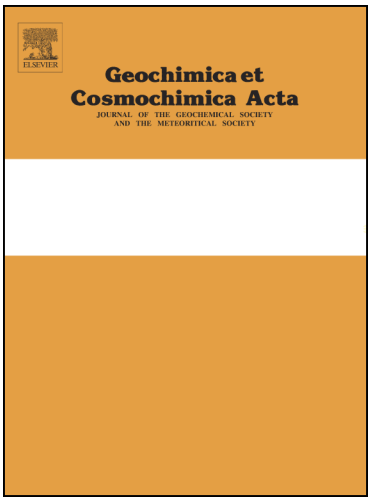

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Intense molybdenum accumulation in sediments underneath a nitrogenous water column and implications for the reconstruction of paleo-redox conditions based on molybdenum isotopes

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Abstract

The concentration and isotope composition of molybdenum (Mo) in sediments and sedimentary rocks are widely used proxies for anoxic conditions in the water column of paleo-marine systems. While the mechanisms leading to Mo fixation in modern restricted basins with anoxic and sulfidic (euxinic) conditions are reasonably well constrained, few studies have focused on Mo cycling in the context of open-marine anoxia. Here we present Mo data for water column particulate matter, modern surface sediments and a paleo-record covering the last 140,000 years from the Peruvian continental margin. Mo concentrations in late Holocene and Eemian (penultimate interglacial) shelf sediments off Peru range from ~70 to 100 µg g^{-1}, an extent of Mo enrichment that is thought to be indicative of (and limited to) euxinic systems. To investigate if this putative anomaly could be related to the occasional occurrence of sulfidic conditions in the water column overlying the Peruvian shelf, we compared trace metal (Mo, vanadium, uranium) enrichments in particulate matter from oxic, nitrate-reducing (nitrogenous) and sulfidic water masses. Coincident enrichments of iron (Fe) (oxyhydr)oxides and Mo in the nitrogenous water column as well as co-variation of dissolved Fe and Mo in the sediment pore water suggest that Mo is delivered to the sediment surface by Fe (oxyhydr)oxides. Most of these precipitate in the anoxic-nitrogenous water column due to oxidation of sediment-derived dissolved Fe with nitrate as a terminal electron acceptor. Upon reductive dissolution in the surface sediment, a fraction of the Fe and Mo is re-precipitated through interaction with pore water sulfide. The Fe- and nitrate-dependent mechanism of Mo accumulation proposed here is supported by the sedimentary Mo isotope composition, which is consistent with Mo adsorption onto Fe (oxyhydr)oxides.