The synthesis of iron-sulfide phases and the incorporation of Mo

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The incorporation of molybdenum (Mo) in marine sediments makes it a useful proxy for past sulfidic conditions. Mackinawite (FeS) is the most kinetically favorable form of iron sulfide and may provide for the earliest removal of Mo to the solid phase[1]. However, the effect on authigenic accumulation of Mo due to subsequent FeS transformation to greigite (Fe_3S_4) and pyrite (FeS_2) must be understood. To properly interpret the appearance of Mo with the pyrite phase in sediments[2], we must understand both the manner in which authigenic Mo accumulation occurs and whether it is susceptible to diagenetic loss during mineral transformation.

Our work has shown that the greatest adsorption of Mo occurs when tetrathiomolybdate is equilibrated with amorphous FeS, whereas less adsorption is apparent when Mo is present as molybdate. Furthermore, adsorption of tetrathiomolybdate drastically decreases when FeS is synthesized with increased crystallinity, which may explain previously observed results[1]. The extent of previously adsorbed tetrathiomolybdate appears to change as FeS undergoes transformation. The solid-state transformation pathways of Fe-S phases are also altered in the presence of adsorbed tetrathiomolybdate. This effect may be similar to the accelerated nucleation of FeS_2 when Ni is present[3] and has implications for the interpretation of Mo-FeS_2 covariation. Whereas we have previously examined the adsorption of Mo to infer past conditions in Fe-S chemistry, we might instead consider whether the adsorption of tetrathiomolybdate might be exerting a measure of control over Fe-S mineral formation.

[1] Helz *et al.* (2004) *Environ. Sci. Technol.* **38,** 4263-4268. [2] Huerta-Diaz and Morse (1992) *Geochim. Cosmochim. Acta* **56**, 2681-2702. [3] Morin *et al.* (2017) *Geochem. Persp. Let.* **5**, 6-11.