

Molybdenum Burial Mechanism: Iron-Sulfide Pathway

TRENT P. VORLICEK^{1*}, GEORGE R. HELZ², ANTHONY
CHAPPAZ³, PAKOU VUE¹ AND AUSTIN VEZINA¹

¹Dept. of Chemistry and Geology, Minnesota State
University, Mankato, MN 56001, USA,

(*correspondence: trenton.vorlicek@mnsu.edu)

²Dept. of Chemistry and Biochemistry, University of
Maryland, College Park, MD 20740, USA

³Institute for Great Lakes Research –Central Michigan
University, Mount Pleasant, MI 48859, USA

Paleoredox interpretations from rock records are hampered by an incomplete understanding of the chemistry controlling Mo burial. One of the major pathways to Mo removal is posited [1] to involve precipitation of a unique but unconfirmed Fe-Mo-S phase. We aimed to characterize any such phase(s) formed via reaction between freshly precipitated FeS and MoS₄²⁻ in mildly alkaline and sulfidic solutions. [2] Initially, test solutions produce a colloidal Mo(VI) solid; thermodynamic data identify the solid as FeMoS₄ with $K_{sp} = 10^{-14.95}$. Elemental analyses of precipitates aged in solution >4 days imply that the natal Mo(VI) solid subsequently undergoes internal reduction, yielding a Mo(IV) solid of analogous composition; XANES data confirms the presence of Mo(IV). Addition of concentrated HNO₃ immediately dissolves the Mo(IV) solid; the solid is insoluble in 1 M HCl. These results weaken support for pyrite as the inferred [3] host of Mo in sulfidic sediments. The Mo(IV) solid partially dissolves in 1 M NaOH; leaching of Mo by NaOH can not be used [4] on its own as evidence of organic-bound Mo in sulfidic sediments. EXAFS spectra point to precipitates consisting of colloidal Mo(IV) polymers with cuboidal Fe₂Mo₂S₄⁴⁺ cores coordinated by two S₂²⁻ ligands. A rare mineral, Jordisite, appears to be a related, though more Mo-rich, phase. Thermodynamic modeling suggests that FeMoS₄ can form in euxinic waters like that of the Black Sea. We propose that colloids similar to FeMoS₄ could assist in accounting for Mo accumulation within euxinic sediments and black shales. [5]

[1] Helz, G.R. et al. *Chem. Geol.* **2011**, *284*, 323-332.

[2] Vorlicek, T.P. et al., *Earth Space Chem.* DOI: 10.1021/acsearthspacechem.8b00016

[3] Huerta-Diaz, M.A. and Morse, J.W. *Geochim. Cosmochim. Acta.* **1992**, *56*, 2681-2702.

[4] Nissenbaum, A. and Swaine, D.J. *Geochim. Cosmochim. Acta* **1975**, *40*, 809-816.

[5] Helz, G.R. et al. *Geochim. Cosmochim. Acta.* **1996**, *60*, 3631-3642.