

Formation and Structure Altering Processes of Iron-Molybdenum-Sulfide Clusters Under Abiotic vs Biotic Conditions- Implications for Molybdenum Paleoredox Proxies

RACHEL PHILLIPS¹, SHERYL SINGERLING², WEINAN LENG² AND JIE XU¹

¹Arizona State University

²NanoEarth, Virginia Tech

Presenting Author: rachelfphillips@aol.com

Molybdenum (Mo) plays an important role in a wide range of natural and engineered processes, including driving biological evolution as a key micronutrient, recording ancient oxygenation events, and controlling rates of industrial/biological reactions as a catalyst. The behavior of Mo in aqueous conditions is closely tied to the chemistry of sulfur, which is regulated by availability of other transition metal cations (i.e., ferrous iron). The formation conditions, structure, reactivity, and stability of Fe-Mo-S clusters in aqueous settings remain poorly understood, however, limiting our ability to accurately and precisely reconstruct ancient geochemical conditions using Mo proxies or to synthesize consistent Fe-Mo-sulfide materials for industrial uses. In this study, we illuminate the formation pathways of Fe-Mo-sulfides in abiotic and bio-stimulated sulfidic conditions through systematic experiments and analyses. We monitored dissolved Mo speciation during reaction with ferrous iron (Fe²⁺) and sulfide using UV-vis spectrophotometry and analyzed FeMoS precipitates using X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) spectroscopy to determine elemental valence and bonding structure. Results indicate Fe is required for Mo sequestration at pH > ~5 in the absence and presence of bacteria. The lack of change observed in the presence and absence of bacteria de-emphasizes the role of bacteria and particulate organic matter in Mo sequestration. The strong effects of pH and Fe²⁺ concentration on Mo sequestration may partially explain the observed sulfide-independent variation of dissolved Mo concentrations among modern euxinic basins. Moreover, the Fe-dependence of Mo sequestration suggests that Fe²⁺ may act as an electron shuttle to enable redox reactions between sulfide (S²⁻) and oxidized Mo(VI), which highlights the importance of future research investigating the effects of other transition metal cations (e.g., Cu, Ni, and Co) on Mo-sulfide interactions. This work will greatly enhance the accuracy and precision of ancient geochemical reconstructions by identifying the range of conditions in which Mo reduction and sequestration occurs.