Formation and Reactivity of Biogenic Iron Microminerals

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Radionuclides and heavy metals (e.g., U, Cr and Ni) pose significant environmental toxicity and health hazards in the subsurface at many of the DOE sites involved in the processing of nuclear materials. The fate and transport of these contaminants are controlled to a large extent by redox chemistry of saturated subsurface sediments and by the nature of the mineral phases that are present. Dissimilatory iron-reducing bacteria catalyze many of the reduction reactions in anoxic, non-sulfidogenic environments and are recognized as important agents impacting the migration of metal contaminants in groundwater. We have examined the effect of a variety of environmental parameters and the influence of bacterial metabolism and surfaces on the biogenic transformation of hydrous ferric oxide (HFO) by iron-reducing bacteria.

To evaluate the effect of pH on the products of HFO transformation, 20 mM Fe(III) as HFO was suspended in buffered, anaerobic media with pH values ranging from 5.5 to 8.5. In the absence of CO_2 and with H_2 supplied as the electron donor, *Shewanella putrefaciens* strain CN32 reduced iron in HFO at all pH values tested except 8.5. The transformation products were influenced directly by initial pH. More than 8 $mmol^{-1}$ of the 20 mmol L^{-1} Fe(III) provided as HFO were reduced at pH values below 6. The crystalline iron oxide goethite was the dominant mineral phase produced during reduction. Biogenic Fe(II) was distributed between the aqueous and mineral phases. Magnetite co-precipitated with goethite at pH 6.5, while magnetite was the dominant phase at pH values >7.0.

Biominerals produced during HFO reduction may be influenced by microenvironmental conditions at the cell-mineral interface. To test this hypothesis, CN32 cells were enrobed in porous sodium alginate beads to physically separate them from the HFO. Anthroquinone-2,6disulfonate (AQDS), an analogue for humic acids, was provided as a soluble electron shuttle between the cells and the HFO. Enrobed cells reduced more than 5 mmol L^{-1} of the initial 20 mmol L^{-1} Fe(III) at pH 5.5 and 6.0 and goethite was the dominant mineral produced; these results were similar to the cell-mineral interface experiments. At pH 6.5, hematite co-precipitated with goethite without forming magnetite. These results contrast with those from experiments where cells were in direct contact with HFO. We hypothesize that iron reduction increases pH at the cell-mineral interface and that this microenvironment favors the formation of magnetite over other crystalline oxide phases. This hypothesis is receiving further investigation.

The biogenic transformation of HFO into goethite and hematite under iron-reducing conditions has until now gone unreported. This transformation has important implications for the bioavailability of Fe(III) and overall biogeochemistry of anoxic sediments and subsurfaces. Substitution of select heavy metal and radionuclides into the crystal structure of these minerals may provide a mechanism for immobilizing the contaminants. We continue to focus upon the role of the cell-mineral interface in directing the formation of biogenic minerals and how these controls may be manipulated for the in-situ stabilization of contaminants.