

Molybdenum heterogeneity in euxinic settings: Implications for the Mo isotopes

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In ancient sedimentary systems, high molybdenum (Mo) enrichments are associated with strong euxinic conditions. Molybdenum isotopes ($\delta^{98}\text{Mo}$) have been used as a paleo-redox proxy for more than two decades. Within sulfidic waters, MoO_4^{2-} can undergo thiolation: Sulfur (S) replaces molecular oxygen (O) to form thiomolybdate species ($\text{MoO}_x\text{S}_{(4-x)}^{2-}$). Thiomolybdates are known to easily concentrate in solid phases at orders of magnitude higher than average crustal backgrounds (e.g., 10–400 ppm) via interactions with organic matter and sulfide mineral phases. Several burial pathways are probably involved and the quantitative importance of each remains an open debate. A common misconception of MoO_4^{2-} thiolation is that it is accompanied by an immediate reduction of Mo(VI) to Mo(IV). Thiolation, however, describes only substitution, and not a reduction reaction. Several studies have showed that Mo speciation can be complex in ancient sediments deposited in sulfidic settings. Characterization of Mo speciation using synchrotron based spectroscopic techniques has demonstrated that Mo can exist in multiple oxidation states associated with different phases (mineral, amorphous and organic).

In sulfidic systems, heavy Mo isotopic signatures are interpreted to represent the thiolation of dissolved Mo toward an estimated equilibrium fractionation for MoS_4^{2-} . The rapid sequestration of Mo into sediments after thiolation leads to near-quantitative removal and a sedimentary isotope composition approaching that of open-ocean seawater ($\delta^{98}\text{Mo} \sim 2.3\text{‰}$). We determined Mo speciation in sedimentary deposits that formed under sulfidic conditions using μ -XANES and μ -EXAFS techniques. Our data, which come from rocks covering several hundred millions of years, confirm that Mo speciation is highly heterogeneous even in settings assumed to be characterized by constantly euxinic conditions. These results show the complexity of Mo geochemical behavior in sulfidic environments and highlight that the interpretation of Mo isotope compositions is not simple, even in the most stable sulfur-reducing environments.