Do distinct molybdenum compounds discern isotope fractionation processes in euxinic settings?

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The Mo isotope composition (δ^{98}Mo) in euxinic shales has been used as a proxy for a) the global distribution of anoxic conditions in ancient oceans [1] and b) sulfide concentrations in depositional environments [2]. However, there is currently no way to distinguish isotope fractionation at low bottom water sulfide concentrations in 'local' basins from 'global' secular isotope variations associated with changing seawater composition. This uncertainty is challenging the use of Mo isotopes for paleoceanographic reconstructions.

We hypothesize that combined information about distinct Mo compounds, Mo enrichments, and relationships between sedimentary Mo enrichment and δ^{98}Mo in euxinic sediments can be used to distinguish local from global isotope effects due to distinct burial pathways from seawater to sediments.

To test this, we collected new isotope data from well-characterized sediments deposited in euxinic Lake Cadagno over the past ~9800 years [3]. Samples were characterized using x-ray absorption fine structure spectroscopy (XAFS), showing the presence of principally two distinct Mo-compounds – a reduced Mo(IV)-S compound (distinct from molybdenite) and oxidized Mo(V)-OS and Mo(VI)-OS compounds [4].

Indeed, we find that the Mo–δ^{98}Mo relationship of Lake Cadagno sediments allows distinguishing between net isotope fractionation occurring in the lake and mixing of shallow, oxic sediments with the deeper euxinic sediments. At certain horizons, we find isotopically fractionated sediments (δ^{98}Mo offset by -0.1 to -0.5‰ from what can be accommodated by mixing) formed by non-quantitative Mo removal during times of frequent injection of O_2- and sediment-rich river water into the deep sulfidic water column. Importantly, this group of isotopically fractionated sediments includes both types of Mo compounds. Hence, the two distinct Mo compounds observed in euxinic Lake Cadagno do not discern isotope fractionation processes in the water column.

[1] Arnold et al. (2004) *Science* **304**, 87–90. [2] Arnold et al. (2012) *Geology* **40**, 595–598. [3] Wirth et al. (2013) *GCA* **120**, 22–238. [4] Dahl et al. 2013 *GCA* **103**, 213–231.