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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 further diagenetic changes.

This proposal is aimed at understanding the effects of formation and transformation of iron sulfide phases—mackinawite (FeS), greigite (Fe₃S₄), and pyrite (FeS₂)—on the ultimate incorporation of Mo into sulfidic sediments. 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, the most kinetically favorable iron sulfide in low-temperature aqueous environments, provides for the earliest removal of Mo to the solid phase and whether Mo-Fe-S mineral phases are formed that could contribute to Mo accumulation in sulfidic sediments (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.

Recent progress includes identifying the influencing factors on the synthesis of mackinawite. We have explored synthetic pathways, identifying those that result in the most crystalline mackinawite that is also stable and resistant to oxidation over time as characterized with powder X-ray crystallography (PXRD) and scanning electron microscopy-energy dispersive spectroscopy (SEM/EDS). Controlling the Fe:S mole ratio (2:3) in combination with heating and stirring provided the best mackinawite, although we are continuing to explore methods that vary the starting reactants.

New insight has been gained into the Mo-adsorption to iron sulfide phases. Using the mackinawite for subsequent adsorption experiments at pH 5.9, the addition of tetrathiomolybdate (MoS₄²⁻) resulted in the retention of mackinawite in both the control (no added Mo) and the adsorbed samples (with added Mo) as determined by PXRD. However, Mo adsorption to the mackinawite surface occurred to a greater extent relative to our earlier work on MoS₄²⁻ adsorption to pyrite. These results confirm the removal of Mo with the formation of the most kinetically favorable iron sulfide 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 whereas stirring appears to destroy the crystallinity of the synthesized iron sulfide. Initial results suggest a preference for pyrite formation upon heating mackinawite and the potential for some control on the iron sulfide phase change dependent on the extent of adsorbed Mo (Figure 1, hypothesis 1b).

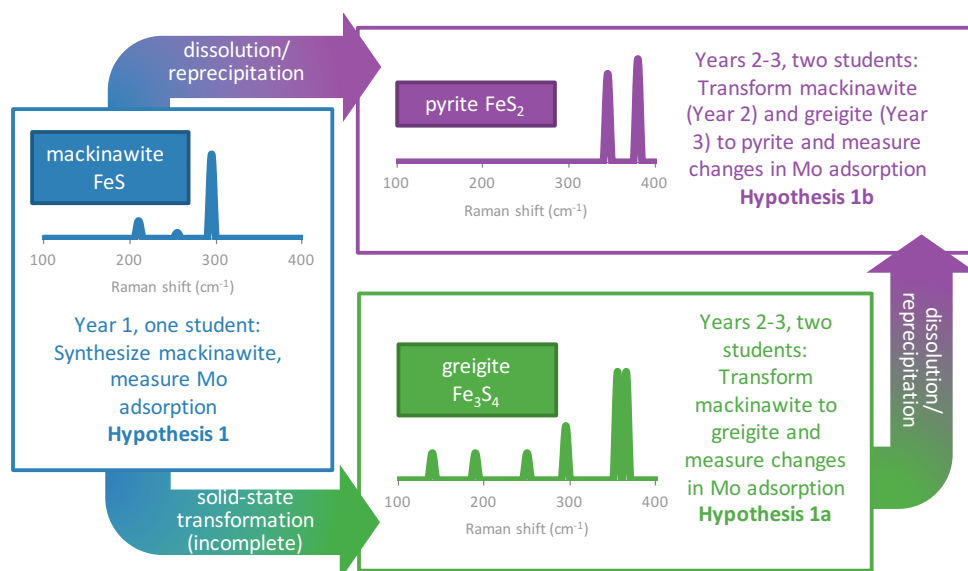


Figure 1. A representation of the relationship between these three iron sulfide phases and how they will be examined to test hypothesis 1. For each phase, a Raman spectrum⁴ is given to demonstrate the ability to differentiate the phases.

This project has solidified collaboration between the PIs. Dr. Morford has guided the aqueous phase analyses and connection to geochemical literature while Dr. Plass has provided extensive expertise regarding solid phase characterization through using instrumentation at F&M (PXRD, SEM/EDS, TEM) and at Pennsylvania State University (Raman). Both faculty members have gained new perspectives through the background and perspective provided by the other, which has already resulted in a successful proposal (American Philosophical Society) and will be the impetus for new ideas and future plans. Students have been continuously and extensively involved in this project, as listed in the personnel report. Students present their results at weekly group meetings to gain a broader perspective while also having individual meetings with each PI to address questions and determine further experiments. During Summer 2017 and 2018, students presented their work at a research group meeting at the Pennsylvania State University and toured the Materials Characterization Lab where their samples were analyzed using Raman spectroscopy. In addition to writing periodic research papers, the summer students have presented research posters at Franklin & Marshall's fall semester research fairs and Kate Myers orally presented her research on this topic at the Intercollegiate Student Chemists Convention at Elizabethtown College in April 2018.

References

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