

Formation of Fe-Mo-S solid(s): Possible sequestration vehicle

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Coastal anoxia is a proliferating environmental problem. Knowledge of the controls on anoxic incidents may assist in creating strategies for mitigating dead zone development. While the geochemistry of Mo may provide the means to acquiring this knowledge, interpreting Mo records is stymied by an incomplete understanding of Mo depositional processes. Although thiomolybdates ($\text{MoO}_{4-n}\text{S}_n^{2-}$; $n = 0-4$) are believed to play a role in Mo removal, the final sedimentary product remains unknown. Some authors¹ suggest Mo deposition ultimately involves uptake of $\text{MoO}_{4-n}\text{S}_n^{2-}$ by pyrite surfaces. A more recent theory² holds that Mo removal involves precipitation of a distinct Fe-Mo-S solid (e.g., $\text{Fe}_5\text{Mo}_3\text{S}_{14}$). This view is largely based on the observation that anoxic basins frequently display dissolved Mo profiles which decrease toward a unique limiting concentration with depth, implying saturation with an insoluble phase. Because dissolved Re profiles often appear to mimic those of Mo, a Fe-Mo-S solid has also been posited³ as a possible vehicle for Re sequestration via a co-precipitation mechanism. Given the potential involvement of a Fe-Mo-S solid in the burial of two paleoredox proxies, research which aims to characterize such solids is imperative. This research seeks to begin defining the chemistry controlling formation of Fe-Mo-S solids. Buffered test solutions initially containing 70 μM Fe^{2+} , 70 μM MoS_4^{2-} , and $\Sigma\text{S}^{2-} = 20$ mM at pH = 8.5 experience near-quantitative loss of ΣFe and ΣMo , implying precipitation of an Fe-Mo-S phase(s)⁴. A small portion (~ 1 μM) of ΣFe and ΣMo is present as aqueous Fe-Mo-S complexes similar to those described elsewhere⁴. Ongoing experiments are designed to quantify stability constant(s) for the solid(s).

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