Thioanions, the forgotten ligands in sulfidic waters

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Many bio-essential trace elements, like Fe, Cu and Mo, form extremely insoluble sulfide minerals, which in principle could starve anoxic microbial ecosystems of critical micronutrients. This outcome is forestalled in part by formation of complexes that are soluble in sulfidic waters. Inorganic ligands responsible for preserving solubility include sulfides, poly-sulfides and thioanions. The last have been largely over-looked. New experimental data [1] as well as earlier studies [2] are used to explore how competition of Fe^{2+} and Cu^{+} for MoS_4^{2-}, as well as competition of MoS_4^{2-} and HS^{-} for both metals would be resolved in sulfidic waters. Thiomolybdate ligands have little effect on Fe solubility but significant effect on Cu in euxinic seawater. As(III) thioanions [3] will have a greater effect owing to their greater solubility, despite the tendency of As(III) to be oxidized to As(V) at intermediate H_2S concentrations. Thioanions have greatest impact at H_2S concentrations near oxyanion-thioanion equivalence points, which for various thioanion-forming elements range over several orders of magnitude. Higher sulfide favors HS^{-} over thioanion ligands. Inorganic clusters structurally related to the $MoFe_7S_9C$ cluster in nitrogenase are conjectured to have helped catalyze prebiotic syntheses of life's organic building blocks. The new data lend no support to the existence of such 3-D clusters as stable dissolved species. Instead linear Fe-Mo-S complexes are found. However the data hint that cuboidal clusters containing Mo(IV) occur as solids that might have been important as heterogeneous catalysts.

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