Trace Metal Interaction with Ferrihydrite: Application to Precambrian Biogeochemical Cycles

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Low atmospheric O_2 levels are thought to have led to a predominance of ferruginous conditions (Fe^{2+} rich) in the Precambrian ocean, evidence for which is found in the sedimentary record of iron formations (IFs). IFs are thought to have formed by chemical precipitation of metastable Fe-bearing precursor minerals followed by diagenetic transformation to stable minerals. One of the suggested precursors to the minerals assemblages in IFs is ferrihydrite (Fh), a hydrous Fe^{III} oxyhydroxide known to be reactive towards various trace metals. Thus, as long as Earth's oceans contained appreciable concentrations of Fe^{2+}, up to the late Neoproterozoic or early Paleozoic oxygenation of the oceans' interior, Fh likely played a role in regulating the trace-metal budget in the early ocean.

To test this hypothesis, we conducted experiments of trace metal (Ni, Zn, Cu, and Mo) uptake by Fh in ancient seawater-analog solutions, at a pH of 7.5 and at 25°C. To investigate both sorption and co-precipitation, experiments were conducted with Fh synthesized in advance and then exposed to the metals, or with Fh synthesized in the presence of the metals. The solids were identified by XRD, TEM and SEM, and trace metals were measured in both solids and supernatants on an Agilent 7700s ICP-MS.

Preliminary results indicate metal reactivity with Fh in the order Mo << Ni < Cu < Zn. Solid-aqueous equilibration times for these metals are about 24, 5, 5 and 0.5 hours, respectively. Mo, present in the experiments as molybdate ions, partitions negligibly onto Fh. In addition to a tendency of the metals to sorb to Fh, Cu and Zn partition more strongly into Fh when the Fh is precipitated in the presence of these metals. This suggests that Cu and Zn co-precipitate with Fe in the Fh, and we observe this over the entire range of experimental metal:Fe. Based on our results, Fh may have had a role in regulating the Precambrian concentrations of some trace metals, with implications for the chemical composition of Earth's oceans, for biological activity, and for geochemical proxies for the oxidation state of the ocean-atmosphere. Experiments to constrain the effect of other suggested precursors to IF mineral assemblages on trace metal budgets are ongoing.