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Project Title: Influence of iron sulfide phase on the incorporation of Mo in marine sediments

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Molybdenum (Mo) in marine sediments is commonly used as a proxy for measuring past anoxic and sulfidic conditions.¹ To best interpret Mo in marine sediments, we must understand the manner in which it became incorporated (authigenic enrichment) and whether it might be susceptible to return to the aqueous phase (diagenetic loss). Recent work has pointed to several possible pathways for Mo accumulation, including Fe-dominated pathways,² and pathways that might instead involve organic carbon,³ with ultimate accumulation as Mo(IV)-species.^{3c} It is critical to determine which process(es) might control the initial removal of Mo from marine waters and whether that initial removal process is suitably inert to safeguard against diagenetic loss.

This proposal is aimed at understanding the adsorption of Mo onto mackinawite (FeS), the most kinetically favorable iron sulfide that forms in low-temperature aqueous environments, and the subsequent effect of transformation to greigite (Fe₃S₄) and pyrite (FeS₂). We hypothesize that the incorporation of Mo in sulfidic sediments must be interpreted in the context of the phase transformations that occur to generate pyrite. To test this, we are investigating whether mackinawite provides for the earliest removal of Mo to the solid phase (Figure 1). Upon understanding initial Mo accumulation routes, we seek to track Mo retention through subsequent phase transitions including the solid-state conversion of mackinawite to greigite and their dissolution and reprecipitation to form pyrite, which could provide pathways for diagenetic loss of previously incorporated Mo. Ultimately, this work should provide more accurate interpretations of Mo concentrations in marine sediments while also answering the broader question of the relative importance of iron sulfides in Mo sequestration.

Research during year two of this grant focused on three approaches to MoS₄²⁻ adsorption. The first approach involved synthesizing mackinawite, isolating and characterizing the material, and then adding MoS₄²⁻ to the material in a subsequent experiment to quantify Mo adsorption. The second approach instead involved the synthesis of a mixture of mackinawite and greigite, followed by isolating and characterizing the material, and the subsequent addition of MoS₄²⁻. The third approach attempted to better simulate environmental conditions – the synthesis of mackinawite followed by the near-immediate addition of MoS₄²⁻. It was hypothesized that the third method would more readily adsorb MoS₄²⁻ due to the likely nanoscale sizing and greater surface area. Solids were characterized with powder X-ray crystallography (PXRD) and transmission electron microscopy (TEM) at F&M and further characterized by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) at the Materials Characterization Laboratory at Penn State University.

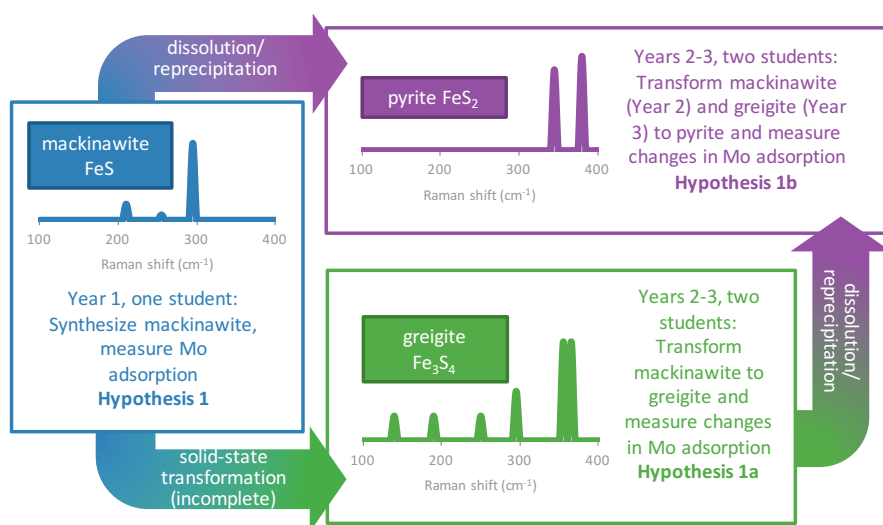


Figure 1. A representation of the relationship between these three iron sulfide phases and how they will be examined to test hypothesis 1. For each phase, a Raman spectrum⁴ is given to demonstrate the ability to differentiate the phases.

New insight has been gained into the Mo-adsorption to iron sulfide phases during year two. Adsorption following the first synthetic approach resulted in a clear adsorption isotherm of MoS_4^{2-} to mackinawite that is similar to that observed for a mixture of mackinawite and greigite. Mo adsorption to the mackinawite surface or the mackinawite/greigite mixture occurred to a greater extent relative to our earlier work on MoS_4^{2-} adsorption to pyrite.⁵ Adsorption following the third approach also resulted in the adsorption of MoS_4^{2-} to the mackinawite surface. Characterization of the solid showed the adsorbed sample (with added MoS_4^{2-}) had a greater amount of mackinawite structure relative to the control (with no added MoS_4^{2-}), suggesting a possible role for Mo in the formation of crystalline mackinawite. XPS confirmed the presence of Mo on the surface of the adsorbed samples in both oxidized [Mo(VI)] and reduced [Mo(IV)] forms. Upon iron sulfide transformation, the mackinawite formed a mixture of greigite and pyrite irrespective of the amount of adsorbed Mo. These results confirm the removal of Mo with the formation of the most kinetically favorable iron sulfide regardless of the experimental approach and prior to the formation of pyrite (Figure 1, hypothesis 1). The subsequent transformation of mackinawite to greigite and pyrite can be somewhat controlled with heat. Results suggest a preference for pyrite formation upon heating mackinawite but more work needs to be done to quantify the potential loss of Mo during this transformation (Figure 1, hypothesis 1b).

This project has continued to solidify the collaboration between the PIs. Dr. Morford has guided the experimental design, the aqueous phase analyses, and the connection to the geochemical literature, overseeing student work in her laboratory. Dr. Plass has provided extensive expertise regarding solid phase characterization through using instrumentation at F&M (PXRD, TEM) and at Penn State (Raman, XPS), overseeing student instrument use and their interpretation of data. Both faculty members have gained new perspectives through the background provided by the other which will be the impetus for new ideas and future plans. Students have been continuously and extensively involved in this project both during the academic year for course credit and during the summer, as listed in the personnel report. Students presented their results at weekly group meetings to gain a broader perspective while also having individual meetings with both PIs to address questions and determine further avenues. This summer, students also participated in a group meeting with faculty and research students from neighboring institutions, in which they practiced giving elevator talks and discussing their work with non-experts. In addition to writing summer research papers, the research students presented their research posters at F&M's Fall Research Fair and one student also presented her research orally at the Intercollegiate Student Chemists Convention at Gettysburg College. Students will continue to present in these venues during the upcoming year.

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