Lawrence Livermore National Laboratory

LLNL SFA OBER–SBR FY17 Program Management and Performance Report:

Subsurface Biogeochemistry of Actinides

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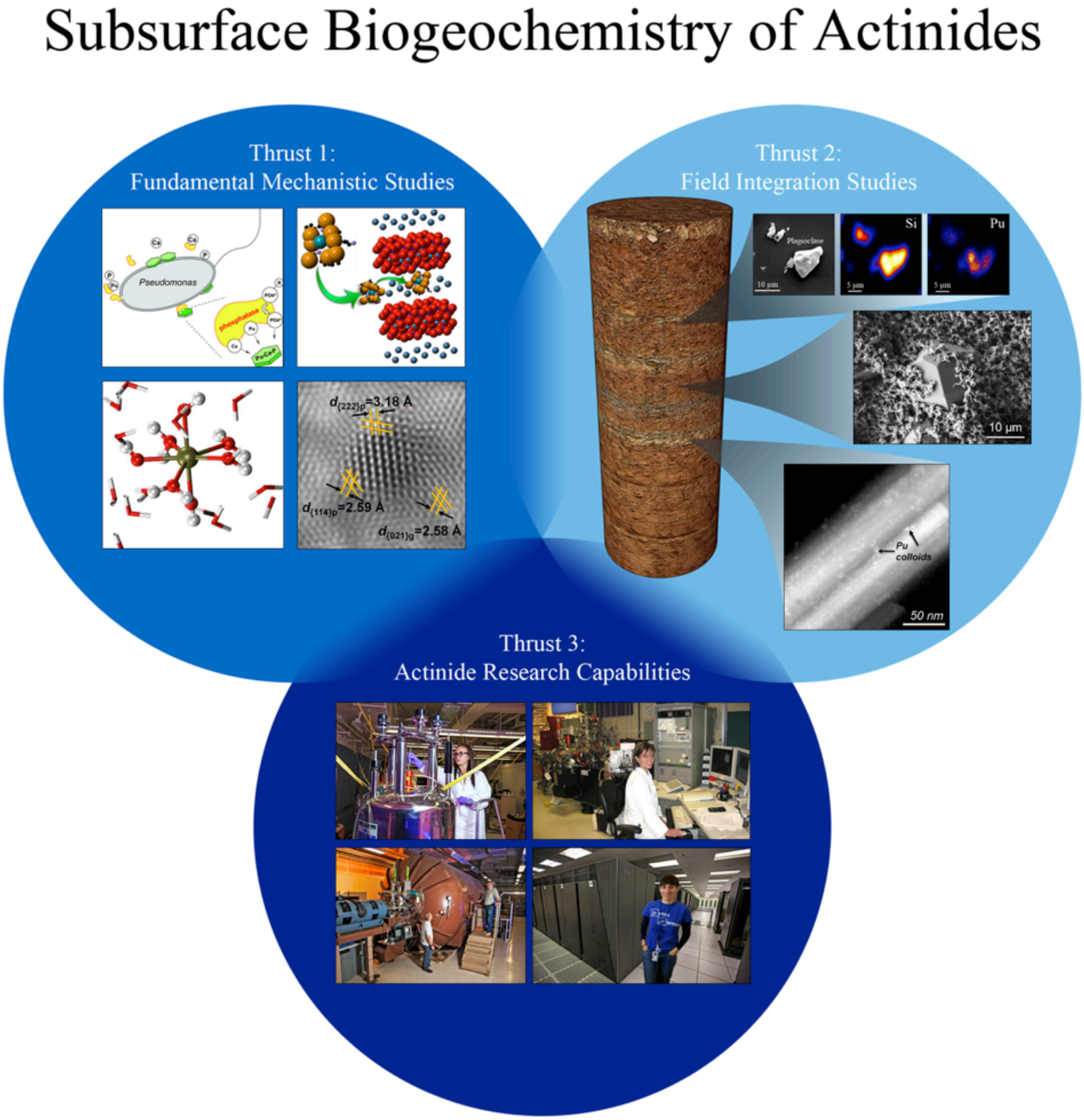

Figure 1. Integration of three research thrust areas in the Subsurface Biogeochemistry of Actinides Science Plan.

1. PROGRAM OVERVIEW

Subsurface Biogeochemistry of Actinides
Lawrence Livermore National Laboratory

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A major scientific challenge in environmental sciences is to identify the dominant processes controlling actinide transport in the environment. It is estimated that currently, over 2200 metric tons of anthropogenic plutonium (Pu) has accumulated worldwide, a number that increases yearly with additional spent nuclear fuel (Ewing *et al*., 2010). Plutonium has been shown to migrate on the scale of kilometers, giving way to a critical concern that the fundamental biogeochemical processes that control its behavior in the subsurface are not well understood (Kersting et al. 1999; Novikov et al. 2006; Santschi et al. 2002). Neptunium (Np) is less prevalent in the environment; however, it is predicted to be a significant long-term dose contributor in high-level nuclear waste. Our focus on Np chemistry in this Science Plan is intended to help formulate a better understanding of Pu redox transformations in the environment and clarify the differences between the two long-lived actinides.

The research approach of our Science Plan combines (1) *Fundamental Mechanistic Studies* that identify and quantify biogeochemical processes that control actinide behavior in solution and on solids, (2) *Field Integration Studies* that investigate the transport characteristics of Pu and test our conceptual understanding of actinide transport, and (3) *Actinide Research Capabilities* that allow us to achieve the objectives of this Scientific Focus Area (SFA) and provide new opportunities for advancing actinide environmental chemistry. These three Research Thrusts form the basis of our SFA Science Program (Figure 1).

Research Thrusts 1 and 2 are guided by broad central hypotheses:

> *Thrust 1 Hypothesis: The biogeochemical mechanisms controlling* ***redox transformations of actinides*** *and their stabilization as aqueous complexes, binary surface complexes, ternary surface complexes, precipitates, and co-precipitates will determine actinide migration in the environment.*
>
> *Thrust 2 Hypothesis: The biogeochemical processes that ultimately control actinide subsurface mobility/immobility are driven by local variations in the geology, geochemical conditions, colloid composition and abundance, and* ***chemical characteristics of the initial actinide source****.*

The success of our program relies on the development and use of state-of-the-art spectroscopic and computational capabilities that are unique to LLNL, and form the basis for Research Thrust 3. Method development is essential to the success of our SFA and will provide new opportunities for the broader actinide and environmental systems science communities. We are focusing on five state-of-the-art capabilities:

- *NMR and EPR of Actinide Complexes*
- *NanoSIMS of Actinides*
- *Actinide TEM-EELS*
- *Actinide Analysis at the Center for Accelerator Mass Spectrometry (CAMS)*
- *f-Element Ab Initio Modeling*

Development of these spectroscopic and computational capabilities is intended to benefit the scientific community as a whole.

New knowledge gained from this Science Plan 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 transport phenomena in environmental systems sciences.

2. SCIENTIFIC OBJECTIVES

The objectives of our Subsurface Biogeochemistry of Actinides SFA are to:

- Advance our understanding of the behavior of actinides by quantifying the dominant biogeochemical processes and the underlying mechanisms that control their fate and transport in the environment.
- Apply our conceptual and numerical models of Pu and Np behavior to field and field-analog sites to test our ability to predict actinide cycling and mobility in the subsurface.
- Develop and use state-of-the-art spectroscopic and computational capabilities and provide new research opportunities for the broader actinide and environmental systems science communities. Capabilities include:
    - NMR (nuclear magnetic resonance) and EPR (electron paramagnetic resonance)
    - NanoSIMS (nanoscale secondary ion mass spectroscopy)
    - TEM-EELS (transmission electron microscopy-electron energy loss spectroscopy)
    - Accelerator Mass Spectrometry
    - f-Element Ab Initio Modeling, and
- Provide the Department of Energy (DOE) with the scientific basis to support decisions for the remediation and long-term stewardship of legacy sites and, more broadly, transport phenomena in environmental systems sciences.

Key Knowledge Gaps that are being addressed in this 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.

3. PROGRAM STRUCTURE

Henry Shaw is the point-of-contact for LLNL's Biological and Environmental Research (BER) Programs and is the Deputy Associate Director for Science & Technology in the Physical and Life Sciences (PLS) Directorate reporting to Glenn Fox, the Associate Director of the PLS Directorate. Dr. Kersting is the program manager and point of contact for this SFA. She is the Director of University Relations and Science Education and reports to Pat Falcone, the Deputy Director for Science & Technology, Director's Office. Dr. Zavarin is the technical co-manager of the SFA and supervises the majority of the experimental work carried out by staff scientists. He is the Director of the Glenn T. Seaborg Institute and reports to Glenn Fox.

Dr. Kersting and Dr. Zavarin co-supervise the graduate students, postdocs, and staff. Program objectives and schedule are reviewed in biweekly SFA program meetings (which includes external collaborators) and weekly meetings with individual postdocs and graduate students. Dr. Kersting, Dr. Shaw, and Dr. Zavarin maintain a dialog to ensure open communication between the Director's office and PLS regarding this SFA.

Education and Outreach

We continue to have a strong educational component to our SFA as we believe that training postdocs and graduate students best serves the scientific community in the area of environmental radiochemistry. Our educational efforts have enhanced the scientific productivity of this program, built a strong collaborative national and international research community, developed future scientific talent, and leveraged current SFA funding. In the last year, we have been collaborating with seven national and international research groups. We have seven postdocs and eight graduate students working with us. To strengthen and expand our university collaborations, we leverage the Seaborg Institute's long-standing Summer Internship Program to bring in students that carry out research specific to this SFA.

Personnel

Annie Kersting—Director of University Relations & Science Education at LLNL; a geochemist with expertise in isotope geochemistry, actinide chemistry, colloid-facilitated transport, and field investigations of contaminant transport. As the program manager for this SFA, she coordinates research and budgets, helps drive the research agenda with Dr. Zavarin, and leads Thrust Area 2: Field Integration Studies. Together with Dr. Zavarin, she co-mentors and directs the research of SFA postdocs Claudia Joseph, Tashi Parsons-Moss, Jennifer Shusterman, Keith Morrison, and Enrica Balboni. She also co-mentors graduate students. Together with Dr. Zavarin she is responsible for building and maintaining external collaborations.

Mavrik Zavain—Director of the Glenn T. Seaborg Institute; a soil scientist involved in experimental and modeling studies of radionuclides at the mineral-water interface, mineral dissolution/precipitation kinetics, colloid-facilitated transport, and radionuclide reactive transport modeling. Dr. Zavarin is the Co-Technical Manager on this SFA, and is responsible for overall planning and execution of the research program. Dr. Zavarin is also leading Thrust Area 1. He co-mentors and directs the research for all the postdocs and graduate students with Dr. Kersting. Together with Dr. Kersting, he is responsible for building and maintaining external collaborations.

James Begg—LLNL staff scientist; Dr. Begg's expertise is in environmental radiochemistry. Specifically, he integrates experimental and modeling approaches to probe the mechanisms of actinide behavior on mineral surfaces. He carries out Pu and Np adsorption experiments investigating actinide interaction with minerals. He leads Thrust 1, Focus Area 1A and is the point of contact for the collaboration between LLNL, the University of Manchester and Karlsruhe Institute of Technology (KIT). Dr. Begg is also responsible for mentoring graduate students.

Brian Powell—Fjeld Professor, Clemson University, Environmental Engineering & Earth Sciences; formerly a postdoctoral fellow at LLNL. Dr. Powell's research focuses on understanding and quantifying the rates and mechanisms of actinide interactions with natural soils and synthetic minerals. Dr. Powell supervises two graduate students and one postdoc who carry out research for this SFA.

Yongqin Jiao—LLNL staff scientist; geobiologist who conducts research at the interface between environmental microbiology and biogeochemistry. She is currently exploring the metabolic activities of microbes and microbial communities in natural, perturbed, or engineered environments, with a focus on microbe–metal interactions. She leads Thrust 1, Focus Area 1D: Probing the role of microbes in manipulating Pu behavior. Dr. Jiao is also responsible for mentoring postdoc Keith Morrison.

Harris Mason—LLNL staff scientist; formerly a postdoctoral fellow at LLNL. Dr. Mason's research focuses on developing advanced solution and solid-state NMR spectroscopic methods to investigate metal sorption reactions at mineral–water interfaces. He leads Thrust 1, Focus Area 1F: Characterizing molecular-level actinide complexes and redox transformations.

Patrick Huang—Assistant Professor at California State University East Bay; formerly a postdoctoral fellow at LLNL. Dr. Huang is a computational chemist whose research interests involve chemical phenomena in condensed phases. He has experience with a variety of *ab initio* methods ranging from quantum chemical techniques to periodic density functional theory, and is collaborating with Brenda Rubenstein to Lead Thrust 1, Focus Area 1E: Simulating the Molecular Level Behavior of f-Elements.

Zurong Dai—LLNL senior staff scientist; physicist and materials scientist with expertise in using transmission electron microscopy (TEM) to understand the structure of natural and man-made materials. His research focuses on crystal growth and crystallography, nanomaterials synthesis and characterization, experimental measurement of electronic structure, and optical properties of materials. Dr. Dai is responsible for the scanning electron microscopy (SEM) and TEM analyses of actinide particles and colloids.

Ruth Kips—LLNL staff scientist; formerly a postdoctoral fellow at LLNL. She has expertise in high-resolution imaging, and microanalysis. She is responsible for our NanoSIMS sample sectioning/preparation, imaging, data analysis, and interpretation. She is also responsible for mentoring graduate student Mary Kathryn (Katie) Hoffman.

Brenda Rubenstein—Former LLNL Lawrence Fellow and now an assistant professor at Brown University; a computational chemist with expertise in quantum simulations. Her research focuses on developing and applying novel quantum Monte Carlo techniques capable of studying systems using quantum statistics.

Keith Morrison—LLNL postdoctoral fellow; microbiologist with expertise in organic chemistry, biochemistry, and geology. He is investigating interactions between microbes, minerals, and Natural Organic Matter (NOM).

Enrica Balboni—LLNL postdoctoral fellow; radiochemist with expertise in actinide chemistry, mineralogy, isotope geochemistry, and mineral synthesis. Dr. Balboni is responsible for experiments that explore the structure of Pu nanocolloids at the mineral–water interface.

Claudia Joseph—LLNL postdoctoral fellow (now a staff scientist at KIT); radiochemist with expertise in conducting and modeling sorption and diffusion experiments with radionuclides. Dr. Joseph is examining Np and Pu interactions with laboratory and field samples.

Tashi Parsons-Moss—LLNL postdoctoral fellow; a radiochemist with expertise in aqueous actinide chemistry, f-element behavior in solution and at solid-liquid interfaces as well as radiological measurements for nuclear forensic applications. She is examining the structure and particle size of Pu nanocolloids.

Jennifer Shusterman—LLNL postdoctoral fellow: a radiochemist with expertise in aqueous actinide chemistry. Her research focuses on the chemical behavior of Pu and other f-elements in solution and at solid-liquid interfaces, and using NMR to probe behavior of metals at solid interfaces.

4. PERFORMANCE MILESTONES AND METRICS

Table 1. Timeline for each task identified in this Science Plan. There were no significant changes to the timeline in FY16-17. There were some tasks that were not initiated due funding limitations (shown in purple). Some tasks were started early (shown in green).

		FY16				FY17				FY18			
THRUST 1	**Focus Area 1A: Identifying the Mechanisms Driving Surface-Mediated Reduction of Pu and Np**												
	Task 1A-1: Role of Fe in controlling Pu redox behavior	🟦	🟦	🟦	🟦	🟦	🟦						
	Task 1A-2: Adsorption/desorption of Pu/Np under controlled atmospheres							🟦	🟦	🟦	🟦	🟦	🟦
	Task 1A-3: Role of aging and concentration in Pu/Np stability on surfaces	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
	Focus Area 1B: Effect of NOM on Actinide Redox Transformations and Sorption Reactions												
	Task 1B-1: Reduction of Pu(V) and Np(V) by NOM	🟦	🟦	🟦	🟦	🟦	🟦						
	Task 1B-2: Stabilization of Pu on mineral surfaces by NOM			🟦	🟦	🟦	🟦	🟦	🟦				
	Task 1B-3: Pu sorption/desorption rates in the presence of NOM	🟦	🟦	🟦	🟦					🟦	🟦	🟦	🟦
	Focus Area 1C: Characterizing the Structural and Chemical Behavior of Pu Nanocolloids												
	Task 1C-1: Structural behavior of Pu oxide on mineral surfaces	🟦	🟦	🟦	🟦	🟦	🟦						
	Task 1C-2: Redox behavior of Pu oxide on mineral surfaces							🟦	🟦	🟦	🟦	🟦	🟦
	Focus Area 1D: Probing the Role of Microbes in Altering Pu Behavior												
	Task 1D-1: EPS-Pu interactions	🟦	🟦	🟦	🟦	🟦	🟦						
	Task 1D-2: Cellular exudates controlling Pu complexation and mobility	🟦	🟦	🟦	🟪	🟪	🟪	🟪	🟪				
	Task 1D-3: Microbial phosphate metabolism in mediating Pu solubility					🟪	🟪	🟪	🟪	🟦	🟦	🟦	🟦
	Focus Area 1E: Simulating the Molecular Level Behavior of f-Elements												
	Task 1E-1: Pu sorption at the mineral/water interface			🟦	🟦	🟦	🟦	🟦	🟦				
	Task 1E-2: Quantum Monte Carlo applied to actinide redox transformations									🟦	🟦	🟦	🟦
	Focus Area 1F: Characterizing Molecular Level Actinide Complexes and Redox Transformations												
	Task 1F-1: Pu complexes on mineral surfaces			🟦	🟦			🟦	🟦			🟦	🟦
	Task 1F-2: Actinide solution complexes	🟦	🟦	🟪	🟪	🟪	🟪	🟪	🟪				
	Task 1F-3: Np ligand exchange	🟦	🟦	🟦	🟦	🟦	🟦						
THRUST 2	**Focus Area 2A: Characterization of Field Samples from Pu Contaminated Sites**												
	Task 2A-1 Hanford Site: Sediments from Area 200	🟦	🟦	🟪	🟪	🟪	🟪						
	Task 2A-2 Savannah River Site: Characterization of sediments associated with the Pu/Np-doped lysimeter coupons			🟩	🟩	🟦	🟦	🟦	🟦				
	Focus Area 2B: Characterization of Pu Behavior in Field and Field-Analog Samples												
	Task 2B-1 NNSS: Colloid stability experiments	🟦	🟦	🟦	🟦								
	Task 2B-2 Hanford: Pu migration under hyper-transient conditions					🟪	🟪	🟦	🟦	🟦	🟦	🟦	🟦
	Task 2B-3 Savannah River Site: field lysimeter experiment				🟩	🟩			🟦				🟦
	Task 2B-4 Influence of NOM on Pu mobility under advective flow conditions			🟦	🟦	🟦	🟦	🟦	🟦				
	Focus Area 2C: Parameterization of the Mechanistic Processes and Integration with Field Observations												
	Task 2C-1 Development of Pu/Np surface complexation/ion exchange models	🟦	🟦	🟦	🟦								
	Task 2C-2 Parameterization of aging processes and associated reaction rates			🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
THRUST 3	**Focus Area 3A: NMR and EPR Analysis of Pu/Np Complexes**	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
	Focus Area 3B: NanoSIMS Analysis of Pu	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
	Focus Area 3C: TEM-EELS of Pu/Np Nanocolloids	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
	Focus Area 3D: CAMS Analysis of Pu/Np at Femtomolar Concentrations	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
	Focus Area 3E: LLNL Computing: Quantum Monte Carlo	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦

4.a REVIEW OF SCIENTIFIC PROGRESS

4.a.i Brief Review of Scientific Progress

Thrust 1: Mechanistic Behavior of Actinides

Thrust 1 Coordinator: M. Zavarin

The objective of Thrust 1 is to develop a mechanistic understanding of the dominant processes controlling actinide migration in the environment. The research is primarily focused on Pu. However, we have expanded some of the research to include Np so as to exploit the similarities and differences between these actinides and develop a deeper understanding of their behavior in the environment.

> *Hypothesis: The biogeochemical mechanisms controlling redox transformations of actinides and their stabilization as aqueous complexes, binary surface complexes, ternary surface complexes, precipitates, and co-precipitates will determine actinide migration in the environment.*

In order to test our hypothesis, we have divided this thrust into the following six **Focus Areas**:

- *1A: Identifying the Mechanisms Driving Surface-Mediated Reduction of Pu and Np*
- *1B: The Effect of Natural Organic Matter on Pu and Np Redox Transformations and Sorption Reactions*
- *1C: Characterizing the Structural and Chemical Behavior of Pu Nanocolloids*
- *1D: Probing the Role of Microbes in Manipulating Pu Behavior*
- *1E: Simulating the Molecular-Level Behavior of f-Elements*
- *1F: Characterizing Molecular Level Actinide Complexes and Redox Transformations*

Focus Area 1A: Identifying the Mechanisms Driving Surface-Mediated Reduction of Pu and Np

Lead: J. Begg

The environmental mobility of Pu and Np depends on the dominant oxidation states present, with each oxidation state displaying a unique solubility (Neck et al. 2007) and sorption affinity (Begg et al. 2013; Keeney-Kennicutt and Morse, 1985; Sanchez et al. 1985; Silva and Nitsche, 1995). Specifically, for Pu, the rates of Pu surface-mediated reduction and oxidation on different minerals are unique; yet, the exact mechanisms driving this redox behavior are unknown.

> *Hypothesis: Pu and Np surface-mediated reduction is driven by the presence of redox active elements (i.e., Fe) on mineral surfaces; the reduction rates will depend on the nature of sorbed Fe (Fe monomers, polymers, or surface precipitates). In addition, the redox transformations are the driving mechanism controlling desorption rates from mineral surfaces.*

Task 1A-1: Role of Fe in controlling Pu redox behavior

Contributors: J. Begg, C. Edelman

Previous work has highlighted the importance of iron in controlling the reduction of Pu(V)/(VI) on mineral surfaces (Hixon et al. 2010; Romanchuk et al. 2011; Zavarin et al. 2012; Begg et al. 2013). In 2016, we carried out a series of batch adsorption experiments to look at the role that structural iron plays in controlling Pu(V) adsorption to montmorillonite. We used 3 montmorillonites with varying structural Fe contents: SWy-1 (3.35% Fe_2O_3; 0.32 % FeO); STx-1 (0.65% Fe_2O_3; 0.15% FeO); and SSM-100 (0.02% Fe_2O_3). Clay suspensions (1 g/L) at pH 4, 6, and 8 were spiked with Pu(V) at an initial concentration of 10^{-10} M, and Pu solution concentration monitored for 6 months.

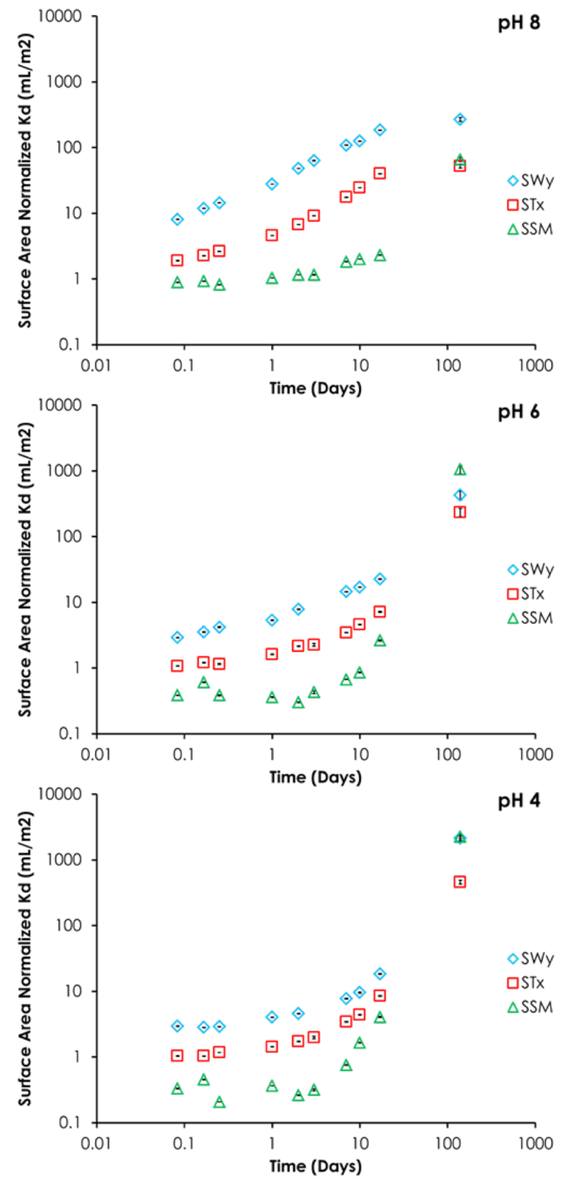

Figure 1A1. Sorption of Pu(V) to SWY-1, STx-1, and SSM -100 montmorillonite clay.

The short-term sorption rate of Pu (1-20 days) showed both a dependence on the clay mineral and pH (Figure 1A1). At pH 8 and 6, the surface area-normalized apparent sorption rates are correlated with the Fe content in the clay (SWy-1> STx-1> SSM-100). The higher the Fe content in the clay, the faster the rate of Pu(V) reduction to Pu(IV) on the clay surface. At pH 4, the effect of Fe content in the clay is less pronounced.

The sorption rates for this early time period were also pH-dependent with respect to each clay. In the case of SWy-1 and STx-1, the rates of sorption were pH 8 > pH 6 > pH 4. For SSM, this order was reversed, with pH 4 > pH 8. The differences in sorption behavior as a function of pH are likely indicative of a change in dominant sorption mechanism from surface complexation to ion exchange.

Importantly, despite differences in the extent of Pu sorption on the clays at 20 days of equilibration, after 6 months the sorption is approximately equal for all three minerals. This indicates that there are two mechanisms controlling the reduction of Pu(V) to Pu(IV) on the mineral surface. While Fe in clays may play an important role in short term sorption/reduction rates, at longer timescales the extent of sorption/reduction of Pu on montmorillonite clays will be independent of the type of montmorillonite and Fe content. This has implications for contaminant transport modeling as well as performance assessment of nuclear waste repository scenarios especially with regards to the choice of clay for repository backfill material.

Task 1A-3: The role of aging and concentration in Pu/Np stability on surfaces

Contributor: J. Begg

One important finding from our recent work is that Pu sorption processes can occur on longer timescales (weeks/months/years) than are commonly investigated in lab experiments (weeks/days) (Begg et al. 2015; Begg et al. 2013; Tinnacher et al. 2011). Typically, these processes may be termed “aging” and defined as “one or more surface process(es) that occurs after the initial sorption reaction and cause(s) changes in contaminant surface speciation over time” (Tinnacher et al. 2011). In 2016 and 2017 we conducted flow cell experiments with goethite at pH 8 aimed at studying the effects of the adsorption aging period on Pu *desorption* behavior. Two initial Pu concentrations (10^{-9} and 10^{-6} M) were used to determine if adsorption and surface precipitation mechanisms lead to similar aging behavior.

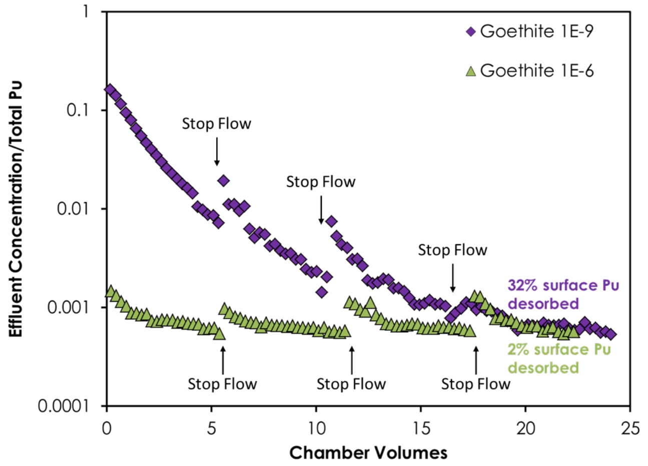

Figure1A2. Desorption of Pu from goethite in 25-day flow cell experiments with initial concentrations of 10^{-9} M and 10^{-6} M Pu(V). Effluent Pu from the flow cell are normalized to the calculated concentration of Pu on the goethite surface at the start of the flow cell experiment.

Results from 10^{-9} M and 10^{-6} M Pu(V) flow cell experiments performed after 25 days of equilibration are shown in Figure 1A2. The desorption profiles show a distinct difference at the two initial Pu concentrations. At 10^{-9} M Pu, the amount of Pu desorbed was 32%. At 10^{-6} M Pu, only 2% is desorbed. These results indicate that predicting the behavior of Pu requires knowledge of the Pu source concentration and the nature of the “sorbed” Pu. We are applying a modeling framework originally developed for Pu desorption from montmorillonite (Begg et al. 2017) to these goethite data to determine the concentration-dependent rates of Pu desorption. Follow-on efforts will examine how desorption rates are affected by adsorption aging time (i.e., 6-month and 1-year adsorption equilibration times).

Focus Area 1B: Effect of NOM on Actinide Redox Transformations and Sorption Reactions

Lead: M. Zavarin

Natural organic matter (NOM) has been shown to play an important role in the migration of Pu in the environment. At the Rocky Flats Environmental Technology Site (RFETS), Pu in soil samples is in the +4 oxidation state and associated with organic macromolecules (Santschi et al. 2002). The NOM associated with mobile Pu was determined to be dominated by cutin-like substances from bacteria (Xu et al. 2008). At the Nevada National Security Site (NNSS), we found that Pu was complexed by NOM and mobilized in tunnels used for underground nuclear testing (Zhao et al. 2011). We have recently shown that Pu may be stabilized on oxide surfaces by NOM and thus lead to increased colloid-facilitated transport (Tinnacher et al. 2015). However, this process could also lead to stabilization of Pu on sediment surfaces and, as a result, minimize Pu transport. Determining the nature of NOM interaction with actinides and its influence on actinide redox transformations and sorption to minerals forms the basis of Focus Area 1B.

> *Hypothesis: Stabilization of Pu as Pu(IV)–NOM binary complexes will depend on the electron-donating capability of the NOM functional groups (e.g., hydroxamates). Stabilization of Pu as Pu(IV)–NOM–mineral ternary complexes will depend on the electron donating capability of the NOM functional groups and the stabilization of NOM on mineral surfaces via bridging cations.*

Task 1B-1: Reduction of Pu(V) and Np(V) by NOM

Contributor: K. Morrison

The cycling of hydroxamate compounds driven by biogeochemical processes is known to influence the transport and reactivity of Pu in the environment. Acetohydroxamic acid (AHA) represents a simple functional moiety belonging to a large class of hydroxamate compounds used by microorganisms for siderophore-mediated iron acquisition. This year we investigated the complexation and reactivity of Pu with AHA by determining the stability of Pu(VI), (V), and (IV)-AHA ligands at environmentally relevant pHs (3–7).

The stability of AHA is influenced by acid concentration and metal ligand binding (Figure 1B1). Previous studies performed with high concentrations of nitric acid (1–4 M) have shown; 1) un-chelated Pu(VI) is rapidly reduced by AHA, while reduction of Pu(V) to Pu(III) is slow (>10 hrs) (Andrieux et al. 2009); 2) reduction of Pu(V) and Pu(IV)–AHA ligands do not occur until hydrolysis of AHA releases the bound metal, which is then reduced by hydroxylamine (Carrott et al. 2008). However, the reactions of Pu–AHA at environmentally relevant pHs (3-7) have not been investigated.

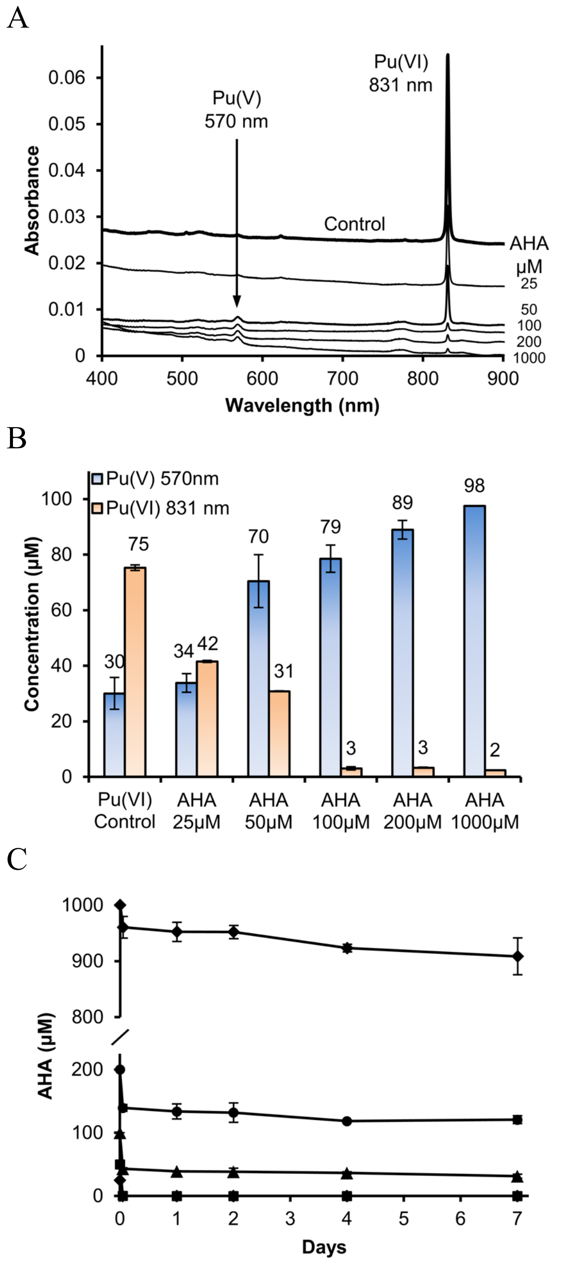

Figure 1B1. AHA reaction mechanisms (A), Pu(VI)–AHA UV-VIS spectroscopy after 7 days (B) Semi-quantitative analysis of Pu(VI) and (V) from UV-Vis spectra (C) and concentrations of AHA reacted with 100 μM Pu(VI).

Last year we developed a gas chromatography-mass spectrometer (GC-MS) capability that allows us to track AHA oxidation products that result from Pu(V) reduction in solution. We tracked the reduction of Pu(VI) by AHA using UV-Vis spectroscopy. Solutions of Pu(VI) (100μM) were adjusted to pH 6 using $NaHCO_3$ and reacted with AHA at 25 to 1000 μM concentrations. After 7 days, samples were acidified with 0.1M HNO_3 to quantify Pu redox state (Fig. 1B1, A and B). The concentration of Pu(VI) decreases with increasing AHA followed by the appearance of a Pu(V) peak. We did not observe any Pu(IV) UV-Vis spectral features throughout the 7-day reaction. Concentrations of AHA and hydroxylamine were tracked using gas chromatography-mass spectrometry. Derivatization of Pu-AHA samples was performed in water using n-hexyl chloroformate, followed by extraction with hexane. When AHA is reacted with Pu(VI) there is an initial drop in AHA concentrations (50 to 75 μM) followed by a slow decrease over 7 days. Starting with a simple organic system we show that Pu(VI) reduction to Pu(V) is driven by direct interaction with AHA, without the formation of hydroxylamine. Pu(IV) was not produced in these experiments, suggesting that the presence of AHA in the environment will not drive the reduction of Pu to the less mobile Pu(IV) oxidation state. We observed a rapid reduction of Pu(VI) to Pu(V) upon reaction with AHA, similar to previous studies (Butler et al. 2000; Carrott et al. 2008). However, our results reveal that hydroxamate hydrolysis and hydrolyxamine mediated Pu reduction will not occur at environmental pH. Therefore, the hydroxamate breakdown products of microbial siderophores in oxidizing zones will not reduce Pu(VI) to Pu(IV). Next we will explore reactions of Pu(V) and Pu(VI) with di- and tri-hydroxamate complexes to determine if chelated Pu exhibits redox activity. This will be followed by a systematic evaluation of the capacity of NOM, cell exudate components, and functional groups to reduce Pu(V) and Pu(IV).

Task 1B-2: Stabilization of Pu on mineral surfaces by NOM

Contributors: B. Powell, N. Conroy,

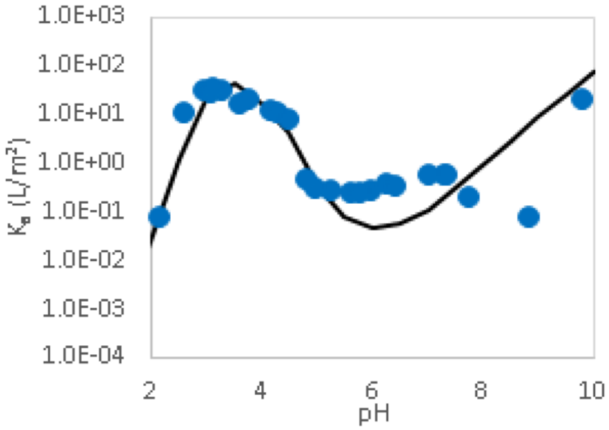

Figure 1B2. Pu sorption to goethite in the presence of 50mgc·L^{-1} citrate; ternary sorption surface complexation model (solid black line) vs. experimental data (blue circles).

Ternary Pu-NOM-mineral surface complexes have been studied previously with pure mineral phases such as kaolinite (Banik et al. 2007), gibbsite (Zimmerman et al. 2014), silica (Roberts et al. 2008), and goethite (Conroy et al. 2017; Tinnacher et al. 2015). In 2016, we produced a simplified surface complexation model which simulated Pu sorption to goethite in the presence of citrate, desferoxamine B, and Leonardite humic acid. The model was based on literature values of Pu complexation with the ligands present is each system (Conroy et al. 2107). However, the model assumed that Pu-ligand complexation affinity would be the same in the bulk solution and on the surface. Based on this model, Pu sorption was underestimated at low pH, the region of greatest NOM sorption. This suggests that ternary Pu-ligand-mineral complexes are preferred over binary Pu-ligand aqueous complexes. In 2017, we began developing a more detailed ternary Pu(IV)-citrate-mineral diffuse layer model for both goethite (α-FeOOH) and gibbsite (γ-Al(OH)$_3$) to address the inadequacy of the previous approach. Batch sorption experiments were performed with citrate concentrations of 0 mg$_C$·L^{-1}, 0.5 mg$_C$·L^{-1}, 5 mg$_C$·L^{-1}, and 50 mg$_C$·L^{-1} (Figures 1B2 and 1B3 for goethite and gibbsite, respectively). A diffuse layer thermodynamic model was then used to simulate the observed adsorption behavior and produce surface complexation binding constants that account for the high affinity of Pu(IV)-citrate complexes for mineral surfaces.

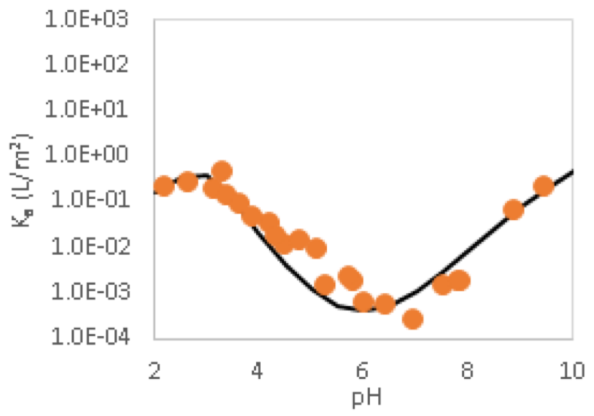

Figure 1B3. Pu sorption to gibbsite in the presence of 50mgc·L^{-1} citrate; ternary sorption surface complexation model (solid black line) vs. experimental data (orange circles).

The surface complexation model (black line in Figures 1B2 and 1B3) required the addition of a hydrolyzed Pu-citrate aqueous species (Pu(OH)$_x$-citrate) at mildly basic pH values. The existence of such a species has been suggested previously. However, no binding constant values could be found in the literature. Validation of the estimated binding constants of these Pu(OH)$_x$-citrate species through additional experimental methods is currently underway.

Focus Area 1C: Characterizing the Structural and Chemical Behavior of Pu Nanocolloids

Lead: A. B. Kersting

At very low Pu concentrations, monomeric actinide complexes on organic or inorganic surfaces will likely be the dominant form of Pu. However, Pu intrinsic nanocolloids are likely to form at field sites where actinides in high concentrations were deposited in the subsurface (e.g., the Hanford Z9 trench (Buck et al. 2014)), or at future radioactive waste repositories where the high-level radioactive waste canisters will, at some point in time, be breached. It is also possible that actinides will co-precipitate with secondary minerals as contaminated waste interacts with the surrounding host rock at both low and elevated actinide concentrations (Buck et al. 2014; Cantrell, 2009; Balboni et al. 2015). The stability of intrinsic colloids, pseudocolloids, or Pu-bearing minerals will control the potential for colloid-facilitated Pu transport. As a result, the conditions that govern their formation and persistence in the environment are critical to predicting the behavior of Pu.

> *Hypothesis: The stability of Pu nanocolloids associated with mineral surfaces (i.e., pseudocolloids) or as free nanoparticles (i.e., intrinsic colloids) will be controlled by the subtle distortions, cation substitutions, and crystallinity of the Pu crystallites, which are a function of the solution conditions that led to Pu precipitation.*

Task 1C-1: Structural behavior of Pu oxide on mineral surfaces

Contributors: E. Balboni, T. Parsons-Moss, J. Shusterman, Z. Dai

Investigations into the structure of Pu nanocolloids on mineral surfaces necessitate a detailed understanding of factors controlling nanocolloid formation. Recent work suggests that nanocolloids as small as 1.25 nm (Soderholm et al. 2008) or as large as 2–4 nm (Zavarin et al. 2014) will form depending on the colloid formation conditions. To investigate Pu colloid formation, we are performing three sets of experiments to systematically determine the 1) aqueous geochemical controls on nanocolloid formation, 2) co-precipitation of Pu on minerals, and 3) structural or chemical controls on Pu nanoparticle formation on mineral surfaces. In 2016 and 2017, we investigated topics 1 and 2 and the results are summarized below. Topic 3 will be investigated in 2018.

Aqueous geochemical controls on nanocolloid formation.

Limited data are available concerning the influence of the solution matrix on the structure, size, and aggregation behavior of Pu nanoparticles. In 2016, experiments were performed to determine how different counter-ions and co-ions impact the properties of Pu colloids formed by hydrolysis of Pu(IV) in mildly acidic and circum-neutral pH solutions. Pu colloid solutions were prepared by adding Pu(IV) in HCl to 1 M salt solutions ($NaClO_4$, $NaNO_3$, LiCl, NaCl, KCl, CsCl, $MgCl_2$, $CaCl_2$, and $BaCl_2$) yielding a total Pu concentration of 10^{-4} M. Each sample was characterized by transmission electron microscopy (TEM) and Pu LIII-edge X-ray absorption spectroscopy (XAS). The X-ray absorption near-edge structure (XANES) of all samples showed no evidence of oxidation states other than Pu(IV). Figure 1C1 shows three Fourier transformed extended X-ray absorption fine structure (EXAFS) spectra, which were similar among all samples and resembled the pattern of $PuO_2(s)$. High-resolution TEM images collected from the different samples were also similar, showing face centered cubic (fcc) crystallites. Differences were observed in the aggregation behavior of the nanoparticles in different electrolytes. For example, aggregates formed in $NaNO_3$ appeared larger and more tightly associated than those formed in NaCl and $NaClO_4$. The nature of the background electrolyte appears to have some effect on the aggregation behavior of PuO_2 but no effect on the crystal structure of Pu nanoparticles. This supports our earlier hypothesis that if non-fluorite structures are observed, it is due to epitaxial growth on host mineral structures (Powell et al. 2011). Interestingly, ongoing TEM characterization is suggesting that crystallite size may be affected by the presence and characteristics of the counter-ions in solution. While the data are still being processed, early results indicate that large crystallites form in the presence of divalent (e.g. Ba^{2+}) ions. These results may provide insight into the growth and stability of intrinsic Pu nanoparticles and their potential for colloid-facilitated transport in the environment.

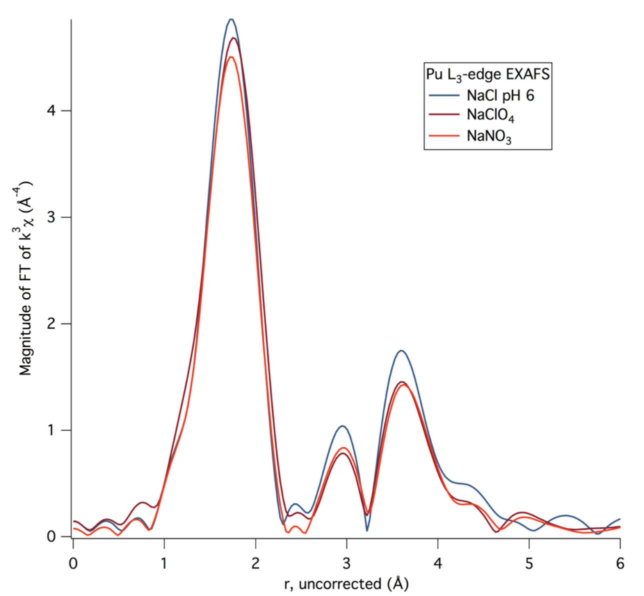

Figure IC1. Fourier-transformed EXAFS spectra measured for samples of $1*10^{-4}$ M Pu(IV) in 1 M NaCl (pH 6), $NaClO_4$, and $NaNO_3$ (pH 4). The first Pu-O shell bond length of 2.34 ±0.02 Å and Pu-Pu shell at 3.69 ± 0.02 Å are consistent with the PuO_2 structure.

Co-precipitation of Pu and environmentally relevant minerals

2016 and 2017 experiments have focused on determining how Pu(IV) and Pu(VI) co-precipitate with environmentally relevant mineral phases. Co-precipitation (or structural incorporation) of co-contaminants into mineral structures most likely involves substitution of the cation site in the mineral or perhaps interstitial incorporation. Crystal chemical constraints that affect incorporation are *i)* the cation coordination environment, *ii)* the cation charge and, *iii)* a charge balancing mechanism.

The goal of this project was to determine the mechanisms of structural incorporation of Pu into synthetic minerals. The minerals that were investigated are: iron oxides and calcite ($CaCO_3$). For the long-term performance assessment of nuclear waste repositories, knowledge about the interactions of actinide ions with mineral surfaces is imperative. Previous studies have demonstrated a high affinity of Pu for Fe-oxide minerals that are ubiquitous in the environment and are characterized by high redox reactivity and surface area (Powell et al. 2011, Zhao et al. 2016). In addition to forming in soil and sediments, iron (oxy)hydroxides form as corrosion products of steel, and are present in intermediate levels of radioactive waste. Calcite is the thermodynamically stable calcium carbonate polymorph at standard conditions and is a major component of many rocks and soils. In the vicinity of nuclear waste disposal sites, it is expected to form as an alteration product of concrete based materials (Heberling, 2011). Clay formations considered in many countries as potential host rocks for nuclear waste repositories may contain as much as 40% of calcite. The reactivity of its surface and its ability to tolerate variations in its chemical compositions make calcite a potentially important sink for environmental heavy contaminants (Heberling, 2011).

Iron oxides: The hydrous ferric oxide, ferrihydrite, is a common, poorly crystalline, metastable early product of both biotic and abiotic precipitation of iron, and is a precursor to other more crystalline iron oxides such as hematite (Fe_2O_3) and goethite (FeOOH). It has been shown that goethite and hematite are able to accommodate various impurities into their structure including Si, Ti, Mn, Ni, and U(VI) (Marshall et al. 2014; Liu et al. 2012). By studying Pu(IV) adsorption and co-precipitation with various synthetic iron oxides, we can determine the mechanism of Pu incorporation and identify the atomic-scale bonding environment of Pu in the various mineral structures. Initially, we studied the adsorption of Pu(IV) onto ferrihydrite. These data indicate that the affinity of Pu(IV) for ferrihydrite is very high and adsorption equilibrium is reached within 24 hours at pH above 7. The fate of Pu(IV) during subsequent ferrihydrite alteration to goethite and hematite was investigated. Upon transformation of Pu(IV)–ferrihydrite, 99% of the initial Pu was associated with the goethite solid; whereas, only 10% of Pu was associated with the hematite. In this work, goethite and hematite were obtained using similar synthetic conditions such as chemicals used, pH, temperature, and time of reaction. Thus, it appears the observed behavior in not a result of synthesis conditions. Our results show that although Pu was structurally incorporated into the metastable ferrihydrite structure, the long-term co-precipitation of Pu into more stable crystalline Fe-bearing minerals is less straightforward, with the hematite structure rejecting the overwhelming majority of the Pu while the goethite structure incorporated most of the Pu.

Differences in Pu co-precipitation behavior may be explained by considering the structural constraints imposed by the goethite and hematite. Future efforts will focus on using XAS at the Stanford Synchrotron Radiation Light source to understand the structural mechanisms by which hematite and goethite incorporate Pu into their structure.

Calcite: To date there have not been any rigorous, published studies of Pu co-precipitation in minerals; however, several studies describing the co-precipitation of actinides (U(IV), U(VI), Np(V), and Cm(III)) in calcite ($CaCO_3$) are reported in the literature (Balboni et al. 2014; Fernandez-Diaz 2006; Holliday et al. 2012; Fernandes et al., 2008). The analyses of a 35-million-years old calcite sample confirmed substitution of a tetravalent uranium for divalent calcium, indicating that U(IV) has a stable location in calcite deposited under reducing conditions (Sturchio 1998). Divalent ions such as Zn^{2+}, Mn^{2+}, and Cd^{2+} have ionic radii that range from0.79-0.97Å and can readily be accommodated in the calcite structure (Fernandez-Diaz 2006). The ionic radius of Pu^{4+} is 0.91Å, thus it might be expected to be readily incorporated into the calcite structure. Natural and synthetic crystals of calcite and aragonite (a calcium carbonate polymorph) can incorporate U(VI) and Np(V) in various amounts (Kelly 2006). Of these, calcite

Table 1C1. Concentration (ppm) of Pu in calcite crystals synthesized with Pu(IV) or Pu(VI). The average was calculated from 15 crystals. The min and max values represent the lowest (min) and highest (max) concentration of Pu for each set of crystals.

	Pu(IV)	**Pu(VI)**
Average (ppm)	100	600
min (ppm)	2	200
max (ppm)	370	2700
# crystals analyzed	15	15

appears to tolerate higher levels of nepunyl incorporation (Heberling 2011, Balboni et al. 2014).

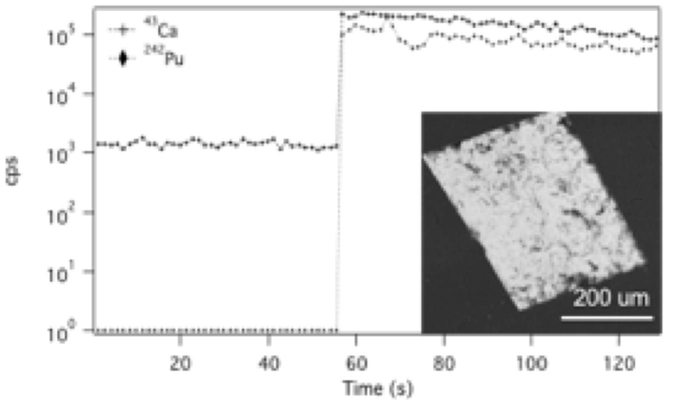

Figure 1C2. ICP-MS data for ^{43}Ca and ^{242}Pu prior to laser ablation (0–55 seconds) and during laser ablation (55–125s) of a calcite crystal (insert).

In 2016, crystals of calcite were synthesized from solution containing 1000 ppm of either Pu(IV) or Pu(VI) following the method described by Balboni et al. 2014. Individual crystals from each synthesis (10 to 100 µm in size) were selected and analyzed for Pu content by laser ablation inductively coupled plasma mass spectrometry (Figure 1C2). Preliminary results indicate that calcite synthesized in the presence of either Pu(IV) or Pu(VI) incorporate Pu to some extent (10s to 1000s of ppm). However, Pu(VI) partitions more strongly onto the calcite solid than Pu(IV) (Table 1C1). Plans for next year are to characterize the material using X-ray photoelectron spectroscopy analysis to determine the oxidation state of Pu, and XAS to determine Pu coordination environment in the calcite structure. Experiments aimed at determining the extent of incorporation of Pu(V) in calcite are planned for 2018.

Focus Area 1D: Probing the Role of Microbes in Altering Pu Behavior

Lead: Y. Jiao

Microorganisms are associated with a variety of radioactive materials at DOE sites (Barnhart et al. 1980; Francis et al. 1980; Frederickson et al. 2004) and it is becoming well-known that Pu speciation and solubility are affected by microorganisms (Gillow et al. 2000; Neu et al. 2005; Panak and Nitsche 2001). Although it has been reported that certain microorganisms can survive in Pu-contaminated environments (Frederickson et al. 2004), little is known about the mechanisms of microbe-Pu interaction. Microbe–metal interactions include reactions with cell wall structures, enzymes, polysaccharides, or ligands excreted by many microorganisms found in natural waters. Furthermore, surface reaction with functional groups on the cell wall can lead to changes in solubility through local nucleation/precipitation or redox reactions (Boukhalfa et al. 2007; Neu et al. 2005; Panak and Nitsche 2001; Wildung and Garland 1982). Besides carbohydrates, enzymes have also been reported to mediate metal precipitation (Beazley et al. 2007; Boukhalfa et al. 2007a; Francis 2007). All these microbial processes must be understood in order to better predict the role of microbes in Pu biogeochemical cycling.

> Hypothesis: *The composition of biomolecules produced from microorganisms (carbohydrates, proteins, and other small ligands) will affect the chemical speciation of Pu and control its sorption onto cell surfaces. Secreted phosphatases will lead to the formation of Pu-P minerals.*

Task 1D-1: EPS-Pu interactions

Contributor: M. Boggs

This work was completed and published in 2016: Boggs, M.A., Jiao,Y., Dai, Z., Zavarin, M., and Kersting, A.B. Plutonium Reaction with Pseudomonas sp. and its Extracellular Polymeric Substances, Applied and Environmental Microbiology, 82: 7093-7101.

In 2011–2012 we isolated and identified the bacterium, *Pseudomonas sp.,* in contaminated groundwater from the NNSS, Nevada. In the recently published work cited above, we examined the redox behavior of Pu on both the outer extracellular polymeric substances (EPS) and the isolated cell surface. We found that biosorption of Pu(V) and subsequent reduction to Pu(IV) was dependent on the presence of EPS and not the cell surface. In addition, we performed TEM to examine the morphology and structure of Pu sorbed on the cell surface and found that EPS influences both the redox transformation and morphology of sorbed Pu. Bacterial cellular and extracellular structures are known to interact with radionuclides including Pu, whereas the role of EPS in Pu(V) reduction and biosorption identified in this study had not been previously reported. Our work highlights the importance of organic macromolecules (e.g. EPS) of microbial origin in affecting the redox transformations, speciation, and basic geochemistry (e.g., environmental mobility and fate) of Pu.

The findings from Task 1D-1 have led to on-going investigations to understand how cellular exudates control the redox behavior, complexation and mobility of Pu (see Task 1B-1).

Focus Area 1E: Simulating the Molecular Level Behavior of f-Elements

Lead: P. Huang

Little direct information is available on the chemical nature and reactivity of aqueous actinides at very low concentrations. This is especially problematic for tetravalent actinide ions such as Pu(IV), which have a strong tendency towards hydrolysis, polymerization, and colloid formation in solution. Although *ab initio* simulations are promising tools for investigating the atomic-scale behavior of Pu(IV), such simulations are not routinely performed. This is due in part to two fundamental difficulties: 1) the need to explicitly account for the local solvation environment, and 2) the accurate treatment of f-electron correlation effects. In this Focus Area, we seek to establish methods and models that will enable the atomic-scale simulation of Pu(IV) at environmentally relevant conditions, i.e., the femtomolar concentration regime.

Hypothesis*: Interfacial water structure and hydrogen bonding is a critical factor in determining the hydration and chemical behavior of actinide ions in solution and at mineral-water interfaces*

Task 1E-1: Pu sorption at the mineral-water interface

Contributors: P. Huang, C. Lo

As a prelude to examining Pu interaction at the mineral-water interface, we continue to study the hydration behavior of a series of actinide and actinide analogs. In 2016, we completed the theoretical characterization of Th(IV) monomeric hydrolysis products using first-principles molecular dynamics (FPMD) techniques. The fully hydrolyzed product, $Th(OH)_4$(*aq*), is a seven-coordinate (CN = 7) complex with four hydroxyls and three coordinated waters in the inner sphere. However, the short time scales typical of FPMD simulations can sometimes yield intermediate states rather than the true ground state. Thus, for 2017 we had proposed to carry out free energy calculations to explore the possibility of a $Th(OH)_4$(*aq*) complex with a different number of coordinated waters. This effort is now complete and the study has been submitted and accepted for publication in *Chemical Physics Letters*. In short, we verified that for $Th(OH)_4$(*aq*) the CN = 7 complex is the lowest energy complex; there is also an eight-coordinate (CN = 8) structure that is higher in energy by ~ 4.5 kcal/mol. This conclusion is based on two complementary approaches: 1) first-principles metadynamics simulations for a 3D-periodic model (Fig. 1E1), and 2) quantum chemical calculations for finite cluster models that employ varying approximations for electron correlation.

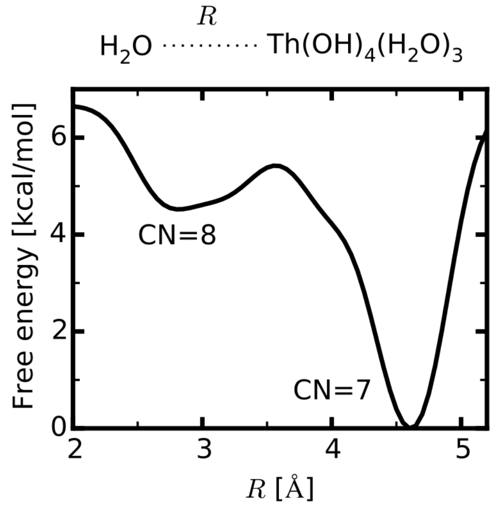

Figure 1E1. Metadynamics free energy profile for the addition of one water molecule to the inner coordination sphere of $Th(OH)_4$(<u>*aq*</u>). *R* is the distance between the Th ion and the incoming water oxygen as illustrated in the upper schematic. The lowest energy minimum represents a structure with a coordination number of seven (CN = 7) and an outer-sphere water at *R* = 4.6 Å. The addition of this water into the inner sphere yields a higher, shallow minimum at *R* = 2.8 Å corresponding to a CN = 8 structure.

The addition and dissociation of coordinated waters is fundamental to reactions of metal complexes in aqueous environments, e.g., actinide substitution reactions that occur in surface complexation processes. Thus, starting with the CN = 7 structure, our next step is to evaluate the free energy differences due to water addition (CN = 7 to 8) and water dissociation (CN = 7 to 6) for the series $Th(OH)_4$(*aq*), $Ce(OH)_4$(*aq*), and $Pu(OH)_4$(*aq*). Of the tetravalent actinides, Th(IV) has the largest ionic radius; Ce(IV) and Pu(IV) are very similar to each other in size and are both smaller than Th(IV). In addition, Pu(IV) also has a partially filled 5f-subshell which may influence bonding. Thus, the comparison between Th(IV) and Ce(IV) will allow us to ascertain the role of size, while the comparison between Pu(IV) and Ce(IV) will allow us to isolate the role of 5f-electrons in Pu(IV). Our preliminary comparison of the bonding between Ce(IV) and Pu(IV) suggests that there is a greater degree of covalency in the Pu(IV)-water coordinate covalent bond; this can potentially result in deviations in the energetic trends for water addition and dissociation, and may be correlated with reactivity differences between Pu(IV) and Ce(IV).

Focus Area 1F: Characterizing Molecular Level Actinide Complexes and Redox Transformations

Lead: H. Mason

The mechanisms of Pu interactions with solid mineral surfaces are still poorly understood at the molecular level. Thermodynamic and/or kinetic models have been used to provide a deeper understanding of the reactions observed at the macroscopic level (Tinnacher et al. 2011, Begg et al. 2015). However, these models are often inherently empirical or semi-empirical, and may lack complete understanding of the underlying molecular mechanisms driving these reactions. The fundamental rates and mechanisms of reaction between actinides and mineral surfaces are still poorly understood.

> *Hypothesis: The interactions of actinides at mineral surfaces are tightly coupled to their redox state and their reactions with dissolved ligands.*

Task 1F-1: Pu complexes on minerals surfaces

Contributors: J. Begg, H. Mason

Investigation of Pu-mineral reactions is hindered by the fact that direct analysis (e.g., x-ray absorption spectroscopy, XAS) must be performed at very high Pu concentrations (>100s ppm) that are often above the solubility of Pu(IV), while investigations at environmentally relevant concentrations rely on indirect methods (e.g., solvent extraction). The inability to directly measure the Pu-mineral reactions limits our conceptual understanding of Pu behavior at the mineral-water interface.

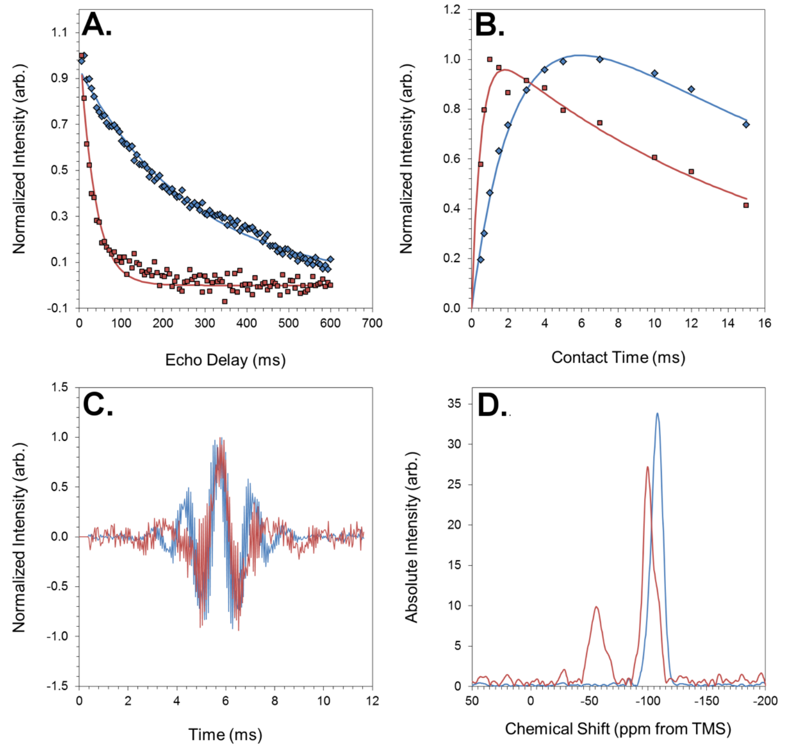

Figure 1F1: Our new statistical analysis method produces a data dense set at a fraction of acquisition time and on much smaller samples than traditional methods. A: T_2 decay curves, B: CP kinetics and C: echo components that can be Fourier-transformed into individual spectral components, D: individual spectral components

We have continued to explore the methods developed in Mason et al. 2012 and 2016 towards the application of these methods to the Pu-quartz system. We have prepared samples from a long-term aging experiment that we plan to analyze with the same statistical methods used to explore divalent and trivalent metal sorption. Due the need for secondary containment, we have devoted effort in this last year to combining our previously reported processing methods with additional NMR experiments designed to boost the signal obtained from small amounts of material. Our new statistical analysis method has been applied to functionalized silica materials and produces data dense spectral sets (Figure 1F1) that contain information about the T_2 decay, CP kinetics, and chemical shift information about unique surface environments. The extracted components again can be assigned to surface and internal silica sites. Further, comparison to standard techniques indicate these methods provide rapid results (less than 1 day) that would otherwise have required weeks of acquisition time. Given the small amount of Pu-quartz material we will be analyzing, we are now confident that this procedure will provide new insight to this interaction.

Task 1F-3: Np ligand exchange

Contributors: H. Mason, C. Pilgrim

The focus of our actinide NMR development efforts in 2016 has been the characterization of Np-ligand complexes and ligand exchange kinetics. These included an examination of the pressure dependence of Np carbonate ligand exchange kinetics, Np(VI)-HEDPA reaction kinetics, and Np(VI)-oxalate ligand exchange kinetics, described below. These experiments were the result of our continued collaboration with U.C. Davis (Bill Casey) which is linked to the Energy Frontier Research Center led by Peter Burns at Notre Dame.

Pressure-dependent measurements of ligand exchange kinetics of the $[NpO_2(CO_3)_3]^{4-}$ complex were completed. Importantly, the results (Figure 3A1) show a pressure dependence that is opposite of the trend seen in the uranyl system. This suggests that the presence of f-electrons in the Np(VI) complex leads to a substantial difference in the mechanism of ligand exchange relative to the equivalent U(VI) complex.

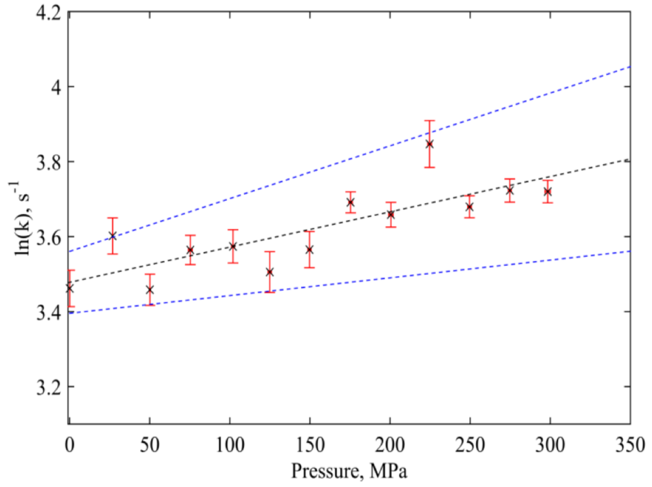

Figure 3A1 Rate coefficient of the self-exchange reaction of $[NpO_2(CO_3)_3]^{4-}$ versus pressure for the pH = 9.72 sample. Taken from Pilgrim et al., 2017

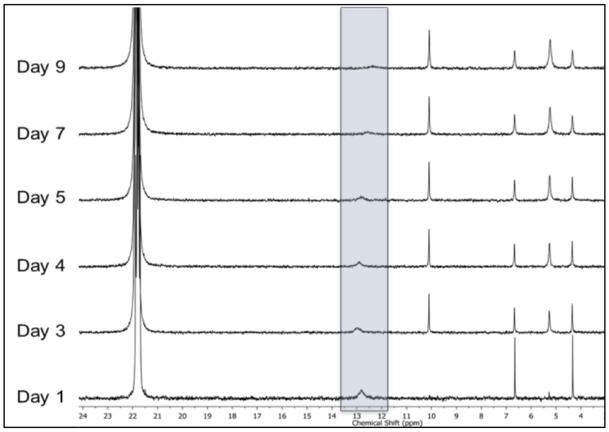

Figure 3A2. ^{31}P NMR of the $[NpO_2]^{2+}$-HEDPA system. Starting from Day 1, the supposed Np-HEDPA complex (gray band) can be seen to degrade over time.

In previous work, Fugate et al. used NMR as a tool for speciation and kinetic studies of U(VI) and Np(V) with 1-Hydroxyethane-1,1-diphosphonic Acid (HEDPA). We were interested in extending this work to Np(VI). In the case of the Np(V) system, it was only studied in an acetate buffered system (pH ~4.6). We were initially interested in looking at a mixture of Np(VI) and HEDPA across a pH range of 4–12 to determine the nature of the Np(VI) complexes. A Np(VI)-HEDPA complex seemed to form around pH 10. However, the complex was unstable with regard to the Np(VI) oxidation state and the signal disappeared with time (Figure 3A2). Subsequent sharp peaks were seen to grow in as well, which led to the conclusion that the Np(VI) reduced to Np(V) while oxidatively decomposing the HEDPA ligands and destroying any complexes that may have formed. While the results are interesting from the standpoint of ligand-facilitated reduction of Np(VI), this was not the primary goal of our investigation, and further examination of the Np(VI)-HEDPA complex will not continue.

Next we examined the oxalate ligand system. Oxalate has been studied with the U(VI) species, by itself and mixed with fluoride in a hetero-ligand arrangement (Aas et al 1999). Oxalate has also been shown to make stable complexes with Np(V), and the titration of Np(V) with oxalate has been studied for speciation via UV/Vis (Rao et al 2010). The kinetics of the exchange of the ligand has yet to be explored. From speciation calculations, $[NpO_2(C_2O_4)_2]^{3-}$ appears to be the dominant complex in solution through a wide range of pH values (pH 6-12). A series of NMR measurements have been run on solutions in this pH range, and as can be seen in Figure 3A3, there are two signals seen (similar to the $[NpO_2(CO_3)_3]^{4-}$ system). With varying temperature, broadening of these two signals occur, which suggests exchange between the free and Np(V)-complexed oxalate. Ongoing experiments are exploring the ligand exchange kinetics of the $[NpO_2(C_2O_4)_2]^{3-}$ complex.

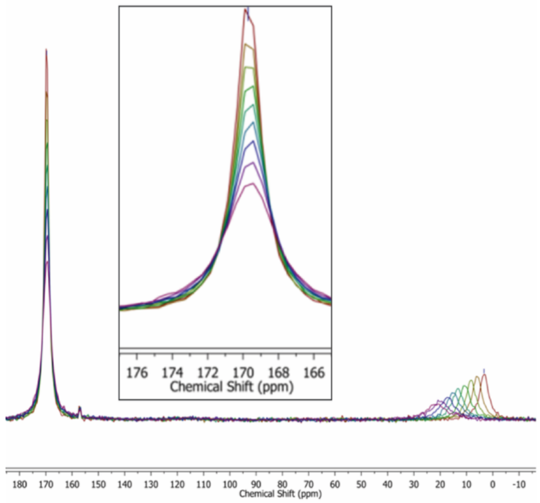

Figure 3A3. ^{13}C NMR of the $[NpO_2(C_2O_4)_2]^{3-}$ system. Two significant peaks are seen, the free oxalate (169 ppm) and the bound oxalate (between 3.3 ppm and 20 ppm). The different traces are at various temperatures, where broadening is seen in the peaks, suggesting exchange is occurring between the sites.

Thrust 2: Identification of Processes Controlling Pu Behavior Under Field Conditions and at Field-Relevant Timescales

Thrust 2 Coordinator: A. Kersting

The objective of Thrust 2 is to understand how individual biogeochemical processes evaluated in Thrust 1 are coupled (or not) to produce the inherent complexity of actinide behavior observed in natural environments. We are evaluating our conceptual and mechanistic understanding in an integrated fashion from the perspective of remediation and long-term stewardship of legacy sites. In particular, Thrust 2 emphasizes actinide behavior under field conditions and at field-relevant timescales.

> *Hypothesis: The biogeochemical processes that ultimately control actinide subsurface mobility/immobility are driven by local variations in the geology, geochemical conditions, colloid composition and abundance, and chemical characteristics of the initial actinide source.*

In order to test our hypothesis, we have divided this thrust into the following three Focus Areas:

- *2A: Characterization of field samples from Pu-contaminated sites*
- *2B: Characterization of Pu behavior in field and field-analog samples*
- *2C: Parameterization of processes and integration with field observations*

Focus Area 2A: Characterization of Field Samples from Pu Contaminated Sites

Leads: R. Kips and B. Powell

In Focus Area 2A, we are characterizing contaminated sediments at the Savannah River Site (SRS) at the SRS-lysimeter field site. In the SRS-lysimeter site, the depositional characteristics are more controlled and allow us to better monitor the evolution of Pu and Np associations under environmentally relevant conditions and timescales, particularly with respect to the evolution of Pu/Np oxidation states and Pu/Np oxide precipitates.

> *Hypothesis: The reaction rates that ultimately control Pu/Np transport in the environment are slow and/or irreversible. As a result, the Pu/Np characteristics in the environment will retain a signature of the depositional history over a timescale of decades.*

Task 2A-2: Savannah River Site: Characterization of sediments associated with the Pu/Np-doped lysimeter coupons

Contributors: M. Maloubier K. Peruski B. A. Powell, and D. I. Kaplan

This project involves characterizing the Pu and Np sources deployed in a field lysimeter facility at the Savannah River Site (RadFLEx: Radiological Field Lysimeter Facility), which is currently operated by Dr. Daniel Kaplan of the Savannah River National Laboratory and Dr. Brian Powell at Clemson University. Twenty-two lysimeters were deployed in 2012 with Pu and Np sources containing $Pu_2^{III}(C_2O_4)_3(s)$, $Pu^{IV}(C_2O_4)_2(s)$, $Pu^{IV}O_2$ nanocolloids, $NH_4Pu^{V}O_2CO_3(s)$, $Np^{IV}O_2(s)$ and $Np^{V}O_2(NO_3)(H_2O)_n$ (note: Np(V) was added as a solution to a filter paper then dried). The sources consist of a ~2-mg solid sample placed between two glass fiber filters. Plutonium bearing lysimeters were deployed in triplicate and Np lysimeters were in duplicate. Triplicate lysimeters for each Pu source were initially deployed with plans to remove them after approximately 5, 10, and 20 years. Duplicate lysimeters for the Np(IV) and Np(V) sources were deployed with planned analysis after 4 and 10 years.

In 2014 and 2015, one of lysimeter for each of the source materials listed above was removed. The Pu(V) sources were removed in November 2014 and all others were removed October 2015. The lysimeters were destructively sampled to: 1) determine the Pu and Np concentration in soil as a function of distance from the Pu/Np sources, and 2) analyze the sources themselves to determine if any changes occurred in their chemical and physical speciation after approximately 4 years of field exposure. Two lysimeters containing oxide sources ($PuO_2(s)$ and $NpO_2(s)$), deployed in the field lysimeter facility for three years, were characterized by X-ray absorption spectroscopy (XAS) during the last year. Additionally, a set of archived Pu and Np sources for each form listed above, stored in an inert atmosphere under controlled temperature and moisture laboratory conditions, were examined.

In 2014, we monitored the archived $Pu^{IV}(C_2O_4)_2(s)$ and $NH_4Pu^{V}O_2CO_3(s)$ sources as well as the $NH_4Pu^{V}O_2CO_3(s)$ sources deployed for 3 years and found transformation to $PuO_2(s)$ occurred in all samples. However, more $PuO_2(s)$ was present in the field deployed samples than the archived samples. This year we have examined the $PuO_2(s)$ and $NpO_2(s)$ sources.

Table 2A1: Pu and Np EXAFS data for both the archived sources controls and field exposed lysimeter data (blue shading).

Sample	First shell	Second shell	Third shell
PuO_2 crystal structure	7 O at 2.34 Å	-	9 Pu at 3.82 Å
PuO_2 colloidal particles	8 O at 2.294 Å	-	3.9 Pu at 3.793 Å
NpO_2 crystal structure	8 O at 2.35 Å	-	12 Np at 3.84 Å
PuO_2 colloidal particles σ^2 (Å^2) =	6.3 O at **2.31(1)** Å 0.008	1.7 O at **3.30**(1) Å 0.01	4.2 Pu at **3.80(1)** Å 0.005
Lys44: PuO_2 colloidal particles σ^2 (Å^2) =	6.3 O at **2.31(1)** Å 0.009	1.7 O at **3.31**(1) Å 0.008	4.4 Pu at **3.79(1)** Å 0.006
Lys31: $NpO_2(s)$ σ^2 (Å^2) =	8 O at **2.35(1)** Å 0.004	-	*Np at **3.84(1)** Å -

*Uncertainty due to the presence of 500 ppm Pu in the NpO2 source hinders fitting coordination numbers beyond the third shell.

The EXAFS spectra of PuO_2 deployed in the field lysimeter facility and the archived 'control' source are similar (Table 2A1). Both show the presence of PuO_2 colloids having a slightly shorter Pu-O and Pu-Pu bond distance compared to crystalline PuO_2 (Ekberg et al., 2013). The EXAFS spectrum of $NpO_2(s)$ deployed in the field lysimeter facility also appears to mostly retain its original reduced state. However, as discussed below, some fraction of the source migrated away from the original source over the course of its 3.5-year exposure in the field.

No aqueous Np was measured in the effluent from the $NpO_2(s)$ lysimeter, which is consistent with the expected low solubility of $NpO_2(s)$ and low mobility of Np(IV). However, approximately 33% of the initial $NpO_2(s)$ source was leached into the soil, suggesting that the Np(IV) source was oxidized to Np(V) while in contact with oxidizing rainwater.

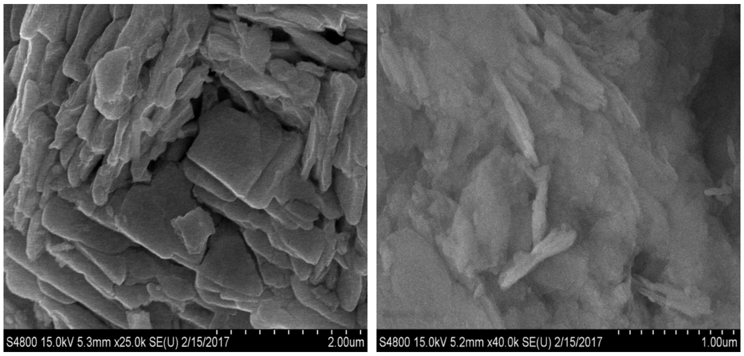

Figure 2A1. SEM images of fresh NpO_2 (left) and NpO_2 source after 3.5 years at RadFLEx (right), showing morphological changes to source material after exposure to field conditions.

$Np^{IV}O_2$ source samples were subjected to autoradiography, EXAFS, and SEM for characterization and comparison to the archived control sources. The alteration of the $Np^{IV}O_2$ surface was observed using SEM (Figure 2A1). Moreover, the presence of the multiple scattering resonance on the XANES spectrum was observed, supporting the hypothesis that the $Np^{IV}O_2$ source was oxidized at the surface while in contact with soil and rainwater, allowing for transport through the soil column. However, the EXAFS spectrum shows that Np is still mainly present as $NpO_2(s)$. The EXAFS fitting could only be performed for the first shell O atoms due to the presence of ~500 ppm Pu in the sample, which led to an interference in the Np EXAFS. In order to better characterize the sources and to evaluate the change after exposure to the lysimeter, the sources will be analyzed by HRTEM and μ-XAS in 2017 and 2018, to determine the crystal structure, particle size, and to probe the oxidation state on the surface.

Focus Area 2B: Characterization of Pu Behavior in Field and Field-Analog Samples

Leads: M. Zavarin and B. Powell

Focus Area 2B is designed to test the transport behavior of Pu associated with field samples and analog field samples from the NNSS, Hanford, and SRS sites. The SRS experiments rely on ongoing experiments at the SRS RadFLEx facility and take advantage of ultralow-level measurement capabilities available at LLNL to monitor Pu migration. Focus Area 2B is intended to test our conceptual understanding of Pu transport and integrate our mechanistic understanding with the more complex conditions that may be present in the field.

> *Hypothesis: Under certain geochemical and Pu depositional conditions, Pu may form an insoluble precipitate, be incorporated into secondary mineral phases, or irreversibly sorbed to minerals. As a result, Pu desorption rates may be much slower and colloid facilitated transport rates much greater than would be predicted based on binary adsorption/desorption kinetics.*

Task 2B-3: Savannah River Site: field lysimeter experiment

Contributors: M. Maloubier and B. Powell

In 2016, we sampled our RadFLex facility effluents using a low-level technique that concentrates Pu from a larger initial sample volume and uses long alpha spectroscopy count times to measure concentration. In a full suite of samples from lysimeters containing $Pu_2(C_2O_4)_3$, $Pu(C_2O_4)_2$, PuO_2, and $PuO_2NH_4CO_3$ sources, Pu concentrations ranged from 3.3×10^{-15} to 9.0×10^{-13} M. These values are near solubility limits for Pu(IV). We have reduced the sampling intervals from the lysimeter facility this year and have combined 9 months of effluent to repeat these measurements at the end of 2018.

Task 2B-4: Influence of NOM on Pu mobility under advective flow conditions

Contributors: J. Wong, and B. A. Powell

Data from a number of column experiments in 2016 showed the influence of organic ligands on Pu mobility in SRS soil (Figure 2B1). In 2017, the majority of our efforts were spent developing quantitative models of these data and testing several conceptual models as described below. The column experiments were performed with a sandy-clay-loam sediment from the Savannah River Site (15-cm column, pH 4.8, 10 mM NaCl, 1 hour fluid residence time). In each experiment, a Pu(IV) spike solution was introduced, followed by ~100 pore volumes of citrate, DFOB, or a control solution containing no organic ligands. The column was sectioned, and the sediment sections were leached with 6 M HNO_3 for 3 days.

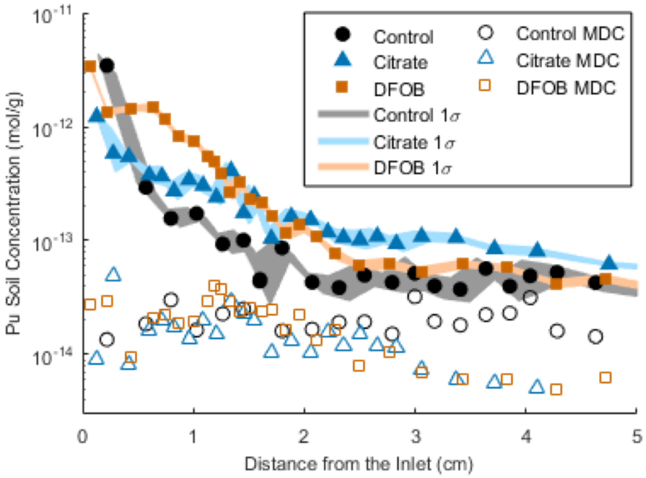

Figure 2B1. Pu sediment profile at the entrance of columns packed with sediment from the Savannah River Site. The Pu spike was added as a 1 PV finite step followed by 2–3 PV background solution and ~100 PV of 278 μM citrate, 278 μM DFOB, or organic-free solution. The 1σ confidence band is shown.

In each of the elution profiles, 10–20% of Pu was recovered. This was neither an effect of citrate nor DFOB, since it was also observed in the control experiment. The retardation factor of this Pu is much lower than would be expected for Pu(IV), but it could be caused by Pu(V), which formed in the spike solutions from the oxidation of Pu(IV).

The majority of the Pu remained within 2 cm of the inlet (Figure 2B1), and it appears that in the presence of citrate and DFOB, Pu transport was slightly enhanced relative to the control experiment. While the exact cause of enhanced transport in the presence of citrate and DFOB cannot definitively be determined, it may be caused by the formation of Pu-ligand aqueous complexes. This is consistent with the behavior previously observed in the 2016 Pu-ligand-goethite flow-cell experiments.

Three possible processes were proposed to explain the distribution of aqueous and sorbed Pu: (1) persistence of Pu(V) during transport, (2) transport facilitated by soil-generated colloids, and (3) transport facilitated by formation of aqueous complexes with native soil organic matter (SOM). One-dimensional reactive transport modeling exploring a wide range of parameter values was unable to predict the data using colloid-facilitated transport or formation of Pu–DOM complexes. The transport of a mixture of Pu(IV) and Pu(V) with a low rate of surface-mediated reduction remains a possible explanation (Figure 2B2). While these data indicate a slight enhancement of Pu mobility in the presence of citrate and DFOB, the overall effect of the organic ligands was small. Thus, it appears that this SRS soil has sufficient sorption capacity to retain Pu, the organic ligands, and any the Pu-ligand complexes. Therefore, NOM may not lead to enhanced Pu mobility in SRS soils. This assumption must be confirmed with other end member soils as the spatial variation in soil mineralogy, leading to differences in Pu and organic matter sorption affinity, could also lead to enhanced transport.

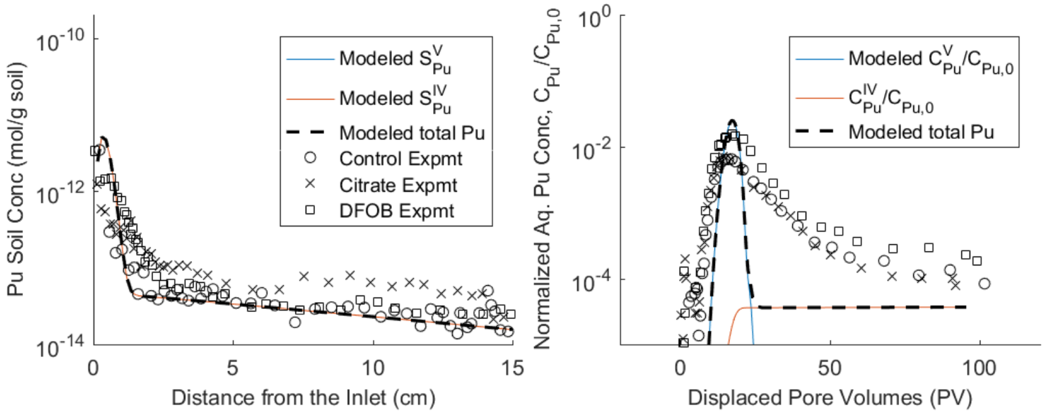

Figure 2B2. An example of a reactive transport model, which includes surface mediated reduction, is superimposed with the Pu soil profile (left) and the Pu elution profile (right). This model assumes 20% of Pu as Pu(V), a first-order surface-mediated reduction rate of 0.0008 min^{-1}, and Pu(IV) and Pu(V) distribution coefficients of 1000 and 8 $\text{mL}\cdot\text{g}^{-1}$, respectively

Focus Area 2C: Parameterization of the Mechanistic Processes and Integration with Field Observations

Lead: M. Zavarin

Since its inception, the LLNL SFA has focused on limited and targeted modeling efforts that quantify the processes controlling Pu redox transformations and adsorption/desorption kinetics at mineral–water interfaces. Within the limited scope of this SFA, we do not intend to develop comprehensive “bottom up” models that simulate Pu transport behavior at a mechanistic level. Instead, modeling is limited to efforts that aid in the development of a conceptual understanding of actinide transport mechanisms. This same approach will be taken when integrating the mechanistic and molecular level studies in Thrust 1 with the more complex observations and experiments conducted at the field scale in Thrust 2.

Hypothesis: The reaction rates that ultimately control Pu transport behavior are sufficiently slow and/or irreversible such that equilibrium models are ineffective in predicting Pu transport behavior at either laboratory or field temporal and spatial scales.

Task 2C-1: Development of Pu/Np surface complexation/ion exchange models

Contributor: M. Zavarin

The need to develop self-consistent surface complexation/ion exchange models, in concert with thermodynamic models, for contaminant transport modeling was identified many years ago (Bradbury and Baeyens 1993). This issue was expressly identified in the recent NEA Sorption project reports (Davis et al. 2005; Ochs et al. 2012). The best path forward for developing such databases remains an open question (Geckeis et al. 2013). However, we have aligned our efforts with the RES^{3}T (Rossendorf Expert System for Surface and Sorption Thermodynamics) project whose aim is to develop a digital open-source thermodynamic sorption database. The RES^{3}T database includes mineral-specific surface complexation constants that can be used in additive models of more complex solid phases such as rocks or soils. However, the database does not provide recommended values or capture the primary sorption data. As a result, the RES^{3}T project provides a foundation for developing a comprehensive surface complexation database but does not go so far as to provide one. Our efforts in FY16 focused on complementing the RES^{3}T project (in collaboration with the RES^{3}T developers) and providing a new approach to develop self-consistent parameterization of surface complexation/ion exchange reaction parameters. This approach was described in our 2016 report. We continue to use this approach in our modeling efforts as part of this SFA (e.g., Conroy et al. 2017) and are applying these surface complexation/ion exchange models (as well as simplified approaches) to integrate observed field and laboratory transport behavior of actinides.

Task 2C-2: Parameterization of aging processes and associated reaction rates

Contributor: J. Begg

Throughout this SFA, we have relied on a semi-empirical approach to simulate both Pu surface-mediated reduction and aging processes on surfaces. In this approach, relatively simple first-order reactions are arranged in-silico (e.g., Figure 2C1) based on a finite difference approach (Euler method). The most recent version of our code was written using Microsoft© Visual Basic 2010 Express Version 10 software and linked to the PEST (Parameter ESTimation) program (Doherty, 2003). PEST is a model-independent parameter optimizer that uses least square minimization based on the Gauss–Marquardt–Levenberg method. These same equations have also been implemented in Matlab, and C-ride/Hydrus. To date, this modeling framework has been used to parameterize Np sorption/desorption on goethite (Tinnacher et al. 2011), Pu surface-mediated reduction on montmorillonite and bentonite (Begg et al 2013, 2015), Pu sorption/desorption rates in the presence of goethite and natural organic matter Tinnacher et al 2015) Pu sorption/desorption on montmorillonite (Begg et al. 2014). Pu desorption from hydrothermally altered nuclear melt glass and Pu transport in Savanah River Site sediments.

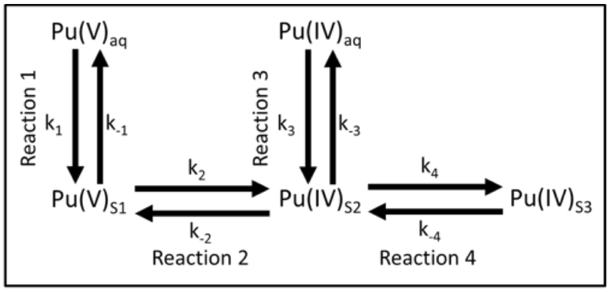

Figure 2C1. Semi-empirical model of surface-mediated reduction and aging processes used for the simulation of Pu sorption/desorption kinetics on mineral surfaces.

The experiments performed to date and associated modeling efforts indicate that plutonium desorption rates are on the order of months and even years. Furthermore, desorption is, in part, controlled by the rates of reoxidation of Pu(IV) on mineral surfaces. Implications of our modeling results are two-fold. First, it is now apparent that sorption/desorption kinetic experiments commonly reported in the literature are performed at timescales that are too short to interrogate sorption reversibility and hysteresis effects. Experiments must be performed on timescales of months or even years to differentiate between hysteretic, reversible, and kinetically limited processes. More importantly, our results thus far imply that adsorption/desorption phenomena on colloids at environmentally relevant timescales (50 to >100 years) may result in limited colloid-facilitated transport. In effect, Pu can remain associated with a colloid on timescales of months to years but will eventually desorb. This has led to our investigation into additional phenomena that may lead to Pu (and contaminants in general) association with colloids at longer, environmentally relevant timescales (e.g. co-precipitation, stabilization on mineral surfaces). These phenomena are the focus of 2018 efforts.

Thrust 3: Development of Spectroscopic and Computational Methods to Probe Actinide Behavior

Thrust 3 Coordinator: H. Mason

The success of our program relies on the development and use of state-of-the-art spectroscopic and computational capabilities that are unique to LLNL. Development of these spectroscopic and computational capabilities is intended to benefit the scientific community as a whole. Our intent is for our SFA to be a hub for world-class, U.S. and international radiochemistry research and education. We have identified five capabilities that will be developed and enhanced as part of this SFA:

A. *NMR and EPR of Actinide Complexes*
B. *NanoSIMS of Actinides*
C. *Actinide TEM-EELS*
D. *Actinide Analysis at the Center for Accelerator Mass Spectrometry (CAMS)*
E. *f-Element Ab Initio Modeling*

Each of the capabilities listed above includes a lead scientist responsible for method development. All advances in capability development are integrated into the appropriate focus areas in both Thrust 1 and Thrust 2.

Focus Area 3A: NMR and EPR Analysis of Pu/Np Complexes

Leads: H. Mason and R. Maxwell

The focus of our actinide NMR development efforts in 2016 and 2017 has been the characterization of Np-ligand complexes and ligand exchange kinetics. This work is discussed in Task 1F-1: Pu complexes on mineral surfaces.

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Focus Area 3B: NanoSIMS Analysis of Pu

Lead: R. Kips

While the focus of our NanoSIMS efforts in recent years has been on the characterization of Pu distribution in Hanford Z-9 trench sediments, we seized an opportunity in 2017 to expand our NanoSIMS capabilities to study ^{137}Cs distribution in contaminated sediments. These analyses were pursued for two reasons. First, ^{137}Cs is often a co-contaminant with Pu in the environment (e.g. Kersting et al., 1999). Thus, its migration relative to Pu may provide insight into the underlying mechanisms controlling transport of both the actinides and ^{137}Cs. Second, two graduate students interested in studying environmental radiochemistry (Chad Durrant, Penn State University and Katie Hoffman, University of Cincinnati) joined our research program on graduate scholarships. Chad Durrant, a current Livermore Scholar, has focused on sorption/desorption kinetics of Cs and Pu from mineral colloids while Katie Hoffman was recently awarded an Office of Science Graduate Student Research fellowship (SCGSR) to study ^{137}Cs distribution in Marshall Islands soils using advanced analytical techniques (e.g. NanoSIMS). NanoSIMS is showing promise for expanding our actinide NanoSIMS capabilities to other radiologic contaminants of interest (Figure 3B1). Initial results indicate that ^{137}Cs is distributed heterogeneously in the carbonate sediments from the Marshall Islands. Additional NanoSIMS and SEM characterization efforts, along with desorption experiments based on the "Float-a-Lyzer" system developed by Chad Durrant (Durrant et al., 2017) will form basis for this fellowship research.

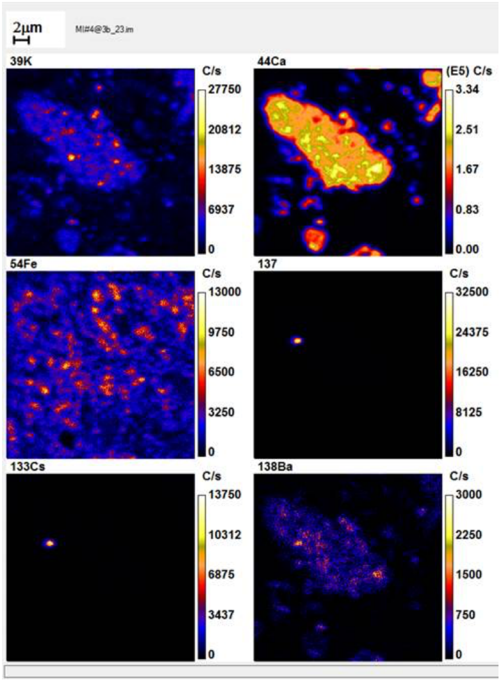

Figure 3B1. Ion images (25×25 um) collected by NanoSIMS on Marshall Island soil samples at m/z ^{39}K, ^{44}Ca, ^{54}Fe, ^{133}Cs, 137 and ^{138}Ba showing a hot spot in the m/z 137 ion image close to the edge of the calcium carbonate grain. The 137/138 ratio was found to be much higher than the natural barium isotope ratio, and given the correlation with the ^{133}Cs ion image, the majority of counts at 137 were attributed to ^{137}Cs.

Focus Area 3C: TEM-EELS of Pu/Np Nanocolloids

Lead: Z. Dai

In 2015, LLNL purchased a Titan STEM (FEI Titan 80-300 FEG STEM), a new generation state-of-the art 80–300 kV analytical transmission electron microscope (TEM). The Titan 80-300 transfers information below 1 Å and routinely obtains high-resolution phase-contrast imaging (HRTEM), atomic-resolution Z-contrast imaging, and atomic-scale mineralogical and petrographic mapping. Key features of the Titan STEM are a high-brightness FEG gun, S-TWIN objective lens, Gatan's UltraScan 1000P (2k x 2k) CCD camera, and GIF Quantum-ER filter. The GIF Quantum filter combines advanced dodecapole-based electron optics with a fast CCD camera system to yield an imaging filter with highly detailed electron energy loss spectroscopy (EELS) and energy-filtered transmission electron microscope (EFTEM) datasets. Energy resolution of the EELS is better than 0.8 eV without a monochromator. This Titan STEM has the potential to be upgraded as an even more powerful Cs-corrected SuperSTEM. This Titan STEM is available to handle radioactive samples.

In FY17, we used the new TEM on several of our projects including the characterization of PuO_2 nanocolloids (Task 1C-1), Pu co-precipitation with iron oxide phases (Task 1C-1), Pu-EPS interaction (Task 1D-1), and field lysimeter Pu coupons (Task 2A-2). An image of the large PuO_2 nanocrystals produced in the presence of Ba^{2+} ions is shown in Figure 3C1). Detailed results are reported in Thrust 1.

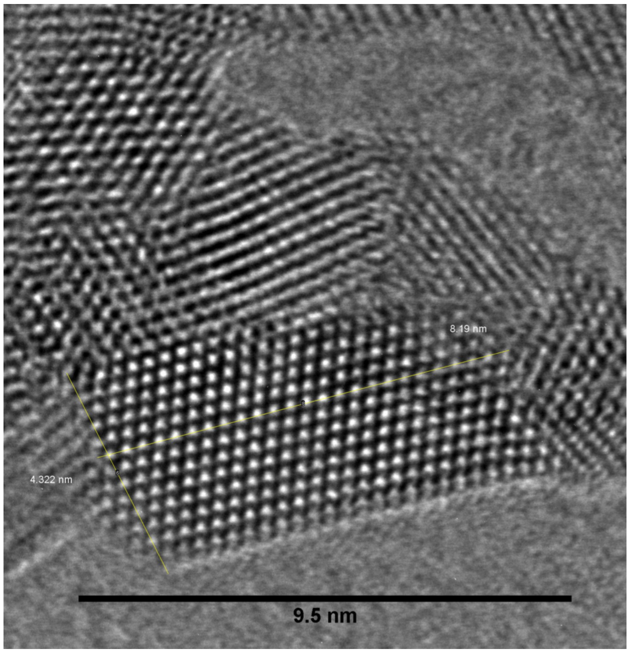

Figure 3C1. TEM of large PuO_2 crystallites formed in the presence of divalent (e.g. Ba^{2+}) ions. These nanocrystals are, by far, the largest we have successfully synthesized under low temperature conditions.

Focus Area 3D: CAMS Analysis of Pu/Np at Femtomolar Concentrations

Leads: S. Tumey

In collaboration with the University of Manchester (UK) and the Karlsruhe Institute of Technology (KIT, Germany), we have begun a study of actinide distribution and release rates from sediments located near the Sellafield Site, UK. The focus of this new effort will be the quantification of actinide release rates from Ravenglass estuary sediments under oxic and anoxic conditions. The 2016 and 2017 effort involves three phases. The first was to collaborate with the University of Manchester team in collecting new sediment cores from the Ravenglass estuary downgradient from the Sellafield Site, and have these cores sent to LLNL for analysis. The cores were collected last summer, have arrived at LLNL, and are currently being maintained under anaerobic conditions. The second phase was to have Dr. Francesca Quinto (KIT) visit LLNL and develop her novel accelerator mass spectrometry (AMS) capability for actinide quantification at LLNL's Center for Accelerator Mass Spectrometry (CAMS). Dr. Quinto visited in April 2016 and successfully demonstrated the target preparation and counting methods that allow analysis of multiple actinides simultaneously using a single AMS target. The third phase will be to return to LLNL in 2018 and quantify actinide distribution in Ravenglass estuary sample.

In the spring of 2017, Dr. Quinto worked with LLNL team members to prepare a series of calibration samples to evaluate the potential for performing multi-isotope actinide measurements on the LLNL AMS. These samples were comprised of a mixture of ^{233}U, ^{236}U, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{242}Pu, and ^{243}Am isotopic standards co-precipitated with iron oxyhydroxide. Two sets of samples, one precipitated from pure water matrix and the other from an artificial seawater matrix, were prepared to test for matrix effects. We determined that the AMS electrostatic bouncing system has an effective mass range of +/- 8 amu, meaning that all isotopes of interest can be measured simultaneously in a single sample. Furthermore, we observed linear response for all isotopes with typical backgrounds of $\sim 10^4$ atoms. The samples prepared from the artificial seawater matrix caused performance issues with the ion source indicating that residual salts are indeed an issue. We have identified additional procedures that can be applied to the AMS targets to remove residual salts and are testing these procedures this summer.

Dr. Quinto will return to LLNL next year to perform analysis on solutions from Ravenglass core samples. In the first of these experiments, we will digest portions of the cores to measure the total concentrations of Np, Pu, and U isotopes. We will then undertake desorption experiments on the sediments under both oxic and anoxic conditions using artificial seawater. The results from this work will help determine the stability of sorbed radionuclides on Ravenglass sediments and the impact of oxygen. The importance of anoxic versus oxic conditions relates to the tendency for deposited Sellafield sediments to be re-mobilized during storm events. Although the accumulation of Sellafield-derived radionuclides in near field and far field sediments has been extensively studied,the processes controlling radionuclide association with sediment particles has not been adequately addressed. Applying CAMS capabilities to the study of actinide mobility at the Ravenglass estuary provides an opportunity to study the long-term fate of actinides in the environment and the factors that may contribute to their mobilization.

4.a.ii Scientific Highlights

- We have identified at least two mechanisms controlling Pu(V) reduction to Pu(IV) on montmorillonite clay surfaces: 1) structural Fe contributes to the rate of Pu(V) reduction to Pu(IV) on the clay surface, and 2) the pH dependence suggests a change in the dominant sorption mechanism from surface complexation at high pH to ion exchange at relatively low pH. Importantly, Fe content in clays can play an important role in short term Pu sorption/reduction rates. However, at longer timescales, the k_d appears independent of Fe content. This suggests that Pu interaction with montmorillonite at environmentally relevant timescales may be less sensitive to the unique composition of montmorillonite clays mined around the world.
- Pu sorption mechanisms at high and moderate concentrations affect their respective desorption rates, which can influence Pu migration in the environment. At high concentrations, the surface precipitated Pu-oxides have lower rates of desorption compared to monomeric Pu sorbed at lower concentrations. (Begg et al. 2017, Zhao et al. 2016).
- Natural organic matter plays an important role in Pu reduction and the transport in the environment. Hydroxamate compounds are used by microorganisms for Fe acquisition and have been implicated in Pu reduction by natural organic matter. We combined gas chromatography-mass spectrometry (GC-MS) with UV-Vis spectrometry to track Pu reduction and hydroxamate oxidation under environmental conditions. We showed that the hydroxamate compound, AHA, can reduce Pu(VI) to Pu(V) but not further to Pu(IV). This suggests that hydroxamate functional groups may not be the primary electron donors in NOM that reduce Pu(V) to Pu(IV).
- Ongoing actinide co-precipitation experiments indicate that calcite synthesized in the presence of either Pu(IV) or Pu(VI) incorporates Pu. However, Pu(VI) partitions more strongly into calcite than Pu(IV). For Fe-oxides, although a significant percentage of Pu is structurally incorporated into the metastable ferrihydrite structure, the long-term co-precipitation of Pu into more stable crystalline Fe-bearing minerals is less straightforward. The hematite structure rejects the overwhelming majority of Pu while the goethite structure incorporates most of the Pu. Structural incorporation of Pu in these minerals could serve to immobilize Pu and has particular importance to actinide migration in nuclear waste repository near fields.
- We have shown that EPS from *Pseudomonous* identified from Pu-contaminated groundwater at the National Nuclear Security Site (formerly Nevada Test Site) can readily biosorb and reduce Pu(V) to Pu(IV). Our findings highlight the importance of organic macromolecules of microbial origin in affecting the redox transformations and morphology of Pu. (Boggs et al. 2016).
- First principles DFT simulation of the coordination environment around the hydrated, monomeric $Th(OH)_4(aq)$ and $Pu(OH)_4(aq)$ complexes and bare ions explain the low coordination numbers predicted for the hydroxides complexes (Huang et al. in press).
- We have established a novel solid-state NMR statistical analysis technique (Mason et al. 2016) that will allow us to investigate Pu coordination chemistry at much lower Pu concentrations using smaller sample sizes. This methodology will be applied to our investigation of the Pu/quartz system.
- We investigated the pressure dependence of $[NpO_2(CO_3)_3]^{4-}$ ligand exchange rates using NMR. Unexpectedly, the experiments show a distinct difference in the pressure dependencies of rates of exchange for the uranyl and neptunyl complexes. This suggests that the mechanisms of ligand exchange may change across the actinide series, possibly due to the influence of f-electrons (Pilgrim et al. 2017).
- We continue to engage in RadFLEx (Radiological Field Lysimeter Facility) research which provides an opportunity to investigate the long-term fate of actinides deposited in the environment. We examined the nature of PuO_2 and NpO_2 sources after 3.5 years of exposure to the environment. EXAFS spectra indicate that PuO_2 sources retained their PuO_2 structure. $NpO_2(s)$ sources also mostly retained their original

reduced state. However, some fraction of the Np source migrated away from the original source. The results are consistent with the faster oxidation of NpO_2 and the significant mobility of Np(V).

- We expanded our NanoSIMS actinide capability to study the ^{137}Cs distribution in contaminated sediments from the Marshall Islands. This project helped establish collaboration with faculty from U. Cincinnati and Penn State by having two of their graduate students work on this project. We successfully developed the NanoSIMS methodology to analyze ^{137}Cs at low ppm concentrations and will be apply this technique to a suite of Marshall Islands carbonates.
- In collaboration with the University of Manchester (UK) and the Karlsruhe Institute of Technology (KIT, Germany), we are developing a new technique to simultaneously measure low levels of actinides using accelerator mass spectrometry (AMS). In 2017, Dr. Quinto (KIT) visited and successfully demonstrated the target preparation and counting methods. In 2018, we will apply this new CAMS capability to the study of actinide mobility downgradient of Sellafield effluent discharge and study the long-term fate of actinides in the environment and the factors that may contribute to their mobilization.

4.a.iii Summary of Publications

We presented our research at a variety of national and international meetings. This included 19 oral or poster presentations, of which 7 were invited and 1 was a keynote talk. In addition, we chaired and organized 3 scientific sessions, were invited to sit on 2 expert panel reviews and participated as a conference organizer in 1 international meeting. We have published 9 peer-reviewed papers, 1 manuscript is in press, and 1 has been submitted.

July 2016–June 2017

1. Durrant, C. B., Begg, J. D., Zavarin, M., Ünlü, K., Kersting, A. B. Cesium sorption reversibility and kinetics on illite, montmorillonite, and kaolinite, *submitted to Sci. Total Environ.* 2017.
2. Huang, P., Lo, C., Zavarin, M., Kersting, A.B., Tetravalent actinide hydration from first principles simulations: Characterization of the monomeric hydrolysis products of thorium(IV), *in press to Chem. Phys. Lett.*
3. Chang C., Rubenstein, B., and Morales-Silva, M. (2016). Auxiliary-field based trial wave functions in quantum monte carlo calculations. *Physical Review B,* 94:235144.
4. Pilgrim, C.D., Zavarin, M. and Casey, W.H. (2017). The pressure dependence of carbonate exchange with [NpO2(CO3)3]4- in aqueous solutions. *Inorg. Chem*, 56: 661-666
5. Boggs, M.A., Jiao,Y., Dai, Z., Zavarin, M., and Kersting, A.B. (2016). Plutonium reaction with Pseudomonas sp. and its extracellular polymeric substances. *Applied and Environmental Microbiology*, 82: 7093-7101.
6. Begg, J., Zavarin, M., and Kersting, A.B. (2017). Desorption of plutonium from montmorillonite: An experimental and modeling study. *Geochim. Cosmochim. Acta*, 197: 278-293.
7. Conroy, N.A., Zavarin, M., Kersting, A.B., and Powell, B.A. (2017). The effect of natural organic matter on plutonium sorption to goethite. *Environ. Sci. Technol.*, 51: 699-708.
8. Joseph, C., Mibus, J., Trepte, P., Müller, C., Brendler, V., Park, D.M., Jiao, Y., Kersting, A.B., Zavarin, M. (2017). Long-term diffusion of U(VI) in bentonite: Dependence on density. *Science Total Environment*, 575: 207-218.
9. Romanchuk, A. Y., Kalmykov, S. N., Kersting, A. B., Zavarin, M. (2016). Behavior of plutonium in the environment. *Russian. Chem. Rev.*, 85: 995-1010. DOI: 10.1070/RCR4602.
10. Zhao, P., Begg, J.D., Zavarin, M., Tumey, S.J., Williams, R., Dai, Z.R., Kips, R., and Kersting, A.B. (2016). Plutonium(IV) and (V) sorption to goethite at sub-femtomolar to micromolar concentrations: Redox transformations and surface precipitation. *Environ. Sci. Technol.*, 50: 6948-6956. DOI: 10.1021/acs.est.6b00605.

11. Mason, H.E., Begg, J.D, Maxwell, R.S., Kersting, A.B., Zavarin, M. (2016). A novel NMR method for the investigation of trivalent lanthanide sorption on amorphous silica at low surface loadings. *Envir. Sci. Process. Impact*, 18: 802-809.

4.b FUTURE SCIENTIFIC GOALS, VISION AND PLANS

The mission of LLNL's Subsurface Biogeochemistry of Actinides SFA is 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.*

Our principal scientific goals are to identify:

- *Mechanisms driving surface-mediated reduction of Pu and Np,*
- *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 Pu colloids,*
- *NOM ligands and functional groups responsible for biologically mediated Pu redox transformations, and*
- *Mechanisms responsible for the observed Pu transport behavior in the field.*

The broad vision is for the LLNL SFA to be a hub for world-class, U.S., and international environmental radiochemistry research and education.

The scientific results produced this fiscal year do not warrant significant changes in direction or focus to our SFA. However, budget constraints have necessitated a delay in some tasks within our original research plan. These delays will affect our scheduled activities in the coming year but we do not anticipate removing them from our scope. Delayed projects are highlighted on our timeline in Section 4 Performance milestones and metrics. Our planned AFQMC effort will continue but will necessitate an external subcontract to Brown University (Brenda Rubenstein). Our external collaboration with KIT and Manchester University regarding actinide migration in Ravenglass estuary sediments has grown in scope. However, we anticipate that the effort can be maintained within the scope of Task 3D: CAMS Analysis of Pu/Np at Femtomolar Concentrations.

4.c NEW SCIENTIFIC RESULTS—*SEE SECTION 4.A.II*

4.d COLLABORATIVE RESEARCH ACTIVITIES

We have a subcontract with Dr. Brian Powell at Clemson University, SC ($100K/yr). Dr. Powell was a former postdoc at LLNL. He co-leads Focus Area 2A: Characterization of Field Samples from Pu Contaminated Sites. In addition, he is co-leading, with M. Zavarin, Focus Area 2B: Characterization of Pu Behavior in Field and Field-Analog Samples. He is responsible for supervising a postdoc, Melody Maloubier, based at Clemson University and two graduate students, Nathan Conroy and Jennifer Wong.

We have a sub-contract with Dr. Patrick Huang at Cal State East Bay, CA ($35K/yr). Dr. Huang was a former postdoc at LLNL. He is responsible for developing new computational methods to simulate the molecular-level behavior of f-elements.

In many of our collaborations, graduate students and postdocs come to LLNL to conduct research as part of the SFA. Faculty, postdocs and graduate students receive access to state-of-the-art facilities at LLNL. Current collaborations include research groups at: Clemson University, Cal State East Bay, UC Davis, UC Berkeley, Lawrence Berkeley National Laboratory, Pennsylvania State University, HZDR Dresden, Germany, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, and the University of Manchester, England.

5. STAFFING AND BUDGET SUMMARY

5.a FUNDING ALLOCATION BY PROGRAM ELEMENT

5.a.i Present Funding

In FY17 our SFA budget was 1.0M. LLNL staff costs are listed below.

Program Element	Costs ($K)
Thrust 1	610
Thrust 2	310
Thrust 3	53
Total	973

LLNL Researcher	Effort (%)	Cost ($K)
Annie Kersting	10	68
Mavrik Zavarin	35	216
Yongqin Jiao	10	48
Enrica Balboni	100	153
James Begg	85	274
Harris Mason	10	40
Claudia Joseph	50	76
Keith Morrison	50	76
Ruth Kips	05	22
Total	3.55 FTE	973K

5.b FUNDING FOR EXTERNAL COLLABORATORS

We have an external collaboration with Brian Powell at Clemson University, SC, at $100K/year, and Patrick Huang at Cal State East Bay for $35K/year. We expect both collaboration to continue. See 4.d for details.

5.c PERSONNEL ACTIONS

Claudia Joseph completed a 3-year postdoctoral fellowship with our group and took a research position at KIT, Karlsruhe, Germany last fall. She will continue to collaborate with this SFA in the area of environmental radiochemistry and waste management. Brenda Rubinstein accepted a faculty position at Brown University. We plan to start a collaboration continuing our efforts to develop quantum Monte Carlo computational methods for actinides in 2018 after she has settled into her new position.

5.d NATIONAL LABORATORY INVESTMENTS

LLNL investments in equipment and infrastructure have enhanced our ability to carry out our program.

- LLNL purchased a state-of-the-art Titan STEM in FY15 that is now available for staff scientists to use on a recharge basis. This Titan is set up to handle actinide samples.
- LLNL has continued to maintain and upgrade its Cameca NanoSIMS 50, keeping it competitive with new NanoSIMS instruments and has had several major upgrades. One was a motorization upgrade for all slits and apertures, which has significantly improved automated operation, enabling efficient 24 hours per day, 7 days per week operation. Another was an upgrade of our Hyperion II RF power supply, enabling higher current operation at spatial resolution. A third was an upgrade of the instrument control processor, control software, and vacuum system.
- LLNL has recently made substantial upgrades to the 500 MHz NMR system including a new triple resonance console and a liquid N_2 cooled cryoprobe to further our work on actinides. A new 4 mm solid state probe installed on the 400 MHz system in FY16 also allows for low gamma nuclei such as ^{14}N and ^{239}Pu to be investigated.
- As an institution, LLNL subsidizes the cost of all postdocs by 25%.

The Seaborg Institute at LLNL covers some of the administrative costs to execute this program (e.g., all visiting postdocs, students, and faculty paperwork). Dr. Zavarin, the Director of the Seaborg Institute, oversees the summer student program that paid for the cost of two summer students working on this program in the summer of 2016 and 2017.

5.e CAPITAL EQUIPMENT

Funding from this program has been used to purchase: a new ultraviolet–visible spectrometer, refurbishment of an existing glovebox to allow experiments under controlled anaerobic conditions, and the refurbishment of a GC-MS. (See 5d for LLNL investments in capital equipment).

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