

## Environmental Transport of Plutonium: Biogeochemical Processes at Femtomolar Concentrations and Nanometer Scales

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A major scientific challenge in environmental sciences is to identify the dominant processes controlling actinide transport in the environment. This is particularly difficult for the light actinides (Pu and Np in this work) due to their complex redox chemistry. Unexpected observations of kilometer scale Pu transport have raised concerns regarding our understanding of the fundamental biogeochemical processes controlling Pu transport. As a result, the mission of LLNL's SFA has been to:

*Identify the dominant biogeochemical processes and the underlying mechanisms that control actinide transport (focusing on Pu and Np) in an effort to reliably predict and control the cycling and mobility of actinides in the subsurface.*

To date, our research has focused on the following five processes:

1. Sorption-desorption and surface mediated redox processes on mineral surfaces,
2. Complexation with organic matter and formation of ternary mineral-ligand-actinide complexes,
3. Pu-oxide precipitation in the presence and absence of mineral surfaces
4. co-precipitation and mineral phase alteration, and
5. direct and indirect microbial interactions.

Highlighted below are recent results (FY14) for each of the five processes investigated above:

- Identified Pu(IV/V) sorption linearity and quantified surface-mediated Pu(V) reductions rates on goethite, montmorillonite, and bentonite over an eight order of magnitude range in Pu concentration ( $10^{-7}$  to  $10^{-15}$  M).\*\*
- Began quantifying Pu sorption/desorption kinetics on goethite, montmorillonite and bentonite to assess field scale colloid-facilitated transport mechanisms (including surface mediated redox transformations).

- Identified the potential role of hydrogen peroxide at environmental concentrations in oxidizing and mobilizing Pu(IV).
- Evaluated the formation of aqueous Pu-NOM and ternary Pu-NOM-mineral complexes for fulvic acid, humic acid, and DFOB in the presence of gibbsite, goethite, and montmorillonite.\*\*
- Developed actinide NMR capabilities at LLNL to probe Np(VI) ligand exchange kinetics and identify the structure of Pu-DFOB complexes responsible for irreversible intercalation into montmorillonite.
- Determined the structure and stability of Pu nanoparticles on goethite as a function of time (3 months) and temperature (25°C and 80°C), and
- Characterized the behavior Pu(V/IV) on bound-EPS and EPS-free cell surfaces of *Pseudomonas* sp. strain EPS-1.\*\*

\*\*Three additional posters discuss our results in further detail.

New knowledge gained from this SFA is advancing our understanding of the behavior of actinides, providing DOE with the scientific basis for remediation and long-term stewardship of DOE's legacy sites and, more broadly, increasing our understanding of actinide behavior in environmental systems.