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Revisiting Mo Burial Pathways: Speciation Reveals Weakly Sulfidic Complexity Beyond Euxinia

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In paleo-redox reconstructions, black shales with high molybdenum (Mo) enrichments and heavy δ^{98}Mo are commonly interpreted as strongly euxinic. This view assumes seawater molybdate (MoO_4^{2-}) undergoes thiolation (O→S substitution) to thiomolybdates, is removed efficiently, and yields sedimentary δ^{98}Mo values approaching open-ocean seawater (≈2.3‰) under near-quantitative burial. However, competing burial pathways can operate in parallel. Here we test whether combined bulk [Mo]–δ^{98}Mo signals uniquely diagnose strongly sulfidic conditions by adding Mo speciation constraints. We pair bulk Mo concentrations (and available isotopes) with micro-focused synchrotron spectroscopy (μ-XANES/μ-EXAFS) on two organic-rich black shale systems deposited under sulfidic bottom waters in contrasting depositional settings.

Across both systems, μ-XANES reveals mixed Mo oxidation states spanning Mo(VI) to Mo(IV), while μ-EXAFS spectra are dominated by Mo–O coordination with only minor Mo–S contributions. These data require multiple Mo hosts, demonstrating that even shales inferred as strongly euxinic from bulk geochemistry can retain incompletely sulfurized Mo. Rather than a monotonic "more H_2S → fully sulfurized Mo(IV)–S" burial model, the observations support heterogeneous sequestration into distinct pools, including association with sulfide mineral phases and organic matter. The discrepancy, in which bulk concentrations and isotope systematics imply efficient sulfidic removal while speciation reveals incomplete sulfidation, demonstrates that δ^{98}Mo-[Mo] pairs may overestimate the intensity and stability of euxinia when speciation is unconstrained. Integrating Mo speciation with bulk δ^{98}Mo provides a pathway-aware framework to refine redox reconstructions and to better leverage Mo as a tracer of weakly sulfidic systems, not just strong euxinia.