

INTRAGRANULAR DIFFUSION OF URANIUM IN SANDS

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RESEARCH OBJECTIVES

Transport of solutes, including contaminants, in soil and groundwater systems can be complex because of the very wide range of time scales associated with basic processes. Although this complexity can be overlooked in volume-averaged measurements of sufficient size (Figure 1a), more mechanistic understanding of reactive transport requires several progressively finer levels of resolution. One such basic scale in porous media is defined by sizes of individual grains. Intragranular diffusion is often invoked to explain slow mass transfer and reaction rates. Our study uses synchrotron x-ray fluorescence microtomography to directly measure intragranular uranium(VI) diffusion in sediments from Oak Ridge National Laboratory, a DOE facility where uranium (U) contamination has occurred.

APPROACH

Experiments involved exposing 50 to 100 μm sand grains from an uncontaminated area of Oak Ridge to U(VI) solutions, and then obtaining fluorescence microtomographs of intragranular U distributions at different times. The sand grains and U(VI) solutions were contained in sealed micropipette tips and scanned at GSECARS beamline 13ID-C, Advanced Photon Source. In addition to fluorescence microtomography, we applied micro-x-ray absorption near-edge structure (μ -XANES) spectroscopy to determine the oxidation state of U within grains.

ACCOMPLISHMENTS

Fluorescence microtomography maps of U were obtained in real time, over two days of intragranular diffusion. Two-dimensional maps within sands (5 μm resolution) revealed very heterogeneous migration of U into individual grains (Figure 1b). Rates of U uptake inferred from the fluorescence

maps of grains are consistent with time scales observed in bulk sorption experiments, indicating that intragranular diffusion is in fact the rate-limiting step. Micro-XANES spectra confirmed that U remained as U(VI) during intragranular sorption. Some spatial correlation between U and Fe was also indicated, as expected from the high sorption affinity of U(VI) to Fe(III)-oxide surfaces.

SIGNIFICANCE OF FINDINGS

These results provide proof that intragranular diffusion exerts a major influence on time scales needed for sorption equilibrium of U(VI) in sediments. The fact that most of the sorbed U(VI) in Oak Ridge sediments occurs in intragranular regions has important implications on its reactivity. If most of the U(VI) diffuses into intragranular regions, it does so through typically less than 100 nm pores that would exclude bacteria. Therefore, intragranular redox transformations of U could not occur via direct contact with bacteria, but instead through other redox active solids and solutes, including electron shuttles.

RELATED PUBLICATION

Tokunaga, T.K., J. Wan, J. Pena, S.R. Sutton, and M. Newville, Hexavalent uranium diffusion into soils from concentrated acidic and alkaline solutions. *Environ. Sci. Technol.*, 38, 3056–3062, 2004. Berkeley Lab Report LBNL-54910.

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