Molybdenum isotope fractionation in a seasonally anoxic fjord

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The molybdenum (Mo) isotopic composition of marine sediments is a potential tracer of ocean redox conditions. In oxic environments, light Mo isotopes are removed from the water column via adsorption to iron (Fe)- and manganese (Mn)-(oxyhydr)oxides, leading to the enrichment of heavy Mo in seawater (δ^{98}Mo = +2.3‰, NIST 3134 = 0.25‰). In euxinic environments, Mo is removed from the water column as a particle-reactive thiomolybdate species, with little net isotope fractionation [1, 2]. Based on isotope mass balance, the contrasting behavior of Mo in oxic and euxinic sediments suggests that seawater δ^{98}Mo should vary with ocean redox state. However, elemental and isotopic Mo cycling in anoxic settings are not well understood and need to be constrained in order to use Mo as a redox tracer [3].

Dissolved and sedimentary Mo were monitored over a two-year period in Saanich Inlet, British Columbia—an anoxic fjord characterized by intense reducing conditions below 120 m water depth punctuated by seasonal deep-water ventilation. Anoxic subsurface waters have significantly heavier δ^{98}Mo values (+2.55±0.05‰) compared to oxic surface waters (+2.23±0.05‰), and samples collected at the redoxcline show both enrichment (+2.45±0.05‰) and depletion (+2.19±0.05‰) of δ^{98}Mo values relative to average seawater. Periods of deep-water ventilation and changes to the magnitude of freshwater inputs are potential explanations for the observed deviations in water column δ^{98}Mo. Sedimentary Mo is a combination of authigenic Mo and particulate Mo scavenged from the water column, and sediment trap samples collected at 50 m, 115 m, and 180 m water depth indicate that Mo adsorbs to particulates in the water column. Therefore, Mo cycling cannot be described by the two fractionation mechanisms found in purely oxic or euxinic environments. Multiple mechanisms including interactions with organic matter and changes to Mo speciation may generate 'non-conservative' Mo behavior prior to deposition in anoxic sediments.

[1] Barling *et al.* (2001) *EPSL* **193**, 447–457. [2] Siebert *et al.* (2003) *EPSL* **211**, 159–171. [3] Poulson Brucker *et al.* (2009) *Geochem Geophys* **10**, Q06010.