

Molybdenum isotope fractionation during continental weathering

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The oceans play a major role in regulating global climate. They both react and drive changes in other geochemical reservoirs (i.e. the atmosphere, surface lithosphere, cryosphere and biosphere) via a series of still poorly understood feedbacks. Quantifying these interactions and the oceanic response is essential for understanding and predicting long term climate change. In recent years, non-traditional isotope systems have become important proxies for changes in oceans chemistry that might for the first time allow quantification of these changes.

Molybdenum isotopes have shown great potential to quantify changes in the oxygenation of the oceans over geological time scales. With an increasing amount of data on the biogeochemical behaviour of Mo in the marine environment, it is now possible to interpret the paleo-record with more confidence. However, important aspects of Mo geochemistry remain poorly understood. These include diagenetic processes at continental margins and continental weathering. Mo behaviour in all of these processes has a potentially large impact on the interpretation of the geological record.

This study investigates the biogeochemistry of Mo in weathering profiles from Hawaii and Puerto Rico. Results verify fractionation of Mo isotopes during chemical weathering. Mo retained in saprolite samples has light isotope compositions of up to -0.5 permil. The extent of fractionation is dependent on redox-conditions, i.e. Mo isotope signals correlate with rainfall gradients. These results could be in accordance with the findings of [1], who observed heavy isotope compositions of dissolved Mo in some of Earth's major rivers. The results also indicate the possible use of Mo isotope signals as paleoredox-proxy in soils. However, soil profiles with large changes in pH show more variable Mo isotope signals with partly positive isotope values. This points to complex behaviour of Mo in terrestrial environments and is likely that there is not a single governing process causing the observed isotope composition of rivers. More data are necessary to judge the influence of these processes on the overall Mo isotope composition reaching the oceans.

[1] Archer&Vance (2008) *Nature Geoscience* Vol.1 p.597

Fungal weathering of black shale and graphite surfaces

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Oxidative weathering of black shale organic matter (OM) plays an important role in diverse processes like atmospheric CO₂ control and acid mine drainage. Fischer & Gaupp (2005) [1] quantified the reactive portions of the black shale surface area during weathering. In addition microorganisms in soils responsible for OM decomposition might have an influence. We wanted to test the contribution of ligninolytic fungi on weathering of black shale (OM). *Schizophyllum commune*, a white-rot fungus, releases enzymes able to oxidize organic compounds [2]. Using vertical scanning interferometry microscopy we were able to visualize and quantify the degradation of black shale OM. After an incubation period of up to 3 months, the surfaces showed typical etch pits with an average minimum depth of 120-150 nm. To prove the ability of OM alteration by fungi we used also graphite surfaces as pure carbon source. In comparison to the black shale surface, the etch pits occur more frequently and with a more continuous elongated morphology on the graphite surface reminiscent of hyphal structures.

[1] Fischer & Gaupp (2005) *Geochimica et Cosmochimica Acta* **69** (5), 1213-1224. [2] Wengel *et al.* (2006) *Science of the Total Environment* **367** (1), 383-393.