Subsurface Biogeochemistry of Actinides Scientific Focus Area

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Identifying biogeochemical processes that control actinide mobility in the environment

All the actinides, which are radioactive, can pose a risk to human health and the environment. However, plutonium (Pu) is the most abundant and chemically complex anthropogenic actinide. Over 2,400 metric tons of Pu are estimated to have been produced worldwide, with approximately 70–90 metric tons added to this inventory each year from spent nuclear fuel. A fraction of this Pu inventory has been released into the environment as a result of nuclear weapons production, weapons testing, poor waste management, and nuclear accidents. Subsurface transport of low Pu concentrations from these environmental releases has been documented on the scale of kilometers. The large Pu inventory, along with its long half-life (~24,000 years), toxicity, and known ability to migrate, represents significant long-term environmental and public health risks.

Neptunium (Np), another long-lived, toxic actinide, is present at much lower concentrations at contaminated Department of Energy (DOE) facilities and, thus, represents a lesser environmental concern. However, both Np and Pu are predicted to be significant long-term dose contributors in high-level nuclear waste. As a result, understanding their behavior in the environment is crucial for the safe, long-term isolation of nuclear waste.

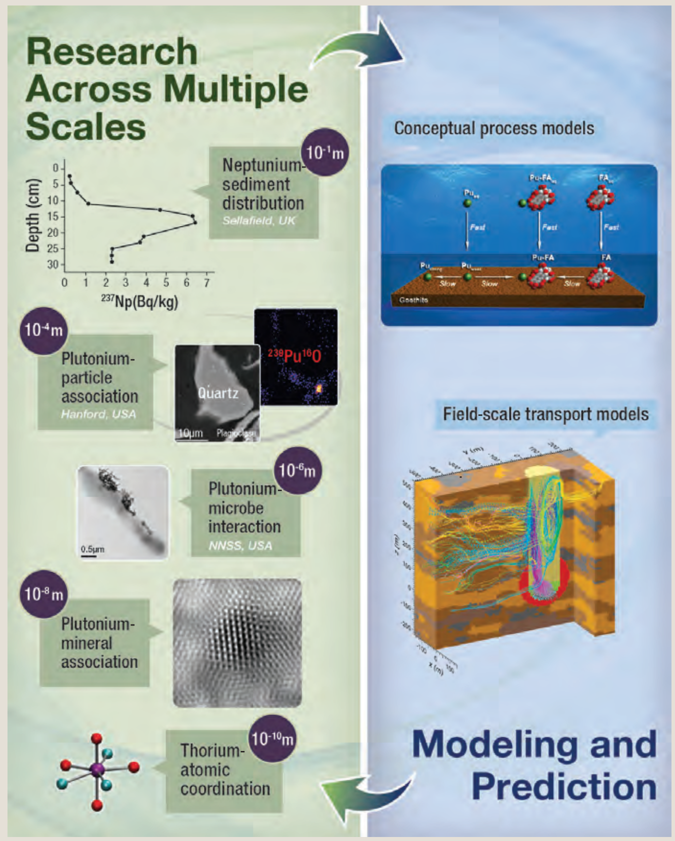
Reliable predictions of how actinides such as Pu and Np will migrate in the subsurface are not currently possible, preventing accurate assessments of risk to human health and the environment. The Subsurface Biogeochemistry of Actinides Scientific Focus Area (SFA) led by Lawrence Livermore National Laboratory (LLNL) is addressing this challenge. By identifying the dominant biogeochemical processes and underlying mechanisms that control actinide transport (focusing on Pu and Np), the SFA is advancing efforts to reliably predict and control actinide cycling and mobility in the subsurface. The project is supported by DOE's Office of Biological and Environmental Research (BER), within DOE's Office of Science, as part of BER's Subsurface Biogeochemical Research (SBR) program.

Key Knowledge Gaps

The LLNL SFA is focused on advancing understanding of subsurface actinide behavior to provide a scientific basis for remediation and long-term stewardship of DOE legacy sites and, more broadly, increase understanding of transport phenomena in environmental system science.

Key knowledge gaps addressed by the LLNL SFA include:

- Mechanisms driving surface-mediated Pu and Np reduction.
- Formation of stable natural organic matter coatings on mineral surfaces and their effect on Pu and Np redox transformations and sorption reactions.
- Factors controlling the stability of intrinsic actinide colloids.
- Natural organic matter ligands and functional groups responsible for biologically mediated Pu redox transformations.
- Mechanisms responsible for observed Pu transport behavior in the field.

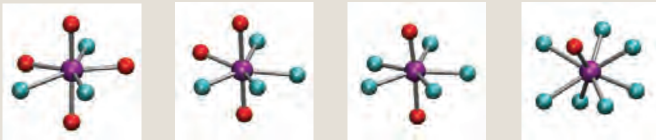


Subsurface Biogeochemistry of Actinides. *The LLNL SFA is building an understanding of actinide behavior from the atomic to field scale. Findings from these observations across scales are used to develop conceptual and numerical models and improve prediction of actinide migration at globally relevant sites.*

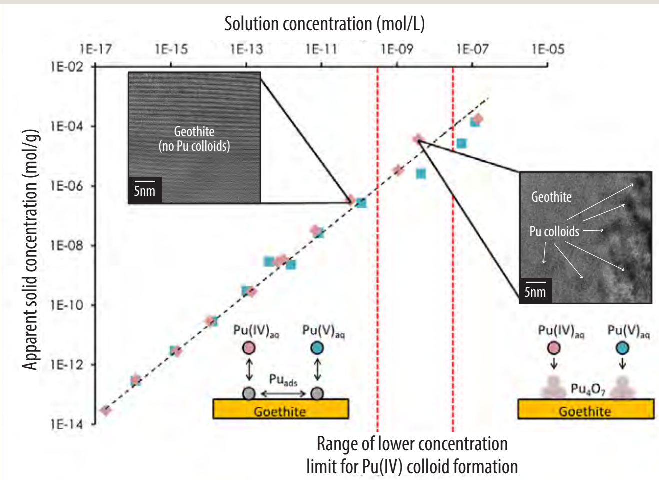
Linking Laboratory and Field Observations

Predicting actinide behavior in the environment necessitates a scaled approach that integrates laboratory experiments and computational models with field observations of actinide transport. Computational models (e.g., quantum mechanical calculations) reveal the fundamental structure of actinide complexes at the atomic level. Laboratory experiments provide quantitative data on the affinities, kinetics, and morphology of actinide associations with mineral surfaces, organic matter, and microbes. Field observations provide the foundation for conceptual understanding of actinide migration.

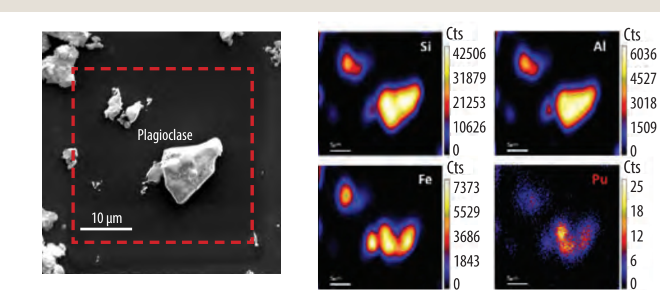
This integrated laboratory- and field-scale approach to subsurface biogeochemistry of actinides is being used to quantify actinide transport at contaminated sites such as the Nevada National Security Site (NNSS), Hanford Site (Richland, Washington), Savannah River



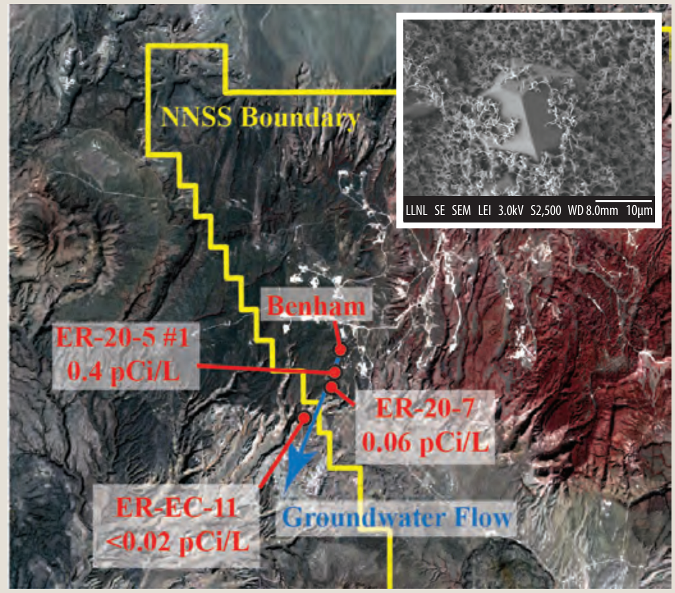
Computational Models Determine Actinide Behavior Under Spectroscopically Inaccessible Conditions. *Snapshots of the first coordination shell for $[Th(OH)_n]^{(4-n)+}(aq)$ as obtained from first-principles molecular dynamics computer models provide insights into the coordination chemistry of Pu and Np. For clarity, only thorium (Th) and the first shell of oxygens are shown. Th is purple, hydroxyl oxygen (OH) is red, and water oxygen (OH_2) is blue. The fully hydrolyzed complex $Th(OH)_4(aq)$* ***(left)*** *is seven-coordinate, with four hydroxyls and three waters in the first shell. Successive removal of hydroxyls* ***(left to right)*** *initially leads to a substitution by water to maintain the seven-coordinate structure. Upon removal of the third hydroxyl* ***(right)****, however, the coordination number increases to eight, and the structure changes to a square antiprism.*



Unique LLNL Capabilities Reveal Actinide Interaction with Mineral Surfaces. *Sorption behavior of Pu at sub-femtomolar concentrations ($<10^{-15}$ mol/L) is examined by accelerator mass spectrometry. At higher concentrations, transmission electron microscopy reveals Pu surface precipitation. These results, spanning the entire range of Pu concentrations observed in nature, provide a new, relatively straightforward conceptual basis for simulating Pu transport behavior in contaminated environments where goethite, a common iron oxide, is present.*



Nanoscale Characterization Tools Identify Pu Associations with Contaminated Sediments. ***(Left)*** *Scanning electron microscopy reveals the presence of plagioclase and other minerals in contaminated sediments recovered 25 m beneath the Z-9 trench at the Hanford Site in Richland, Washington.* ***(Right)*** *NanoSIMS is used to identify the spatial distribution of silicon (Si), aluminum (Al), iron (Fe), and plutonium (Pu) in these same grains and indicates a strong correlation between Pu and Fe.*



Laboratory and Field Data Provide a Comprehensive View of Plutonium Migration Rates at the Nevada National Security Site. *Hydrothermal alteration of nuclear melt glass* ***(inset)*** *yields colloidal clay with associated Pu. Laboratory colloid formation experiments along with field measurements reveal the mechanisms of trace Pu migration from the Benham underground nuclear test. (Note: The U.S. Environmental Protection Agency regulates Pu in drinking water at 15 pCi/L.)*

Site (Aiken, South Carolina), and Sellafield (Cumbria, England). At NNSS, for example, detailed adsorption and desorption experiments, hydrothermal colloid formation experiments, and field actinide groundwater analyses suggest that Pu will migrate in groundwater for decades. However, actinide concentrations are likely to decline over time and unlikely to reach hazardous levels. Such SFA findings are providing the scientific foundation for understanding actinide transport phenomena and applying scientifically defensible management decisions at actinide-contaminated sites worldwide.

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