Introduction

Biorreductive transformations of iron (hydr)oxide minerals are critically important processes controlling the fate and transport of contaminants in soil and aquifer systems. Heterogeneity arising from both chemical and physical conditions can lead to various biorreductive products of iron oxides and will additionally alter reactions controlling the partitioning of hazardous elements such as uranium. We are presently exploring chemical and mineralogical transformations within physically complex material having a range of pore-size distribution and chemical environments. Here we discuss the impact of calcium on the reactive transport of uranium and the spatial heterogeneity in iron hydroxide mineralization and concomitant uranium reduction along a diffusive flow path.

Iron Biomineralization

Biorreduction of ferrihydrite by dissimilatory iron reducing bacteria is driven largely by dissolved concentrations of ferrous iron (Gachérie et al., 2002; Benner et al., 2002; Hansel et al., 2003). A complex mineral assemblage results that is dominated by the production of goethite and magnetite with small quantities of green rust (unless specific ligands, such as sulfide, are enhanced in concentration). As a consequence, adsorption properties will be modified appreciably with the shift in mineralogy and the development of reactive ferrous iron bearing phases will have important ramifications on reductive stabilization. While the extent of contaminant adsorption on ferrihydrite (hydr)oxides will generally decrease upon biomineralization (a consequence of the crystallization and diminished surface area), the potential for reductive stabilization will be enhanced.

Spatial and Geochemical Heterogeneity Impacts on Iron Biomineralization and Uranium Sequestration

Reduction of uranyl, U(VI), by S. putrefaciens proceeds rapidly in batch culture. However, imparting an important criterion on uranyl reduction are the aqueous and solid matrices. Owing to alterations controlling the formation of highly stable Ca-uranyl-carbonato complexes, which will dominate the aqueous speciation of uranium at circumneutral pH values (right panel), reduction can be severely limited (Brooks et al., 2003). With alternate electron acceptors available, e.g., ferric-iron, uranyl reduction may be completely inhibited—a possibility we test here.

Heterogeneity in Biomineralization Processes

While biorreduction of ferrihydrite will increase geochemical heterogeneity, physical complexity (heterogeneity) will be a dominant factor controlling biorreductive process. Transport limitation and size-exclusion within structure media (as depicted below for ORMIL) will lead to diffusive gradient reaction paths. A cross-section flow field (a) containing a low hydraulic conductivity (low-K) zone (top) leads to the development of 2 mineral phases (magnetite and goethite, shown in bottom two panels) during reductive transformation of iron oxides. The simulations is made using MIN3P (Mayer et al., 2002) and iron biomineralization parameters revealed in Benner et al. (2002) and Hansel et al. (2003b). (b) Schematic diagram of the low-K region modeled in (a) depicting the biogenic products and impact on uranium sorption, reduction, and transport (magnification increases from right to left and top to bottom).

Conclusions

Natural environments possess physical and chemical heterogeneity of varying degrees. Owing to diffusive transport of organic carbon, biomineralization of iron oxides will result in a complex assemblage of products within soils and sediments, while uranium reduction will dominate near advective-flow regimes. Furthermore, uranium reduction will be critically dependent on both the aqueous and solid-phase chemistry of the environment. Formation of a calcium-uranyl carbonate complexes retard U(VI) reduction with total inhibition occurring when ferric (hydr)oxides are present.

References