Exploring Mo-Dissolved Organic Matter (DOM) Interactions as a Control on the Mo Paleoproxy

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Molybdenum (Mo) has long been used as a proxy for diagnosing anoxic, sulfidic conditions in both modern and ancient sediments. Additionally, Mo isotopes have emerged as a novel tool for revealing the history of deep ocean oxygenation. However, accurate proxy interpretation requires a thorough understanding of their biogeochemical cycling, including how an element or isotope is delivered to and preserved in sediments.

In oxygenated water, molybdate (MoO_4^{2-}) dominates Mo speciation, but in sulfidic water MoO_4^{2-} is transformed to highly reactive tetrathiomolybdate (MoS_4^{2-}) via intermediates ($MoO_xS_{4-x}^{2-}$). Observed correlations between sedimentary Mo enrichments and organic carbon content suggest an association of Mo with organic matter, but the geochemical mechanistic pathways remain unclear.

In this study we explore Mo-dissolved organic matter (DOM) interactions via an experimental approach using small organic molecules that mimic functional groups present in DOM, with the objective of identifying functional groups reactive toward MoO_4^{2-} and MoS_4^{2-}. Although the molybdate ion is typically unreactive under normal environmental conditions, the bisphenol catechol forms a complex with molybdate. These results imply that Mo-DOM complexes incorporating naturally-occurring polyphenol ligands potentially exist in oxygenated freshwater and terrestrial systems.

Likewise, preliminary data suggest that MoS_4^{2-} also may react with catechol, and that Mo-DOM complexes may be present in anoxic sediments. Molybdenum-DOM interactions are therefore likely to affect Mo isotopic fractionation during transport to and burial in marine sediments. Furthermore, Mo-DOM complexes are currently unaccounted for in models of Mo geochemical cycling, and could help to explain geographic variation in Mo isotopic values of riverine input to the ocean.