SLAC-SFA: Structural Basis for Ferrihydrite Reactivity in Subsurface Environments

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Ferrihydrite is a reactive and relatively abundant Fe-oxyhydroxide phase that coats subsurface sediments at redox transition zones in aquifers, such as occur in and around artificially and naturally bioreduced zones, hyporheic boundaries, and near the surface of the water table. In these environments, ferrihydrite plays important roles in mediating the cycling of carbon, sulfur, and contaminants such as uranium. The reactivity of ferrihydrite derives from its exceptionally large surface area, high sorptive capacity for organic carbon, metal ions, silicate and phosphate, and from its poor crystallinity and metastability. Ferrihydrite forms in the presence of natural organic matter (NOM, *e.g.*, humic and fulvic substances), aluminum and silica, all of which are common in aquifers and interfere with its crystallization. These interactions profoundly modify the reactivity and stability of ferrihydrite. In spite of its importance, a structural basis that conceptually and quantitatively relates these constituents to the behavior of ferrihydrite and linked elemental cycles in aquifers is lacking. This portion of the SLAC SFA is addressing the fundamental molecular- and nano-scale physico-chemical factors that control ferrihydrite reactivity in complex subsurface environments.

We have evaluated the structural and physico-chemical characteristics of ferrihydrite formed in the subsurface at the Rifle, CO IFRC site. Rifle ferrihydrite was found to be closely associated with Si and NOM. Synchrotron-based X-ray diffraction (XRD), X-ray total scattering, and Pair Distribution Function (PDF) analysis show that Rifle ferrihydrite is smaller in size and more structurally disordered than pure synthetic ferrihydrite. When structural details are combined with compositional analyses, we find that NOM and Si appear to be responsible for these structural perturbations. Surprisingly, Rifle ferrihydrite bears close structural resemblance to ferrihydrites formed in natural environments ranging from acid mine drainage systems to deep-sea microbial mats, which also contain significant amounts of NOM, Si, and/or Al.

We have subsequently explored the individual and combined effects of organic matter, Si, and Al on synthetic ferrihydrite structures. In the case of Al, X-ray scattering/PDF, scanning transmission X-ray microscopy, and nuclear magnetic resonance (NMR) spectroscopy show that up to ~25 mol. % Al^{3+} replaces Fe^{3+} in octahedral sites in the ferrihydrite structure. Si, on the other hand, does not appear to structurally incorporate in ferrihydrite but rather forms as a poorly ordered Si-rich surface coating. Si strongly impacts the crystal size of ferrihydrite and increases lattice strain. Finally, we have used hydroxybenzoic acids as well-defined model substances to probe the impact of structural organics on the formation and structure of ferrihydrite. Here, we have found that hydroquinone structures in particular strongly impact ferrihydrite formation and size, as well as also increasing strain. This information is providing a fundamental scientific basis to account for ferrihydrite stability and reactivity in sediments.