Toward a predictive model for molybdenum speciation and isotope ratio in sulfidic waters

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Molybdenum (Mo) is a well established paleoredox proxy for sulfidic environments. However, the conventional approach to determining Mo systematics (i.e., bulk Mo concentration analyses and isotope signature) from water and/or sediments does not constrain specific mechanisms regulating Mo burial under fluctuating anoxic to sulfidic conditions. The widest range of isotopic values (δ^{98}Mo) and concentrations are linked to these particular redox settings, confounding geochemical interpretations of the paleoproxy. The large variations of δ^{98}Mo are likely associated with Mo speciation. Equilibrium isotope fractionations among various Mo species have been estimated using quantum chemical models. Traditionally, these models have relied on thermodynamic predictions to define species and associated isotopic fractionations. Yet, this approach often falls short when explaining natural system data, where predicted results often don't conform to empirical observations. This inconsistency may be due to an oversimplification of the geochemical components or reactions in these complex natural systems.

To address this research gap, we synthesized multiple thiomolybdate species in the laboratory and measured their δ^{98}Mo values. Using these data and in order to capture the isotopic behaviour of Mo under dynamic, reactive-transport conditions, we created a fully kinetic model that outputs thiomolybdate speciation and δ^{98}Mo fractionation based on sulfide concentration. Through comparison with published Mo geochemical measurements, we demonstrate the potential of this approach further refine the Mo paleoproxy, and thereby improve interpretations of sulfidic systems in the geologic record.