Mo and U Fractionation: new Proxies for the Quantification of Oceanic Anoxia

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The oceans were likely dominantly oxygenated throughout the Phanerzoic. Periods with major evidence of increased extents of anoxic environments include the oceanic anoxic events (OAEs) during the Mid-Cretaceous and the lower Jurassic. The establishment of the anoxic conditions and the reasons for enhanced deposition of black shales may vary for the individual OAEs. They are generally linked to environmental changes, i.e. variations in the primary production, the ventilation of the oceans, the climate or to an enhanced volcanic activity. These environmental changes result in significant shifts of carbon isotope compositions, however, quantification of the extent of anoxic environments in the ancient oceans remains difficult.

Molybdenum and U are redox sensitive trace metals and thus suitable proxies to study the redox conditions of the oceanic environments. Additionally, their burial into sediments is associated with isotopic fractionation. Both elements show a considerable fractionation between oxic and anoxic environments (up to 2‰ in δ^{97}Mo and 1.3‰ in δ^{238}U) although the fractionations are contrary in direction and extent. Mo displays no or little fractionation in anoxic settings. Accordingly, Mo isotope compositions of black shales are similar to that of seawater. In contrast, it is highly fractionated towards light isotope compositions in oxic environments Arnold et al. (2004). In contrast, U is fractionated towards heavier isotope compositions during anoxic conditions (relative to seawater) and towards lighter isotope compositions in oxic environments Weyer et al. (2008). Thus, a shift in the abundance of oxic versus anoxic sinks should affect the oceanic mass balance for U isotopes as well as Mo isotopes.

We studied Mo and U isotope compositions of ancient black shales from the mayor Mesozoic oceanic anoxic events such as OAE-2 (Mid-Cretaceous) and the Toarcian OAE (Jurassic). Preliminary results for OAE-2 show δ^{97}Mo ranging from 0.68‰ to 0.82‰ and δ^{238}U ranging from -0.24‰ to 0.07‰. Toarcian black shales display a range of isotope compositions from 1.17‰ to 1.66‰ for Mo and from -0.18‰ to 0.10‰ for U. Both, Mo and U isotopes of ancient black shales are lighter than those observed in modern euxinic environments, e. g. the Black Sea and the Cariaco basin (1.10‰ to 1.71‰ for Mo and -0.2‰ to 0.44‰ for U Arnold et al. (2004); Weyer et al. (2008). This shift towards lighter isotope compositions (and closer to crustal values) may indicate an enhancement of anoxic sinks of Mo and U during these periods. Thus, both isotope systems together may be suitable to quantify the expansion of oceanic anoxic environments throughout geological time scales.

References

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