# Molybdenum burial with organic matter in sulfidic settings

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Molybdenum is a redox sensitive element utilized to track the presence and abundance of $O_2$ and $H_2S$ in ancient environments from the sedimentary record. Yet, our ability to make robust interpretations from elemental, isotopic and structural analyses rests on how well we understand the scavenging and preservation mechanism in modern sulfific sediments. In a seminal paper from 1996, George Helz and colleagues highlighted the need for understanding the chemical mechanism responsible for concentrating molybdenum in euxinic sediments [1]. They concluded that both organic matter and iron sulfides can fulfill the role of scavenging agent. Helz and others have since shown that inorganic removal pathways with Fe-sulfide minerals are efficient [2,3,4] and produce insoluble Mo(IV)-Fe sulfides with XAFS spectra similar to the amorphous Mo-sulfide phases found in euxinic sediments [5,6]. Still, the organic scavenging pathway has received much little attention.

Here, I present elemental and structural data from Mo precipitates in culture experiments with sulfate-reducing bacteria grown at four different Mo concentrations (0.1 to 2 mM) and neutral pH. The results show that Mo(VI) is reduced in the presence of particulate organic matter (represented by sulfate-reducing bacteria) [7]. Molybdenum was immobilized at the surface of both living cells and dead/lysed cells, but not in cell free control experiments. The cell- associated Mo precipitates contained little or no Fe, consisting of mainly Mo(IV)-sulfide compounds with XAFS spectra similar to natural euxinic sediments [6]. I conclude that Mo scavenging with organic particulates may operate in sulfidic settings, *e.g.* in parallel with Fe-assisted pathways.

The XAFS spectra of cell-associated precipitates are indistinguishable from the Mo-cofactor in all (~30), but one class (nitrogenase), of Mo enzymes, suggesting the same four basal Mo- S ligands (e.g., pterin side chains) and various ligands at the pole depending on Mo oxidation state (Mo=O, Mo-OH and Mo-S). This comparison gives important clues to the formation pathways at play both in culture experiments and in natural sulfidic environments.

[1] Bostick et al., *ES&T* 2003; [2] Freund et al., *GCA* 2016; [3] Helz et al., *ES&T* 2004; [4] Xu et al., *Chemosphere,* 2006; [5] Vorlicek et al. *E&SC* 2018; [6] Dahl et al. *GCA* 2013; [7] Dahl et al. *Geobiology* 2017.