Controls on Mo isotope fractionations

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Mo isotopes are employed as a palaeoredox indicator, particularly in terms of quantifying the spatial extent of different redox conditions [e.g. 1]. However, the controlling factors on Mo cycling and isotopic fractionations under distinct redox conditions remain poorly understood. Mn and Fe (oxyhydr)oxides, Fe-sulphides, and organic mater have all been proposed to exert an influence on Mo isotope fractionations during diagenesis [2, 3]. To evaluate past ocean redox conditions it is necessary to understand the controls on redox sensitive element and isotope cycling in modern sedimentary environments, as well as the degree of Mo fractionation during Mo uptake by different substrates.

Sediment cores from Danish and Swedish waters were investigated for this purpose. The redox chemistry ranges from Mn- to Fe-rich to sulphidic sediments and pore-waters. An examination of dissolved and particulate Mo isotope measurements with porewater and solid phase Mn, Fe and sulphide characterization, reveals that adsorption and desorption processes heavily influence the porewater δ^{98}Mo values. The highest δ^{98}Mo values, converging towards the global modern seawater (~2.3‰), are recorded in highly sulphidic sediments. Our results suggest that for modern anoxic marine sediments, where deposition occurs beneath an oxic to suboxic water column, sedimentary δ^{98}Mo is dominantly controlled by the relative availability of Mn and Fe (oxyhydr)oxides, and the production of dissolved sulphide [4].

A mechanistic investigation of the isotopic fractionation of Mo during different mineral uptake pathways was also employed. The focus here is on fractionations during redox transformations involving iron-based phases, including those upon Mo interaction with Fe oxides and their sulphide-promoted reductive dissolution. This is a key process affecting Mo cycling in the environment. Preliminary results exhibit species dependant fractionations. The findings add to our understanding of Mo isotope fractionations during syn- to early-diagenesis and their relation to the interpretation of Mo isotope data for ancient sediments.

[1] Kendall et al. (2011) *EPSL* **307**, 450-460. [2] Siebert et al. (2006) *EPSL* **241**, 723-733. [3] Poulson-Brucker et al. (2009) *G*^{3} **10**, 1-25. [4] Goldberg et al. (2012) *Chem.Geol.* **296-297**, 73-82.

On the evolution of Earth's "Geo-bio" atmosphere

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On of the first predictions of Gaia hypothesis was that the biota exerted dominant control of evolution of the composition of Earth's atmosphere - including for the major atmospheric constituents, oxygen and nitrogen [1]. Here we review this in light of four decades of study. We argue that, other than water vapour (which is controlled by temperature) and the noble gases, all constituents of the atmosphere are controlled by a mix of geological and biological processes. In particular, recent work on nitrogen has shown that there is more nitrogen buried in the mantle than there is in the atmosphere. This is not primordial, but grew from the subduction of biologically fixed NH_4^+ [2]. It is evidence of both the biological contamination of the mantle, and billion-year timescale, non-steady state interaction of life and the atmosphere. By contrast, cycles of other gases range from years (methane) to millions of years (CO_2 via carbonate silicate weathering), and others display strongly non-linear behaviour (oxygen [3]). Can one weave these timescales together to a coherent narrative of coupled geosphere-atmosphere-climate interaction through the history of life on Earth?

[1] Lovelock (1972) *Atmos. Env.* **6**, 679-580. [2] Goldblatt et al. (2009) *N. Geosci.* **2**, 891-896 [3] Goldblatt et al. (2006) *Nature*, **443**, 683-683.