

The bioinorganic chemistry of the ancient ocean: the co-evolution of cyanobacterial metal requirements and biogeochemical cycles at the Archean-Proterozoic boundary?

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Recent evidence from the sulfur isotopic record indicates a transition ~2.5 billion years ago from an ocean chemistry first dominated by iron and then by sulfide. It has been hypothesized that the selection of metal centers in metalloenzymes has been influenced by the availability of metals through geological time, in particular as a result of large differences in the solubility of metals-sulfides. We examine the trace metal requirements and sensitivities of marine cyanobacteria and use recent stability constants to model the abundance and chemical speciation of metals across this chemical transition ~ 2.5 billion years ago. Two major results are reported here: (1) the marine cyanobacterial species studied thus far show trace metal preferences and sensitivities that are consistent with their evolution in a sulfidic marine environment, and (2) in an ancient ocean dominated by high fluxes and concentrations of iron, the relative availability of trace metals would have been similar to that of a sulfidic system - Fe > Mn, Ni, Co >> Cd, Zn, Cu - as a result of the formation of dissolved sulfide complexes. Thus, the formation of strong aqueous metal-sulfide complexes was likely as important as the precipitation of minerals in influencing the selection of metals in biology. These results suggest that marine biogeochemical cycles and marine bioinorganic chemistry have co-evolved, and that the evidence for this co-evolution has been preserved in the physiology and genomes of modern descendants of the early cyanobacteria. Genomic data from modern cyanobacteria will be interpreted in light of these results.