Spatial and Geochemical Heterogeneity Impacts on Iron Biomineralization and Uranium Sequestration

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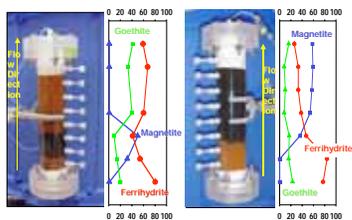
Introduction

Bioreductive transformations of iron (hydr)oxides are a critically important processes controlling the fate and transport of contaminants in soil and aquifer systems. Heterogeneity arising from both chemical and physical conditions will lead to various biomineralization 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
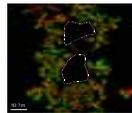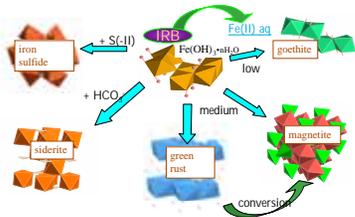
Biomineralization of ferrihydrite by dissimilatory iron reducing bacteria is driven largely by dissolved concentrations of ferrous iron (Zachara et al., 2002; Benner et al., 2002; Hansel et al., 2003). A complex mineral assemblage results that is dominated by the production of goethite and magnetite 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 ferric (hydro)oxides will generally decrease upon biomineralization (a consequence of the crystallization and diminished surface area), the potential for reductive stabilization will be enhanced.

Uranyl Reductive Stabilization

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 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.
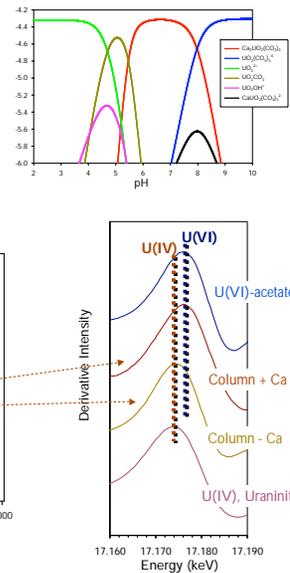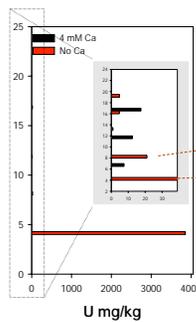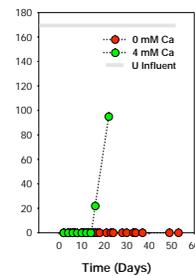
Uranyl reduction within ferrihydrite coated sands inoculated with *S. putrefaciens* strain CN32 undergoes rapid and extensive reduction (see above, left). Breakthrough is not observed within 52 d of reaction (in fact, dissolved U(VI) does not even progress beyond the bottom sampling port over this time period). Utilization of U(VI) impedes, albeit only slightly, Fe(III) reduction and leads to the development of goethite. In contrast, when equilibrated with calcite at pH 7 (2.9 mM Ca), uranyl reduction is greatly retarded and U(VI) breakthrough is observed after 15 d (above, left). Owing to reductive precipitation of uranium (above, right) in the absence of calcium, nearly 4 g/Kg of U are deposited within the initial section of the flow-field (above, middle). In contract, uranium remains in the hexavalent state with calcium present (above right) and minimal uranium, as compared to columns without calcium, is incorporated into the solid phase (above, middle). Lower calcium concentrations, down to 0.5 mM, have similar inhibitory effects on uranyl reduction.

0 mM Calcium
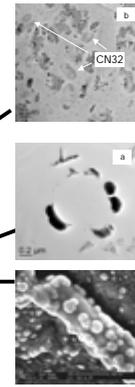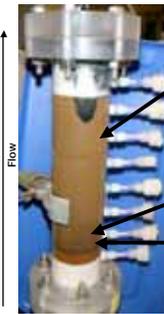
Transmission electron micrographs of column solids illustrate differing bacteria-to-uranium spatial relationships along the flow-path. Extra-cellular precipitation of uraninite on the bacterial cell surface is noted at the inlet (a). Cells in the down-flow column section illustrate no visible uranium precipitation (which is minimal, 5 mg/Kg) in associated with the cells (b).

Scanning Electron micrograph (c) showing *S. putrefaciens* on the surface of a silica sand grain. This cell exhibits extra cellular precipitates of uraninite (U(IV)).
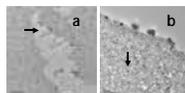
4 mM Calcium
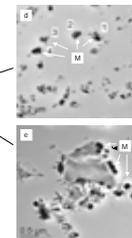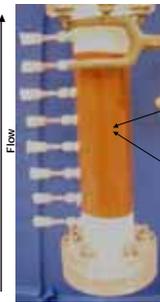
Transmission Electron Micrographs of solids from uranium enriched (1 mg/ Kg) zones in columns containing calcium illustrating magnetite (24% by wt) formation and the concomitant retention of uranium.

Heterogeneity in Biomineralization Processes

Biomineralization of ferrihydrite resulting from the dissimilatory iron reducing bacterium *S. putrefaciens* strain CN32 at different advective flow velocities. The right panel above (from Benner et al., 2002) illustrates a mature column and an extensive magnetite domain that is truncated with a decrease in flow rate by a factor of 4 (left panel). The two columns have identical initial conditions; the single difference is flow-rate, illustrating the importance of hydrodynamics on biomineralization processes.

A further consequence of the biomineralization process is the development of micro-scale heterogeneity. As illustrated in the TEM images below, the original ferrihydrite substrate transitions into a complex assemblage of goethite (laths shown in "a") and magnetite (arrows and upper surface in "b").

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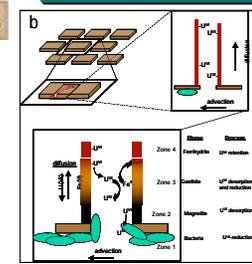
A cross-section flow field (a) containing a low hydraulic conductivity (low-K) zone (top) leads to the development of 2 mineral phases (magnetite and goethite, shown in bottom two panels) during reductive transformation of iron oxides. The simulations is made using MIN3P (Mayer et al., 2002) and iron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

Conclusions

Natural environments posses physical and chemical heterogeneity of varying degrees. Owing to diffusive transport of organic carbon, biomineralization of iron minerals will results 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 carbonato complexes retard U(VI) reduction with total inhibition occurring when ferric (hydr)oxides are present.

References:
Benner, S.G., C.H. Hansel, B.W. Wielinga, T.M. Barber, and S. Fendorf. 2002. Environ. Sci. Technol. 36: 1705.
Brooks, S.C., et al. 2003. Environ. Sci. Technol. 37: 1850-1858.
Hansel, C.M., S. Benner, Dohnalikova, A., R.K. Kukkadapu, and S. Fendorf. 2003. Geochim. Cosmochim. Acta 67: 2977-2992
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