Subsurface Biogeochemistry of Actinides

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LLNL SFA OBER–SBR FY16 Program Management and Performance Report:

Subsurface Biogeochemistry of Actinides

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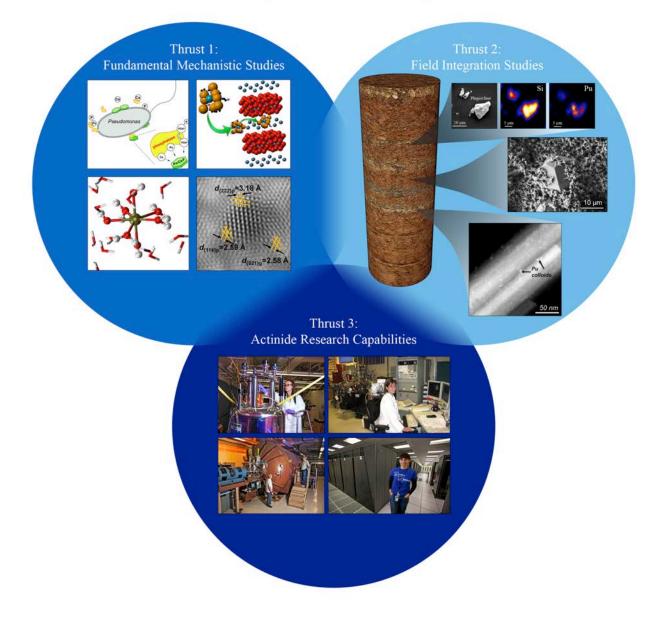## TABLE OF CONTENTS

Subsurface Biogeochemistry of Actinides

Figure 1. Figure shows the 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 plutonium (Pu) have been deposited in the subsurface 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:

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*

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 of state-of-the-art spectroscopic and computational capabilities and provide new research opportunities for the broader actinide and environmental systems science communities. Capabilities include:

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

- Provide the 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.

3. PROGRAM STRUCTURE

Henry Shaw is the point-of-contact for LLNL's 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. Until February, 2016, she was the Director of the LLNL branch of the Glenn T. Seaborg Institute (Seaborg Institute) in PLS and reported to Glenn Fox. She is currently the Director of University Relations and Science Education and reports to Pat Falcone, the Deputy Director for Science & Technology, Director's Office. She has retained her role as program manger for this Science Plan. Dr. Zavarin is the technical co-manger of the SFA and supervises the majority of the experimental work carried out by staff scientists. He was recently appointed as the Director of the Glenn T. Seaborg Institute and reports to Glenn Fox.

The interaction between Dr. Kersting and Dr. Zavarin will remain the same. Dr. Kersting and Dr. Zavarin will continue to co-supervise the graduate students, postdocs, and staff. The interactions include a biweekly SFA program meeting (which includes external collaborators) and weekly meetings with individual postdocs and graduate students. Dr. Kersting will continue to interact frequently with Dr. Shaw and Dr. Zavarin to make sure excellent communication continues 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 8 national and international research groups. We have five 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 will coordinate research and budgets, help drive the research agenda with Dr. Zavarin, and is leading 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 radionuclide chemistry 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; formerly a postdoctoral fellow at LLNL, 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. Dr Begg is also responsible for mentoring graduate students.

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.

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 the mineral–water interface. He leads Thrust 1, Focus Area 1F: Characterizing molecular level actinide complexes and redox transformations

Robert Maxwell—Division Leader of the Materials Division in PLS and Director of the NMR center at LLNL; He is interested in the development and use of nuclear magnetic resonance (NMR) to study the structure and dynamics of materials. He coordinates activities in the NMR facility and mentors staff in the NMR center.

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.

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.

Pihong Zhao—LLNL senior staff scientist; radiochemist with experience in environmental radiochemistry, waste forms, and actinides separations. Dr. Zhao serves as lab manager for the program and carries out experiments on actinide–inorganic interactions. She is responsible for training new postdocs and graduate students in actinide analytical chemistry.

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.

Keith Morrison—*new* 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—*new* 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.

Mark Boggs—LLNL staff scientist, *was* a LLNL postdoctoral fellow, has recently taken a position as staff scientist at LANL; Dr. Boggs's expertise is in organic interactions with radionuclides and his research focuses on understanding plutonium interactions with anthropogenic, natural, and biological organic matter.

Claudia Joseph—LLNL postdoctoral fellow; 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.

Adele Panasci—LLNL postdoctoral fellow; chemist with expertise in aqueous actinide chemistry and NMR. She is using NMR to study the mechanisms of Np ligand exchange and redox reactions that control actinide mobility.

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 as a function of geochemistry.

Brenda Rubenstein—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.

Jennifer Shusterman—*new* 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 NMR to probe behavior of metals at solid interfaces.

4. PERFORMANCE MILESTONES AND METRICS

The timeline for each task identified in this Science Plan is listed in Table 1.

	FY16		FY17		FY18	
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: The role of aging 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	▓	▓	▓			
Focus Area 2A: Characterization of Field Samples from Pu Contaminated Sites						
Task 2A-1 Hanford Site: Sediments from beneath the Z-9 crib	▓	▓	▓			
Task 2A-2 SRS: Sediments associated with the Pu-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 SRS: RadFLEx facility field lysimeter experiments		▓		▓		▓
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		▓	▓	▓	▓	▓
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	▓	▓	▓	▓	▓	▓

THRUST 1 · THRUST 2 · THRUST 3

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 the development of a mechanistic understanding of the dominant processes controlling actinide migration in the environment. The research is primarily focused on plutonium. 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
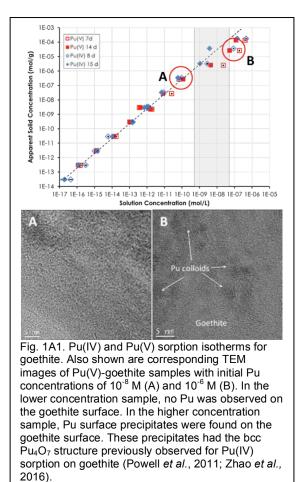*Lead: J. Begg*

The environmental mobility of Pu and Np is dependent 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; desorption rates will be affected by both pH and Eh.

Task 1A-1: Role of Fe in controlling Pu redox behavior
Contributors: P. Zhao, J. Begg, Z. Dai, S. Tumey, R. Williams

Previous work has highlighted the importance of iron hydroxide minerals in controlling the fate of Pu in the environment (Novikov *et al.*, 2006). Recently, we tested Pu sorption to goethite over a range of concentrations that span field observations. This has implications for understanding how Pu will behave both close to, and far from, initial Pu source terms and is especially relevant to locations such as Hanford, U.S., or Mayak, Russia, where Pu concentrations span many orders of magnitude (e.g., Mayak: $10^{-12} - 10^{-9}$ M in the near field and $10^{-14} - 10^{-12}$ M in the far field) (Novikov *et al.,* 2006).

Fig. 1A1. Pu(IV) and Pu(V) sorption isotherms for goethite. Also shown are corresponding TEM images of Pu(V)-goethite samples with initial Pu concentrations of 10^{-8} M (A) and 10^{-6} M (B). In the lower concentration sample, no Pu was observed on the goethite surface. In the higher concentration sample, Pu surface precipitates were found on the goethite surface. These precipitates had the bcc Pu_4O_7 structure previously observed for Pu(IV) sorption on goethite (Powell *et al.*, 2011; Zhao *et al.*, 2016).

Isotherm experiments were performed over a wide range of Pu(IV) and Pu(V) concentrations ($10^{-15} - 10^{-5}$ M) to compare the behavior of the two most environmentally common Pu oxidation states and test whether initial oxidation state and/or concentration affects equilibrium sorption behavior. Experiments with initial Pu concentrations of 10^{-15}–10^{-8} M produced linear Pu sorption isotherms, demonstrating that Pu sorption to goethite is not concentration-dependent across this concentration range (Figure 1A1). The high sorption affinity of both Pu(IV) and Pu(V) for goethite suggests that when present, it will play an important role in the subsurface mobility of Pu, as observed at the Mayak site. Equivalent Pu(IV) and Pu(V) sorption Kd values obtained at 1- and 2-week sampling time points indicated that Pu(V) is rapidly reduced to Pu(IV) on the goethite surface. At initial concentrations $>10^{-8}$ M, both Pu oxidation states exhibited deviations from linear sorption behavior. NanoSIMS and HRTEM analysis of samples with initial Pu concentrations of $10^{-8} - 10^{-6}$ M indicated that Pu surface and/or bulk precipitation was likely responsibility for the non-linearity. HRTEM analysis showed the formation of a body-centered cubic (bcc) Pu_4O_7 structure on the goethite surface, confirming that reduction of Pu(V) occurred on the mineral surface and that epitaxial distortion previously observed for Pu(IV) sorption occurs with Pu(V) as well.

Importantly, our results demonstrate that Pu solubilities reported in the literature can effectively predict the transition from adsorption to precipitation of Pu. The finding that Pu sorption behavior on goethite can be described by a combination of linear adsorption behavior at $<10^{-8}$ M Pu and surface precipitation at $>10^{-8}$ M Pu, regardless of whether it is initially present as Pu(IV) or Pu(V), provides a relatively simple conceptual basis for simulating transport behavior of Pu where the common Fe-oxide, goethite, is present (Zhao *et al.*, 2016).

Task 1A-3: The role of aging in Pu/Np stability on surfaces
Contributor: J. Begg

One important finding from our current 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). We have begun experiments with goethite at pH 8 aimed at studying the effects of the adsorption equilibration period on Pu *desorption* behavior. Further, we have used two initial Pu concentrations (10^{-9} and 10^{-6} M) to determine if the different adsorption mechanisms previously observed at these concentrations (Task 1A-1) affect desorption behavior. Initial results from the first desorption sampling time point, taken after 21 days of adsorption equilibration,
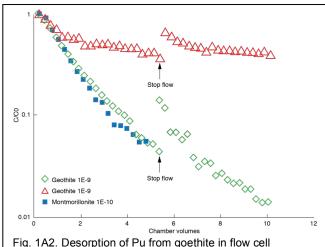

Fig. 1A2. Desorption of Pu from goethite in flow cell experiments with initial concentrations of 10^{-9} M Pu(V) (diamonds) and 10^{-6} M Pu(V) (triangles). Also shown is Pu desorption from montmorillonite in an experiment with an initial Pu(IV) concentration of 10^{-10} M. Arrows denote stop flow events; the increase in concentration following the stop flow indicates desorption is rate limited under the experimental conditions.

are shown in Figure 1A2. There is a marked difference in the desorption behavior in the experiment with 10^{-9} M Pu(V) compared to that at 10^{-6} M Pu(V). Further characterization of the nature of the Pu on the goethite surface with transmission electron microscopy is planned. Desorption experiments at 100 days and 200 days adsorption equilibration and characterization of the surface Pu will help determine if Pu stability increases over time and if so, what mechanisms contribute to this process.

Focus Area 1B: Effect of NOM on Actinide Redox Transformations and Sorption Reactions
Lead: M. Zavarin

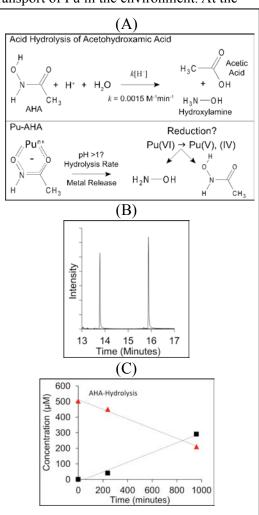Natural organic matter has been shown to play an important role in the transport of Pu in the environment. At the Rocky Flats Environmental Technology Site (RFETS), Pu in soil samples is in the +4 oxidation state and associated with organic macromolecules (Santschi *et al*., 2002). The NOM associated with Pu was determined to be dominated by cutin-like substances (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.
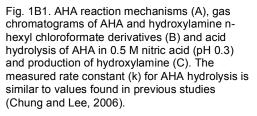
Hypothesis: Stabilization of Pu as Pu(IV)–NOM binary complexes will depend on the electron-donating capability of the NOM functional groups (e.g. hydroxamates). Stabilization of Pu as Pu(IV)–NOM–mineral ternary complexes will depend on the electron donating capability of the NOM functional groups and 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 are exploring the complexation and reactivity of Pu with AHA by determining the stability of Pu(VI), (V), and (1V)-AHA ligands at environmentally relevant pH ranges (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 showed 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

Fig. 1B1. AHA reaction mechanisms (A), gas chromatograms of AHA and hydroxylamine n-hexyl chloroformate derivatives (B) and acid hydrolysis of AHA in 0.5 M nitric acid (pH 0.3) and production of hydroxylamine (C). The measured rate constant (k) for AHA hydrolysis is similar to values found in previous studies (Chung and Lee, 2006).
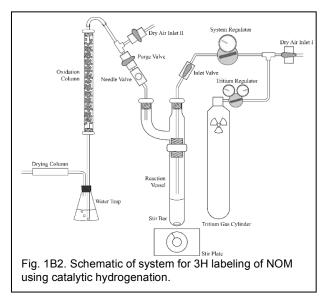
Pu(V) and (IV)-AHA ligands does not occur until hydrolysis of AHA releases the bound metal, which is then reduced by hydroxylamine (Carrott *et al.*, 2008). However, the reactions of Pu-AHA at environmentally relevant pHs (3-7) have not been investigated.

We have developed a gas chromatography-mass spectrometer (GC-MS) capability that will allow us to track AHA oxidation products that result from Pu(V) reduction in solution. Pu oxidation states can also be monitored by UV-Vis and solvent extraction. This approach will be expanded to systematically evaluate the capacity of NOM and cell exudate components and functional groups to reduce Pu(V) and Pu(VI).

Task 1B-2: Stabilization of Pu on mineral surfaces by NOM
Contributors: B. Powell, N. Conroy

To date, stability constants for Pu(IV)-FA complexes are unavailable across a wide pH range. To quantify the interaction of Pu with FA, we have, 1) developed a new technique to produce ^3H-labeled FA and other NOM and, 2) begun a systematic study of Pu(IV)-FA complexation starting with Pu(IV)-polyaspartic acid complexes as model compounds.

A new method for producing NOM tracers has been developed using catalytic hydrogenation in the presence of tritium gas (Figure 1B2). This method of labeling is intended to produce a more robust tracer that does not undergo rapid exchange with water. The new method opens an ethylene bond to create a direct C-^3H bond. This method has produced fulvic acids with tritium concentrations of approximately 0.21 $\mu Ci \cdot mg_{fulvic}^{-1}$, which can be used for Pu-FA complexation and ternary complexation studies with mineral surfaces.
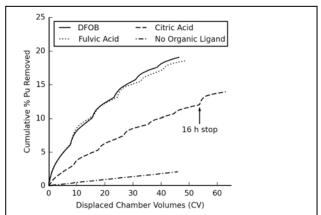

Fig. 1B2. Schematic of system for 3H labeling of NOM using catalytic hydrogenation.

Pu(IV)-fulvic acid (Suwannee River) complexation constants are being determined using a ligand exchange technique. The method exploits the well-established Pu(IV)-EDTA complexation constants and measures Pu(IV) partitioning between the two ligands by employing a semi-permeable membrane. In addition to determining Pu(IV)-fulvic acid complexation constants, the effect of ligand size on complexation strength was studied using various sized polyaspartic acids (PAAs), all of which have identical complexation sites. Pu(IV)-PAA results suggest little or no effect of PAA size on Pu(IV) complexation strength (Figure 1B3).

Fig. 1B3. Plutonium complexation with PAA; PLD 30/50/100 denotes PAA size range.
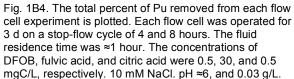
Task 1B-3: Pu sorption/desorption rates in the presence of NOM
Contributors: B. Powell, J. Wong

Experiments to investigate Pu(IV) desorption from goethite, both in the presence and absence of DFOB were performed to complement earlier flow cell experiments with citrate and fulvic acid. The percent Pu removed from each flow cell experiment (Figure 1B4) demonstrates that DFOB, fulvic acid, and citric acid are effective at enhancing Pu desorption from goethite, relative to an organic-free system. Much higher fulvic acid concentrations (30 mgC/L) were necessary

Fig. 1B4. The total percent of Pu removed from each flow cell experiment is plotted. Each flow cell was operated for 3 d on a stop-flow cycle of 4 and 8 hours. The fluid residence time was ≈1 hour. The concentrations of DFOB, fulvic acid, and citric acid were 0.5, 30, and 0.5 mgC/L, respectively. 10 mM NaCl. pH ≈6, and 0.03 g/L.

to yield equivalent Pu desorption behavior as DFOB and citric acid (a lower total C concentrations (0.5 mgC/L). The desorption behavior was modeled with two consecutive linear sorption sites. Assuming pseudo-first-order reaction rates for sorption, the two-site sorption model demonstrates a good fit to the experimental data for both experiments. This modeling effort builds on the sorption/desorption modeling framework developed as part of this SFA.

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 the formation, reactivity and stability of intrinsic actinide nanocolloids, and the concomitant understanding of their long-term 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 surface
Contributors: Z. Dai, T. Parsons-Moss, E. Balboni, J. Shusterman

Investigations into the structure of Pu nanocolloids on mineral surfaces using TEM 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 5 nm (Zavarin *et al.*, 2014) will form depending on the colloid formation conditions. We started three sets of experiments to systematically determine the 1) solution chemistry controls on nanocolloid formation, 2) structural or chemical controls of Pu nanoparticles on mineral surfaces, and 3) co-precipitation of Pu on minerals.

Aqueous geochemical controls on nanocolloid formation.

The pH, ionic strength and background electrolyte composition are being controlled to systematically evaluate Pu nanocolloid formation. Neither temperature (25–80ºC) nor aging (~3 months) appears to increase Pu nanocolloid size, so these variables will
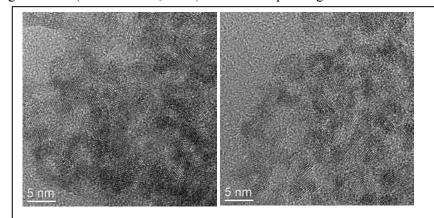

Fig. 1C1. Example high-resolution TEM images of PuO_2 nanocrystals formed in 1M NaCl (left) and 1 M CsCl (right), pH 4 solution. The particles are very similar, but the average size appeared slightly smaller and the morphology more regular in the CsCl sample.

not be further investigated (Lloyd and Haire, 1968; Zavarin *et al.*, 2014). TEM analysis showed that the PuO_2 nanocrystals formed in pH 4, 1 M salt solutions (NaCl, $NaNO_3$, $NaClO_4$, LiCl, CsCl) were all FCC. The nanoparticles ranged from approximately 2 to 4 nm, and the aggregates of Pu nanoparticles ranged from approximately 1 to 100 μm. There may be some subtle differences in size and crystallinity of the particles formed in different salt solutions. Figure 1C1 shows the high-resolution TEM images of PuO_2 nanocrystals formed in 1M NaCl (left) and 1 M CsCl (right), at pH 4. The Pu nanoparticles formed in the CsCl solution appeared slightly

smaller and the morphology perhaps more regular than those formed in NaCl solution. However, more analysis is needed before conclusions can be drawn.

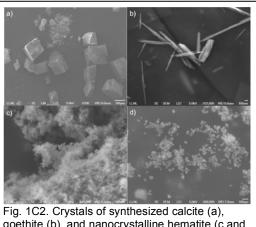*Mineral surface chemical or morphological controls on nanocolloid formation*

This project was recently initiated. The goal is to determine if the formation of plutonium nanocolloids on mineral surface is mediated by either the chemical or structural properties of the mineral substrate. The minerals chosen are environmentally relevant and have a range of structural and chemical properties. The minerals chosen for this study include goethite (FeOOH), diaspore (AlOOH), magnetite (Fe_3O_4), quartz (SiO_2), biotite $K(Mg,Fe^{2+})_3[AlSi_3O_{10}(OH,F)_2]$, muscovite $KAl_2[AlSi_3O_{10}(OH)_2]$, calcite ($CaCO_3$) and apatite ($Ca_{10}(PO_4)_6(OH)_2$). Powders of the selected mineral phases have been ground (micrometer size range) and characterized by powder x-ray diffraction. After completing our mineral characterization (SEM-EDS and BET), Pu nanocolloids will form both in presence and absence of these minerals. The structure of Pu nanocolloids will be studied by TEM.

Co-precipitation of Pu and environmentally relevant minerals

These experiments are focused on determining how Pu(IV) and Pu(V) 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 is to determine the mechanisms of structural incorporation of Pu into synthetic minerals. The proposed minerals are: calcite ($CaCO_3$), iron oxides, and clay minerals. The syntheses of calcite ($CaCO_3$), goethite (FeOOH), and hematite (Fe_2O_3) have been optimized (Figure 1C2). Yield and purity of the material was confirmed by powder x-ray diffraction (not shown). Mineral syntheses in the presence of Pu(V) or Pu(IV) is ongoing. Crystals of calcite will be analyzed for Pu content by laser ablation inductively coupled plasma mass spectrometry and NanoSIMS. The morphology of the Pu-bearing, synthesized crystalline products will be compared to the Pu free synthetic material by secondary electron microscopy (SEM). EXAFS will be used to determine the coordination environment and oxidation state of structurally incorporated Pu.

Fig. 1C2. Crystals of synthesized calcite (a), goethite (b), and nanocrystalline hematite (c and d).

Focus Area 1D: Probing the Role of Microbes in Altering Pu Behavior
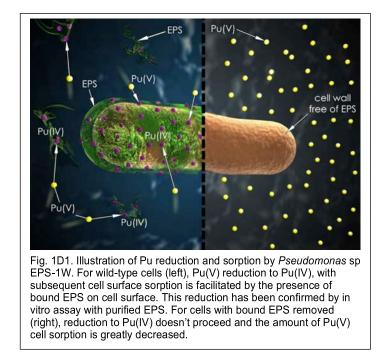*Lead: Y. Jiao*

Microorganisms are associated with a variety of radioactive materials at DOE sites (Barnhart *et al.*, 19080; 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 of 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

We examined Pu sorption onto the cell surface of a bacterium *Pseudomonas sp.* isolated from the Nevada Nuclear Security Site. In particular, we examined the effect of extracellular polymeric substances (EPS) on Pu redox and cell surface sorption. We found that the cell-bound EPS did not affect biosorption of Pu(IV). However, biosorption of Pu(V) was dependent on the presence of EPS. Pu(V) sorption is likely controlled by Pu(V) reduction to Pu(IV) mediated by cell-bound EPS (Figure 1D1). The EPS-mediated reduction of Pu(V) was confirmed using purified EPS.

In addition, we performed TEM to examine the morphology and structure of Pu sorbed on the cell surface. Comparing Pu(IV) sorption onto cell surface with and without cell-bound EPS, a

Fig. 1D1. Illustration of Pu reduction and sorption by *Pseudomonas* sp EPS-1W. For wild-type cells (left), Pu(V) reduction to Pu(IV), with subsequent cell surface sorption is facilitated by the presence of bound EPS on cell surface. This reduction has been confirmed by in vitro assay with purified EPS. For cells with bound EPS removed (right), reduction to Pu(IV) doesn't proceed and the amount of Pu(V) cell sorption is greatly decreased.

higher degree of Pu crystallinity appears to be associated with EPS-free cells. This suggests 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 has not been previously reported. Our findings highlight the importance of organic macromolecules of microbial origin in affecting the redox transformations, speciation, and basic geochemistry (*e.g.,* environmental mobility and fate) of Pu.

Task 1D-2: Cellular exudates controlling Pu complexation and mobility

This task had a planned start date of FY16 but was put on hold due to funding constraints. Some aspects of this task are being carried forward in Task 1B-1: Reduction of Pu(V) and Np(V) by NOM.

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: i) the need to explicitly account for the local solvation environment, and ii) 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.

The motivation for this work is the elucidation of the chemical nature and reactivity of aqueous Pu(IV) at environmentally relevant conditions, i.e., the femtomolar concentration regime. The development and application of *ab initio* simulations at LLNL hold promise in studying the electronic structure of f-elements at concentrations unattainable experimentally.

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

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. Up to this point, we have performed first principles molecular dynamics (FPMD) simulations of fully hydrolyzed An(OH)$_4$(*aq*) complexes, whose characterization is an essential first step towards elucidating the chemical behavior of tetravalent actinide ions at interfaces. The results from our prior simulations found a coordination number of seven for both Th(OH)$_4$(*aq*) and Pu(OH)$_4$(*aq*), with four hydroxyls plus three waters of hydration in the first coordination shell. This is rather low; while coordination numbers for monomeric An(OH)$_4$(*aq*) at neutral pH have not been experimentally
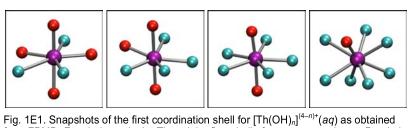

Fig. 1E1. Snapshots of the first coordination shell for [Th(OH)$_n$]$^{(4-n)+}$(*aq*) as obtained from FPMD. For clarity, only the Th and the first shell of oxygens are shown. Purple is Th, red is hydroxyl oxygen (OH), and blue is water oxygen (OH$_2$). The fully hydrolyzed complex Th(OH)$_4$(*aq*) (left) is seven-coordinate, with four hydroxyls and three waters in the first shell. Successive removal of hydroxyls (left to right) initially leads to a substitution by water to maintain the seven-coordinate structure. But upon removal of the third hydroxyl (right), the coordination number increases to eight and the structure changes to a square antiprism.

characterized for any of the actinides series, in related species such as the An^{4+}(*aq*) aquo ions or oligomeric An complexes, coordination numbers are typically eight or higher.

We have determined that interactions between the inner sphere hydroxyls are responsible for the low coordination numbers. This is demonstrated by successive removal of hydroxyls in the FPMD model, whose effects are summarized in Figure 1E1. Starting with Th(OH)$_4$(*aq*), removal of the first two hydroxyls simply results in a substitution by a water molecule to maintain the seven-coordinate structure. Removal of the third hydroxyl to give [ThOH]$^{3+}$(*aq*) changes the coordination number to eight and yields a square antiprism structure. Thus, the seven-coordinate structure is favored when electrostatic repulsions between negatively charged hydroxyls are present; in the absence of OH–OH repulsions, the first shell can accommodate additional waters of hydration (Huang *et al.*, 2016 submitted). Now that we have established the nature of the coordination environment around the hydrated, monomeric Th(OH)$_4$(*aq*) and Pu(OH)$_4$(*aq*) complexes, our next step is to characterize the free energy differences associated with the gain or loss of waters of hydration. This information can be correlated with the mechanism of An^{4+} substitution reactions that occur in surface complexation processes.

Focus Area 1F: Characterizing Molecular Level Actinide Complexes and Redox Transformations
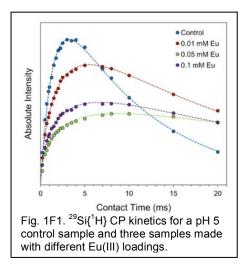*Leads: R. Maxwell and H. Mason*

Although the thermodynamic and empirical kinetic models developed by our group have increased our understanding of the processes controlling Pu transport in the environment (Begg *et al.*, 2015; Begg *et al.*, 2013; Tinnacher *et al.*, 2015; Tinnacher *et al.*, 2011), a direct mechanistic understanding of those processes is needed to develop a broader conceptual model of the relevant mechanisms controlling Pu migration. In this Task, we use novel spectroscopic NMR measurements developed in our SFA to directly probe Pu interfacial reactions on simple mineral surfaces and evaluate the coordination chemistry of actinide–aqueous ligand complexes.

Hypothesis: The stabilization of Pu(IV) complexes with various types of NOM (HA, FA, EPS) is a function of the specific functional groups present in the NOM (e.g. carboxamate) and their electron donating capacity.

Task 1F-1: Pu complexes on minerals surfaces
Contributor: J. Begg

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 (>10's 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.

Fig. 1F1. ^{29}Si{^{1}H} CP kinetics for a pH 5 control sample and three samples made with different Eu(III) loadings.

In FY15, we used the techniques pioneered in Mason *et al.*, 2012 to investigate the Eu(III) interactions with the silica surface at low pH to mimic a solubility-limited Pu system. We successfully investigated the interactions of Eu(III) at surface loadings of 0.1 to 0.15 nmol m^{-2} (Figure 1F1). These loadings are well below the limits for comparable studies with either XAS or TRLFS methods. The results indicate monomeric coverage for all loading levels investigated, but also hint at surface precipitates forming at higher initial solution concentrations (Mason *et al.* 2016). This study shows promise for differentiating between surface sorption and precipitation in the solubility-limited Pu(IV) system using these NMR techniques.

Recently, we have initiated long-term Pu(IV) quartz sorption experiments. We have shown that the methods above can be successfully applied in static NMR experiments. However, challenges 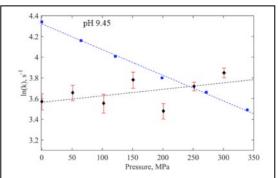have arisen from the necessary containment and sample size requirements to handle radioactive solid samples. Advanced NMR collection techniques employing CPMG acquisition will be combined with the statistical analyses to maximize the observed signal intensity for the Pu samples. We will build on this approach to include electron paramagnetic resonance (EPR) methods that have the potential to directly probe the Pu oxidation state (Focus Area 3A). These data will provide important constraints on how redox reactions occur on mineral surfaces, what conditions drive the surface mediated reduction of Pu, and the solution and surface conditions that lead to surface precipitation of Pu nanocolloids.
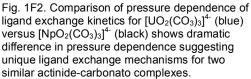
Task 1F-2: Actinide solution complexes

This task had a planned start date of FY16 but was put on hold due to funding constraints (in concert with Task 1D-2).

Task 1F-3: Np ligand exchange
Contributors: A. Panasci, C. Pilgrim

Previously, we had investigated the ligand exchange for the tris-carbonato Np(VI) species and compared it to the U(VI) analogue. The kinetics of carbonate exchange were determined using variable temperature NMR (Panasci *et al.* 2014). In FY16, we investigated the pressure dependence of the rates of ligand exchange for the same $[NpO_2(CO_3)_3]^{4-}$ aqueous complex in order to complement existing data on the isostructural $[UO_2(CO_3)_3]^{4-}$ complex and identify the exchange mechanism. Experiments were conducted at pH conditions where the rate of exchange is independent of the proton concentration. Unexpectedly, the experiments show a distinct difference in the pressure dependencies of rates of exchange for the uranyl and neptunyl complexes (Figure 1F2). 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.* 2016 submitted). This research was performed in collaboration with W. Casey, U.C. Davis.

Fig. 1F2. Comparison of pressure dependence of ligand exchange kinetics for $[UO_2(CO_3)_3]^{4-}$ (blue) versus $[NpO_2(CO_3)_3]^{4-}$ (black) shows dramatic difference in pressure dependence suggesting unique ligand exchange mechanisms for two similar actinide-carbonato complexes.

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.*

Thrust 2 is composed of three Focus Areas:

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

Focus Area 2A: Characterization of Field Samples from Pu Contaminated Sites
Leads: R. Kips (LLNL) and B. Powell (Clemson)

In Focus Area 2A, we are characterizing contaminated sediments at two field sites. In collaboration with A. Felmy, we are characterizing additional sediments from below the Z-9 crib, higher up in the vadose zone from the 25 and 30 m samples we have already analyzed. At the Savannah River Site (SRS), we are characterizing the nature of Pu that was originally deposited in sediments at the SRS-lysimeter field site. In the SRS lysimeter experiments, the depositional characteristics are more controlled and allow us to better monitor the evolution of Pu associations under environmentally relevant conditions and timescales, particularly with respect to the evolution of Pu oxidation states and Pu oxide precipitates.

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

Task 2A-1: Hanford Site: Examination of sediments from beneath the Z-9 Crib

This task had a planned start date of FY16 but was delayed to FY17 to allow for an earlier start of Task 2A-2.

Task 2A-2: Savannah River Site: Characterization of sediments associated with the Pu-doped lysimeter coupons
Contributors: M. Maloubier (Clemson), E. Black (Clemson)

This task had a planned start date of FY17 but was begun in FY16 due to the availability of unique field samples.

This project involves characterizing the Pu sources deployed in a field lysimeter facility at the Savannah River Site (RadFLEx: Radiological Field Lysimeter Facility), which is currently operated by Daniel I. Kaplan of the Savannah River National Laboratory and Brian Powell at Clemson University. The lysimeters were deployed in 2012 with Pu sources containing $Pu_2^{III}(C_2O_4)_3(s)$, $Pu^{IV}(C_2O_4)_2(s)$, $Pu^{IV}O_2$ nanocolloids, and $NH_4Pu^VO_2CO_3(s)$. The sources consist of a ~2-mg solid sample placed between two glass fiber filters. Triplicate lysimeters for each of these sources are currently in the field with plans to remove them at three time intervals over the next 10 years. Additionally, a set of archived plutonium sources stored in an inert atmosphere under controlled temperature and moisture laboratory conditions is available. To date, the characterization has been performed using X-ray absorption spectroscopy (XAS) for three archived sources ($Pu^{IV}(C_2O_4)_2(s)$, $Pu^{IV}O_2$ nanocolloids, and $NH_4Pu^VO_2CO_3(s)$) and two sources exposed in lysimeters ($NH_4PuO_2CO_3$ with and without organic matter respectively) for 2.5 years.

Archived $Pu^{IV}(C_2O_4)_2$(s) and $NH_4Pu^VO_2CO_3$(s) sources were observed to have changed with time. Pu(IV)-oxalate is known to be susceptible to decomposition by alpha radiation with a half-life of 64 days. The EXAFS spectra of $NH_4PuO_2CO_3$(s) indicated that more than one species is present, including approximately 70% PuO_2. This same source, after exposure in the field lysimeter for 2.5 years with and without presence of organic matter, is mainly composed of PuO_2 (Table 2). In order to evaluate and demonstrate the impact of the soil (with and without OM) on the source, a new $NH_4PuO_2CO_3$(s) source will be synthesized. The degradation of this source will be followed over the time with and without the presence of the soil to determine if the soil accelerates the formation of PuO_2. Regarding the archived PuO_2(s) nanocolloid source, the EXAFS results are consistent with previously observed colloidal particles with slightly shorter Pu-O and Pu-Pu distance compared to bulk PuO_2 (Ekberg *et al.*, 2013). The morphology of plutonium particles in sources will be examined using TEM at LLNL.

Table 2: EXAFS data on Pu in both the archived and lysimeter data (blue shading).

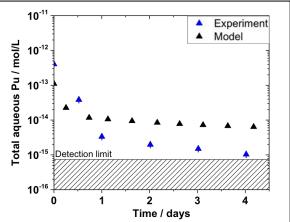|	Pu-O	Pu-Pu
PuO_2	7 O at 2.34 Å	9 Pu at 3.82 Å
Pu colloidal particles	8 O at 2.294 Å	3.9 Pu at 3.793 Å
Pu(IV) colloids σ^2 (Å^2) =	8 O at **2.30** Å 0.0123	3.9 Pu at **3.77** Å 0.0048
Lys22: $NH_4Pu(CO_3)$ with OM σ^2 (Å^2) =	8 O at **2.31** Å 0.0086	4.6 Pu at **3.81** Å 0.0036
Lys41: $NH_4Pu(CO_3)$ σ^2 (Å^2) =	8 O at **2.30** Å 0.0118	4.0 Pu at **3.77** Å 0.0043

Desorption experiments using sediments from field lysimeters
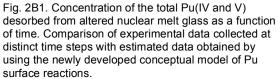Desorption experiments were conducted on soils that were in contact with the $NH_4PuO_2CO_3$(s) sources (with and without OM amendment in the soil) after 2.5 years in the field. Three desorption periods of 3, 14, and 60 days under aerobic and anaerobic conditions were performed in 10 mM NaCl. Select samples were also filtered (30k MWCO) to evaluate the potential impact of colloidal particles. Under anaerobic conditions, aqueous plutonium concentrations in the aqueous phase were low. Thus, oxidation of Pu(IV) to Pu(V) is likely a controlling factor in the desorption of Pu. Desorption rate constants and potential aging effects will be examined in the coming months.

Focus Area 2B: Characterization of Pu Behavior in Field and Field-Analog Samples
Leads: M. Zavarin (LLNL) and B. Powell (Clemson)

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 NNSS experiments are focused on characterizing the stability of Pu associated with colloids and hydrothermally altered clays that represent the dominant Pu transport mechanism at this site. The Hanford experiments will investigate the transport behavior of several forms of Pu when incorporated in the complex mixed waste deposited at the Z9 Trench. The SRS experiments rely on ongoing experiments at the SRS RadFLEx facility and take advantage of ultra low-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.

Fig. 2B1. Concentration of the total Pu(IV and V) desorbed from altered nuclear melt glass as a function of time. Comparison of experimental data collected at distinct time steps with estimated data obtained by using the newly developed conceptual model of Pu surface reactions.

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-1: NNSS: Colloid stability experiments
Contributors: C. Joseph, P. Zhao

To determine what causes the observed colloid-facilitated Pu transport at NNSS (Kersting *et al.*, 1999), the interaction of Pu(V) and Pu(IV) with well-characterized montmorillonite colloids was intensively studied by batch sorption (Begg *et al.*, 2013) and flow-cell experiments (Begg *et al.*, 2016). Based on these results, a numerical model of the surface reactions was developed consisting of five Pu species (two aqueous species: $Pu(V)_{aq}$ and $Pu(IV)_{aq}$; three surface species: $Pu(V)_{S1}$, $Pu(IV)_{S2}$, and $Pu(IV)_{S3}$) interacting with each other by sorption, desorption, aging, and surface redox reactions (see Task 2C). In FY16, the numerical model was tested under conditions that better reflect field conditions at NNSS.

Nuclear melt glass obtained from an underground nuclear test at NNSS and containing about 950 ± 108 pCi Pu/g was hydrothermally altered in a Parr pressure vessel at 200 °C (using $5 \cdot 10^{-3}$ mol/L NaCl/$7 \cdot 10^{-4}$ mol/L NaHCO$_3$, pH 8). These hydrothermal conditions are representative of the underground nuclear test cavities when groundwater has re-saturated the nuclear melt glass and glass dissolution occurs. Within 994 days, the morphology of the nuclear melt glass altered to smectite and zeolite structures. This is in agreement with observations at NNSS, where the migrating Pu was mainly associated to clay and zeolite colloids. The colloidal fraction of the altered nuclear melt glass sample was separated and used in a flow-cell experiment (1 g/L colloids, 3817 ± 1260 pCi Pu/L, $5 \cdot 10^{-3}$ mol/L NaCl/$7 \cdot 10^{-4}$ mol/L NaHCO$_3$, pH 8, room temperature, 4.4 days). The experiment was conducted to study the Pu desorption from the colloids similar to the experiments with Pu and montmorillonite.

In Figure 2B1, the comparison between the desorbed Pu measured and the Pu estimated by our numerical model is presented. The total amount of Pu removed from the colloids was reliably estimated by the conceptual model (experiment: 0.4%; model: 0.6% in relation to the initial Pu content). The current numerical model was also able to predict desorption *rates* of Pu from nuclear melt glass colloids within one order of magnitude. However, it appears that the model overestimates the short-term desorption rates and underestimates the long-term desorption rates. Additional desorption experiments and sample characterization is ongoing. However, these initial results suggest that a fraction of the Pu associated with hydrothermally altered clays may not be a simple adsorbed species.

Task 2B-3: Savannah River Site: field lysimeter experiment
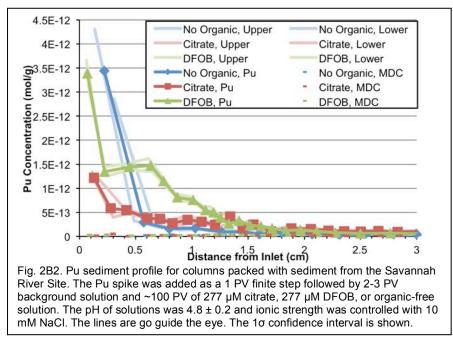*Contributor: M. Maloubier*

We have begun sampling 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 lysimiters 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 plan to continue our effluent sampling to determine the longterm migration of Pu; advanced methods such as MC-ICPMS and CAMS will be employed for select samples as Pu attenuation is observed.

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

In order to examine the effect of organic ligands on Pu transport, 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 pore 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.

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 2B2), and it appears that in the presence of citrate and DFOB, Pu transport was 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 Pu-ligand aqueous complexes. This is consistent with the Pu-ligand goethite flow-cell experiments as shown in Figure 1B4. Transport modeling to quantify the mobility of Pu in these columns is still underway.

Fig. 2B2. Pu sediment profile for 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 277 µM citrate, 277 µM DFOB, or organic-free solution. The pH of solutions was 4.8 ± 0.2 and ionic strength was controlled with 10 mM NaCl. The lines are go guide the eye. The 1σ confidence interval is shown.

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.*
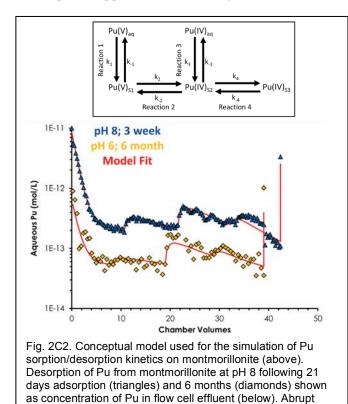
Task 2C-1: Development of Pu/Np surface complexation/ion exchange models
Contributor: M. Zavarin

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), particularly in cases where there is a need to model radionuclide behavior over a very broad range of solution and mineralogic conditions.

The RES³T (Rossendorf Expert System for Surface and Sorption Thermodynamics) project is a recent effort by HZDR to develop a digital open-source thermodynamic sorption database. It includes mineral-specific surface complexation constants that can be used in additive models of more complex solid phases such as rocks or soils. However, this database does not provide recommended values. It also does not capture the primary sorption data or provide information on the aqueous speciation constants used in determining those surface complexation constants. As a result, the RES³T project provides a foundation for developing a comprehensive surface complexation database but does not go so far as to provide one. Our recent efforts have focused on complementing the RES³T project (in collaboration with the RES³T developers) and providing a new approach to develop self-consistent parameterization of surface complexation/ion exchange reaction parameters (Figure 2C1). This approach is being applied to available actinide sorption data.

Task 2C-2: Parameterization of aging processes and associated reaction rates
Contributor: J. Begg

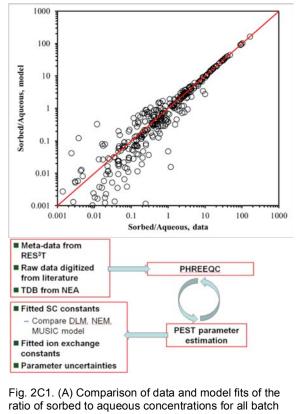An empirical approach to simulating both surface-mediated

Fig. 2C1. (A) Comparison of data and model fits of the ratio of sorbed to aqueous concentrations for all batch sorption data contained in references identified by the RES³T database for U(VI) sorption to quartz and (B) a proposed approach for developing and testing surface complexation/ion exchange modeling approaches for the actinides.

Fig. 2C2. Conceptual model used for the simulation of Pu sorption/desorption kinetics on montmorillonite (above). Desorption of Pu from montmorillonite at pH 8 following 21 days adsorption (triangles) and 6 months (diamonds) shown as concentration of Pu in flow cell effluent (below). Abrupt changes in Pu concentration are from changing flow rates. Red lines are best model fits to the data.

reduction and additional aging processes has been under development as part of this SFA We have taken the montmorillonite flow cell experimental data generated in FY12–14 and developed a conceptual model for Pu adsorption/desorption that incorporated known surface-mediated Pu redox reactions (Figure 2C2). The details of this approach are discussed fully in Tinnacher *et al.,* (2011). Relatively simple first-order reactions were arranged in-silico based on a finite difference approach (Euler method). The 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 optimiser that uses least square minimization based on the Gauss–Marquardt–Levenberg method.

The model was used to generate good fits to the experimental data and allowed us to parameterize rates for the adsorption, desorption, and surface-mediated reduction reactions (Figure 2C2). The resulting rate constants indicated processes occurring on timescales of months and even years. By quantifying these rates, we are able to make predictions about the long-term fate of Pu adsorbed on mineral surfaces. Moreover, this

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model can be tested on other Pu-mineral interactions (see Task 1A-3). Importantly, our results thus far imply that migration of Pu adsorbed to montmorillonite colloids at long (50-100 year) timescales under oxic conditions may not be possible without considering additional phenomena, such as co-precipitation.

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 will have a lead scientist responsible for method development. All advances in capability development will be 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

NMR spectroscopy can be used to derive the rates and mechanisms of water/ligand exchange in actinide complexes. This is important because in order for actinide complexes to bind to surfaces, they must first lose either their solvating water or their complexing ligands. Understanding such reactions is thus crucial to understanding actinide-surface interactions. Variable pressure NMR of actinides was recently implemented at LLNL to determine the nature of actinide–ligand exchange for the Np(VI) tris-carbonate species. This capability is now available study patterns in ligand exchange kinetics and mechanisms for a number of relevant actinide solution complexes.

We are studying the interaction of various electrolytes with PuO_2 nanocolloids and their impact on the subsequent size and structure of the colloids. We have formed nanocolloids in alkali metal salts and began an examination with XAS, NMR, and TEM. Previous work has indicated that the anions in the electrolyte surround the outside of a PuO_2 crystal, and these crystals are charge-balanced by the cation (Sodeholm *et al.*, 2008). Using ^7Li NMR, we can get a better understanding of whether the Li ions are exchanging with charged sites on the PuO_2 surface, incorporating into the PuO_2 cluster network, or remaining evenly dispersed in the bulk solution. Thus far we have begun work looking at Pu in LiCl solutions at pH 4 and sub-pH 1. This will allow for comparison of Pu as primarily a colloid versus as a bare cation in solution. This work will be extended to ^{23}Na and ^{133}Cs NMR to look at the NaCl and CsCl matrices as well.

We are using electron paramagnetic resonance (EPR) to study the electronic structure of metal complexes. This new capability has the potential to reveal detailed information about actinide solution complexes. Preliminary EPR spectra have been collected for aqueous neptunyl (V) and (VI). Future work will proceed, by placing Np solution into a capillary in order to minimize the solvent effect on the EPR spectra. The EPR spectra of Np(V), Np(VI), and Pu(VI), and their ligand complexes will be collected and compared to determine similarities and differences in the electronic structure.

Focus Area 3B: NanoSIMS Analysis of Pu
Lead: R. Kips

LLNL has been one of the pioneers in the use of the CAMECA NanoSIMS 50 for the detection and characterization of radionuclides in the environment. This secondary ion mass spectrometer combines several key characteristics essential for the isotopic and chemical analysis of inhomogeneous and/or particulate samples, including dust particles, meteorite samples, microorganisms and mineral grains. The NanoSIMS is a destructive surface analysis technique that uses a primary ion beam and double-focusing magnetic sector analyzer to probe ppm-level sample constituents in complex organic and inorganic matrices. This ion imaging capability, together with a high sensitivity (e.g., capability of detecting ~200 Pu atoms) and high mass resolving power, has been applied to visualize the distribution of ^{239}Pu across mineral grains from contaminated soil samples, including mineral, organic, and microbial surfaces.

In FY14, the NanoSIMS' conventional duo-plasmatron primary ion source was replaced with a Hyperion inductively coupled plasma ion source from Oregon Physics (now manufactured for CAMECA). In FY15, this new ion source was tested and has resulted in an increased beam brightness of the Hyperion ion source allowing for a reduction in the spatial resolution for oxygen primary ion beams from 150–250 nm to ~50 nm. This improved NanoSIMS capability will be applied to Hanford and SRS sediments to characterize the spatial distribution of Pu.
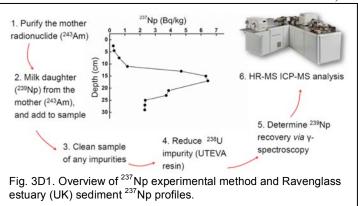
Focus Area 3C: TEM-EELS of Pu/Np Nanocolloids
Lead: Z. Dai

In FY15, 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 obtaining high-resolution phase-contrast imaging (HRTEM), atomic-resolution Z-contrast imaging, atomic-scale mineralogical and petrographic mapping. Key features of the Titan STEM are 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) data sets. Energy resolution of the EELS is better than 0.8 eV without 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.

Focus Area 3D: CAMS Analysis of Pu/Np at Femtomolar Concentrations
Lead: S. Tumey

In collaboration with the University of Manchester (UK) and the Karlsruhe Institute of Technology (Germany), we have begun a study of actinide distribution and release rates from sediments located near the Sellafield Site, UK. In 2015, summer student Daisy Ray (Manchester) visited LLNL and quantified Np distribution in Ravenglass estuary sediments using ultratrace Np analysis methods developed as part of this SFA (Figure 3D1). In 2016, we collected new sediment cores from the Ravenglass estuary. These cores are being maintained under anaerobic conditions and will be shipped to LLNL for characterization. Dr. Francesca Quinto (KIT) has been working at the VERA AMS facility in Vienna. Dr. Quinto will visit LLNL during 2016/2017 to collaborate on the development of novel AMS capabilities for actinide quantification
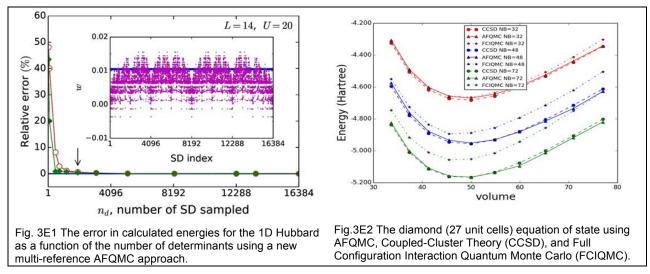

Fig. 3D1. Overview of ^{237}Np experimental method and Ravenglass estuary (UK) sediment ^{237}Np profiles.

using AMS. The focus of this new effort will be the quantification of actinide release rates from Ravenglass estuary sediments.

Focus Area 3E: LLNL Computing: Quantum Monte Carlo
Lead: B. Rubenstein

The ability to accurately predict the electronic structure of actinide complexes is critical to enhancing our understanding of their redox and transport properties. Nevertheless, the accurate determination of actinide electronic structure has been hampered by the paucity of methods capable of capturing both the relativistic effects and strong electron correlation that are at play within these complexes. One particularly promising method well-suited for satisfying these aims is the Auxiliary Field Quantum Monte Carlo (AFQMC) method. AFQMC is a Quantum Monte Carlo technique that projects out the ground state wave function of a system from an appropriate trial wave function. The more accurate the trial wave function, the more accurate the computed ground state energy and related ground state properties. Over the past year, we have embarked upon three different routes aimed at developing AFQMC into a highly useful tool for actinide research. We have made significant progress toward understanding how to best: 1) Incorporate Relativity into AFQMC Calculations, 2) Create Accurate Multi-reference Trial Wave Functions, and 3) Model Solids in the Thermodynamic Limit.

Although this work is still underway, we have so far found that the use of small-core ECPs in AFQMC (as well as in a variety of other standard quantum chemistry techniques, including MP2 and CCSD) is essential for accurate predictions of bond lengths. We have also found that using multideterminant trial wave functions as starting points is essential for simulations of these fundamentally multireference simulations. As shown in Figure 3E1 below, using increasingly accurate versions of this compact wave function as a starting point, we obtain increasingly accurate estimates of the ground state energy.

Fig. 3E1 The error in calculated energies for the 1D Hubbard as a function of the number of determinants using a new multi-reference AFQMC approach.

Fig.3E2 The diamond (27 unit cells) equation of state using AFQMC, Coupled-Cluster Theory (CCSD), and Full Configuration Interaction Quantum Monte Carlo (FCIQMC).

While we have demonstrated our basic technique on a well-known lattice model, the 2D Hubbard model, we are currently adapting this approach so that it can be applied to actinide complexes and other strongly correlated chemical systems. With the goal of eventually being able to model actinide solids, we have started to perform AFQMC simulations on a variety of network covalent and ionic solids. As shown in Figure 3E2 for diamond, we find that AFQMC yields estimates of the ground state energy that are virtually identical to results obtained using CCSD(T), the gold standard for electronic structure calculations.

4.a.ii Scientific Highlights

- Pu solubilities reported in the literature can effectively predict the transition from adsorption to precipitation of Pu, providing a relatively simple conceptual basis for simulating transport behavior of Pu where Fe-oxide, goethite, is present (Zhao *et al.*, 2016).

- A new method for producing NOM tracers has been developed using catalytic hydrogenation in the presence of tritium gas.
- A novel GC-MS methodology was implemented that allows us to follow redox reactions between actinides and natural organic matter.
- The role of EPS in Pu(V) reduction and biosorption was identified. Our findings highlight the importance of organic macromolecules of microbial origin in affecting the redox transformations and morphology of Pu.
- We have established the nature of the coordination environment around the hydrated, monomeric $Th(OH)_4(aq)$ and $Pu(OH)_4(aq)$ complexes and bare ions which explains the low coordination numbers predicted for the hydroxides complexes using DFT (Huang et. al., submitted).
- We investigated the pressure dependence of $[NpO_2(CO_3)_3]^{4-}$ ligand exchange rates. 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.*, submitted).
- Our current numerical model of Pu sorption/desorption was also able to predict desorption rates of Pu from hydrothermally altered nuclear melt glass colloids to within one order of magnitude. However, these initial results suggest that a fraction of the Pu associated with hydrothermally altered clays may not be a simple adsorbed species. This has significant implications to the long-term transport of Pu at the Nevada National Security Site and elsewhere.
- We have made a number of new theoretical and computational advances, including the development of a new method for sampling and generating multideterminant expansions for describing multireference systems, that enable the direct simulation of actinide complexes using quantum Monte Carlo methods for the first time.
- We have established that the solid-state NMR spectroscopic techniques that we have developed are capable of investigating loading levels lower than traditional spectroscopic methods and hold potential for investigating the solubility limited Pu/quartz system.

4.a.iii Summary of Publications

We presented our research at a variety of national and international meetings. This included 29 oral or poster presentations, of which 12 were invited and 1 was a keynote talk. In addition, we organized three scientific sessions and participated as a conference organizer for one international meeting. We have published 8 peer-reviewed papers, 3 are in review and 4 have been submitted.

July 2015-June 2016

1. Huang, P., Lo, C., Zavarin, M., Kersting, A.B., Hydration of tetravalent actinides from first principles simulations: Structure and energetics of monomeric Th(OH)4(aq), *Submitted to J. Phys. Chem. B*.

2. Chang C., Rubenstein, B., and Morales-Silva, M.. Auxiliary-Field Based Trial Wave Functions in Quantum Monte Carlo Calculations. *Submitted to Physical Review B*, March 2016. arXiv:1604.00345.

3. Pilgrim, C.D., Zavarin, M. and Casey, W.H. The pressure dependence of carbonate exchange with $[NpO_2(CO_3)_3]^{4-}$ in aqueous solutions. Letter. *Submitted to Inorganic Chem*

4. Boggs, M.A., Jiao,Y., Dai, Z., Zavarin, M., and Kersting, A.B. (2016) Plutonium Reaction with *Pseudomonas* sp. and its Extracellular Polymeric Substances. *Submitted to Applied and Environmental Microbiology*.

5. Begg, J., Zavarin, M., and Kersting, A.B. Desorption of plutonium from montmorillonite: An experimental and modeling study. *In revision Geochim. Cosmochim. Acta.*

6. Conroy, N.A., Zavarin, M., Kersting, A.B., and Powell, B.A. The Effect of Natural Organic Matter on Plutonium Sorption to Goethite. *In revision Environmental Science & Technol.*

7. Joseph, C., Mibus, J., Trepte, P., Müller, C., Brendler, V., Park, D.M., Jiao, Y., Kersting, A.B., Zavarin, M. (2016) Long-term diffusion of U(VI) in bentonite: Dependence on density. *In press Science Total Environment.*

8. Romanchuk, A Yu, Kalmykov, S N, Kersting, A B, Zavarin, M. Behavior of plutonium in the environment. *in press Russian. Chem. Rev.*, 2016, **85**, DOI: 10.1070/RCR4602

9. Zhao, P., Begg, J.D., Zavarin, M., Tumey, S.J., Williams, R., Dai, Z.R., Kips, R., and Kersting, A.B. Plutonium(IV) and (V) Sorption to Goethite at Sub-Femtomolar to Micromolar Concentrations: Redox Transformations and Surface Precipitation. *In press Environ. Sci. Technol.* DOI: 10.1021/acs.est.6b00605.

10. Mason, H.E., Begg, J.D, Maxwell, R.S., Kersting, A.B., Zavarin, M., A novel NMR method for the investigation of trivalent lanthanide sorption on amorphous silica at low surface loadings, *In press Envir. Sci. Process. Impact.*

11. Uribe, E.C., Mason, H.E., Shusterman, J.A., Bruchet, A., Nitsche, H., (2016) Probing the interactions of U(VI) with phosphonate-functionalized mesoporous silica using solid-state NMR spectroscopy. *Dalton Trans.*, 45:10447-10458 doi: 10.1039/C6DT01200K.

12. Parsons-Moss, T., Jones, S., Wang, J.X., Wu, Z.X., Uribe, E., Zhao, D.Y., and Nitsche, H. (2015) Reduction of Plutonium in Acidic Solutions by Mesoporous Carbons. *J. Radioanalytical and Nucl. Chem.* 307(3):2593-2601. DOI: 10.1007/s10967-015-4647-7.

13. Xiong, Q., Joseph, C., Schmeide, K. and Jivkov, A. P. (2015) Measurement and modelling of reactive transport in geological barriers for nuclear waste containment. *Phys. Chem. Chem. Phys.*, 17: 30577-30589. doi: 10.1039/c5cp05243b.

14. Shusterman, J.A., Mason, H. E., Bowers, J., Bruchet, A., Uribe, E.C., Kersting, A.B., Nitsche, H. (2015) Development and Testing of Diglycolamide Functionalized Mesoporous Silica for Sorption of Trivalent Actinides and Lanthanides. *ACS Appl. Mater. Interfaces*, 7: 20591-20599. doi:10.1021/acsami.5b0448.

15. Wong, J.C., Zavarin, M., Begg, J.D., Kersting, A.B., and Powell, B.A. Effect of Equilibration Time on Pu Desorption from Goethite. *Radiochim. Acta*, 103:695-705. doi: 10.1515/ract-2015-2404.

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. Our planned AFQMC effort will continue but may necessitate the inclusion of an external subcontract to Brown University (Brenda Rubenstein). Our external collaboration with KIT and Manchester University regarding actinide redistribution in Ravenglass estuary sediments has increased. 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 will co-lead with R. Kips Focus Area 2A: Characterization of Field Samples from Pu Contaminated Sites. In addition, he will co-lead with M. Zavarin, Focus Area 2B: Characterization of Pu Behavior in Field and Field-Analog Samples. He will be responsible for supervising a postdoc, based at Clemson University, and two graduate students.

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 will develop new computational methods to simulate the molecular-level behavior of f-elements.

We collaborate with Dr. Andrew Felmy, Washington State, WA (formerly at PNNL) to provide contaminated sediments from the 200 Area at Hanford. He is helping us to to understand Pu migration through the vadose zone. This collaboration is unfunded.

Many of our collaborations involve having graduate students and postdocs come to LLNL to conduct research as part of the SFA. Collaborations involve providing faculty/national laboratory staff access to state-of-the-art facilities at LLNL. These collaborations include research groups at: UC Davis, UC Berkeley, LBNL, Penn State, HZDR Dresden, Germany, K.I.T., Karlsruhe, Germany and U. Manchester, England.

5. STAFFING AND BUDGET SUMMARY

5.a FUNDING ALLOCATION BY PROGRAM ELEMENT

5.a.i Present Funding

In FY15 our SFA budget was 1.0M (subcontracts total 130K). LLNL staff costs are listed below.

Program Element	Costs ($K)	LLNL Researcher	Effort	Cost ($K)
Thrust 1	623	Annie Kersting	10%	85
Thrust 2	72	Mavrik Zavarin	35%	180
Thrust 3	220	Pihong Zhao	15%	52
Total	**.915M**	Zurong Dai	5%	20
		Yongqin Jiao	10%	30
		Enrica Balboni	30%	50
		Mark Boggs	10%	42
		James Begg	85%	143
		Harris Mason	20%	58
		Claudia Joseph	80%	170
		Keith Morrison	30%	50
		Ruth Kips	10	30

5.b FUNDING FOR EXTERNAL COLLABORATORS

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

5.c PERSONNEL ACTIONS

We converted one postdoc, Mark Boggs, to a staff position at LLNL in 5/15. This last year he worked about 20% on our SFA. We hired two new postdocs: 1) Keith Morrison (start 12/15), a microbiologist working 50% time on our SFA, and 2) Enrica Balboni (start 3/16), a mineralogist and geochemist, working 100% time on this SFA.

5.d NATIONAL LABORATORY INVESTMENTS

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

- NMR facility is available to use at no cost to our program. A new Electron Paramagnetic Resonance (EPR) spectrometer that includes the capability to run samples at liquid He temperatures was purchased in FY14 and is now available for our program to use.
- 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.
- 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). The Director of the Seaborg Institute (currently Mavrik Zavarin) oversees the summer student program that paid for the cost of one summer student working on this program in FY15.

5.e CAPITAL EQUIPMENT

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

6. REFERENCES

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