

Inorganic Fixation of Molybdenum

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Knowledge of the factors controlling Earth's redox history may prove useful in developing strategies for adapting to the consequences of anthropogenic changes upon the aquatic environment. The geochemistry of Mo offers a means to this knowledge, but unlocking the full potential of Mo requires a precise definition of the chemistry leading to its final burial. Sulfidic ($\text{H}_2\text{S} > 10^{-5} \text{ M}$) test solutions containing Fe^{2+} and MoS_4^{2-} rapidly yield colloidal Fe-Mo-S phases. Initially, $\text{FeMo}^{\text{VI}}\text{S}_4(\text{s})$ appears to form; $K_{\text{sp}} = 10^{-14.95}$ is calculated for this phase. Within hours, $\text{FeMo}^{\text{VI}}\text{S}_4$ undergoes S^{2-} ligand-induced reduction and irreversibly transforms to a similar product but containing Mo in a +IV oxidation state. XAFS data imply that the solid is a cuboidal cluster and yields coordination numbers and interatomic Mo-S and Mo-Fe distances consistent with those obtained for the form of Mo present in Lake Cadagno sediments¹ as well as Phanerozoic black shales². These data and quantitative elemental analyses on selected precipitates point to cuboids with an $\text{Fe}_2\text{Mo}_2\text{S}_4^{4+}$ core coordinated by external S_2^{2-} ligands. The poor symmetry of such a structure may explain why precipitates in our test solutions resist crystallization. Jordisite, a mineral nominally described as amorphous MoS_2 , actually appears to contain essential iron according to published analyses. Thus, jordisite may be a naturally-occurring mineral that shares similarities with our synthesized solids. A thermodynamic model has been developed that demonstrates the prevailing pH and HS^- concentrations in contemporary anoxic basins are sufficient to cause precipitation of much of the dissolved Mo in seawater. The model also indicates that reported correlations between Mo and organic carbon in black shales are largely explained by biological sulfate reduction which is itself fuelled by organic matter and controls the pH and dissolved sulfide concentrations that ultimately dictate Mo uptake within euxinic water columns and pore waters.

1. Dahl, T.W.; Chappaz, A.; Fitts, J.P.; Lyons, T.W. (2013). *Geochim. Cosmochim. Acta* **103**, 213-231.
2. Helz, G.R.; Miller, C.V.; Charnock, J.M.; Mosselmans, J.F.W.; Patrick, R.A.D.; Garner, C.D.; Vaughan, D.J. (1996) *Geochim. Cosmochim. Acta* **60**, 3631-3642.