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Examining the Molybdenum Paleo-Redox Proxy in Modern Ferruginous Waters

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The abundances and isotope compositions of trace metals are commonly used as paleo-redox proxies to reconstruct the chemistry of Earth's oceans, and to consider the bioavailability of these elements to Earth's earliest metabolisms. Molybdenum (Mo) is a trace element with special paleo-biological and paleo-chemical significance: Mo plays a vital role in the key enzyme responsible for most nitrogen fixation (Mo-nitrogenase), and its distribution in aquatic environments is sensitive to redox conditions. In order to refine our interpretations of Mo geochemistry in the geologic record, it is imperative that we develop a framework for Mo cycling in modern environments. However, few studies consider Mo geochemistry in anoxic and iron-rich (*i.e.*, ferruginous) redox regimes, complicating how we use Mo as a paleo-redox proxy during times wherein ferruginous conditions dominated Earth's oceans (*e.g.*, the Archean; 4.0–2.5 Ga).

We are exploring Mo abundances and isotope compositions in the waters of Brownie Lake, MN, an Archean ocean analog environment with pervasive ferruginous waters at depth. Dissolved Mo concentrations are greater in the oxic surface waters (0.83 ± 0.19 ppb) than in the ferruginous deeper waters (0.26 ± 0.11 ppb), indicating a removal pathway for Mo at depth. Preliminary dissolved $^{98/95}$Mo values were obtained for three depths in the water column: the chlorophyll maximum (3.4 m; 0.77 ± 0.04 ‰), turbidity maximum (3.9 m; 0.45 ± 0.03 ‰), and deeper, ferruginous waters (7.40 m; 77 ± 0.03 ‰). Similar $^{98/95}$Mo values observed in the chlorophyll maximum and deeper waters– despite 80% less dissolved Mo in the latter– suggest a removal mechanism for Mo in the ferruginous waters that does not fractionate Mo isotopes. Curiously, the lighter $^{98/95}$Mo values in the turbidity maximum imply fractionation at this depth independent of the conservation of 98/95Mo in deeper waters. Future work will continue to explore Mo geochemistry in the water column and sediments, allowing us to identify Mo fractionation pathways and burial mechanisms in Brownie Lake, and ultimately providing insights into Mo isotope systematics on the early Earth.