

Formation of Iron Molybdenum Sulfur Clusters Under Abiotic and Biotic Euxinic Conditions

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Molybdenum (Mo), a redox-sensitive trace metal, plays an important role in a wide range of natural and engineered processes, including driving biological evolution and diversification as a key micronutrient, recording ancient oxygenation and deoxygenation events as a paleoredox proxy, controlling rates of industrial or biological reactions as hetero-catalysts, and enabling new technologies as structurally and electronically innovative nanomaterials. The mobility and reactivity of Mo in aqueous environments are closely tied to the chemistry of reduced sulfur species, which are regulated by availability of transition metal cations (M^{n+}). Mixed M-Mo-sulfur systems may therefore represent some of the most complex yet pivotal compounds in environmental chemistry. Our current knowledge for the formation, structure, reactivity, stability, and condensation pathways of M-Mo-S clusters in aqueous settings is limited. Here, we experimentally investigate the interactions between dissolved Mo, transition metal cation ferrous iron (Fe^{2+}), and sulfide (σH_2S_{aq}) in comparative abiotic and biological euxinic (anoxic and sulfidic) systems. We aim to determine the pH and stoichiometric conditions necessary for the formation and precipitation of Fe-Mo-sulfides abiotically and biotically, the oxidation state of Mo in such precipitates, and whether bacteria in the biological systems play an active or passive role in Fe-Mo-sulfide precipitation. The sample solutions are monitored with ultraviolet-visible spectroscopy (UV-vis) to track the evolution of dissolved Mo species, and precipitates formed are analyzed with x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) to determine their composition, Mo oxidation state, and structure. Initial results indicate that Fe^{2+} and certain species of bacteria strongly increase the rate at which Mo reacts with sulfide and precipitation occurs. If corroborated through further analyses, this initial finding that Mo-sulfide precipitation is iron-dependent and/or biologically mediated may reshape our understanding of ancient reconstructions using Mo geochemical proxies. Moreover, the planned compositional and structural analyses of the Fe-Mo-sulfides will illuminate the mechanisms behind the reaction and precipitation pathways involved and further our understanding of these geochemically, biologically, and industrially significant materials.