e-mail: georg.amthauer@sbg.ac.at

Natural chrysoberyl from Rio das Americas, Minas Gerais, Brazil, was studied by electron microprobe analysis, X-ray single-crystal diffractometry, magnetization and $^{57}$Fe Mössbauer spectroscopy. The aim of this study is the structural and magnetic characterisation of the sample.

Microprobe measurements of two chrysoberyl crystals were performed with high grid resolution leading to the average chemical composition Al$_{1.96}$Fe$_{0.03}$BeO$_4$. The crystals seem to be homogenous.

Single-crystal data were collected and refined on a BRUKER Smart Apex 3-circle diffractometer using the ideal chemical composition, Al$_2$BeO$_4$, space group Pnma with four formula units per unit cell and the initial fractional coordinates given by [1]. The results of the refinement show, that the untwinned chrysoberyl has a hexagonal closed packed structure of oxygen ions, slightly distorted with Al$^{3+}$ and Be$^{2+}$ occupying the octahedral and tetrahedral sites of chrysoberyl [2], respectively.

Magnetization data taken down to 3 K reveal paramagnetic moment behavior with $S=5/2$ as expected for high spin Fe$^{3+}$. No indications for magnetically ordered impurities were found. The $^{57}$Fe-Mössbauer spectra, collected at different temperatures between 20 K and room temperature, reveal a superposition of several subspectra. Isomer shifts and quadrupole splittings are typical for Fe$^{3+}$ in a comparably weakly distorted six-fold coordination of the M1 and M2 position, the latter with point symmetry m (AlII, 4c-site) in accordance with the EPR measurements of [3]. Remarkable is a strong spectral contribution revealing a magnetic hyperfine splitting, indicative for magnetic order of part of the sample or slow spin relaxation effects. Several scenarios for the origin of this magnetic contribution will be discussed, e.g., defect sites as reported for alexandrite [4], superparamagnetic iron oxide precipitates, or slow paramagnetic spin relaxation of dilute Fe$^{3+}$.

Magnesium carbonate bio-mineral formation in the presence of metabolically active and dead cyanobacteria species: implications for CO₂-sequestration

Sebastian Weber¹ and Raul E. Martinez²

Institut für Geo- und Umwelt naturwissenschaften, Albert-Ludwigs-Universität, Albertstraße 23b, D-79104 Freiburg, Germany

¹sebastian.weber@minpet.uni-freiburg.de
²raul.martinez@minpet.uni-freiburg.de

Carbonation of olivine minerals (e.g. forsterite, Mg₂SiO₄) is a leading CO₂ sequestration process candidate. Olivine deposits are sufficient to support regional implementation of above-ground sequestration (Martinez et al., 2010, Béarat et al. 2006). Even when inorganic carbonation processes have been extensively studied, the interaction of the olivine surface with metabolically active photosynthetic microorganisms, and bio-organic ligands, has not yet been fully quantified. This project is, therefore, motivated by the lack of a detailed quantification of the extent to which forsterite dissolution contributes to magnesium carbonate biomineral formation in the presence of metabolically active and passive photosynthetic cyanobacteria and the implications of this process to CO₂ sequestration. In this regard, the goals of this research are: (1) to quantify the rates of Mg rich olivine dissolution in batch bio-reactors with constant air bubbling, in the presence of metabolically active and dead cyanobacteria biomass, (2) to identify the aqueous surface species of Mg on the olivine surface by means of FTIR-spectroscopy, and (3) to model the rates of Mg-carbonate formation by monitoring the pH, alkalinity, temperature and cyanobacteria biomass concentration, in the batch reactors with continuous input of CO₂. Preliminary results show an enhanced Mg release from olivine as a function of ionic strength at constant pH, and a decrease in the rate of Mg release form the mineral surface in the presence of active cyanobacteria species. Current FTIR and SEM/EDS are being performed to show the presence of magnesium carbonate minerals on the surface of active or dead cyanobacteria biomass.

References


Fluorine and chlorine influence magmatic and metasomatic-hydrothermal processes, and in combination with the lesser halogens, bromine and iodine, are useful tracers of geochemical processes in magmas - even though halogen abundances typically are less than those of the primary magmatic volatile components water, carbon dioxide, and sulfur. To differing extents, F and Cl affect melting and crystallization; magma evolution; melt viscosities; the dissolution, transport, and precipitation of ore metals in mineralizing magmas; fluid phase equilibria; volcanic degassing; and chemical exchanges of volatile components between Earth’s reservoirs.

The cycling of halogens between the mantle, crust, and atmosphere is controlled fundamentally by their sequestration in minerals and their solubilities in aluminosilicate melts and fluid phases. Some experimental data on F and Cl partitioning between fluids and hydrous minerals (amphiboles, micas, and/or apatite) or silicate melts and hydrous minerals are available, but these experimental constraints are limited. Much more is known about F and Cl partitioning between fluids and melts, but less so for Br and I. Hydrothermal experiments that simulate felsic melts at shallow-crustal conditions, for example, demonstrate the halogens partition (i.e., wt% halogen in fluid(s)/wt% halogen in melt) in the order: I > Br > Cl > F. Typically with geologically relevant halogen abundances in the system, I, Br, and Cl are more strongly enriched in the fluid(s) whereas F concentrates in silicate melts. These experimental relationships are consistent with observations from magmatic systems, where I, Br, and Cl are readily degassed to the atmosphere in volcanic vapor but the volcanic emission of F is generally much less significant.

Chlorine controls the phase equilibria of hydrothermal fluids (i.e., the stability of vapor or brine versus vapor plus brine) in magmas at shallow-crustal pressures, and the chloride ion is one of the most effective anions involved in ore metal-complexation in aqueous hydrothermal fluids. These relationships depend on the solubility of Cl in fluid(s) versus Cl solubility in silicate melts, i.e., Cl partitioning, and Cl solubility in melt varies strongly with pressure, temperature, and the compositions of melt and fluid. This is well demonstrated by results of new hydrothermal experiments on Cl solubility in rhyolitic to basaltic melts at 0.1 to 800 MPa and 786-1250°C. These experimental data have been used to generate an empirical model that allows computation of Cl solubility in a wide variety of magmas as they ascend through the crust toward the surface, cool, crystallize, and differentiate chemically.

Experimental constraints on Br and I partitioning between fluid(s) and melt are currently limited to melts of albitic, haplogranitic, rhyolitic, and pantelleritic compositions. Additional experiments are needed to determine the solubilities of these trace halogens in fluids and less-evolved melts in order to better apply their abundances in natural samples to interpret processes of volcanic eruption and recycling between mantle and crustal reservoirs.
Sedimentary records of the Japan Trench: The impact of the Tohoku-Oki Earthquake and its implications

Wefer, G., Fink, H., Ikehara, K., Kanamatsu, T., Strasser, M. and R/V Sonne Cruise SO219A participants

gwefer@marum.de
hfink@marum.de
k-ikehara@aist.go.jp
michael.strasser@erdw.ethz.ch

The Tohoku-Oki mega-earthquake (Mw 9.0) off the Pacific coast of Japan hit northern Japan on March 11, 2011. The earthquake has induced large co-seismic slip along the plate boundary fault resulting in a horizontal displacement of the continental plate of 50 m toward the east. The large sea-floor displacement, in combination with earthquake triggered submarine slumps, generated a devastating tsunami which hit large areas of the coast of Honshu. In order to contribute to a better understanding of the mechanisms of such large events, the region was investigated during a joint German-Japanese Cruise with RV SONNE in March/April 2012.

Repeated bathymetric surveys showed prominent changes in seafloor morphology east of the epicenter. Based on the bathymetric data and sedimentary records sampled from this area, a large rotational slump related to the Tohoku-Oki earthquake was identified. This slump significantly impacted the geometry and evolution of the shallow plate boundary system by emerging a submarine fold-and-thrust belt and abruptly narrowing the trench up to 3 km in width during this single-event, large mega-thrust earthquake.

The deep Japan Trench (>7500 m water depth) is a remarkable depression near the epicenter, where earthquake triggered gravity flows might result in the deposition of turbidites. In a north-south transect sediment cores were obtained along the Japan Trench axis. All records revealed several turbidite sequences of same lithology. One unique turbidite unit is characterized by calcareous nanno fossil bearing mud, suggesting a transport from the upper-mid slope. Volcanic ash (Towada-a) deposited above this unit, allows the correlation to onshore deposits on the Sendai Plain. Here, the same Towada-a ash occurred above the deposits of the large Jogan tsunami which hit Honshu in 869 AD. These result indicate that turbidite deposits along the Japan Trench might give us important information on the spatio-temporal occurrence of the past earthquakes and tsunamis.
Constraining fluid flow of supercritical geothermal resources

Philipp Weis¹ and Thomas Driesner²

¹Institute of Geochemistry and Petrology, ETH Zurich, philipp.weis@erdw.ethz.ch
²Institute of Geochemistry and Petrology, ETH Zurich, thomas.driesner@erdw.ethz.ch

High-enthalpy geothermal systems in magmatic-hydrothermal environments such as the Taupo Volcanic Zone in New Zealand or the active rift zones of Iceland host the most productive geothermal energy systems worldwide. Geothermal up-flow is normally considered to represent isenthalpic ascent and fluids in these systems typically have specific enthalpies near 1.2-1.5 MJ/kg [1,2]. In an attempt to increase energy production by up to an order of magnitude, supercritical conditions beneath these systems have been targeted and a supercritical resource was tapped at the IDDP-1 well at Krafla, Iceland, in 2011 [3]. These systems may reach enthalpies in the order of 3 MJ/kg. The average system-scale permeability of the rock has a major influence on hydrothermal convection, eventually governing the temperature-profile of natural geothermal systems. Numerical simulations can thus far explain the hydrology of high-enthalpy geothermal systems but cannot reproduce supercritical systems with these simple convection models [1,2]. Rather, a hydrologic divide may be required that at least partially separates two flow regimes from each other. Such a divide proved to be essential to provide a mechanism for metal enrichment to economic grades in porphyry-copper deposits [4]. These mineral resources formed within magmatic-hydrothermal systems that can be regarded as fossil analogues of active geothermal systems. In our simulations, the hydrologic divide self-organizes from an intimate interplay of fluid flow and dynamic permeability mimicking hydraulic fracturing and the transition from brittle to ductile rock behavior in a geologically reasonable way [4-7]. These recent modelling results suggest that similar physical processes may also be crucial to constrain the fluid flow of potential geothermal resources beyond high-enthalpy systems.

Long-lived crustal-scale fluid-flow:

The hydrothermal mega-breccia of Hidden Valley,

Mt. Painter Inlier, South Australia

Anett Weisheit\textsuperscript{1}, Paul D. Bons\textsuperscript{1}, Marlina A. Elburg\textsuperscript{2}

\textsuperscript{1}Department of Geosciences, Eberhard-Karls University Tübingen, Wilhelmstraße 56, 72074 Tübingen, Germany

\textsuperscript{2}Geology Division, SAEES, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa

The Palaeozoic Hidden Valley breccia in the Northern Flinders Ranges of South Australia is exceptional for (1) its size of about $10\ \text{km}^2$, (2) the large continuous range in clast sizes from tens of microns to hundreds of meters and (3) thorough mixing of lithologies of different provenance, some originally kilometres apart stratigraphically. The size distribution follows a single fractal dimension of about unity over at least 6 orders of magnitude, implying that a single process was responsible for diminution from the $100\ \text{m}$ scale, down to $<\text{mm}$. The breccia formed during $>12\ \text{km}$ exhumation which lasted about 200 Myrs, starting during the $\sim500\ \text{Ma}$ Delamerian Orogeny and continuing during the Alice Springs Orogeny. Fluids released during exhumation were structurally focussed towards Hidden Valley, where an estimated 20 (5-30) $\text{km}^3$ total fluid volume caused the extensive brecciation. Brecciation initiated in Neoproterozoic cover meta-sedimentary rocks, at a level that is now fully exhumed. As hydrothermal fluid ascent continued with ongoing exhumation, the level of brecciation shifted down into the underlying Mesoproterozoic basement rocks, taking with it clasts of cover rocks. In this model, rocks pass through the zone of brecciation, which can thus incorporate a variety of lithologies that were originally kilometres apart.
Facies architecture of an Upper Jurassic carbonate platform in the Marib region/Yemen.

Christian Weiss

Geozentrum Nordbayern, University of Erlangen/Nuremberg, Loewenichstr. 28, 91054 Erlangen, Germany

The Upper Jurassic Amran Group in the Yemen Mountains consists of thick carbonate deposits. The base consists of sandstones and sandy limestones with a thickness of about 50 m, which are described as clastic sequences. They are overlain by limestone-marl alternations and nodular limestones that form the major part of the sequence with about 250 m thickness. The top consists of massive limestone beds that reach a thickness of about 60 m. In several areas occur reefs, which are composed of stromatoporoids, corals and coral-stromatoporoid associations. The microfacies description distinguishes 27 microfacies that contain mainly wacke-, pack and grainstones, with several types of mudstones; siltstones and sandstones are counted as separate microfacies types. The clastic sequences consist of poorly sorted sandstones, fossiliferous wacke-, to grainstones and sporadic intercalated mudstones. Nodular limestones are dominated by microfacies types, which have a high amount of micritic; but pure mudstones occur only subordinate. The massive limestones at the top consist of grainstones predominantly, with scattered wacke- to packstone intercalations.

The biostratigraphic subdivision of the profiles is based on benthic foraminifera and dasycladaceans resulting in 5 zones, which reveal an age from the Upper Oxfordian to Lower Tithonian. According to the biostratigraphic subdivision the lithostratigraphical classification shows a dominance of shallow marine sediments in the Oxfordian, which contain numerous siliciclastic units. The Lower Kimmeridge is made of shallow marine carbonate series developing into a deeper marine micritic facies. The Middle Kimmeridge consists of deep marine units predominantly. The Tithonian sediments are shallow marine carbonates. The result corresponds with several transgressive cycles that extend over the entire Arabian Peninsula and the Horn of Africa.

In summary a slowly evolving carbonate platform can be interpreted. During the Oxfordian, the sedimentation begins with the formation of small deltas and general sand deposits in marginal marine areas, which were connected with small carbonate ramps and lagoons. The Lower Kimmeridgian is characterized by the transition into pure carbonate sedimentation that take place on a carbonate platform. Carbonate sands were formed in high-energy, shallow marine environment with isolated lagoons or smaller basins. During the Middle Kimmeridgian the sedimentation took place in deeper environments on the platform slope or in deeper pools and lagoons. Scattered reefs, particle-rich limestones and grainstones indicate a continued shallow marine influence. In the Upper Middle Kimmeridgian a regression is indicated continued in the Upper Kimmeridgian. Sediments of a vast shallow marine carbonate platform are prevailing. The Tithonian is characterized by shallow marine units, which consist of carbonate sands laterally interfingering with coral reefs.
Fluvial sediments of the Yeha area – sedimentological and archaeological implications.

Christian Weiß¹, Dana Pietsch², Roman Koch¹ und Iris Gerlach³
¹Geozentrum Nordbayern, University of Erlangen/Nuremberg, Loewenichstr. 28, 91054 Erlangen, Germany
²Physical Geography and Soil Science, Eberhard Karls University of Tübingen, Rümelinstraße 19-23, 72070 Tübingen, Germany
³Deutsches Archäologisches Institut, Podbielskiealle 69-71, 14195 Berlin, Germany

Yeha is placed in the North of Ethiopia. The village is known for an ancient settlement with several large buildings that were influenced by the Sabaean culture introduced by South Arabian migrants dating between 800 B.C. and 600 B.C. Near to these monumental buildings occur fluvial sediments that contain high amounts of anthropogenic remains like obsidian tools, bones pottery and some figurines. Along river outcrops several profiles where taken. They contain of fine to coarse grained sands with intercalations of calcareous tufa. The C¹⁴ determined age of the profiles is between 1030 B.C. and 130 B.C..

The mineral composition of the sediments is made of feldspars with few quartz grains and rock fragments that are encrusted with iron oxides. The clay mineral composition is made of illite, kaolinite, montmorillonite and a low amount of chlorite. The form and preservation of the archaeological artefacts suggest that the river was used for waste deposition. The bones belongs mostly to domestic animals and have a similar distribution in all profiles while stones tools and obsidian remains are concentrated in older parts mainly before 800 B.C. while the pottery is made of similar ware groups of local material and has also a homogeneous distribution in all profiles. The calcareous tufa’s are made of cyanobacterial crusts and phytoherm framestones. They can be subdivided sin several microfacies types that form crusts with a thickness up to 60 cm or build dams with a high up to 3 m. The cyanobacterial crusts are made of thin laminated, homogenous layers. They can be rich in organic carbon and crusts of iron oxides. The phytoherm framestone is made of dense micritic crusts with a high content of iron oxides. The microfacies types and stable isotopes indicate continuously humid conditions with several interruptions during the deposition.

Questionable is the origin of the carbonate. The geology of the area consists completely of volcanic rocks (mainly phonolites and trachytes) or of metamorphites like shists and gneiss. All units these units are free of carbonate. An origin by weathering of carbonate can be excluded by the absence of calcareous deposits on natural outcrops and springs. Possible sources seem to be anthropogenic activity like mining or metal production.
Microbial life in Muschelkalk - activities in calcification

Aileen Weist¹, Manu Singh¹, Anne Kastner¹, Gerd Gleixner², Georg Büchel³, Erika Kothe¹

¹FSU Jena, Institute of Microbiology, Microbial Communication, Neugasse 25, D-07743 Jena, Germany
²Max Planck Institute, Biogeochemical cycles, Hans-Knöll-Str. 10, D-07745 Jena
³FSU Jena, Institute of Earth Sciences, Applied Geology, Burgweg 11, D-07749 Jena, Germany,
corresponding author: aileen.weist@uni-jena.de

The carbon cycle is an important natural process which involves the exchange of carbon between different reservoirs such as atmosphere and biosphere. The metabolic activities of organisms within the cycle affect the fluxes, including organic carbon, atmospheric CO₂ and carbonates. Formation and weathering of carbonates are influenced by CO₂ and milieu changes, both mechanisms being controlled by geogenic processes as well as bacterial activity.

In this study, microbial diversity in limestone and associated groundwater aquifers has been investigated to determine microbial signatures. Groundwater, rock, and soil samples were studied from Middle and Lower Muschelkalk. Bacteria were isolated from the Thuringian Basin, which is surrounded by layers of Muschelkalk, and analyzed on their ability to form carbonates.

The (expected) low colony forming units (cfu) from rock and groundwater as well as higher cfu’s for soil samples, rich in nutrients, revealed prevalence of γ-proteobacteria in groundwater, Pseudomonas and Bacillus in rock samples and actinobacteria in soil. On calcium containing media, the ability to form carbonates could be demonstrated for most isolates, visible by formation of crystals. These represented different morphologies, and SEM/XRD analyses verified carbonate presence in the biominerals.
The role of bubble ascent in magma mixing

S. Wiesmaier\textsuperscript{1}, D. Morgavi\textsuperscript{1}, D. Perugini\textsuperscript{2}, C. De Campos\textsuperscript{1}, K.-U. Hess\textsuperscript{1}, Y. Lavallée\textsuperscript{3}, D. Dingwell\textsuperscript{1}

sebastian.wiesmaier@min.uni.muenchen.de

\textsuperscript{1}Ludwig-Maximilians-Universität München, Earth and Environmental Sciences, Munich, Germany
\textsuperscript{2}Department of Earth Sciences, University of Perugia, Perugia, Italy
\textsuperscript{3}School of Environmental Sciences, University of Liverpool, Liverpool, UK

The mechanical interaction between two distinct batches of magma has commonly been attributed to shear and folding movements between two distinct liquids. A mode of mechanical interaction scarcely invoked is the advection of mafic material into a felsic one through bubble motion. Yet, experiments with analogue materials demonstrated that bubble ascent has the potential to enhance the fluid mechanical component of magma mixing [Thomas et al., 1993].

Here, we present results from bubble-advection experiments. For the first time, experiments of this kind were performed using natural materials at magmatic temperatures. Cylinders of Snake River Plain (SRP) material were prepared for a static layered set-up, with basalt glass placed underneath rhyolite glass. Upon heating, trapped air from the interstices between glass cylinders and the crucible expanded, forming bubbles in the now molten basalt. The bubbles rose, thus entraining a portion of basaltic material into the rhyolite.

The plume-like structure that the advected basalt formed within the rhyolite was characterized by microCT and subsequent high-resolution EMP analyses. The diffusional gradient around the plume tail showed a progressive diffusional equilibration from top to bottom, consistent with increasing time of interaction towards the bottom end of the plume tail. Furthermore, single protruding filaments at the bottom end of the plume tail indicate that the plumous structure is a composite of many smaller plume tails. The first bubble rising probably created a preferential pathway for subsequently rising bubbles. Notably, the normalised variance, which serves as a proxy of cation diffusion rate at the interface of rhyolite and basalt, is unsystematic. This is most likely a result of the many small plume tails combined in the hybridised region. In turn, stretching and folding experiments produce very systematic normalised variances. The normalised variance measured in natural magma mixing structures may thus provide characteristic evidence to distinguish between mixing induced by bubble action or scenarios of stretching and folding.
Experimental studies of phase stability and fluid content of nephelinitic melts from the Oldoinyo Lengai volcano, Tanzania

Sören Wilke¹ Roman Botcharnikov² Francois Holtz³

¹s.wilke@mineralogie.uni-hannover.de
²r.botcharnikov@mineralogie.uni-hannover.de
³f.holtz@mineralogie.uni-hannover.de

This study presents experimental data about the magmatic evolution of Oldoinyo Lengai nephelinites with particular attention to the role of water and of immiscible carbonatitic melt. Two nephelinitic synthetic compositions representative of different stages of the magmatic evolution and containing different amounts of carbonate and water were used as starting materials. Crystallization experiments were conducted in fluid-present conditions in the T and P range 650 °C - 850°C and 100 MPa - 300 MPa. The produced silicate melts span a SiO$_2$ range from ~39 wt% to 50 wt% and a peralkalinity range (molar (Na+K)/Al) from 1.95 to 8.04. The presence of an immiscible carbonatitic phase was found to influence the evolution of the coexisting nephelinitic melt in several ways. One crucial observation is that the presence of a carbonatitic melt leads to an enrichment in SiO$_2$ with ongoing crystallization in the nephelinitic melts, due to the concomitant increase of the proportion of nearly SiO$_2$-free carbonatite. On the other hand, nephelinite melts without coexisting carbonatite show no such evolutionary trend towards higher SiO$_2$, as the SiO$_2$ content of the crystallized minerals is close to or even above that of the melt. The fluid content of the melt is also controlled by the presence of immiscible carbonatite. Nephelinitic melts without coexisting carbonatite were found having a wide range of CO$_2$ concentrations between 3.1 wt% and 8.6 wt% and the CO$_2$ concentration increases with decreasing temperature (accumulating due to increasing crystal content). In contrast, nephelinitic melts coexisting with an immiscible carbonatite phase have CO$_2$ concentrations which do not exceed 5-6 wt% and the CO$_2$ concentration tends to decrease with decreasing temperature. The experimental results indicate that the conditions at which immiscibility of nephelinite and carbonatite is reached are an important key to the understanding of the Oldoinyo Lengai magmatic system. While the peralkalinity of nephelinitic melts is widely accepted in literature as the controlling factor for the occurrence of carbonatite melts, the experimental results of this study indicate that the composition (XCO$_2$) of the coexisting fluid phase is an additional important parameter. For a given melt composition (fixed peralkalinity value of 7), the experiments demonstrate that the occurrence of immiscibility is only attained in nephelinitic melts with CO$_2$ concentrations higher than 9 wt%. The exsolution of carbonatite then leads to a decrease of the peralkalinity value in the residual nephelinitic melts, causing a decrease in CO$_2$ solubility, which in turn enhances the continuous growth of the immiscible carbonatite phase. This process is coupled with an increasing amount of water in the residual nephelinitic liquid (up to 7-8 wt% H$_2$O at 200 and 300 MPa). With magma ascent and decompression, the high volatile concentrations may result in efficient exsolution of large amounts of fluid and may explain the plinian eruptive behavior repeatedly observed during eruptions of nephelinites.
The conservative character of the modern Mo seawater reservoir is represented by its long ocean residence time of ~750 ka and its uniform and heavy Mo isotopic composition. Adsorption and co-precipitation with iron- and manganese- oxides on one hand and Mo removal from pore water or the water column under reducing environmental conditions on the other hand are thought to be the main control on the isotopic composition of the seawater reservoir. Reductive Mo removal from the water column can be found in restricted basins while Mo accumulation from pore water is dependent on the redox processes within the diagenetic regimes.

Here we present the stable Mo isotopic composition of sediments, clays containing different amounts of calcareous material, sampled along the active Banda Arc (East Indonesia), which were deposited under oxic water conditions. The range of 1.71‰ in $\delta^{98/95}$Mo values within these sediments is more than half the total variation observed within the entire redox diversity of the modern ocean ranging from oxic to euxinic. Correlations of the Mo concentration and isotopic composition with depositional depth indicate that authigenic Mo supply is controlled by organic carbon burial, which fuels the Mo redox cycling within the sediment during diagenesis.

We imply that next to water column redox conditions the Mo incorporation and isotopic composition within sediments at continental margins are mainly controlled by the rate of primary production of organic matter and its supply to the sediments which is dependent on sedimentation rate and depth.
Influence of fluid flow and deformation on $^{40}\text{Ar}^{39}\text{Ar}$, Rb-Sr, and fission track ages of very low to low grade metamorphic processes in SE Cape Breton Island (Nova Scotia, Canada)

Willner, A.P.¹, Barr, S.M.², Glodny, J.³, Massonne, H.-J.⁴, Sudo, M.⁵, Thomson, S.N.⁶, van Staal, C.R.⁷, White, C.E.⁸

¹arnes.willner@rub.de, Universität Stuttgart, Stuttgart, Germany, ²sandra.barr@acadiau.ca, Acadia University, Wolfville, Canada., ³glodnyj@gfz-potsdam.de, Deutsches GeoForschungsZentrum (GFZ), Potsdam, Germany, ⁴h-j.massonne@imf.uni-stuttgart.de, Universität Stuttgart, Stuttgart, Germany, ⁵masafumi.sudo@geo.uni-potsdam.de, Universität Potsdam, Potsdam, Germany, ⁶thomson@email.arizona.edu, University of Arizona, Tucson, USA, ⁷cees.vanStaal@NRCan-RNCan.gc.ca, Geological Survey of Canada, Vancouver, Canada, ⁸whitece@gov.ns.ca, Natural Resources Nova Scotia, Halifax, Canada

In the Avalonian Mira terrane of SE Cape Breton Island, various belts of Neoproterozoic volcanic arc rocks and overlying Neoproterozoic to Cambrian platform sedimentary rocks were metamorphosed under peak conditions near 3.5±0.4 kbar and 280±30°C. Maximum dehydration occurred in a narrow window at ~240-280°C. During metamorphism water was present between reactants and reaction products, which mainly precipitated in clusters. As a result, transient equilibrium conditions were present throughout the prograde P-T path.

Formation of white mica clusters during this fluid release was dated in six metavolcanic samples by $^{40}\text{Ar}^{39}\text{Ar}$ in situ UV laser ablation resulting in predominant spot age peaks between 366±14 Ma and 396±5 Ma. Independently, studies of Rb-Sr systematics of minerals and mineral clusters in metavolcanic rocks resulted in two Rb/Sr isochrons at 370±10 Ma and 391±7 Ma. These ages match the $^{40}\text{Ar}^{39}\text{Ar}$ spot ages, and hence indicate equilibrium-conditions at very low grade, because micro-chemical equilibria are matched by Sr-isotopic equilibria. The dated white mica is oriented parallel to foliations produced by prominent sinistral strike-slip faulting and/or by folding, thus relating ages also to deformation. $^{40}\text{Ar}^{39}\text{Ar}$ spot age spectra also show relict age peaks at 420-424 Ma and 439-475 Ma. The age peak of 420-424 Ma may be attributed to deformation and fluid access, possibly related to the collision of Avalonia with composite Laurentia. The age peaks at 439-475 Ma occur in two pyroclastic samples which also contain slate clasts which are ca. 550 Ma or older as documented by earlier workers. Hence the 439-475 Ma ages may be due to partial resetting or isotopic inheritance from the protolith (excess Ar). The dominant ages of ca. 396-366 Ma are similar to emplacement ages of I-type plutons in the Mira terrane and are likely related to Neoacadian collisional and transcurrent assembly of the Avalonia microplate.

Fission track ages of zircon from Mira terrane samples are between 215±21 and 233±52 Ma, dating cooling of the Mira terrane to below 250-280°C. Although these temperature conditions are close to previous peak metamorphic temperatures, similar Mesozoic ages were not found in the $^{40}\text{Ar}^{39}\text{Ar}$ spot age spectra, suggesting that the rocks remained entirely dry during the process dated by the fission track ages. Fission track ages are most likely related to early Atlantic rifting.
Trace element partitioning in peralkaline iron-rich melts

Andreas Winterhalder¹, Christopher Giehl*,¹, Regina Mertz-Kraus², Michael Marks¹ and Marcus Nowak¹

¹Fachbereich Geowissenschaften, Eberhard Karls Universität Tübingen, Germany
²Institut für Geowissenschaften, Johannes Gutenberg Universität Mainz, Germany

*correspondence: christopher.giehl@uni-tuebingen.de

Phase equilibrium experiments based on an iron-rich peralkaline phonolitic composition were performed to investigate mineral/melt trace element partitioning. The starting material resembles a parental composition of the peralkaline Ilímaussaq complex/South Greenland (Marks & Markl 2003). Previous experiments show that this starting composition is suited to crystallize mineral assemblages that occur in natural Ilímaussaq rocks (Giehl et al. 2013). Accordingly, identical experimental conditions of 100 MPa, 850 – 700 °C, low /fO₂ and nominally H₂O-free were applied; and experiments were conducted in hydrothermal rapid-quench cold seal pressure vessels. A two-step fractional crystallization strategy utilizes a residual melt composition coexisting with mineral phases as subsequent starting material. Major and trace element (Nb, La, Ce, Y, Sr) compositions of mineral phases and coexisting glasses were determined with electron microprobe analysis (EMPA) and laser-ablation quadrupol ICP-MS, respectively.

Besides residual melt the following minerals crystallized: titano magnetite, Fe-rich olivine, clinopyroxene, aenigmatite (Na₂Fe₅TiSi₆O₁₈), alkali feldspar, nepheline, fluorite, sodalite (Na₈Al₆Si₆O₂₄Cl₂), hiortdahlite ((Ca,Na)₆(Zr,Ti)₂Si₄O₁₄F₄) and a wöhlerite group mineral (WGM). The coexisting melt shows increasing concentrations of FeO*, Na₂O, F and an increasing alkalinity index (molar Na+K/Al), as well as decreasing concentrations of SiO₂, Al₂O₃, CaO and K₂O. Trace element melt concentrations of Nb, La and Ce increase, whereas Y and Sr are fairly constant.

Phase stabilities and the liquid line of descent are similar to experiments using the same starting composition without trace elements. However, trace elements are incorporated in aenigmatite, hiortdahlite and the additionally stabilized WGM. Schematic chondrite-normalized trace element patterns show that hiortdahlite and the WGM are enriched in LREE’s and concentrations increase up to 13 wt% with decreasing T in the WGM at 700 °C (Nb 2.5 wt%, La 2.5 wt%, Ce 6.2 wt%, Y 1.9 wt%).

Partially open grain- and phase boundaries as fluid pathways in magmatic and metamorphic rocks

Richard Wirth¹, Jörn H. Kruhl², Luiz F.G. Morales¹

¹ GFZ German Research Centre For Geosciences, Helmholtz Centre Potsdam, Germany; wirth@gfz-potsdam.de; morales@gfz-potsdam.de

² Technical University Munich, Tectonics and Material Fabrics Section, Munich, Germany; kruhl@tum.de

Focused ion beam (FIB) sample preparation, transmission electron microscopy (TEM), and 3D slice and view imaging show that in metamorphic rocks quartz grain boundaries are partially open, with widths of several hundred nanometres, and form a connected network that serves as pathway for fluids (Kruhl et al, 2013). During uplift, opening results from cooling-induced anisotropic volume reduction of quartz below the diffusion threshold of ca. 300 °C. The volume reduction is not balanced by decompression-induced anisotropic volume expansion. The degree of measured grain-boundary opening is in agreement with semi-quantitative modelling which indicates that, due to temperature-pressure-related volume change, at least 50% of the total grain-boundary area is open.

New measurements on grain and phase boundaries of various rock-forming minerals (calcite, quartz, plagioclase, K-feldspar, amphibole, pyroxene) from magmatic and high-grade metamorphic rocks (basalt, syenite, marble, metagabbro, eclogite) confirm the widespread existence of partially open grain as well as phase boundaries with widths of several hundred nanometres. In addition to quartz, these boundaries are partially filled with newly grown biotite, chlorite or amphibole. This proves that in magmatic or high-grade metamorphic rocks the grain and phase boundaries opened already at conditions of at least greenschist facies. This is in agreement with the model that boundary opening starts below the diffusion threshold of the respective minerals, i.e., below ca. 500 °C for feldspars and below at least ca. 600 °C for pyroxenes and amphiboles. Since these minerals are common in rocks of the middle and lower continental crust, which partly cooled from temperatures above the diffusion thresholds, partially open grain and phase boundaries should be already present at deeper crustal levels, with all consequences for, e.g., rock strength, permeability and reactivity. The volume of open grain and phase boundary porosity in quartzite was estimated as 0.1 to 2.2 % for grain sizes of ca. 0.2 to 1 mm. Probably it is higher in finer-grained rocks, specifically in basalt where cooling-induced shrinking of grains is not reduced by decompression expansion. Last but not least, it can be expected that open grain- and phase-boundary networks strongly promote weathering and disaggregation of rocks to various extent, depending on mineral composition and cooling-decompression history.

Multi-stage hydrothermal alteration of the lower oceanic crust – Evidences from a layered gabbro series of the Oman ophiolite (Wadi Tayin Massif)

Paul Eric Wolff¹, J. Koepke², J. Berndt³, D. Garbe-Schönberg⁴, S. Schuth⁵, A. McCaig⁶

¹e.wolff@mineralogie.uni-hannover.de
²j.koepke@mineralogie.uni-hannover.de
³j.berndt@uni-muenster.de
⁴dgs@uni-kiel.de
⁵s.schuth@mineralogie.uni-hannover.de
⁶a.m.mccaig@leeds.ac.uk

Hydrothermal circulation within the oceanic crust is one of the key processes in controlling the cooling of the oceanic crust. During hydrothermal circulation, the crust undergoes extensive chemical exchange with seawater. If during the accretion of the lower crust in-situ crystallization of deep gabbros plays a significant role (so-called "sheeted sill model"), thermal models suggest that extensive hydrothermal circulation within the lower section of the oceanic crust must exist.

However, the extent and temperature of hydrothermal circulation within the lower oceanic crust and related petrological record are still poorly constrained. In this study, we present petrological, geochemical and isotopic data from hydrothermal dikes and veins crosscutting a layered olivine gabbro from the Wadi Tayin Massif in the Southern Oman ophiolite, forming the deepest parts of the crustal series in the Oman ophiolite. Our results show that hydrothermal activity within the lower crust starts at very high temperature and very low water/rock ratios (0.5-1) with the production of amphibole-bearing dikes and veins. Characteristic mineral assemblages and trace element modeling suggest partial melting of the layered gabbro triggered by aqueous fluids at temperatures of about 1000 °C (based on amphibole thermometry). Rims of amphibole extremely enriched in chlorine (up to 4 wt%) indicate the influence of very Cl-rich fluids (brines?) at the transition between the magmatic and metamorphic regime (temperatures: 500-800 °C). At lower temperatures, hydrothermal circulation produced veins consisting of greenschist facies minerals (epidote, chlorite, and actinolite). Isotopic data indicate an interaction between gabbro and hydrothermal fluid at temperatures between 300-500 °C and water/rock ratios between 0.5-1. In a final stage, cm-thick monomineralic prehnite veins indicate low temperature hydrothermal circulation at temperatures around 100 °C and the highest water/rock ratios of up to 3.

Our results suggest that the hydrothermal alteration within the lower oceanic crust proceeds in multiple stages from magmatic to very low temperatures with increasing water/rock ratios with decreasing temperature. Our study highlights that the same pathways were used at different temperatures for hydrothermal circulation. Conclusively, hydrothermal circulation at magmatic temperatures needs to be considered for thermal models regarding cooling of the deep oceanic crust via fluid circulation.
Superposition of burial and hydrothermal events: Post Variscan thermal evolution of the Erzgebirge, Germany

R. Wolff1, I. Dunkl2, J.-M. Lange3, Ch. Tonk4, T. Voigt5, H. v. Eynatten6

1rwolff@gwdg.de; 2idunkl@gwdg.de; 3jan-michael.lange@senckenberg.de; 4christian.tonk@amtc-dresden.com; 5Thomas.Voigt@uni-jena.de; 6heynatt@gwdg.de

The Erzgebirge forms part of the Saxothuringian unit of the Variscan mountain belt, located at the northern margin of the Bohemian Massif. It exposes mainly metamorphic rocks intruded by Carboniferous and Permain igneous rocks. This basement block was probably buried and covered by marginal deposits of the Permo-Mesozoic sequence of the Central European basin. During Jurassic and early Cretaceous significant uplift led to the next exhumation of the Erzgebirge. The eastern part of the basement adjacent to the Elbe Zone was re-buried in late Cretaceous. This (second) sedimentary cover was nearly completely removed in early Cenozoic time. In the western Erzgebirge the basement is partly covered by Miocene fluvial deposits and mafic lavas (21 Ma), indicating limited Neogene subsidence and later uplift.

The Erzgebirge hosts numerous ore deposits of variable genetic origin. Two major periods of hydrothermal activity were recognized: (1) hydrothermal ore deposits related to late Variscan granitoid magmatism; and (2) long-lasting Mesozoic hydrothermal activity. The latter causes intense vein formations that were probably driven by major tectonic events affecting the European continent, such as the Triassic opening of the Tethys and the Jurassic to Cretaceous opening of the Central and North Atlantic (e.g. Romer et al. 2010).

The post-Variscan thermal evolution is thus influenced by both sedimentary burial and ore-generating hydrothermal fluids. We analyzed 45 samples from the Variscan basement and Permian rocks of the Erzgebirge. These 170 new zircon and apatite (U-Th)/He ages combined with the existing apatite fission track data (Lange et al. 2008; Ventura 2008) describe the timing and areal extend of the thermal evolution of the Erzgebirge. The zircon (U-Th)/He age pattern clearly delineate areas of dominantly Permian cooling ages in the east while the western Erzgebirge experienced a significant reset of the zircon (U-Th)/He thermochronometer in Jurassic time. This was probably due to deep burial under Mesozoic sediments. This method is sensitive enough to detect the Mesozoic hydrothermal pulses, also. The Apatite (U-Th)/He cooling ages reflect the final exhumation of the basement in late Cretaceous times. Additionally it marks an “island” of Jurassic cooling ages in the central part of the exposed basement. This gives a limit to post-Jurassic erosion. The results of this work point to a more differentiated evolution of central European basement blocks than described so far.

Characterization of the physiology and cell-mineral interactions of the marine anoxygenic phototrophic Fe(II)-oxidizer *Rhodovulum iodosum* – implications for Precambrian banded iron Formation deposition

Wenfang Wu\(^1\), Elizabeth D. Swanner\(^2\), Yongxin Pan\(^3\), Andreas Kappler\(^4\)

\(^1\)wuwenfang@mail.iggcas.ac.cn
\(^2\)elizabeth.swanner@ifg.uni-tuebingen.de
\(^3\)yxpan@mail.iggcas.ac.cn
\(^4\)andreas.kappler@uni-tuebingen.de

\(^1,3\)Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China

\(^1,2,4\)Department of Geoscience, University of Tuebingen, Tuebingen, Germany

Anoxygenic phototrophs are able to oxidize Fe(II) to Fe(III) photosynthetically in the absence of oxygen. Discovery of this metabolism lent support to the suggestion that photoferrotrophs participated in the deposition of iron oxide minerals in banded iron formations (BIFs) prior to the rise of significant amounts of oxygen in the Precambrian atmosphere. Previous studies of the involvement of photoferrotrophs in BIFs deposition focused on freshwater strains. However, the complement of inorganic (and organic) ligands present in seawater vs. freshwater should control the rates, mechanisms and products of Fe(II) oxidation. Because we lack an understanding of the physiological behavior of marine photoferrotrophs, the mineral products they form and their relevance to marine Fe(II) oxidation, we investigated Fe(II) oxidation by a marine photoferrotroph *Rhodovulum iodosum*, isolated from a mud flat in the North Sea. In growth experiments, Fe(II) was fully oxidized at 250 h incubation, and Fe(II) oxidation rate increased with the initial Fe(II) concentration to a maximum rate of ~1.98 mM/day obtained at 5 mM Fe(II). Adding silicon (Si) to 2.2 mM, a concentration inferred for the Precambrian ocean, has no significant effect on the Fe(II) oxidation rate, except for a longer lag phase before oxidation initiated. Goethite was the final product of Fe(II) oxidation. The minerals precipitated near extracellular polymeric substances (EPS) but were spatially separated from cells. The presence of an aqueous or ligand-bound Fe(III) species within EPS, as visualized with a fluorescent sensor, leads us to suggest that EPS play a role for cells to prevent encrustation. This study establishes not only rates and conditions under which marine phototrophic Fe(II) oxidation occurs, relevant to BIFs deposition, but also a possible mechanism for Fe(III) precipitation away from cells.
Hydrothermal activity along strike-slip faults: cyclicity of movements and fluid flow

T. Yilmaz1, G. Prosser2, D. Liotta3, J.H. Kruhl1

1 Technical University of Munich TUM, Tectonics and Material Fabrics Section, Munich, Germany. tim.yilmaz@tum.de
2 Università della Basilicata, Dipartimento di Scienze, Potenza, Italy. giacomo.prosser@unibas.de
3 Università degli Studi di Bari, Dipartimento di Scienze della Terra e Geo-Ambientali, Bari, Italy. domenico.liotta@uniba.de

Fault zones serve as pathways for large amounts of fluids that may change rock composition and structure, generating ore deposits and geothermal fields. Quartz may crystallize from these fluids in numerous generations reflecting cyclicity of deformation and fluid-flow.

Structures and quartz mineralization of the dextral strike-slip shear zone „Bavarian Pfahl“ (Germany) were analyzed. Polarizing microscopy and hot cathode CL analyses reveal several stages of fluid flow, quartz crystallization and fragmentation: (i) At least three early stages of silicification of granitoid basement rocks result in µm-sized quartz matrices with variable amounts of kaolinite. (ii) Fragmentation during shear-zone activity and fluid flow leads to mm-cm wide veins roughly parallel to the fault zone and filled with blocky 100-500 µm-sized quartz grains. (iii) Brittle deformation in a central fault-parallel zone causes a massive quartz dyke with complex patterns of fragmentation and quartz overgrowth. (iv) Continued dextral shearing produces a set of steep, N-S oriented and cm-dm spaced fractures that locally form mm-cm wide quartz veins with voids, indicating decreased fluid flow, (v) followed by at least two generations of µm-thin quartz veins with ghost veinlet overgrowth textures. (vi) µm-thin partly open quartz veins represent the final stage of fragmentation and fluid flow.

The Pfahl shear zone, characterized by brittle deformation during fluid flow, represents long-term activity of a large-scale hydrothermal system. It is an excellent example of cyclic stress and strain-rate variation, fluid flow and mineralization.
Siberian Arctic paleoclimate: insights from clay minerals and organic data from New Siberian Islands Paleogene sections

Daichi YOON¹, Johann SCHNYDER¹, Guillaume SUAN², François BAUDIN¹, Speranta-Maria POPESCU-SUC³, Jean-Pierre SUC¹, Loic LABROUSSE¹ & K. PIEPJOHN¹

¹UPMC-Univ. Paris 06, ISTeP, case 117, 4 Place Jussieu F- 75252 Paris
²UMR CNRS 5276 LGLTPE Université Lyon 1, Campus de la Doua, F-69622 Villeurbanne
³GeoBioStratData. Consulting 385 Route du Mas Rillier, F-69149 Rillieux la Pape
⁴BGR, Geozentrum Hannover, Stilleweg 2, D-30655 Hannover

Lower Palaeogene times saw abrupts climate change episodes (PETM, ETM2, …) extensively evidenced at low latitudes but still poorly documented at higher latitudes. However, the extreme sensitivity of high Arctic system to global climate fluctuations inferred at present day has to be evidenced for past episodes. The joint expedition « CASE 15 New Siberian Island Geological Excursion » allowed high resolution sampling of Palaeogene sections from Bel’kovsky and Fadeevsky island, both dominated by silty deposits with numerous amber-rich coal beds.

Determination of organic matter (Rock-Eval pyrolysis, δ13Corg, palynofacies and pollen analysis) on these two sections evidenced a type III continental organic content well preserved and weakly matured (Tmax < 435°C) with a high proportion of C3 plants and lacustrine algae in coal beds. Sediment mineralogy, studied by RX diffraction on bulk rock and clay fraction, shows a high quartz content and illite in clay fraction along both profiles. Coal layers exhibit a systematic increase in kaolinite content (up to 60%) suggesting warm and wet climate for those intervals.

These sections represent bog to swamp depositional environments next to high reliefs responsible for the observed detrital influx (Verkhoyansk fold-and-thrust belt and rejuvenated Taimyr for instance) and drained by the Khatanga and Lena paleo-equivalents. Analysis of pollen content yield a Paleocene age for Belkovsky and Eocene age for Fadeevsky series, with relatively warmer and wetter conditions in Eocene times on Fadeevsky.
Deep partial melting (anatexis) in the continental crust has a critical effect on weakening rocks and promoting deformation, which finally cause architectural rebuilding, chemical differentiation and rapid exhumation of thick mountain belts. Such a partial melting-induced crustal evolution scenario might be in progress for the active Himalaya, and might have played an important role in the exhumation processes of numerous ancient continental collision orogens, such as the Variscan orogen of central Europe, the Appalachian orogen of North America, and the Qinling-Dabie orogen of central China. To dissect the mechanisms controlling mountain exhumation, structural evidences and petrogenetic modeling have merits for decoding the deformation and metamorphism paths, while petrological microstructures are of particular importance in recognizing anatexis. Despite the critical role of anatexis in promoting crustal rock exhumation of the Dabie orogen, little has been known about the mechanism and pressure-temperature (P-T) condition of anatexis in the Dabie core complex, and thus the genetic relationship between anatexis and exhumation is still vague.

We present for the first time unequivocal anatexis-indicating microstructures in the core complex migmatite of the Dabie orogen, which show incongruent partial melting of amphibolitic protolith by which peritectic clinopyroxene has been produced. The rare earth element pattern of partial melt modeled from trace element compositions of clinopyroxene analyzed by LA-ICP-MS is consistent with in-situ leucosome composition, which are both characterized by relative enrichment in heavy rare earth elements (Yb and Lu) compared to middle rare earth elements (Dy and Ho) and consistent with experimental partial melt forming at low pressures (<10 kbar). The quartz enclosed in clinopyroxene which might have crystallized from anatectic melt, show a variable Ti concentration within 25-140 ppm. The majority of amphibole compositions reveal a near-isothermal decompressional evolution by ca. 4 kbar within 800-850 °C, which is well consistent with the results applying Ti-in quartz thermobarometry. The previously assumed decompression-induced Ti increase in quartz has been observed in this case concerning orogenic doming. The significant effect of anatexis on weakening core complex rocks and promoting extensional tectonics might be responsible for the strong exhumation which diminished ca. 15 km thickness at a near-isothermal condition for the migmatitic core complex.
Anatexis and differentiation during formation of felsic melts at the roof of axial magma chamber: Evidence from IODP Hole 1256D

Chao Zhang¹, Jürgen Koepke¹, Lydéric France², Marguerite Godard³

¹Institut für Mineralogie, Leibniz Universität Hannover, Callinstr. 3, 30167 Hannover, Germany
c.zhang@mineralogie.uni-hannover.de (C. Zhang), koepke@mineralogie.uni-hannover.de (J. Koepke)

²CRPG-CNRS, Nancy-Université, BP 20, F-54501 Vandœuvre-les-Nancy, France

³Géosciences Montpellier, CNRS, Université Montpellier 2, 34095 Montpellier, France

Author e-mail address

Whole-rock major and trace element compositions, and mineralogical major and trace element compositions of a variety of lithologies recovered from the IODP Hole 1256D have been analyzed in order to investigate possible anatexis and differentiation processes which might have contributed variably to the ubiquitous felsic veins at the roof of axial magma chamber. The newly analyzed 38 whole-rock samples were collected during IODP Expeditions 312 and 335 at depths between 1404.2 and 1521.6 m below seafloor (mbsf), and can be classified into 6 rock types based on petrographic observations, including leucocratic vein, medium-grained diorite, coarse-grained diorite, granoblastic dike, hydrothermal vein and gabbroic pluton. Their petrological and geochemical characteristics are believed to genetically relate to substantial and thermal exchanges in the conductive boundary layer, between the convective hydrothermal system above and the axial magma chamber below.

The major compositional variations of all rock types are generally overlapping with the compositions of global mid-ocean ridge glasses (PetDB). With decreasing MgO content from gabbro, granoblastic dike and hydrothermal vein to coarse-grained diorite, medium-grained diorite and leucocratic vein, all the rock types show continuous strong decrease in CaO but modest decrease in Al₂O₃; the Fe₂O₃⁺TiO₂ and P₂O₅ first increase to their peaks at ca. 4 wt% MgO but then decrease dramatically till the low MgO end (ca. 0.5 wt%). The only discrepancy between the Hole 1256D samples and the global mid-ocean ridge glasses is the extremely low K₂O content in the former (<0.4 wt%, mostly <0.25 wt%), which does not rise with decreasing MgO. The coarse-grained diorites have relatively higher Fe₂O₃, TiO₂ and MgO but lower SiO₂ contents than the medium-grained diorites and leucocratic veins, although they are similar in mg-number and other major element concentrations.

Comparatively, the melt inclusions and host glasses from East Pacific Rise show very similar major element contents with the majority of these fossilized gabbros and granoblastic dikes but with slightly higher MgO and mg-number. Compared to partial melts of hydrous melting experiments of sheeted dike or gabbro, the felsic rocks recovered from Hole 1256D clearly show much lower Al₂O₃ and K₂O but higher P₂O₅ contents, as well as higher Sm/Yb and Zr/Hf ratios, and these discrepancies can hardly be explained by the compositional difference of protoliths, possibly indicating that multiple processes such as magma replenishment, assimilation and fractional crystallization might have contributed variably.
How to evaluate a huge dataset of pollen and spores to reconstruct palaeoenvironment and palaeoclimate in terrestrial settings: A Mesozoic case study (Junggar and Tarim Basins, NW-China)

Jianguang Zhang¹, Jens Hornung², Olaf K. Lenz³, Matthias Hinderer⁴, and Pujun Wang⁵

¹zhangjianguang108@126.com
²hornung@geo.tu-darmstadt.de
³lenz@geo.tu-darmstadt.de
⁴hinderer@geo.tu-darmstadt.de
⁵wangpj@jlu.edu.cn

Adjacent to the Tian Shan in NW China the Junggar and Tarim basins provide a continuous continental record of climatic and tectonic parameters during the entire Mesozoic. This makes them a natural laboratory to study how geodynamic processes interplay with surface topography and climate on a local, regional, and global scale. Of overall scientific interest is the role and intensity of the Early Mesozoic mega monsoon system at the easternmost end of Pangea and its evolution with repeated collisional events and increasing continental vs. global humidification and rearrangement of atmospheric circulation patterns.

To reconstruct palaeoenvironmental parameters on a regional scale a huge literature-dataset of about 64 papers was evaluated in terms of fossil distribution and lithofacies. Therefore a specially designed MS Access database was used, which automatically can crosslink all data. This study focusses on quantitative sporomorph data to identify palaeoenvironmental changes, because palynomorphs are the most abundant microfossil group in this area. Hence, until now, nobody has tried to establish a palaeo-community model based on such a huge database in that region. Therefore 337 genus of pollen and spores in 283 samples were used covering both basins. A program was compiled to create a cluster analysis, which show very pronounced quantitative sporomorph distribution patterns.

The resulting clusters reveal sporomorph assemblages that correlate well with known sporomorph ecogroups from NW-Europe (Abbink et al. 2004), but show also new or missing members compared to the European ecogroups. In conclusion specific and unique assemblages could be established which are characteristic for that region and contribute to better understanding palaeoecological conditions. Based on the interpretation of these new sporomorph assemblages and their spatial distribution, new palaeoenvironmental maps could be automatically generated in a GIS system. This offers the unique possibility to study the sensitivity of compositional variations of the ecogroup-assemblages, to eliminate misinterpretations of palaeoenvironment and palaeoclimate of single species and to map lithofacies and sporomorph shifts in time and space. As an outcome this dataset will reveal new insights into the relationship of climate and tectonic processes in central Asia.

Reference

Mineralogical and geochemical studies on sedimentary copper mineralization in the western Thuringer Wald

ZIEROLD, S., MAJZLAN, J.
Inst. of Geoscience, Friedrich-Schiller-University, Jena, Germany (steven.zierold@uni-jena.de)

The western part of Thuringer Wald is an old mining region, with exploitation of iron ores documented already in the 11th century south of Ruhla, later with mining of copper ores, today no longer viable. Geologically, the area belongs to the Mid German Crystalline Complex, the Ruhla Crystalline Complex (Zeh and Gerdes, 2009). The study area is located south of the city of Eisenach around the triangle Eisenach-Ruhla-Gumpelstadt (near Bad Liebenstein). Here, a sequence of Permian sediments is cropping out from the Werra basin.

In this study, we investigated the mineralogy and element distribution in the copper-bearing marly slates (so-called Kupferschiefer) and the basal conglomerate in this region at four sites, two outcrops, and two drill cores from 1953/54 (Hoyningen, 1955). The copper concentration at the outcrops are 0.61 and 0.62 wt% in the bottommost layer. The overlying layers are poorer in copper, with 0.21 and 0.41 wt%. The following overlying layers are significant more depleted in copper, from 0.48 weight percent decreasing to 60 and 720 ppm on the top. The main ore phases are chalcopyrite, sphalerite, pyrite, with less frequent galena in a clay-rich matrix in the form of concretions. In the organic-rich matrix, we observed abundant frambooidal pyrite throughout the entire investigated profile.

Interestingly, the most metal-enriched zone is not the Kupferschiefer itself but rather the top few centimetres of underlying basal conglomerate, with up to 2.07 wt% Cu. A drill core sample shows the mineralisation below the hydraulic barrier of marly slates. On the top of the conglomerate (but not directly on the contact between the conglomerates and the slates), there is a millimetre thick layer, where the clay-organic matrix is almost completely replaced by chalcopyrite and subordinate bornite, pyrite, sphalerite, and galena. Beneath this layer, there is another very thin layer with abundant massive pyrite. The spatial element distribution changes markedly in the oxidised and weathered samples. Top portions of the profile are enriched in iron oxides, followed by a zone of copper carbonates and a thicker zone with manganese dendrites.

We are further planning to analyse three samples with copper minerals from the bottom of Permian reefs and the rhyolitic basement rocks near Ruhla, with ore microscopy, electron microprobe and X-ray diffraction.

This is the abstract submission template. Please use this file to fill out and upload your abstract(s). Ensure that it fits into one column and one page.

Metastability and crystallisation of metamict minerals

P. Zietlow¹, T. Beirau², B. Mihailova³, Th. Malcherek⁴, J. Schlüter⁵, C. Paulmann⁶, R. · koda⁷, L.A. Groat⁸, U. Bismayer⁹

¹ peter.zietlow@mineralogie.uni-hamburg.de

Institute of Mineralogy, Crystallography and Petrography, Hamburg University, Germany

⁷ Institute of Geological Sciences, Masaryk University, Brno, Czech Republic

⁸ Dept. of Earth and Ocean Sciences, University of British Columbia, Vancouver, Canada

Natural metamict minerals show damaged crystallographic long range order, mainly resulting from the · -decay of built-in uranium and thorium atoms. Because of a prolonged low dose radiation, such minerals can be considered as natural laboratories to study composites of amorphous, quasi-amorphous, and crystalline material. Studies on such samples are highly relevant for our better understanding of the behaviour of radioactive waste embedding materials. Radiogenic · -particles and recoiled atoms produce locally amorphized regions in the order of several thousand atoms surrounded by a non-periodic gradient structure. During heating such minerals recrystallize to a certain extend and, hence, the radiation damage may be healed. [1]

We analyse changes of the long range order and the recrystallization kinetics of pyrochlores and titanites of different amorphization levels. For in-situ studies of local metamictization effects of the untreated samples as well as after annealing, Raman, and FTIR spectroscopy were used and correlated with integrating XRD measurements. [2]


Toarcian-Bajocian (Jurassic) deltaic systems in the North German Basin: Controls on the development from high-constructive fluvial-dominated to high-destructive wave-dominated deltas

Jens Zimmermann1, Matthias Franz2, Carmen Heunisch3, Friedrich Wilhelm Luppold4, Eckhard Mönnig5, Markus Wolfgramm6

1jenser.zimmermann@gmail.com; ²franz@mailserver.tu-freiberg.de; ³Carmen.Heunisch@lbeg.niedersachsen.de; ⁴FriedrichWilhelm.Luppold@lbeg.niedersachsen.de; ⁵e.moennig@naturkunde-museum-coburg.de; ⁶markus.wolfgramm@gtn-online.de

Toarcian-Bajocian deltaic sediments in the North German Basin (NGB) have been subject to a basin-scale study incorporating outcrop analog studies, more than 15 cored wells (> 1500 m cored intervals) and more than 500 logged wells. The high-resolution facies architecture of Toarcian-Bajocian deltas and their controls was investigated using an integrated approach of sedimentological, palaeontological, petrological and sequence-stratigraphic methods.

The analysis of lithofacies, an intense data set on biofacies and biostratigraphy (macro- and micropalaeontology, palynology) (>1500 evaluated samples) as well as stratal pattern architecture provide the basis for a high-resolution sequence-stratigraphic framework spanning from the Early Toarcian to Late Bajocian. The succession is bounded within two 2nd order Transgressive-Regressive Cycles (T-R cycle) with two maximum flooding zones (mfs) in the Lower Toarcian and Upper Bajocian and further subdivided into six 3rd order T-R cycles. Major flooding surfaces of basin-wide importance have been identified in the (1) Lower Toarcian (falciferum zone), (2) Lower Aalenian (opalimum zone) and (3) Upper Bajocian (parkinsoni zone). Based on the sequence-stratigraphic framework deltaic systems and their depositional environments are reconstructed within 10 time-slices to differentiate between allogenic and autogenic controls and visualised in 10 high-resolution facies maps.

Since Rhaetian times Scandinavian source areas supplied clastics to an epeiric sea of the Tethyan Ocean. High sediment input relative to wave energy resulted in high-constructive fluvial-dominated deltas in the Toarcian. These large and elongated deltas are mainly located in the NE part of the NGB, characterised by a distributive network of distributary channels with progradational and aggradational stacking pattern resulting in thick sandy delta plain and delta front deposits with steep facies gradients. From the Upper Aalenian to the Bajocian the delta plain shifted successively towards the West and deposition of lobate shaped high-constructive fluvial-dominated deltas focused in the NW part of the NGB. In the NE high-destructive wave-dominated deltas evolved characterised by a rather parallel to subparallel network of thin distributary channels dissecting a thin sandy delta plain. These deltas show progradational to retrogradational stacking pattern and their mouth bars are connected by elongated shoreface sandbars comprising longshore elongated oolitic shoals. The change in delta types marks an increase in wave energy time-constrained to the new connection between the NGB with the Tethyan realm via the Polish Basin in the Early Bajocian.

Toarcian-Bajocian deltaic systems in the NGB were sensitive to eustatic fluctuations and changes in circulation pattern, show typical lateral shifts and are therefore a considerable good example to demonstrate the interactions of allogenic and autogenic controls.
Anorthosite dikes from Cyprus: phase relations in the system
$\text{CaAl}_2\text{Si}_2\text{O}_8 - \text{CaMgSi}_2\text{O}_6 - \text{Mg}_2\text{SiO}_4$ at 5 wt.\% $\text{H}_2\text{O}$

Aurelia Zirner$^1$, Chris Ballhaus$^2$, Raúl Fonseca$^3$, Carsten Müncker$^4$.

$^1$azirner@uni-bonn.de
$^2$ballhaus@uni-bonn.de
$^3$rfonseca@uni-bonn.de
$^4$c.muenker@uni-koeln.de

Massive anorthosite dikes are documented for the first time from the Limassol Forest Complex (LFC) of Cyprus, a deformed equivalent of the Troodos ultramafic massif. Both the Troodos and LFC complexes are part of the Tethyan realm consisting of Cretaceous oceanic crust that formed within a backarc basin 90 Ma ago and was obducted during late Miocene.

From crosscutting relations with the sheeted dike complex, it follows that the anorthosites belong to one of the latest magmatic events on Cyprus. In hand specimen, the rocks appear massive and unaltered, although in thin section magmatic Plagioclase ($\text{An}_{93}$) is partially replaced by Albite and Chabazite (Zeolithe). Where magmatic textures are preserved, Plagioclase forms cm-sized, acicular, radially arranged crystal aggregates reminiscent of spinifex textures.

The origin of these anorthosites remains poorly understood. Even though they occur as intrusive dikes, it is evident they cannot represent liquid compositions, at least under dry conditions. Whole-sale melting of a pure $\text{An}_{93}$ would require temperatures in excess of 1450 °C, which is a quite unrealistic temperature of the modern Earth’s crust.

We are exploring experimentally if such lithologies can be generated by medium-pressure fractional crystallization of hydrous basaltic melts followed by decomposition-degassing. High pH$_2$O stabilizes Olivine and Spinel but tends to suppress Plagioclase, hence may allow the An-component to be accumulated in late-stage melts. Hydrous melts do occur on Cyprus, in form of high-Ca boninites with ~ 5 wt.\% H$_2$O. Experiments are being performed in the Ol-Cpx-Pl-H$_2$O system, with Ol (Fo$_{95}$), Pl (An$_{93}$), and Di (Di$_{95}$) separates as starting materials. The separates are ground, mixed in the desired proportions, then equilibrated with 4 wt. \% H$_2$O at 0.5 GPa total pressure from 1000 to 1300 °C in a piston-cylinder press. Preliminary experimental results indicate the validity of the working hypothesis.

Aim is to delineate the Anorthite saturation field in the Ol-Cpx-Pl-H$_2$O system, and assess to what extent Plagioclase can be suppressed as a liquidus phase in basalt fractionating under hydrous conditions.
Thermodynamic properties of libethenite [Cu2PO4(OH)], pseudomalachite [Cu5(PO4)2(OH)4], and olivenite [Cu2AsO4(OH)]

Arne H. Zittlau1, Juliana Boerio-Goates2, Brian F. Woodfield2 and Juraj Majzlan1

1Institute of Geosciences, Friedrich-Schiller University, Jena, Germany, (*correspondence: Arne.Zittlau@uni-jena.de)
2Department of Chemistry and Biochemistry, Brigham Young University, Provo UT 84602, USA

Weathering of primary copper minerals (e.g., chalcopyrite, bornite) leads to the formation of secondary copper sulfates, phosphates, and arsenates. In this work, we focused on Cu arsenates and phosphates minerals olivenite [Cu2AsO4(OH)], libethenite [Cu2PO4(OH)], and pseudomalachite [Cu5(PO4)2(OH)4]. We synthesized these phases in the laboratory and measured their thermodynamic properties.

The synthesis procedures of olivenite including boiling of a solution of 0.1 M As2O5 with 0.05 M Cu(OH)2 for 2.30 h, hot filtration, and drying in air on the filter for 24 h. Libethenite was produced after a hydrothermal synthesis procedure of Gallego et al. (2009). Pseudomalachite was synthesized similarly as libethenite by a hydrothermal synthesis procedure which was modified after Xu et al. (2010). A suspension of 0.010 M Cu(COOH)2, 0.028 K3PO4·H2O, and 0.001 M Cu(OH)2 was titrated to pH of 7 with a 85 % H3PO4 and transferred to a hydrothermal bomb. This bomb was heated to 200 °C for 24 h, the smaragd green crystals were filtered and washed with deionized water.

All these samples were characterized by X-ray diffraction (XRD). Subsequently, the best samples were analyzed by scanning electron microscopy (SEM) and infrared spectroscopy (FT-IR) for phase purity and prepared for calorimetric measurements.

The calorimetric measurements were carried out by an acid-solution calorimeter at T = 298.15 K in 5 N HCl as the solvent, using CuO, KH2PO4, KH2AsO4 and KCl as the reference compounds. For all measurements, appropriate thermochemical cycles were constructed. The formation enthalpies (ΔfH) of olivenite, libethenite and pseudomalachite are -1000.3±4.6 kJ/mol, -1385.7±4.3 kJ/mol, and -3230.1±10.5 kJ/mol, respectively. Measurements of heat capacity were carried out and standard entropies for each phase were calculated as 179.5±1.8 J/mol·K, 162.2±1.6 J/mol·K, and 374.5±3.8 J/mol·K, for olivenite, libethenite and pseudomalachite, respectively. The standard Gibbs free energies of formation (ΔfG) of olivenite, libethenite and pseudomalachite are -851.1±4.7 kJ/mol, -1229.7±7.3 kJ/mol and -2823.0±10.6 kJ/mol, respectively.

Our ultimate goal is a comprehensive model of Cu- and sulfate-rich fluids present in oxidation zones of ore deposits and tailings of Cu ores.


Establishing willow and poplar short rotation forestry on marginal lands can help in CO₂ sequestration by reducing soil gas emissions

Kamal Zurba¹, Cornelius Oertel², Jörg Matschullat³

¹Author e-mail address: zurba@ioez.tu-freiberg.de
²Author e-mail address: Cornelius.Oertel@ioez.tu-freiberg.de
³Author e-mail address: joerg.matschullat@ioez.tu-freiberg.de

Interdisziplinäres Ökologisches Zentrum (IÖZ) - TU Bergakademie Freiberg

Contaminated soils with e.g. trace metals due to different human activities like mining inhibit food production due to potential risks for human and animal health. Such sites may be suitable however, for willow and poplar short rotation forestry (SRF) to extract biomass for energy purposes. SRF can be applied to marginal lands and brown fields. Thus SRF can help in decreasing the conflict between food and energy crops by reducing competition on arable lands. Yet is SRF truly sustainable? Does SRF positively influence the GHG balance in comparison with other land-use alternatives? The aim of this study is to investigate the reduction of CO₂ emissions from SRF soil. To achieve this aim, a SRF site and two alternative energy crop production sites (rye, field mustard and rapeseed) were compared under the same weather and soil type conditions.

Initial results show that the CO₂ emission rate at both alternative sites was significantly higher than at the SRF site during the growing season. In June, one site was 188% higher, and in August, it was 150% higher. In November (after the end of the vegetation period) it was lower (78%), however. At that time, field mustard plants were still growing, while the trees were completely barren at the SRF site. This could explain the related higher CO₂ emissions, since no photosynthesis occurred to absorb the carbon dioxide. At the second alternative site, emissions were 306% higher in August, and no significant difference was observed in November. No significant difference occurred between both the alternative site 2 and the SRF site in November.

To help reduce CO₂ emissions in summer (vegetation period), we recommend planting SRF on marginal land and brownfields. Such land-use will reduce the demand for fertile and non-contaminated arable land for energy crops. As well, it will help in CO₂ sequestration. Consequently more fertile land remains available for food and animal feed production. At the same time, SRF contributes on a longer term to soil quality and biodiversity improvement, groundwater protection, and soil erosion prevention.