Insights into Fe and S Biogeochemistry in Redox Dynamic Environments

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Biogeochemical cycling of Fe and S in the terrestrial subsurface affects contaminant mobility, nutrient availability, and groundwater chemistry. Predicting the flow of electrons through these elements requires a fundamental, molecular-level understanding of the coupled biotic and abiotic processes responsible for these transformations.

Natural Fe^{III} oxides typically contain a range of trace elements that can include P and we examined the bioreduction of lepidocrocite and maghemite containing 0–3 mass% P. Kinetic dissolution studies showed congruent release of Fe and P, indicating that the P in these materials was incorporated within the particles. In the absence of P, lepidocrocite was rapidly and stoichiometrically reduced to magnetite by *Shewanella putrefaciens* CN32, and over time the magnetite was partially transformed to chukanovite. Doping with 0.2–0.7 mass% P significantly inhibited the initial reduction of lepidocrocite but ultimately resulted in greater Fe^{II} production and the formation of carbonate green rust; doping with 3.0% P resulted in the formation of green rust and vivianite. However, the bioreduction of both maghemite and P-doped maghemite resulted in solid-state conversion to magnetite, with subsequent formation of chukanovite.

In separate bioreactor experiments, we show that at pH 9, dissimilatory metal-reducing bacteria (DMRB) can respire S^0 but not goethite because the reduction of the latter is not thermodynamically favorable under oligotrophic conditions. Because the reaction of HS^- with Fe^{III} minerals produces S^0, DMRB in alkaline aquifers may require active respiration by sulfate-reducing bacteria (SRB) to respire. Under these conditions, Fe^{III} reduction will proceed via S^0–mediated electron-shuttling pathways through a mutualistic partnership between DMRB and SRB rather than the direct enzymatic reduction of Fe^{III} minerals by DMRB alone.

Accurate determination of Fe^{II} concentrations and distribution is key to understanding iron redox processes in environmental systems. Acid extraction followed by colorimetric assay is a widely used approach for determination of Fe^{II} in soil and sediment samples that under sulfidogenic conditions can contain both metal sulfides and Fe^{III} oxides. Our comparisons of Fe^{II} concentrations determined by 0.5 N HCl extraction/colorimetric assay (ferrozine) and XAFS analysis showed that the presence of sulfide resulted in overestimation of Fe^{II} concentrations by acid extraction by a factor of 1.5 to 3 depending on the Fe^{III} oxide; the extent of Fe^{II} overestimation was higher with ferrihydrite and lepidocrocite than with goethite. These results illustrate the need for caution when using acid extraction/colorimetric analysis to determine Fe^{II} concentrations in samples containing Fe^{III} oxides and ferrous sulfide.