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Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments

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PROJECT SUMMARY

Widespread subsurface contamination at DOE sites has resulted from past mining, processing, and disposal processes. *In situ* remediation technologies can sequester uranium on site by transforming uranium to stable, low solubility species. While most recent research has investigated biogeochemical reduction of U(VI) to less soluble U(IV) species, this approach may have limited long-term sustainability because of the potential for reoxidation of U(IV) to more mobile U(VI) species. Phosphate addition is an alternative remediation approach that can enhance the sequestration of uranium without requiring chemically reducing conditions. Phosphate addition can be used as a stand-alone treatment process or as a complementary process to increase the longevity of reduction-based bioremediation methods. The U(VI)-phosphate-sediment-groundwater system is complex. Phosphate can immobilize U(VI) through both enhanced adsorption and the formation of uranyl phosphate solids. The geochemical factors that determine the dominant immobilization mechanisms are insufficiently understood to design efficient remediation strategies or accurately predict uranium transport in treated systems.

The overall objective of the proposed research is to determine the dominant mechanisms of U(VI)-phosphate reactions in subsurface environments. Specific objectives are to: (1) resolve uncertainty regarding the specific uranyl phosphate solids that form in homogeneous solutions; (2) determine the molecular mechanisms controlling U(VI) speciation in heterogeneous phosphate-bearing systems and the conditions where specific mechanisms dominate; (3) characterize how the interaction of competitive and cooperative reactions controls uranium speciation in sediments; and (4) identify chemical divides that separate regimes where specific mechanisms dominate U(VI) speciation in subsurface sediments.

We will pursue these objectives through an integrated research approach involving two parallel modules that links fundamental geochemical processes with their roles in heterogeneous field sediments. In Module I we will investigate the formation of U(VI) phosphate precipitates in homogeneous aqueous solutions and then study the adsorption and precipitation of U(VI) and phosphate in heterogeneous systems containing goethite and montmorillonite. Module II will use sediments from the Hanford and Rifle IFRC sites to examine the dominant U(VI)-phosphate reactions at field-relevant conditions in batch and column experiments. By performing these two modules in parallel, studies of fundamental processes can focus on those that are found to be dominant in field sediments and insights regarding specific processes can be tested in field sediments. We will combine aqueous analyses, geochemical modeling, and solid phase characterization to measure macroscopic U(VI) behavior and elucidate the molecular-scale mechanisms responsible for the behavior. Solid phase characterization will benefit from an array of spectroscopic, microscopic, and diffraction tools performed at Washington University and at DOE national user facilities. Our team has the complementary expertise in environmental geochemistry, engineering, and advanced spectroscopic techniques to successfully implement the research approach.

The research results will advance the scientific basis for phosphate-based remediation at uranium-contaminated DOE sites. The investigation will identify the geochemical factors governing the precipitation of specific uranyl phosphate solids. The proposed research will also identify the conditions where other U(VI) reactions with phosphate, such as ternary surface complexation and association with calcium phosphates, control contaminant fate. These processes may provide additional long-term attenuation of U(VI) transport in systems where uranyl phosphates are dissolving or bioreduced U(IV) is reoxidizing. By studying fundamental processes at field-relevant conditions, the results will enable site-specific decision making regarding remediation and site management. This work will provide the knowledge base needed to evaluate the efficacy of phosphate-amendment treatment methods.

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EXECUTIVE SUMMARY

Widespread subsurface contamination at DOE sites has resulted from past mining, processing, and waste disposal processes. *In situ* remediation technologies can sequester uranium on site by transforming uranium to stable, low solubility species. While substantial recent research has investigated biogeochemical U(VI) reduction, this approach may have limited long-term sustainability because of the potential for reoxidation to occur. Phosphate addition is an alternative approach that can enhance the sequestration of uranium without requiring sustained reducing conditions. However, the geochemical factors that determine the dominant immobilization mechanisms are insufficiently understood to design efficient remediation strategies or accurately predict uranium transport in treated systems.

The overall objective of the proposed research is to determine the dominant mechanisms of U(VI)-phosphate reactions in subsurface environments. Specific objectives are to: (1) resolve uncertainty regarding the specific uranyl phosphate solids that form in homogeneous solutions; (2) determine the molecular mechanisms controlling U(VI) speciation in heterogeneous phosphate-bearing systems and the conditions where specific mechanisms dominate; (3) characterize how the interaction of competitive and cooperative reactions controls uranium speciation in sediments; (4) identify chemical divides that separate regimes where specific mechanisms dominate U(VI) speciation in subsurface sediments. The proposed work is designed to test the following hypotheses: (1) mineral surfaces modify uranyl phosphate precipitation through both competitive and cooperative processes; (2) uranyl phosphate ternary surface complexes dominate uranium speciation in phosphate-rich systems undersaturated with respect to uranyl and calcium phosphates; (3) complex interactions between U(VI), phosphate, sediments, and groundwater components yield systems where uranium speciation is controlled by only one or a few reactions.

We will pursue these objectives through an integrated research approach that links fundamental geochemical processes with their roles in heterogeneous field sediments. In Module I we will investigate the formation of U(VI) phosphate precipitates in homogeneous aqueous solutions and the adsorption and precipitation of U(VI) and phosphate in heterogeneous systems containing goethite and montmorillonite. Module II will use sediments from the Hanford and Rifle IFRC sites to examine the dominant U(VI)-phosphate reactions at field-relevant conditions in batch and column experiments. By performing the two modules in parallel, studies of fundamental processes can focus on those that are found to be dominant in field sediments and insights regarding specific processes can be tested in field sediments. We will combine aqueous analyses, geochemical modeling, and solid phase characterization to measure macroscopic U(VI) behavior and elucidate the molecular-scale mechanisms responsible for the behavior. Solid phase characterization will benefit from an array of spectroscopic, microscopic, and diffraction tools performed at Washington University and at DOE national user facilities.

The proposed research will support the BER Long Term Measure by advancing the scientific basis for phosphate-based remediation at uranium-contaminated DOE sites. The investigation will identify the geochemical factors governing the precipitation of specific uranyl phosphate solids. The proposed research will also identify the conditions where other U(VI) reactions with phosphate, such as ternary surface complexation and association with calcium phosphates, control contaminant fate. These processes may provide additional long-term attenuation of U(VI) transport in systems where uranyl phosphates are dissolving or bioreduced U(IV) is reoxidizing. By studying fundamental processes at field-relevant conditions, the results will enable site-specific decision making regarding remediation and site management. This work will provide the knowledge base needed to evaluate the efficacy of phosphate amendment treatment methods.

I. INTRODUCTION

Widespread contamination of the subsurface at DOE sites with uranium and other contaminants has resulted from historical deliberate and accidental discharge of nuclear waste into the environment. It is estimated that these sites contain 6 billion cubic meters of contaminated soil and groundwater. In addition, mining and milling operations have produced additional sizable areas of subsurface uranium contamination. Management of such sites has consisted of either monitored natural attenuation or active alteration of biogeochemical conditions to increase uranium partitioning to the solid phase. While bioreduction of U(VI) to U(IV) has received great interest as it results in a substantial decrease in aqueous U concentrations because of the low solubility of U(IV), the long-term sustainability of such an approach is questionable in many locations because of their natural oxic conditions. Reoxidation of bioreduced uranium can release the uranium back to groundwater and renew its migration [1-7]. Alternative remediation approaches that immobilize uranium in situ but that do not require biological or chemical U(VI) reduction may serve as both stand-alone treatments or as complements to bioreduction. Phosphate addition to promote the precipitation of low solubility U(VI) phosphates is the most frequently proposed alternative [8-18], although other methods have also been suggested [19].

The use of phosphate to enhance U(VI) sequestration has analogues in both natural and contaminated sites. Uranyl phosphate solids are common forms of U(VI) in contaminated soils and sediments at DOE facilities, most notably beneath the Hanford 300 Area. Solid-phase uranium sources in the 300 Area vadose zone are sustaining the large groundwater plume [20]. Uranium species in the source-term have been identified as primarily U(VI) adsorbed onto phyllosilicate surfaces and uranyl phosphate minerals [21-24]. Uranyl phosphates have also been observed in contaminated soils and sediments at the Oak Ridge Reservation [25, 26] and at the Fernald Site [27-29]. In natural settings, phosphate has been found to immobilize uranium(VI) in the oxidized zone of uranium ore deposits, often as uranyl phosphate minerals [30-34]. Uranyl phosphates have also been observed to form during alteration of a granite through the replacement of apatite [35].

Phosphate-based remediation methods have been designed to take advantage of the stability of uranyl phosphates seen in natural and contaminated environments. Uranium remediation by addition of calcium phosphate solids to sediments or soils is well established and the resulting reduction in uranium concentration is thought to occur through both enhanced adsorption and formation of secondary uranyl phosphate solids [11, 12, 36]. However, introduction of solid phosphate sources, such as in permeable reactive barriers, is not practical for the treatment of large areas of contaminated subsurface sediments. New technologies under development are thus focused on addition of phosphate in an aqueous form. Methods proposed for releasing phosphate into the subsurface involve either injections of polyphosphates that disperse and then decay to orthophosphate through hydrolysis [13, 15, 37] or biodegradation of injected organophosphate compounds [8, 9, 16]. These methods are intended to induce the precipitation of uranyl phosphate solids or the adsorption of uranyl on newly formed calcium phosphates. Field-scale testing of the polyphosphate method was not fully successful in its first implementation because of limited mixing of Ca- and P-bearing fluids [38]. This mixing was intended to induce the formation of calcium phosphate solids which would attenuate U transport.

The widespread occurrence of uranyl phosphates in natural and contaminated settings and the proposed phosphate-based treatment methods point to the importance of phosphate in controlling U(VI) fate in the environment. Although recent studies have investigated phosphate-induced immobilization in laboratory and field-scale systems, the understanding of the fundamental mechanisms controlling U(VI) immobilization is not sufficient to provide a sound scientific basis for such approaches. Recent studies have identified an array of potential uranium-phosphate reactions that include ternary surface complexation [39, 40] and uranium phosphate precipitation by calcium phosphates [12, 17] in addition to direct precipitation of uranium phosphates. The limited success of

field-scale demonstrations may be due in part to testing an engineering solution with insufficient knowledge of the controlling scientific processes. Fundamental aspects of uranium-phosphate reactions in sediments must be understood in order to predict U migration and the efficacy of proposed treatment methods.

The complexity of the Uranium-Phosphate-Sediment-Groundwater system presents challenges to developing a predictive understanding of immobilization processes. This complex system has multiple components and a series of competing and cooperating reactions. These include uranium and phosphate binary and ternary adsorption reactions onto sediment minerals, formation of uranyl phosphate precipitates of varying composition, and precipitation of calcium phosphates which may incorporate U(VI) as a substituting cation, adsorb U(VI), or nucleate uranyl phosphate solids. Each of these processes affects the U(VI) and phosphate concentrations in groundwater, altering the favorability of other reaction pathways. These inhibitory or cooperative effects may create chemical divides delineating regimes where a subset of these mechanisms dominates. The dominant mechanisms responsible for controlling uranium fate in phosphate-bearing subsurface sediments, and the ways multiple processes interact, are currently poorly understood.

II. PROJECT OBJECTIVES

The overall objective of the proposed research is to determine the dominant mechanisms of U(VI)-PO₄ reactions in subsurface environments. Specific objectives include:

1. *Resolve uncertainty regarding the specific uranyl phosphate solids that form in homogeneous aqueous systems.*
2. *Determine the molecular mechanisms controlling U(VI) speciation in heterogeneous phosphate-bearing systems and the conditions where specific mechanisms dominate.*
3. *Characterize how the interaction of competitive and cooperative reactions controls uranium speciation in sediments.*
4. *Identify chemical divides that separate regimes where specific mechanisms dominate U(VI) speciation in subsurface sediments.*

III. SCIENTIFIC BACKGROUND

A. Hanford and Rifle IFRC Sites

Proposed research activities (see Section V) involve work with sediments from the Hanford and Rifle IFRC sites. Relevant aspects of the groundwater geochemistry, sediment mineralogy, and uranium subsurface speciation are reviewed.

Groundwater Compositions. Groundwater at the Hanford IFRC [20], located in the 300 Area adjacent to the Columbia River, is slightly alkaline (pH 7.7 to 8.1) with a total ionic strength of 4 to 8 mmol/L. The dominant cations, in order of concentration, are Na⁺, Ca²⁺, and Mg²⁺, and the dominant anions are HCO₃⁻, Cl⁻, SO₄²⁻, and NO₃⁻. P_{CO2} values range from 10⁻³ to 10^{-2.5} atm, and the groundwater is nominally in equilibrium with calcite. While spatially variable, U(VI) concentrations typically range from 0.1 to 5 μmol/L (24-1200 μg/L).

Groundwater at the Rifle IFRC is similar in that it is also near calcite saturation but average P_{CO2} values are near 10^{-1.5} atm [41]. Reflecting the higher P_{CO2}, the range of pH values (6.6 to 7.4) is also higher than at Hanford. The groundwater at this site has a higher ionic strength than at Hanford (average of 33 mmol/L). Na⁺ is the dominant cation followed by roughly equimolar concentrations of Ca²⁺ and Mg²⁺. The dominant anions are HCO₃⁻ and SO₄²⁻ with lower concentrations of Cl⁻ and

still lower concentrations of NO_3^- . In a 1998 site characterization the U(VI) concentrations ranged from 0.1 to 1.1 $\mu\text{mol/L}$ (27-270 $\mu\text{g/L}$) [41], and similar values have been reported in recent field activities [42-44].

Sediment Mineralogy. The sediments at the Hanford IFRC are dominated by quartz, feldspars, and hornblende; calcite is typically not present [45]. These minerals occur primarily as sand-sized grains, often composed on multi-mineralic rock fragments, coated in a mixture of phyllosilicate clays [24]. Smectite, muscovite, chlorite, vermiculite, and illite are the major clays present [20, 22-24, 46]. Trace biotite present appears to be oxidized and coated with the iron oxides hematite and ferrihydrite [24]. Rifle IFRC site sediments are dominated by quartz and feldspars, with minor calcite, clay minerals (illite, vermiculite, chlorite, and kaolinite), and iron oxides (goethite, hematite, and magnetite) [47-49].

Uranium Speciation in IFRC Sediments. Recent studies have investigated the solid-phase uranium in contaminated Hanford IFRC sediments. Uranium predominantly occurs adsorbed to phyllosilicates and iron oxides and precipitated as autunite group uranyl phosphate minerals at this site [21-24]. The dominant sorbent phase was recently suggested to be chlorite [23], although uranium is found to associate with many phyllosilicates and their weathering products [24]. Chlorite and other Fe(II)-bearing phyllosilicates are known to reduce U(VI) to U(IV) [50, 51], but only U(VI) has been detected in the Hanford IFRC subsurface [21-23]. As Fe(II)-bearing phyllosilicates in the site sediments appear to be highly weathered, with iron oxides partially coating their surfaces [24], it is likely that pristine chlorite itself is not the adsorbing phase. Rather, secondary iron oxides associated with weathered chlorite, oxidized chlorite surfaces, and other phyllosilicates likely dominate U(VI) adsorption. The uranyl phosphate mineral was identified as metatorbernite $[\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$, an autunite group mineral, by X-ray microdiffraction ($\mu\text{-XRD}$) and electron microprobe measurements [21, 23, 24]. Minor amounts of cuprosklodowskite, a copper uranyl silicate mineral, have been identified in some samples [23].

Uranium at the Rifle IFRC is predominantly U(VI), except in a naturally bioreduced zone where U(IV) was found associated with framboidal pyrite [52]. A generalized composite surface complexation model indicates uptake of U(VI) by adsorption to reactive surface coatings on sediment grains [47], which would include iron oxides and clay minerals. During the biostimulation of Rifle sediments in column experiments, the reduction of U(VI) to U(IV) was tracked with X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra of sediments from complementary batch experiments indicated the formation of UO_2 nanoparticles [53]. However, we are unaware of studies that have directly characterized the speciation of U(VI) in the original sediments.

C. Aqueous Geochemistry and Mineralogy of Uranium(VI) in Environmental Systems

U(VI) is known to display complex speciation in natural waters, forming aqueous complexes of UO_2^{2+} with OH^- , CO_3^{2-} , PO_4^{3-} , SO_4^{2-} , $\text{H}_4\text{SiO}_4(\text{aq})$, F^- , Cl^- , and NO_3^- [54-57]. In addition, U(VI) has recently been shown to form ternary $\text{UO}_2^{2+}\text{-CO}_3^{2-}\text{-X}^{2+}$ complexes in solution, where X^{2+} is Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} [58-61]. Under circumneutral to slightly alkaline pH conditions (pH 6 to 9) and in a groundwater composition representative of the IFRC sites, U(VI) aqueous speciation is dominated by carbonate complexes, especially ternary complexes that also contain Ca^{2+} or Mg^{2+} . In a similar system with added phosphate, carbonate complexation is still dominant above pH 7.5, but complexation by phosphate dominates below this pH.

Phosphate also affects the solubility of U(VI) in these systems, with uranyl orthophosphate $[(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$ and a range of autunite group minerals (generally $\text{MUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}$, where $\text{M} = \text{Na}^+$, K^+ , H_3O^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} and $x = 3$ to 6) being the most thermodynamically stable phases observed under ambient conditions [54, 56, 57, 62]. The predicted stability field for each of these phases has a complex dependence on pH, P_{CO_2} , electrolyte cation type and concentration, and

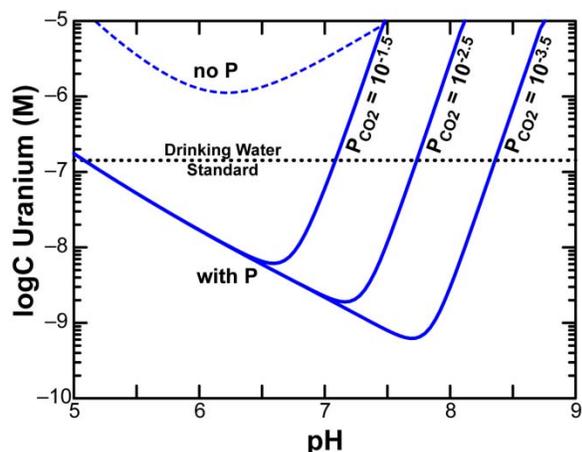


Figure 1. *U(VI) solubility in the absence (dashed) and presence (solid) of 5 mmol/L phosphate in a solution of 10 mmol/L NaCl and 1 mmol/L CaCl₂ at different CO₂ partial pressures. Autunite [Ca(UO₂)₂(PO₄)₂·11H₂O] is the solubility limiting phase in the presence of phosphate.*

intermediate phase in the formation of uranyl phosphates [66].

Once formed, autunite group minerals may undergo transformations through cation exchange reactions [67-71]. Autunite minerals also partially dehydrate to meta-autunite minerals (e.g., torbernite dehydrates to metatorbernite). This transformation often occurs when autunite minerals are exposed to the atmosphere. Some meta-autunites, like chernikovite, do not have an autunite counterpart, and are likely the stable phase in the presence of water. In contrast, transformation of autunites to uranyl orthophosphate must occur through a dissolution and reprecipitation mechanism, as uranyl orthophosphate has a markedly different structure from that of autunites [72]. The formation of an autunite as a precursor to uranyl orthophosphate formation suggests that there are mechanistic controls that favor the nucleation and precipitation of autunite-type sheets over other uranyl phosphate structural units. Similar controls have been demonstrated for uranyl silicates [73].

D. Effect of P_{CO₂} on U Solubility and Aqueous Speciation

P_{CO₂} is widely identified as a critical parameter determining the solubility and aqueous speciation of U(VI). At slightly alkaline pH conditions, the solubility of U(VI) solids increases as P_{CO₂} increases because of the formation of soluble U(VI)-carbonate complexes. However, this effect is often overestimated when comparisons are made between two P_{CO₂} conditions at a fixed pH value. In real systems pH and P_{CO₂} are not independent, with pH decreasing as P_{CO₂} increases; this is observed in Hanford and Rifle IFRC groundwater [20, 41]. In calcite-saturated systems, pH increases from 8.2 at a P_{CO₂} = 10^{-3.5} to 6.9 at P_{CO₂} = 10^{-1.5}. The effect of increasing P_{CO₂} on U solubility is thus more complicated and often results in only a moderate increase in U concentration. As an example, in calcite-

phosphate concentration. As an example, in a mixed NaCl-CaCl₂ solution equilibrated with atmospheric CO₂, U(VI) solubility is greatly reduced in the presence of phosphate, with a minimum solubility a factor of 100 less than the drinking water standard of 30 µg/L (Fig. 1).

The specific uranyl phosphate solid that forms in an aqueous system may not necessarily be the thermodynamically most stable phase. Chernikovite (H₃OUO₂PO₄·3H₂O), an autunite group mineral, is often described as precipitating under conditions where uranyl orthophosphate is expected to form, and chernikovite transforms to uranyl orthophosphate after boiling, digestion in water, or washing in a solvent [62-64]. Chernikovite has been identified at the Shinkolobwe mine and suggested to be a precursor to later-formed uranyl phosphates [65]. Chernikovite may be a short-lived but important

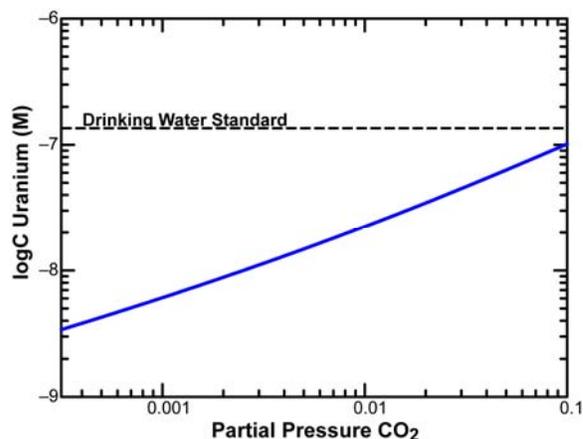


Figure 2. *Autunite solubility in a calcite-saturated system amended with 50 mM NaH₂PO₄ as a function of CO₂ partial pressure.*

equilibrated systems amended with sodium phosphate at a concentration proposed for use in treatment methods [15], U concentrations are maintained below the drinking water standard at P_{CO_2} values relevant to most contaminated sites, including the Hanford and Rifle IFRC sites, in the western United States (Fig. 2). The increase in solubility between a P_{CO_2} of $10^{-3.5}$ and $10^{-1.5}$ is about a factor of 10. The effect of P_{CO_2} on aqueous speciation is similarly small. For all conditions illustrated in Fig. 2, the U(VI) speciation is dominated by $Ca_2UO_2(CO_3)_3(aq)$ and $CaUO_2(CO_3)_3^{2-}$ in a nearly constant ratio.

E. Adsorption and Precipitation in UO_2^{2+} - PO_4^{3-} - CO_3^{2-} Systems

The concentration of uranium in environmental aquatic systems is primarily controlled by adsorption and precipitation reactions. Adsorption of U(VI) to sorbent minerals present in aquifers increases significantly with increasing pH at pH 4-5 [74]. Adsorption becomes unfavorable above pH 8-9 because of aqueous complexation of U(VI) by carbonate [74]. Phosphate increases uranium adsorption at low pH, presumably through the formation of ternary surface complexes [39, 75-77]. The presence of phosphate enhanced adsorption and limited transport of uranium in goethite-coated sand [40]. One previous EXAFS spectroscopic study [78] has suggested that the speciation of U(VI) sorbed to sediments from DOE sites is dominated by uranyl phosphate ternary surface complexes under acidic conditions. However, spectroscopic confirmation of uranyl phosphate ternary surface complexation is generally lacking.

Precipitation of uranyl phosphates also occurs in natural and contaminated environments. Murakami et al. [34] observed the formation of nanocrystalline uranyl phosphates downgradient of the Koongarra ore deposit in Australia that were associated with iron oxides. They hypothesized that these formed by adsorption of the many constituent ions onto ferrihydrite followed by precipitation during ferrihydrite recrystallization into goethite or hematite. Uranyl phosphates have also been found in contaminated soils and sediments at a number of DOE facilities [21, 22, 25-29]. Fuller et al. [12] observed that apatite may adsorb U(VI) at low coverages and induce the precipitation of chernikovite at higher U concentrations. A similar observation was made in the presence of bone charcoal and bone meal apatite [11]. These studies suggest that the transition between adsorption and precipitation of U(VI) and phosphate may be either part of a gradual continuum or may be controlled by chemical divides (i.e., tipping points). Further, the presence of mineral surfaces may facilitate U(VI) phosphate precipitation through heterogeneous nucleation of the solids. The complexity of U(VI)-phosphate interactions in contaminated subsurface systems requires further investigation to elucidate the mechanisms controlling uranium speciation and mobility.

IV. RECENT RESULTS AND PRELIMINARY DATA

A. U-P Goethite Interactions

We have previously investigated the effect of phosphate on immobilization mechanisms of U(VI) in the presence and absence the iron oxyhydroxide goethite (α -FeOOH). We performed a series of batch experiments at pH 4 that were supported by aqueous analyses, direct solid-phase characterization, and a chemical equilibrium model that integrated adsorption and precipitation processes. By combining these methods we were able to identify geochemical conditions favoring adsorption of U(VI) and precipitation of U(VI) phosphates.

At sufficiently high phosphate loadings, phosphate addition induced the formation of U(VI) phosphate solids both in the presence and absence of goethite. In the absence of goethite, phosphate induced the precipitation of chernikovite (Fig. 3a), although uranyl orthophosphate was predicted to be the thermodynamically most stable phase. Consequently, chernikovite formed as a metastable phase that could persist for reaction times of more than one year. In the presence of goethite, when

phosphate was added to provide strongly supersaturated solutions, chernikovite precipitation occurred rapidly. Precipitates were stable over long periods even when equilibrium calculations predicted that adsorption to goethite would have been dominant (**Fig. 3b**). There is a critical phosphate level (between 15 and 130 μM for the experimental conditions) required for precipitation of U(VI) phosphates instead of adsorption. Near the critical level, we found evidence for heterogeneous nucleation of U(VI) phosphate precipitates on the goethite surface (**Fig. 3c**).

Phosphate also influenced the adsorption of U(VI) to goethite at conditions undersaturated with respect to U(VI) phosphates. A surface complexation model developed through the integration of models from several previous studies [39, 40, 79] indicated that a ternary U(VI)-phosphate-goethite surface complex is the dominant U(VI) surface species at pH 4. While previous studies used only macroscopic data to suggest a ternary surface complex, our EXAFS measurements yielded spectroscopic evidence for a U(VI)-bridging ternary surface complex. Through the linear combination fitting of the spectra of U(VI)-phosphate-goethite samples to endmembers of a U(VI) phosphate precipitate and U(VI) adsorbed to goethite, we were able to quantify the relative contributions of adsorption and precipitation to U(VI) immobilization (**Fig. 4**). The spectrum of adsorbed U(VI) in the presence of phosphate indicated a contribution of phosphate even for conditions for which precipitates definitely did not form. Further characterization of the spectrum for this sample led to an optimal EXAFS fit that included a ternary surface complex. While this evidence is strongly suggestive of ternary surface complexation, further study can identify the structure of the surface complexes and determine the range of conditions over which they may be significant.

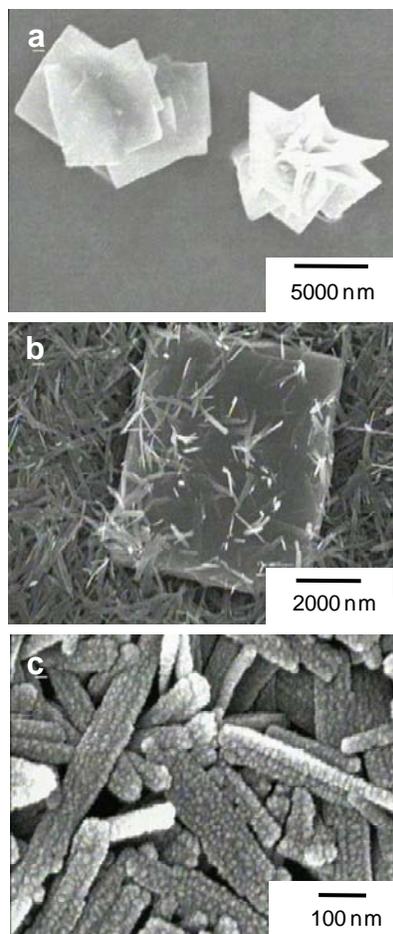


Figure 3. Electron micrographs of solids resulting from reaction of 100 μM U(VI) and 130 μM phosphate in the (a) absence and (b) presence of 0.6 g/L goethite and of (c) 100 μM U(VI) and 15 μM phosphate in the presence of goethite.

We developed a geochemical equilibrium model to predict the conditions favoring adsorption versus precipitation for U(VI) in the presence of phosphate and goethite. The model

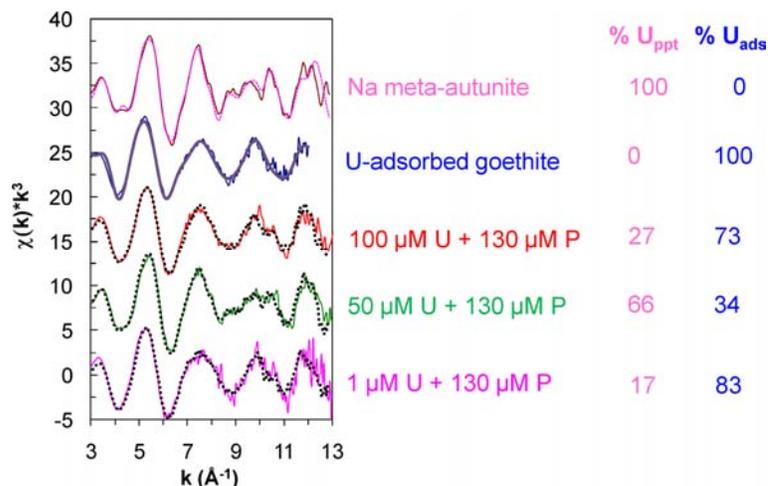


Figure 4. EXAFS spectra of pure sodium meta-autunite ($\text{NaUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$), U(VI) adsorbed to goethite, and samples (bottom three spectra) from reaction of U(VI), phosphate, and goethite at pH 4. Linear combination fitting (dashed lines) of the sample spectra was used to determine relative proportions of precipitated and adsorbed U(VI). The spectrum of 1 μM U(VI) adsorption in the presence of phosphate is suggestive of a ternary surface complex.

could also identify the dominant solid-associated U(VI) species. The model was developed by integrating thermodynamic equilibrium constants from recent critical reviews [54, 55, 80, 81] and previous surface complexation models for U(VI) and phosphate [39, 79]; an approach developed by Sverjensky was used to integrate studies of sorbents with different surface areas and site densities [82]. With increasing U(VI) loading at pH 4, the dominant form of solid-associated U(VI) gradually transitions from adsorbed U(VI) complexes to U(VI) phosphate precipitates, and equilibrium predictions suggest the coexistence of both forms (Fig. 5a). In the presence of phosphate, a ternary U(VI)-phosphate surface complex ($\equiv\text{FePO}_4\text{UO}_2$) is predicted to be the dominant species over a broad environmentally relevant pH range (Fig. 5b).

B. U-P-Smectite Interactions

We have also identified potential uranyl phosphate ternary surface complexes on montmorillonite [83]. At pH 7 and $P_{\text{CO}_2} = 10^{-3.5}$ bar in a NaNO_3 electrolyte, solution conditions supersaturated with respect to uranyl phosphate solids clearly precipitate an autunite-like phase, based on EXAFS analyses (Fig. 6A). However, at conditions undersaturated with respect to uranyl phosphates the EXAFS spectra still differ from that of uranyl adsorbed to montmorillonite in the absence of PO_4^{3-} . The 3.0 Å feature in the Fourier transform EXAFS spectrum, typically associated with Fe or Al second shell neighbor and multiple scattering from the axial oxygens, increased in amplitude and shifts slightly in the presence of phosphate (Fig. 6B). The resulting EXAFS spectrum is well modeled as a uranyl phosphate ternary surface complex. This assignment is made with confidence because of the clear change in the spectrum in the presence of phosphate. While further study is clearly warranted, this is

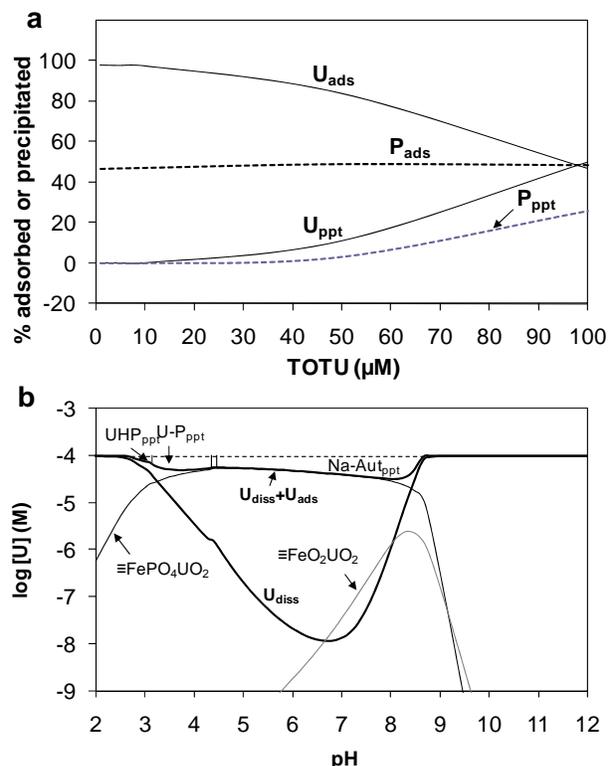


Figure 5. Predicted equilibrium speciation of U(VI) in the presence of 130 μM phosphate, 0.6 g/L goethite, and 0.01 M NaNO_3 as a function of (a) total U(VI) loading at pH 4 and (b) pH at 100 μM total U(VI). The predicted U(VI) precipitates [chernikovite (UHP), uranyl orthophosphate (U-P), and sodium meta-autunite (Na-Aut)] and surface complexes are noted in b.

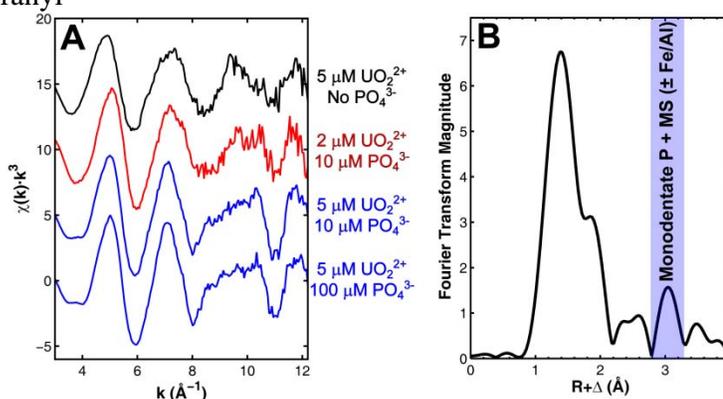


Figure 6. (A) Comparison of U EXAFS spectra of U(VI) sorbed to montmorillonite in the absence of PO_4^{3-} and in the presence of PO_4^{3-} at conditions undersaturated (2 μM UO_2^{2+}) and supersaturated (5 μM UO_2^{2+}) with respect to uranyl phosphate minerals. (B) Fourier transform of the undersaturated spectrum showing the presence of a P shell consistent with uranyl phosphate ternary surface complex.

additional evidence for such complexation at undersaturated conditions, in this case on a smectite at circumneutral pH.

V. RESEARCH APPROACH

A. Major Hypotheses

The proposed work is designed to test the following major hypotheses:

1. *Mineral surfaces modify uranyl phosphate precipitation through both competitive (e.g., sorbing solutes that are reactants for precipitation) and cooperative (e.g., promoting nucleation through the formation of uranyl phosphate ternary surface complexes) processes.*
2. *Uranyl phosphate ternary surface complexes dominate uranium speciation in phosphate-rich systems undersaturated with respect to uranyl and calcium phosphates.*
3. *Complex interactions between uranium, phosphate, sediments, and groundwater components yield systems where uranium speciation is controlled by one or a few reactions; chemical divides separate regimes where sets of specific mechanisms dominate uranium speciation.*

B. General Research Strategy

Our team will test these hypotheses through an integrated research approach involving two parallel modules that links fundamental geochemical processes with their roles in heterogeneous field sediments (**Fig. 7**). In Module I we will study specific uranium-phosphate reactions to isolate the chemical controls on immobilization mechanisms and characterize the complex interactions among different mechanisms. We will investigate the mechanisms controlling uranium speciation in phosphate-treated field sediments in Module II. These two modules will be performed in parallel to optimize identification of the major processes and the conditions under which they are dominant in actual subsurface systems. This approach will combine wet chemistry, geochemical and surface complexation modeling, and advanced spectroscopic, microscopic, and diffraction tools both at Washington University and at national user facilities, including the Advanced Photon Source (APS), the Stanford Synchrotron Radiation Lightsource (SSRL), and the Environmental Molecular Sciences Laboratory (EMSL). Unfamiliar aspects of specific analytic methods are explained below in Section E.

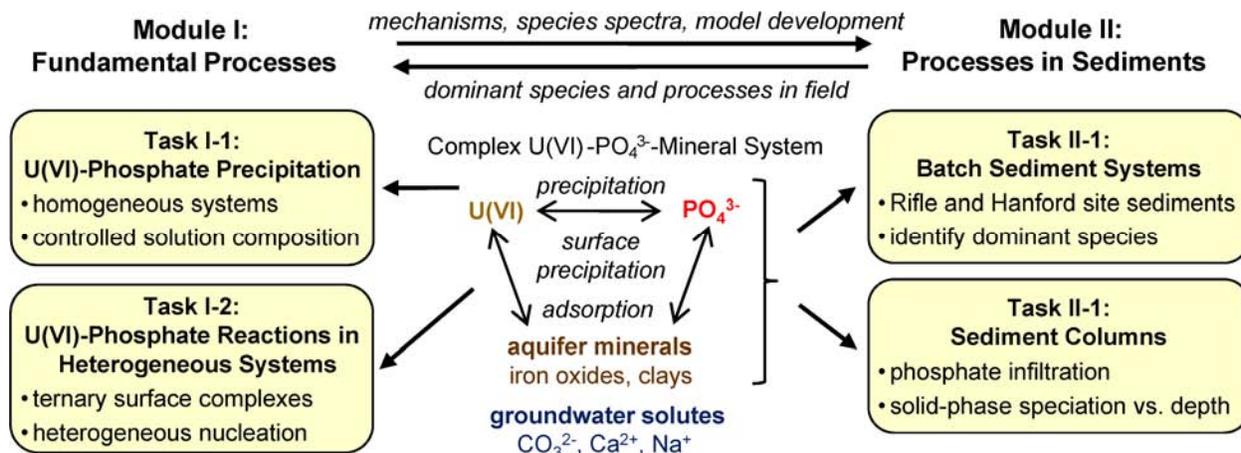


Figure 7. Research approach that integrates investigation of fundamental mechanisms with determination of their roles in sediments from field sites.

C. Module I: Fundamental U(VI)-PO₄ Processes

This module is designed to characterize the fundamental reactions that occur between uranium and phosphate, the chemical conditions under which they occur, and how competing processes affect the mechanisms controlling U speciation.

Task I-1. Formation of U(VI) Phosphate Precipitates in Homogeneous Systems

Before examining the role of sediment mineral surfaces on U(VI)-phosphate reactions, we will probe unresolved questions regarding the precipitation of U(VI) phosphate solids. While phosphate definitely promotes uranyl phosphate precipitation, the conditions that will result in the formation of specific phosphate solids are unknown. The first solid phase to form is often not the most thermodynamically favorable solid. Consequently, U(VI) phosphate precipitation may be kinetically controlled and metastable phases may play important roles in controlling dissolved U(VI) concentrations. The exact solution chemistry of a given site will also determine which specific U(VI) phosphate solids precipitate, especially considering the diversity of U(VI) phosphate solids with structural incorporation of common groundwater cations. Fundamental aspects of U(VI) phosphate precipitation will be investigated in a research approach that combines aqueous and solid phase analyses.

Batch Experiments. Batch U(VI) phosphate precipitation experiments will be performed in stirred glass reactors (200 mL) over a broad range of solution compositions. To simulate the formation of U(VI) phosphates in subsurface environments, experiments will be limited to 25°C; synthesis methods often employ high temperatures to promote the formation of specific U(VI) phosphate solids. The reactors will be loaded with solutions of UO₂(NO₃)₂ and H₃PO₄. Depending on the specific solution composition being probed, the pH, cation composition, and dissolved inorganic carbon will be set to desired values by addition of the necessary solutions.

The aqueous phase and the solids will be sampled at 10 prescribed times from 1 hour to 6 months (**Fig. 8**). Because of the possible transformation of metastable phases that may precipitate first, long reaction times are necessary. Samples (10 mL) of the suspension will be filtered using 0.2 μm filters, and the filtrates will be acidified and then analyzed for dissolved U, P, Ca, and Na by inductively coupled plasma mass spectrometry (ICP-MS). The pH will also be measured at each sampling time. The solids retained on the filters will be air-dried and then examined using X-ray diffraction (XRD) and scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS). We have used this integrated approach to track the transformation of other U(VI) solids in previous work [84, 85]. Because U(VI) phosphate precipitation may involve the formation of stable nanoparticles [56], selected filtrates from the 0.2 μm step will be further filtered using 0.02 μm filters and the filtrate will be analyzed. If this sequential filtration approach suggests the formation of colloids, then we will measure the size distribution of the suspended particles by performing dynamic

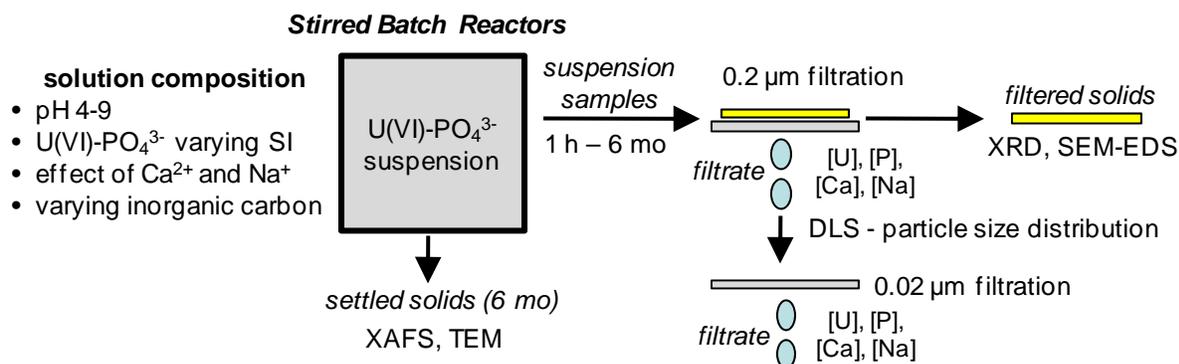


Figure 8. Experimental approach to study U(VI) phosphate formation by integrating aqueous phase analysis and solid phase characterization.

light scattering (DLS) on a portion of the filtrate from the 0.2 μm filtration. After the last sampling period, the solids remaining in the 200 mL batch reactor will be collected and saved for analysis.

The effect of dissolved inorganic carbon (DIC) on U(VI) phosphate formation will be assessed by performing experiments in both the absence and presence of DIC. DIC-free experiments will be performed in an Ar-filled glovebox with a system that removes trace amounts of CO_2 . For experiment with carbonate, the DIC will be provided by two separate methods. In the first method, the solutions will be equilibrated with atmospheric CO_2 . In the second method the solutions will receive dissolved inorganic carbon (DIC) equivalent to that in equilibrium with calcite for the given pH by addition of CO_2/TBAOH , NaHCO_3 , or CaCO_3 , depending on the desired cation composition of a given experiment.

Solution Compositions. To focus on fundamental processes and gradually add complexity, the approach progresses from simple solution compositions, to solutions containing a single groundwater cation, to complex real-world groundwater compositions.

Ultrapure Water. The first precipitation experiments will be performed with solutions containing only U(VI) and phosphate. The expected solids will be chernikovite ($\text{H}_3\text{OUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$) at below pH ~ 4 and uranyl orthophosphate [$(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$] at higher pH. Experiments will be conducted from pH 4 to 9 with 1 pH unit increments. The pH will be adjusted by addition of tetrabutylammonium hydroxide (TBAOH) because the tetrabutylammonium ion is unlikely to be structurally incorporated into the U(VI) phosphate precipitates. For later experiments with groundwater cations, NaOH or $\text{Ca}(\text{OH})_2$ will be used. A key experimental variable in these experiments will be the degree of solution supersaturation. The reactors will be loaded with 1-100 μM U(VI) from uranyl nitrate; within this range the higher concentrations will be used at lower pH values. The reactors will then be dosed with phosphate solutions to provide P:U ratios of 1:1 and greater. The range of total phosphate concentrations will be selected to provide saturation indices from 0 (anticipated equilibrium) to 2 (two orders of magnitude supersaturation) for chernikovite and uranyl orthophosphate. The saturation indices will be calculated from the solubility products of the two solids and the set of equilibrium constants for aqueous reactions involving U(VI), OH^- , and PO_4^{3-} , and CO_3^{2-} . The constants used will be selected from recent critical reviews [55, 80, 81]. The final dissolved concentrations from these experiments will be compared with the predicted equilibrium solubility.

Sodium-Containing Solutions. The role of common groundwater cations on U(VI) phosphate precipitation will first be investigated with sodium. Experiments will be conducted with Na^+ to promote the formation of sodium-metaautunite ($\text{NaUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$). Sodium concentrations will be chosen to encompass those encountered in Rifle and Hanford groundwater.

Calcium-Containing Solutions. Similarly to sodium, the presence of calcium can promote the formation of U(VI) phosphates with structurally incorporation of Ca^{2+} (i.e., autunite [$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 11\text{H}_2\text{O}$]). The addition of calcium also adds the possibility of precipitating calcium phosphate minerals (e.g., brushite [$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$], apatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$]). If calcium phosphate solids precipitate, then U(VI) may be removed by precipitation in a separate U(VI) phosphate solid, adsorption to the calcium phosphate, or incorporation into the calcium phosphate. Calcium and uranium concentrations will be studied at environmentally relevant values that include (1) compositions favoring U(VI) phosphate (including autunite) precipitation and (2) compositions for which calcium phosphate is expected. For the calcium phosphate solids precipitated, we will characterize the samples using EXAFS in addition to the SEM/EDS and XRD characterization planned for all solids in this task. EXAFS can determine whether discrete U(VI) phosphate solids still form or whether the U(VI) is adsorbed on or incorporated into the calcium phosphate precipitates.

Groundwater. Building on the insights gained from studying sodium and calcium, precipitation experiments will be conducted in actual or synthetic groundwater for the Rifle and

Hanford sites. These groundwater solutions will first be amended with additional U(VI) to provide a constant initial concentration, and then they will be dosed with dissolved phosphate at levels ranging from equimolar to the U(VI) to a tenfold excess of phosphate. Ideally groundwater will be collected at the sites, filtered, and shipped to our laboratories for these experiments. If real groundwaters cannot be obtained, then we will use measured compositions from the sites to prepare synthetic groundwaters that include all of the relevant anions and cations; we have used such an artificial groundwater for the Rifle site in previous work on the stability of UO_2 [86]. Aqueous samples from these experiments will be analyzed for a whole suite of groundwater constituents (we routinely use a 25 element ICP-MS method) in addition to U, P, Na, and Ca.

Task I-2. Uranyl and Phosphate Reactions in Heterogeneous Systems

Heterogeneous systems containing mineral sorbents are inherently more complex than homogeneous systems because multiple competing or cooperative processes may occur. We seek to identify the conditions where specific reactions dominate U(VI) speciation in heterogeneous systems containing phosphate. This will be accomplished through a series of batch studies containing suspensions of a single mineral sorbent phase (**Fig. 9**). In order to build on our recent results and preliminary data, we will focus on goethite and the montmorillonite SWy-2 from the Source Clay Repository. These phases were selected because the fine fraction of the Hanford and Rifle IFRC sediments are dominated by phyllosilicate clays and iron oxides. Selection of an example of each of these mineral types allows us to compare how sorbent structure influences uranium-phosphate reactions in heterogeneous systems.

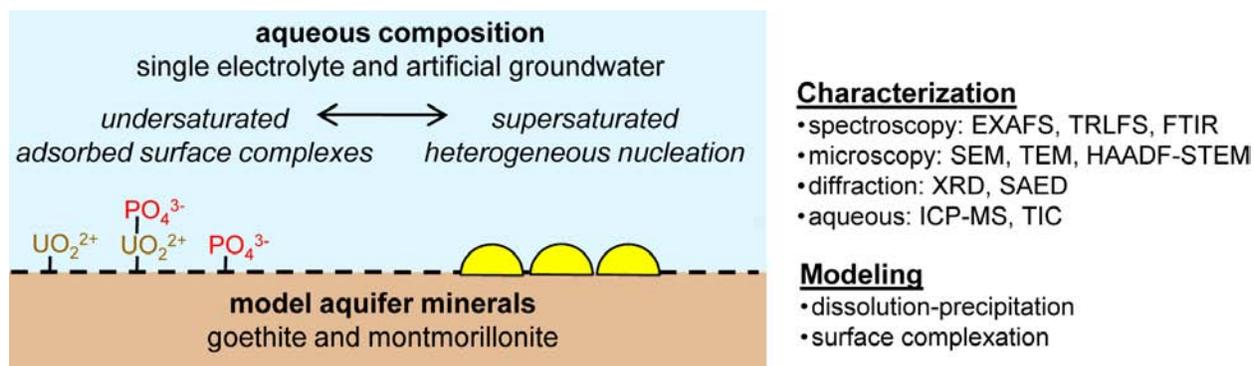


Figure 9. Approach to investigation of uranyl phosphate reactions in heterogeneous systems.

A range of chemical conditions will be explored in a series of systematic studies in order to determine the occurrence and distribution of ternary surface complexes, the conditions where uranyl phosphates form, and the composition of such solids. These topics are being addressed in a single task as small changes in composition can alter which reactions control U(VI) speciation. In addition, we seek to assess competition and cooperation among these processes. First, solutions that are undersaturated with respect to uranyl phosphate solids will be studied to investigate the formation and structure of ternary surface complexes, and then supersaturated solutions will be used to investigate the nucleation and composition of uranyl phosphate solids in the presence of goethite and montmorillonite. Solution analyses and solid-phase characterization of U(VI) speciation will be used to optimize geochemical and surface complexation models of the systems under investigation. Specific aspects of uranyl phosphate reactions will be investigated as follows:

Identification of the Presence and Structure of Uranyl Phosphate Ternary Surface Complexes. There is ample evidence from past studies and our recent results that uranyl phosphate ternary surface complexes occur, although little work has been conducted under circumneutral to

alkaline conditions near calcite saturation. In addition, the identification of uranyl phosphate ternary surface complexes in unknown samples, such as individual contaminated sediment samples, using EXAFS spectroscopic methods is challenging because of overlapping features in spectra. Analysis of macroscopic solution chemistry data in the context of a surface complexation model also poses challenges to determining the occurrence and abundance of such species as adsorption behavior is difficult to translate between systems [77] and complex sediments often cannot be modeled using electrostatic surface complexation models [47]. These barriers may be overcome by employing a systematic approach where multiple spectroscopic, microscopic, and wet chemistry methods are integrated to characterize U(VI) surface speciation under a range of conditions.

We will use such an integrated approach to investigate uranyl phosphate ternary surface complexation on goethite and montmorillonite for conditions that are undersaturated with respect to uranyl phosphate precipitates. The effect of phosphate on uranium(VI) adsorption as a function of pH, [U(VI)], [PO₄], P_{CO2}, and electrolyte cation will be characterized. The order of PO₄ and U(VI) addition will also be explored. Element concentrations will be measured using ICP-MS, and DIC will be measured with a total organic carbon (TOC) analyzer. These measurements will be coupled to spectroscopic determination of U speciation in a series of related samples prepared under conditions where critical solution parameters are varied. Measurements of EXAFS and time-resolved laser fluorescence (TRLFS) spectra will be employed in concert to identify and quantify the distribution of U(VI) between distinct surface species.

Use of these two spectroscopic methods to probe a single system will provide substantial synergy and allow us to determine speciation with a confidence and accuracy not possible using these methods separately. TRLFS provides an indication of the number of distinct U(VI) species in a sample and, through comparison with spectra of known samples, the identity of the major species. TRLFS spectra however display non-linear mixing of spectral components and may suffer from quenching effects; this method is thus not suitable for quantifying the distribution between species. In addition, clear models for uranyl phosphate ternary surface complexes are not available (their identification is a goal of this project), so these results need to be coupled to another method, such as EXAFS spectroscopy.

EXAFS spectroscopy will be used to determine the structure and stoichiometry of surface complexes under conditions where TRLFS identifies a single species. EXAFS spectra of a set of samples where chemical conditions are expected to produce mixtures of surface species will be examined using principal component analysis (PCA). This will identify the number of spectral components (i.e., U(VI) species) in a dataset [87-89], which will be confirmed by TRLFS analysis on select samples. Iterative transformation factor analysis (ITFA) of the EXAFS spectra [90-92] can then be used to extract the real spectral components from the dataset assuming that specific spectra represent end-member states, i.e., conditions where only one species dominates. As noted above, such conditions will be identified by TRLFS; this is an essential role of this method in the project. Linear-combination fitting of the EXAFS spectra will then be used to quantify the proportion of the U(VI) species present. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra will also be collected on select samples to determine variations in phosphate speciation and to support the conclusions of the EXAFS and TRLFS studies. This general approach, but utilizing only EXAFS spectra, has been successfully applied to study U(VI) complexation in solution [90], uranyl carbonate ternary surface complexation on ferrihydrite [93], and metal speciation in contaminated soils [94, 95].

By combining EXAFS and TRLFS analyses with the wet chemistry results we will be able to map out U(VI) surface speciation under a range of chemical condition, effectively creating U(VI) surface phase diagrams. This will allow us to assess a number of aspects about the chemical behavior of uranyl phosphate ternary complexes. By exploring speciation as a function of pH and the U:P ratio we will assess whether single or multiple uranyl phosphate ternary surface species exist.

Aqueous complexation of uranyl by phosphate is dependent on these parameters and results in a number of complexes between uranyl and PO_4^{3-} , HPO_4^{2-} , and H_2PO_4^- . While all past surface complexation models have assumed $>\text{MOUO}_2\text{PO}_4$ surface complexes, a species with a partially protonated phosphate group could occur under slightly acidic conditions given the known aqueous speciation. A change in phosphate protonation is expected to show the largest effect in the TRLFS and ATR-FTIR spectra as it should have a larger impact on fluorescence decay lifetimes and vibrational frequencies than on U-O or U-P interatomic distances. The distribution of surface species among binary uranyl or phosphate surface complexes, uranyl phosphate ternary surface complexes, and uranyl carbonate ternary surface complexes will be investigated using the changes in speciation caused by variations in P_{CO_2} and pH. Together these measurements will determine the conditions where uranyl phosphate ternary surface complexes occur and their ability to compete with carbonate for controlling U(VI) surface speciation.

Nucleation and Composition of Uranyl Phosphate Solids. We will extend our studies of uranyl phosphate ternary surface complexation to conditions where precipitation of uranyl phosphate solids is expected. This will be guided by the conditions identified in Task I-1 that are favorable for the formation of specific uranyl phosphate solids. We hypothesize that there may be a relationship between conditions where uranyl phosphate ternary surface complexation is favorable and those where surface nucleation dominates. Metastable uranyl phosphate solids may precipitate in the presence of solids, and sorbent phases may alter particle size and morphology or the saturation state at which precipitation occurs. Our recent results (Section IV) suggest that under some conditions small nuclei of uranyl phosphates may form and coat mineral surfaces whereas at higher degrees of initial supersaturation apparent homogeneous precipitation occurs. In the presence of mineral surfaces multiple pathways to uranyl phosphate precipitation may occur that will affect particle size and their physical association with mineral sorbents, both of which may affect their stability and dissolution rate.

Using the same combination of wet chemical and spectroscopic tools that we will use in Task I-1, we will determine the conditions where precipitation occurs and the phase that forms. We will also explore the competition among precipitation and adsorption processes in the presence of goethite and montmorillonite through extending these studies to additional fluid compositions, including real (if available) or artificial Hanford and Rifle groundwater. This will be aided by the collection of EXAFS and TRLFS spectra of model compounds we have collected for prior studies [22, 96-100]. In addition, we will explore the nature of uranyl phosphate ternary surface complex properties at conditions near supersaturation with respect to uranyl phosphate solids to determine if molecular-scale changes in surface complex structure (e.g., multinuclear complex formation) occur prior to precipitation. These measurements will be further supported by microscopic and diffraction methods to determine the phase(s) that form and whether they were surface nucleated. SEM/EDS and transmission electron microscopy (TEM) observations will verify that precipitates have formed and estimate their overall composition. High-resolution TEM (HRTEM) and selected area electron diffraction (SAED) will be used to identify the mineral phase, and HRTEM and high-angle annual dark field scanning TEM (HAADF-STEM) will directly probe the substrate-uranyl phosphate interface to look for evidence of heterogeneous nucleation. This will be complemented by both laboratory- and synchrotron-based powder XRD measurements in order to further identify the precipitated phase(s). These studies will determine the role of surfaces in controlling uranyl phosphate precipitation, the phase(s) that form, and whether surface complexes serve as precursors to some phases.

Integration of Studies through Chemical Modeling. The conditions where distinct reactions dominate the processes controlling U(IV) speciation may be separated by sharp chemical boundaries. Investigating any one aspect requires analysis to ensure that other processes are not really at work, e.g., precipitation is not occurring when ternary complexation is expected. In addition, many of the

conditions explored will contribute to datasets needed to evaluate multiple factors. To investigate fundamental mechanisms controlling U(VI) fate effectively and efficiently these studies will be integrated through geochemical modeling. We will integrate information from the latest available thermodynamic databases for U(VI) solution complexes and precipitates with surface complexation models for U(VI) adsorption to goethite and montmorillonite. The integrated results will be used to expand existing surface complexation models for goethite ([39, 40, 79] and from our recent results) and montmorillonite [101] in order to create overall chemical models for these complex systems. The direct characterization of the solid phase speciation of U(VI) and phosphate will be used to constrain the reactions included in modeling.

D. Module II: Dominant Processes in Sediments

This module seeks to determine the dominant U-P reactions that actually occur in sediments under circumneutral to alkaline systems near calcite saturation.

Task II-1. Identifying Dominant Processes in Batch Systems

Natural sediments display substantially greater complexity than single mineral sorbents. While the simple heterogeneous systems studies in Task I-2 are essential for evaluating the processes that may potentially control U(VI) fate in phosphate-bearing systems, different behavior may be observed in real sediments because of heterogeneous mineral assemblages, common ion effects, and intraparticle diffusion. This task seeks to identify the dominant processes controlling U(VI) speciation in the presence of phosphate in sediment samples from the Hanford and Rifle IFRC sites (see attached letters of support from Dr. John Zachara and Dr. Phil Long). We will acquire both contaminated and uncontaminated sediments. The Rifle and Hanford IFRC sediments are complementary as both generally occur under calcite-saturated groundwater conditions but differ in the fine fraction mineralogy, with Hanford being phyllosilicate clay dominated with minor iron oxides whereas iron oxides are much more abundant in the Rifle sediments. This task will thus also provide insight into the role of sediment mineralogy in determining the processes affecting U(VI) speciation. These studies will be accomplished through a set of related activities (Fig. 10).

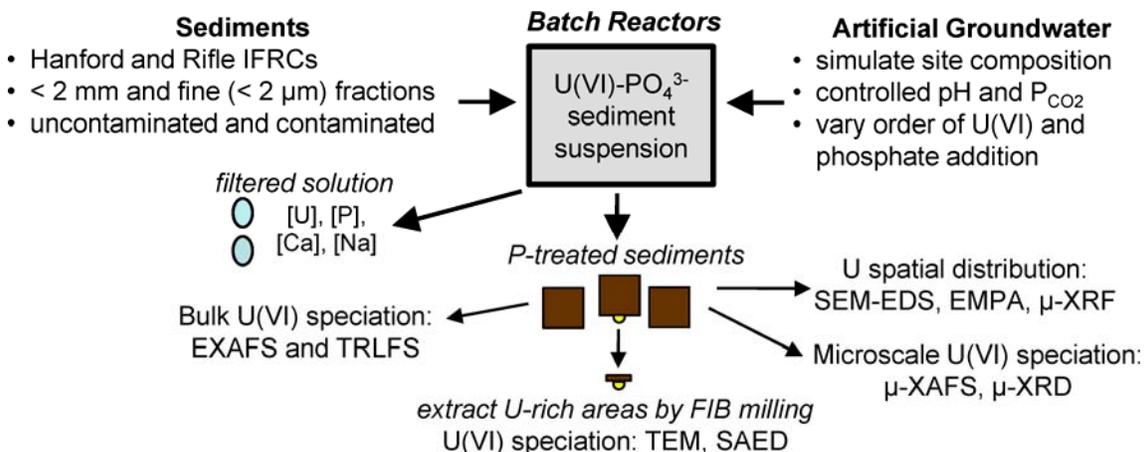


Figure 10. Approach to identifying dominant U(VI) species and reaction mechanisms during phosphate treatment of field sediments in batch systems.

UO₂²⁺-PO₄³⁻ Reactions in IFRC Background Sediments. Sediments from Rifle and Hanford IFRC will be acquired from portions of the site considered to be under background conditions. The <2 mm fraction of each will be used in batch studies to investigate the conditions where specific adsorption and precipitation mechanisms control U(VI) speciation in the presence of phosphate.

Artificial groundwaters will be the reaction solutions. For each site, an artificial groundwater reflective of the general groundwater composition but varying in pH and P_{CO_2} along a calcite-saturation trend will be employed. 3-5 pH/ P_{CO_2} conditions will be used for each sediment sample. At each condition the U and phosphate concentrations in solutions and their order of addition will be varied to establish conditions where U(VI) adsorption, precipitation, and binding by precipitating calcium phosphates are predicted to dominate speciation. Dissolved concentrations of U, P, and major elements will be determined by ICP-MS and dissolved inorganic carbon by a TOC analyzer.

The solid phase speciation of U will be characterized in select samples that are either predicted to be dominated by one adsorption or precipitation mechanism or are near transition conditions between different regimes (e.g., final solution near saturation with a uranyl phosphate mineral). A subset of each selected sample will be embedded in epoxy and prepared as thin sections for microanalysis. Electron probe microanalysis (EPMA) and SEM/EDS will be used to identify areas of clear uranium precipitation, which will appear as bright, electron-dense material. The elemental composition of these areas will also be determined, and the distribution of any calcium phosphate precipitates will be characterized. For samples with low U concentration, synchrotron-based micro-X-ray fluorescence (μ -XRF) mapping will be used to determine the U distribution; the resulting images will be indexed to the EMPA images to study element associations. Areas where uranyl phosphate precipitation has occurred and other areas dominated by distinct materials in the clay size fraction will be examined by TEM after extraction using focused ion beam (FIB) milling. This will explore nanometer-scale spatial relationships between uranium and sediment minerals, identify possibly U-bearing nanoparticles, and aid in phase identification through the use of SAED. Synchrotron-based μ -EXAFS and μ -XRD on thin sections will also be used to identify U species and any calcium phosphate phases that form.

These microscopic solid characterization techniques will be complemented by bulk EXAFS and TRLFS spectroscopy on each selected sample. Based on the microscopic studies and the TRLFS time-decay results, samples reflective of end-member conditions dominated by a single major U(VI) species will be identified. EXAFS spectroscopy will then be used to quantify the distribution of U between distinct species in each selected sample. The EXAFS analysis will employ the PCA, ITFA, and linear-combination fitting techniques described in Task I-2. Together, these studies will identify the conditions where specific mechanisms controlling U(VI) speciation dominate in these sediments.

Reactivity of Sediment Fines. The clay (<2 μ m) size fraction of the sediments will be separated by wet sedimentation in CO_2 -free deionized water to minimize the release of any existing surface-bound U. Sonification will be explored to enhance the release of the clay size fraction from the sediments. Grains will be examined using electron microscopy after sonification to identify any sign of fracture; if this occurs then sonification will not be employed. Sonification has been used in a prior study of Rifle sediments to assist size fractionation [47]. The mineralogy of the clay size fraction will be determined by powder XRD and further characterized by TEM. These materials will then be reacted in their respective artificial groundwaters in the presence of variable U(VI) and PO_4 concentrations. Solid phase U speciation will be characterized using EXAFS and TRLFS. The formation of U precipitates will be confirmed by SEM/EDS and TEM.

Phosphate-reacted U-Contaminated Sediments. The <2 mm fraction of Hanford and Rifle sediment samples contaminated with U will be reacted with phosphate-bearing simulated groundwater to determine the effect P-addition has on the speciation of preexisting U. This artificial groundwater will also contain dissolved U at concentrations typical of groundwater near the point of sediment collection. Solid-phase U speciation before and after phosphate addition will be determined using TRLFS and EXAFS spectroscopy, synchrotron-based X-ray microbeam methods, and electron microscopy, including TEM of slices obtained by FIB milling.

Task II-2. Distribution of Dominant Processes in Column Systems

Column experiments with phosphate injection will examine phosphate-induced immobilization of uranium in sediments at conditions relevant to uranium-contaminated DOE sites (Fig. 11). Laboratory-scale glass columns ($r = 1.25$ cm, $L = 15$ cm) will be loaded with sediments from the Hanford 300 Area and the Rifle Integrated Field Research Challenge Site. Fresh sediments for experiments will be collected through collaboration with site managers at Hanford and Rifle (see attached letters of support from Dr. John Zachara and Dr. Phil Long). The sediments will be sieved, and the columns will be wet-loaded with the fraction smaller than 2 mm. The porosities of the packed columns will be measured, and the values are anticipated to be close to their field values of 15-27% for Hanford and Rifle.

The initial uranium loading of the sediments will be achieved through three different approaches. U-contaminated field sediments will be loaded into the columns in their as-received forms. Uncontaminated sediments from the field sites will be pre-loaded with uranium for the other two approaches. In one method, uncontaminated sediments will be loaded with uranium by batch reaction with U-containing solutions at compositions similar to those used in Task II-1. In the other method, the uncontaminated sediments will be loaded into a column and then treated with at least 100 pore volumes of U-containing artificial groundwater. Comparison of the phosphate-induced immobilization for the contaminated field sediments with the laboratory-loaded uncontaminated field sediments can provide insights into the impacts of field aging on the accessibility of sediment U(VI) to reaction with added phosphate.

Water amended with dissolved phosphate will be introduced to the columns at compositions and flow rates relevant to the Hanford and Rifle sites. Artificial groundwater solutions will be prepared at the pH, alkalinity, and compositions of major cations and anions present for the two sites, and these solutions will be spiked with 1 mM Na_2HPO_4 (31 mg P/L) to provide phosphate to promote U(VI) immobilization. This is comparable to the orthophosphate concentration used in previous column experiments for phosphate immobilization at the Hanford 300 Area [38]. For each sediment, two columns will be treated with phosphate-containing solutions and a control column will also be operated without the addition of phosphate. The influents will be spiked with LiBr to provide a conservative tracer for assessing solute dispersion in the columns. Constant flow will be provided to the columns from peristaltic pumps at flow rates that will provide a pore velocity of 0.5 m/d. This velocity is within the wide range of values measured at the Hanford 300 Area [102] and just slightly faster than those at the Rifle site (~0.3-0.4 m/d pore velocity) [43, 103]. The columns will be

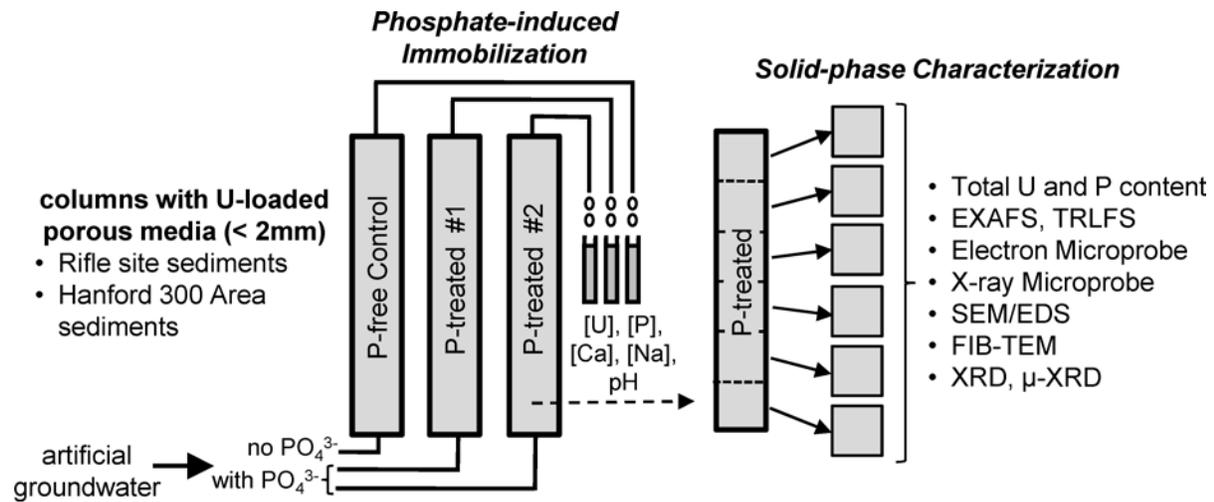


Figure 11. Column experiments with an approach that integrates measurements of phosphate-induced immobilization, solid phase characterization, and uranium release.

operated in an upflow mode, which helps to maintain water saturation of the pores, for 30 days. This time is equivalent to 100 column pore volumes. Column effluents will be sampled twice a day and analyzed for pH and the dissolved concentrations of U, P, Na, Ca, Li, and Br as well as other groundwater constituents that may affect solution complexation and precipitation processes (e.g., Mg, Si, V). The concentrations of 25 elements, including U, P, Na, Ca, and Li, will be determined by ICP-MS, Br⁻ will be analyzed with an ion selective electrode, and DIC will be quantified using a TOC analyzer. Comparison of the effluent U(VI) profiles of the columns with and without phosphate addition will provide a quantitative measure of the U(VI) immobilization induced by the phosphate.

The speciation and spatial distribution of solid-phase U(VI) after phosphate treatment will be determined by comprehensive characterization of sediments from the phosphate-treated columns. The sediments will be removed in six 2.5 cm increments, and each increment will be physically homogenized. U(VI) phosphate speciation is expected to be variable along the length of the column. Precipitation extents will be greatest at the zones where the infiltrating phosphate front encountered the highest U(VI) concentrations, so the investigation of discrete segments of the columns is important. A portion of each increment will be treated with concentrated HNO₃ to extract U and P and measure the total solid-phase U and P. The molecular-scale speciation of the U in the sediments will be investigated with EXAFS and TRLS spectroscopy. In addition, portions of the sediments will be fixed in epoxy and thin sectioned. The identity and grain-scale spatial distribution of U(VI) phosphate precipitates in the sediment thin sections will be investigated by SEM/EDS, EMPA, and synchrotron-based μ -XRF mapping. Synchrotron-based μ -XAFS and μ -XRD on thin sections will also be used to identify U species and any calcium phosphate phases that form. Selected areas of U precipitates and U-enriched mineral coatings will be further investigated by FIB milling followed by TEM analyses, including mineral identification using SAED.

E. Characterization Methods

A number of advanced characterization methods will be used in the proposed work. Relevant aspects of select methods are discussed below.

Synchrotron-based X-ray Methods. A number of synchrotron-based X-ray methods will be utilized in the proposed work. EXAFS spectroscopy is an element-specific technique that will provide information on the local coordination environment of uranium. EXAFS spectra can serve to distinguish between adsorbed and precipitated uranium, determine the structure of adsorption complexes, and identify precipitate phases, and quantify the distribution of an element between distinct species. Practical EXAFS detection limits have improved over the last decade because of synchrotron, beamline and detector advances. This can be illustrated by comparing data quality of U EXAFS spectra of contaminated Hanford sediments. Catalano et al. [22, 97] published EXAFS spectra for samples from the Hanford 300 Area and BX tank farm containing 140 ppm or greater U. The lowest concentration samples could be analyzed but did contain substantial noise. Singer et al. [23] more recently published good quality spectra of Hanford 300 Area samples containing as little as 70 ppm U. Based on simple counting statistics, a sample with half the concentration would have a signal to noise ratio roughly 30% worse and thus also could be analyzed. New 100-element segmented planar germanium detectors that are now available and increases in beamline flux because of optic and ring current improvements are expected to provide another factor of 3 or 4 improvement in detection limits. Practical EXAFS detection limits during the proposed project will thus be as low as 10-20 ppm, depending on interferences, making most sample conditions accessible to EXAFS measurements.

X-ray microprobe methods (μ -XRF, μ -EXAFS, μ -XRD) will be used to determine the spatial variation in U solid-phase concentration and speciation with micrometer resolution. These methods involve focusing a X-ray beam to a 1-5 μm spot. Rastering a sample while collecting XRF data produces elemental maps analogous to those obtained from an electron microprobe. EXAFS spectra and powder XRD patterns (using an area detector) can then be collected on individual spots on the sample. Synchrotron-based measurements will be conducted at the Advanced Photon Source (APS) and the Stanford Synchrotron Radiation Lightsource (SSRL), both DOE-support national user facilities.

TRLFS Spectroscopy. Uranyl, UO_2^{2+} , and its compounds absorb strongly in a broad spectral range from deep UV to visible (≤ 500 nm) and the majority of solid uranyl compounds and aqueous uranyl complexes display fluorescence emission in the visible wavelength range, typically characterized as a progression of nearly evenly-spaced vibronic bands [104-106]. The fluorescence spectral position, intensity, lifetime and the spacing of the vibronic bands vary as a function of ligand coordination and thus allow identification of uranyl species by comparison with spectra of compounds with those of known structures and compositions [29, 99, 107]. Using either as a standalone techniques or in combination with X-ray and Raman spectroscopy, TRLFS has been used to identify uranium in a broad array samples with different origins, including contaminated soils and sediments [29, 107-109], uranium mill tailings [59, 110], uranium adsorbed at various minerals surfaces [111-117] as well as uranium in homogeneous aqueous solutions [60, 118-121]. Further combination of TRLFS and optical microscopy makes it possible to differentiate U(VI) species in solids with high spatial resolution [100, 109]. Exploiting the enhanced spectral intensity and resolution at cryogenic temperatures, we have successfully applied TRLFS to study uranyl speciation in various complex, highly contaminated Hanford sediments for which weak, broad and featureless fluorescence spectra are usually observed at room temperature [99, 100, 122-124]. For the first time, direct fluorescence spectroscopic observation of several environmentally important uranyl complexes with carbonate: $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$ was achieved [124].

In this project, TRLFS measurements, in conjunction with chemometric analysis of the resulting spectra, will be performed for the solid phases (as well as aqueous phase) to investigate U(VI) speciation and how different U(VI) species distribute in the solids as a function of reaction conditions. The fluorescence lifetimes as well as peak-spacings, which correspond to the symmetric stretching frequency of the $\text{O}=\text{U}=\text{O}$ molecule, will further aid the analysis. Such information, along with data from XAS analysis will allow assignment of uranium species in the precipitated solid phases. The high sensitivity and the time-resolved capability will make it an ideal complimentary method to identify uranium species at U(VI) concentration levels that XAS analysis can be applied satisfactorily. TRLFS measurements will be conducted at the Environmental Molecular Sciences Laboratory (EMSL), a DOE-support national user facility.

TEM Sample Preparation by FIB Milling. Micron-scale areas of interested identified as of importance in a sample in the SEM or electron microscope will be extracted using focused ion beam (FIB) milling for higher resolution imaging with TEM. A FIB instrument bombards a sample with a narrow ion beam; instruments typically also have an integrated SEM. This instrument will be used to precisely mill out slices of thin sections that are suitably thin for TEM analyses. FIB milling and associated TEM analyses will be conducted at EMSL.

HADDF-STEM Measurements. HAADF-STEM is a power tool for observing nanoparticles composed of high-Z elements, such as uranium, in complex matrices [125]. Heavy atoms strongly induce incoherent diffuse electron scattering at high angles. By measuring this high-angle diffuse electron scattering intensity as the STEM beam is rastered across a sample, a map can be generated of electron-dense regions with sub-nm resolution and directly compared to conventional bright-field

images. HAADF-STEM has been previously applied to identify nanoparticles of high-Z materials in As-contaminated bedrock, urban atmospheric particles, arsenian pyrite deposits, 3.1 to 4.4 Ga zircon grains, and Nevada test site groundwater [126-130]. It has also been used to identify amorphous U nanoclusters adsorbed to muscovite [131]. In the proposed work HAADF-STEM will complement other analyses to investigate nucleation of uranyl phosphates at conditions near saturation. These measurements will be performed at the Center for Materials Innovation at Washington University.

VI. EXPECTED SCIENTIFIC CONTRIBUTIONS

The proposed work will lead to an enhanced understanding of the processes through which phosphate addition controls U(VI) fate in contaminated subsurface environments. Key molecular-scale mechanisms involved in U(VI) phosphate precipitation and adsorption will be characterized, and the effects of these mechanisms on sediment-scale processes will be determined. We expect to make the following specific major contributions: (1) Determine the chemical controls on the U(VI) phosphate phase that forms under a range of relevant conditions; (2) Identify the structure and significance of U(VI) phosphate ternary surface complexes; (3) Establish how competition and cooperation among adsorption and precipitation reactions control U(VI) fate in phosphate-bearing systems; (4) Assess the behavior of U(VI) in such systems under realistic flow conditions; and (5) Characterize the chemical regimes where particular mechanisms that control U(VI) fate are dominant.

VII. RELEVANCE TO THE BER LONG TERM MEASURE

The proposed project will support the BER Long Term Measure of providing “sufficient scientific understanding such that DOE sites would be able to incorporate coupled physical, chemical and biological processes into decision making for environmental remediation and long-term stewardship.” This proposal seeks to advance the scientific understanding of the processes that control U(VI) fate in phosphate-bearing subsurface sediment systems. Uranyl phosphates occur frequently in contaminated soils and sediments at DOE sites, and substantial quantities of additional uranyl phosphate solids are expected to form as a result of phosphate-based remediation methods now under pilot testing. Understanding the conditions under which these species form and the chemistry that controls their behavior is essential to proper decision making regarding remediation and site management. In addition, this proposal will identify the conditions where other U(VI) reactions with phosphate, such as ternary surface complexation and association with calcium phosphates, control contaminant fate. These processes may provide additional long-term attenuation of U(VI) transport in systems where uranyl phosphates are dissolving or bioreduced U is reoxidizing. This work will thus provide a fundamental knowledge-based needed to evaluate the efficacy of primary or complementary phosphate-amendment treatment methods.

VIII. PROJECT TIMELINE

The proposed work is arranged in two parallel modules so that insights gained from each module can be used to actively guide the specific activities of the other module. The timeline of the proposed activities, including results will feedback into parallel studies, are described below:

Year 1: Complete Task I-1 on uranyl phosphate precipitation in homogeneous systems. Study uranyl phosphate ternary surface complexation in single mineral systems (Task I-2) and begin to study such complexes in sediments (Task II-1). Obtain sediments after site visits to Rifle and Hanford IFRC sites by PI Catalano and co-PI Giammar. Project kickoff meeting with all PIs during Hanford IFRC visit.

Year 2: Precipitation and competition studies in single mineral systems (Task I-2) with input on conditions from Task I-1. Complete surface complexation in batch sediment systems and begin studies of competing processes in sediments (Task II-1). Initial column experiments (Task II-2) with conditions influenced by Task I-2 and II-1 results to date. Follow-up homogeneous precipitation studies to support unexpected observations in Tasks I-2 and II-1.

Year 3: Experiment completion, data analysis, and modeling of results in Task I-2. Further batch sediment studies (Task II-1) to support column work. Completion of column experiments (II-2). Completion of spectroscopic and microscopic analyses.

All results will be published in peer-reviewed journals in a timely manner. We expect to be able to submit our first manuscripts in Year 1 based on Task I-1 results, with initial Task I-2 and II-1 results ready for submission in Year 2 and final results submitted in Year 3.

IX. PROJECT PERFORMANCE SITE

The proposed activities will take place at Washington University in St. Louis, MO and Pacific Northwest National Laboratory in Richland, WA.

X. PROJECT MANAGEMENT

A. Project Team

The proposed research is a collaborative effort among Dr. Jeffrey Catalano (PI), Dr. Daniel Giammar (Co-PI), and Dr. Zheming Wang (co-PI). Catalano will lead this interdisciplinary team as his research expertise encompasses much of the proposed work. Catalano has also previously collaborated with both co-PIs [99, 132, 133]. A postdoctoral researcher supervised by Dr. Catalano and a graduate student supervised by Dr. Giammar will also participate in this project.

B. Management Plan

Catalano will be responsible for overall project management and administration. All of the PIs on this project will be responsible for individual tasks or components of tasks as specified below. The Washington University component of the project team will hold bi-weekly meetings to discuss experimental results and coordinate activities. Dr. Wang will join these meetings using videoconferencing monthly to discuss TRLFS results and to stay abreast of current project developments. An initial project kickoff meeting will take place at PNNL during the visit of Catalano and Giammar to the Hanford IFRC site. The project team will also confer at the SBR Annual PI Meeting.

C. Distribution of Activities

Project activities will be distributed as follows:

Catalano (PI): Responsible for overall project management and coordination. Will also assist with synchrotron-based data collection and analysis and will obtain time at national user facilities through proposal submission. Supervise postdoctoral researcher who will conduct Tasks I-2 and II-1, synchrotron-based analyses, and all thin section, FIB, and TEM work.

Giammar (co-PI): Responsible for managing Tasks I-1 and II-2, column study experimental design, and development of chemical models. Supervise graduate student who will perform laboratory experiments, develop chemical equilibrium models, and assist with synchrotron-based analyses.

Wang (co-PI): Responsible for TRLFS analyses for Tasks I-2, II-1, and II-2.

APPENDIX A: LITERATURE CITED

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APPENDIX B: BIOGRAPHICAL SKETCHES/CONFLICTS OF INTEREST

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Publications:

Dr. Catalano has published 32 journal articles and 4 technical reports. Those most relevant to the proposed research are listed below.

1. Brown C.F., Serne J.R., **Catalano J.G.**, Krupka K.M., Icenhower J.P. (2010) Mineralization of contaminant uranium and leach rates in sediments from Hanford, Washington. *Applied Geochemistry* **25**, 97-104.
2. Zeng H., Singh A., Basak S., Ulrich K.-U., Biswas P., **Catalano J.G.**, Giammar, D.E. (2009) Nanoscale size effects on uranium (VI) adsorption to hematite nanoparticles. *Environmental Science & Technology* **43**, 1373-1378.
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4. Wellman D.M., **Catalano J.G.**, Icenhower J.P., and Gerner A.P. (2005) Synthesis and characterization of sodium meta-autunite, $\text{Na}_2[(\text{UO}_2)(\text{PO}_4)]_2 \cdot 3\text{H}_2\text{O}$. *Radiochimica Acta* **93**, 393-399.
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6. **Catalano J.G.**, and Brown G.E., Jr. (2005) Uranyl adsorption onto montmorillonite: Evaluation of binding sites and carbonate complexation. *Geochimica et Cosmochimica Acta* **69**, 2995-3005.
7. **Catalano J.G.**, Trainor T.P., Eng P.J., Waychunas G.A., Brown G.E., Jr. (2005) CTR diffraction and grazing-incidence EXAFS study of U(VI) adsorption onto $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ (1102) surfaces. *Geochimica et Cosmochimica Acta* **69**, 3555-3572.
8. **Catalano J.G.**, Warner J.A., Brown G.E., Jr. (2005) Sorption and precipitation of Co(II) in Hanford sediments and alkaline aluminate solutions. *Applied Geochemistry* **20**, 193-205.

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Synergistic Activities:

1. **Reviewer**, National Science Foundation, Geobiology and Low-Temperature Geochemistry Program (2008-Present)
2. **Panelist**, Chemical, Biological, and Environmental Scattering Proposal Review Panel, Advanced Photon Source (2009-Present)
3. **Panelist**, Green Action's 7th Hour Panel Discussion, "Facts and Fission... nuclear power and the 2008 election", Washington University, October 30, 2008
4. **Reviewer** for Scholarly Journals (In last 12 months: *Chemical Geology*, *Chemosphere*, *Environmental Science & Technology*, *Geochimica et Cosmochimica Acta*, *Geosphere*, *Journal of Contaminant Hydrology*, *Surface Science*).
5. **Mentor**, Students and Teachers As Research Scientists (STARS) program (2009-Present)

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Amend, J. (Washington U.), Arvidson, R.E. (Washington U.), Bedzyk, M.J. (Northwestern U.), Bell, J.F. III (Cornell U.), Bellutta, P. (JPL), Biswas, P. (Washington U.), Brown, C.F. (PNNL), Brown, G.E., Jr. (Stanford U.), Cabrol, N.A. (NASA Ames), Chaka, A.M. (NIST), Cohen, J. (Honeybee Robotics), Crumpler, L. (NM Mus. Nat. Hist. & Sci.), Cull S. (Washington U.), Des Marai, D.J. (NASA Ames), Eng, P.J. (U. Chicago), Estlin, T. (JPL), Farrand, W. (Space Sci. Inst.), Fenter, P. (ANL), Gellert, R. (U. Guelph), Giammar, D.E. (Washington Univ.), Ghose, S.K. (U. Chicago), Grant, J.A. (Smithsonian Inst.), Greenberger, R. (Washington U.), Guinness, E.A. (Washington U.), Heald, S.M. (ANL), Herkenhoff, K.E. (USGS), Herman, J.A. (JPL), Iagnemma, K. (MIT), Icenhower, J.P. (VSI Analytics), Johnson, J.R. (USGS), Jun, Y.-S. (Washington Univ.), Kelly, S.D. (ANL), Klingelhöfer, G. (Johannes Gutenberg U.), Lemmon M.T. (Texas A&M), Li, R. (Ohio State U.), Lichtenberg, K.A. (Washington U.), Lo, C. (Washington U.), Maxwell, S. (JPL), McKinley, J.P. (PNNL), Mellon, M.T. (U. Colorado), Ming, D.W. (NASA JSC), Morris, R.V. (NASA JSC), Nagy, K.L. (U. Illinois), Park, C. (ANL), Pasteris, J.D. (Washington Univ.), Petitto, S.C. (U. Alaska), Pierce, E.M. (PNNL), Rice, M. (Cornell U.), Rosso, K.M. (PNNL), Ruff, A. (Arizona St. U.), Serne, J.R. (PNNL), Shaw, A. (Washington U.), Siebach, K. (Washington U.), Singer D.M. (LBNL), Smith, S.C. (PNNL), de Souza, P. (CSIRO), Stroupe, A. (JPL), Sturchio, N.C. (U. Illinois), Squyres, S.W. (Cornell U.), Sullivan, R.J. (Cornell U.), Talley, K. (JPL), Tanwar, K. (U. Alaska), Townsend, J. (JPL), Trainor, T.P. (U. Alaska), Wang, A. (Washington U.), Waychunas, G.A. (LBNL), Wellman, D.M. (PNNL), Wright, J. (JPL), Yen, A. (JPL), Zachara, J.M. (PNNL), Zhang, Z. (ANL)

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Former and Current Graduate and Postdoctoral Students: Andrew Frierdich (Ph.D. exp 2012); Alison Beehr (Ph.D. exp. 2013); Yun Luo (Post-doc 2009-Present)

APPENDIX C: FACILITIES, RESOURCES, AND MAJOR EQUIPMENT

Research will be performed at Washington University in St. Louis and Pacific Northwest National Laboratory, with additional measurements made at DOE-supported national user facilities such as the Advanced Photon Source, Stanford Synchrotron Radiation Lightsource, and the Environmental Molecular Science Laboratory. Research facilities and other resources available are summarized below.

WASHINGTON UNIVERSITY

Environmental Geochemistry and Mineralogy Laboratory (PI: Catalano)

Dr. Catalano's Environmental Geochemistry and Mineralogy Laboratory is located in the new Earth and Planetary Sciences building and consists of two general purpose wet chemical laboratories equipped with standard equipment needed for solution chemistry, mineral-water interface geochemistry, and sample preparation. This equipment includes multiple fume hoods, two environmental chambers for studies under anaerobic or CO₂-free conditions, pH meters, analytical balances, UV/Vis spectrophotometer, a wheel and fixtures for polishing crystalline substrates, muffle and tube furnaces, ultrapure water system, centrifuges, magnetic stir plates, and syringe pumps. The laboratory includes an Agilent Technologies (formerly Molecular Imaging) atomic force microscope (AFM) model 5500, capable of imaging mineral surfaces under aqueous conditions. The laboratory also maintains computing facilities needed for analysis of X-ray scattering and spectroscopic data and geochemical modeling, as well as equipment needed for making XANES, EXAFS, and Surface X-ray Scattering measurements at X-ray light sources.

Aquatic Chemistry Laboratory (PI: Giammar)

Dr. Giammar's Aquatic Chemistry Laboratory is a recently renovated 650 sq. ft. space with state of the art facilities. The laboratory is equipped with two fume hoods, purified air, vacuum, deionized water, and a point-of-use ultrapure (18.2 MΩ-cm) water system. The laboratory has an environmental chamber for conducting experiments at anaerobic or carbon dioxide-free conditions. The laboratory contains all of the equipment necessary for conducting a large set of bench-scale experiments including pH meters, magnetic stir plates, peristaltic pumps, fraction collectors, a general purpose centrifuge, an orbital shaker, temperature control baths, and a drying oven. The laboratory also houses a freeze-drier for the preparation and isolation of fine particles in aqueous suspension.

Department of Earth and Planetary Sciences

The department of Earth and Planetary Sciences maintains microscopic, spectroscopic, and diffraction facilities for sample characterization. A new (circa 2007) JEOL-8200 electron microprobe is available for element mapping and quantitative compositional analysis of solids using both energy-dispersive and wavelength-dispersive spectrometry. X-ray powder diffraction is done on a Rigaku Geigerflex D-MAX/A Diffractometer using Cu-Kα radiation. The instrument is equipped with a vertical goniometer and a scintillation counter. Maximum power is 1.5kW operating at 50kV and 50mA. PC-based Datascan software by Materials Data, Inc. (MDI) controls the diffractometer and MDI's Jade software can be used to analyze mineral

diffraction patterns. A Nicolet Nexus 670 FTIR spectrometer with ATR accessory and a HoloLab 5000 Raman microprobe are available for vibrational spectroscopy measurements. A total organic carbon (TOC) analyzer is also available.

Department of Energy, Environmental, and Chemical Engineering

Shared analytical facilities in the Department of Energy, Environmental and Chemical Engineering include the Environmental Nanoscale Analysis Laboratory and the Jens Environmental Engineering Laboratory. These laboratories are common, centralized facilities maintained by full time technicians. Analytical equipment housed in these laboratories include a BET surface area analyzer, an inductively coupled plasma mass spectrometer (ICP-MS), a 96-well plate reader, an atomic absorbance spectrophotometer, a UV-visible spectrophotometer, a gas chromatograph mass spectrometer (GC-MS), three gas chromatographs (equipped with flame-ionization, photo-ionization, electron-capture, and thermal-conductivity detectors), a high-performance liquid chromatograph (HPLC) with diode array detector, and a Fourier transform infrared spectrometer with accessories for the analysis of solids, liquids, and suspensions.

Center for Material Innovation (CMI)

Advanced transmission and scanning electron microscopy instrumentation is available in the Center for Materials Innovation, an interdisciplinary research effort of which Dr. Catalano and Dr. Giammar are members. A JEOL 2100F scanning field emission transmission electron microscope [(S)TEM] equipped with an electron-energy-loss spectrometer, a high resolution CCD camera, and an array of BF, DF, and HAADF detectors is available for imaging, diffraction, and chemical mapping. A JEOL JSM-7001FLV field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectrometer is available for high resolution imaging and element identification.

Nano Research Facility (NRF)

The NRF contains numerous characterization tools and is a member of the National Nanotechnology Infrastructure Network (NNIN), supported by the National Science Foundation. Tools available for use in the project include an FEI Nova 2300 SEM, an FEI Spirit TEM, a Scanning Mobility Particle Sizer, and a gold coater is available for preparing SEM samples for analysis. The NRF also operates a Malvern Zetasizer ZS for dynamic light scattering (DLS) and zeta potential measurements of particle suspensions and Perkin Elmer Elan DRC II ICP-MS and Optima 7300DV ICP-OES systems for determining the composition of aqueous samples, including from solid phase digestions. The NRF also operates a gold coater for SEM sample preparation.

PACIFIC NORTHWEST NATIONAL LABORATORY

EMSL Laser Spectroscopy Facility

At the Environmental Spectroscopy Laboratory, Environmental Molecular Science Laboratory operated by the Pacific Northwest national Laboratory, is equipped with two general types of time-resolved laser-induced fluorescence spectroscopy (TRLFS) systems, several Nikon inverted optical microscopes, electrochemistry, a BioLogic four-syringe stopped-flow system, two Bruker IFS-66 FT-IR/FT-Raman spectrometer both integrated with an optical microscope

and an Asylum scanning atomic force microscope. For fluorescence imaging, a Nikon 2000U and a Nikon TE-300 inverted optical microscopes with dichroic beam splitters is placed on a mobile optical table and located in the vicinity of the laser systems, and can be easily coupled with any of the lasers.

Of the two TRLFS systems, one is designed for fluorophores that have fluorescence lifetime on the order of nanoseconds (ns) to milliseconds (ms) and up, and the other is for fluorophores that have fluorescence lifetimes on the order of picoseconds (ps) to nanoseconds(ns). A late model Horiba Spex Fluorolog III fluorimeter is also available for either xenon-lamp excitation or laser induced fluorescence spectroscopic measurement in CW mode.

The ns-ms TRLFS system consists of nanosecond laser excitation sources of either a Spectra-Physics Quanta-Ray PRO Nd:YAG/BeamLok laser pumped MOPO-730 laser equipped with a FDO-900 scanning frequency doubler or a Light Age, Inc. Model 101 PAL Alexandrite laser and an Acton SP-300 triple turret double monochromator spectrograph equipped with a 1024 elements Princeton Instruments PIMAX intensified time-gated CCD camera and a thermoelectrically cooled Hamamatsu time-gated photo multiplier tube. The MOPO-730 laser allows continuous scanning in the spectral ranges of 440 nm – 690 nm, 735 nm – 1800 nm, and, with the FDO-900 frequency doubler, of 220 nm – 440 nm. The Light Age 101 PAL laser covers 700 nm – 800 with peak power up to 16 W and up to 4 W and 0.18 W for the second and third harmonic conversions. A Nikon 2000U inverted optical microscope is integrated with the MOPO-730 laser, an Acton Research 2150i dual turret spectrograph and a second ICCD camera allowing the acquisition of laser-induced time-resolved fluorescence images and fluorescence spectra at selected spot with micro-level spatial resolution.

The ps-ns system consists of a Spectra-Physics Millennia Nd:YO4 laser pumped Clark-MXR NJA-5 Ti:Sapphire laser (76 MHz) and a Coherent Vanguard 2000 laser (76 MHz) pumped dye laser system. Currently, two dye lasers, a Coherent 702 and a Coherent Satori, are equipped with the system, providing laser output with a pulse width of a few ps with the Coherent 702 laser and laser output with a pulse width of 100 fs with the Coherent Satori laser. Fluorescence detection is accomplished by either a Hamamatsu 3680 High Speed Streak camera or a home-built time-correlated-single-photon-counting system, with time resolutions of 2 ps and 40 ps, respectively.

For fluorescence measurement under cryogenic conditions, two conventional Cryo Industries cryostats, RC152 and RC102 each fitted with four sealed quartz optical windows, and a third cryostat fitted on a Nikon 2000U inverted microscope, readily replace the existing sample holder. The cryostats are equipped with two sets of internal heating elements, Lakeshore 330 auto-tuning temperature controllers and connected to both an Edwards 12 mechanical pumps and an Edwards turbo molecular pumps, allowing spectroscopic measurement from ambient pressure to 10⁻⁷ torr and from room temperature to 4.2 K.

NATIONAL USER FACILITIES

Advanced Photon Source (APS), Argonne National Laboratory

The APS is a DOE-supported national user facility for the study of matter using brilliant X-ray beams. Users may access this facility at no cost through a competitive, peer-reviewed proposal system. The X-ray absorption spectroscopy measurements described in this proposal can be performed at a numbers of different beamlines, including 5-BM, 10-ID, 12-BM, 13-BM,

13-ID, 20-BM, and 20-ID. X-ray microprobe measurements can be made at beamlines 10-ID, 13-ID, 20-BM, 20-ID. Powder XRD measurements can be conducted at beamlines 5-BM-C, 11-BM, and 13-BM-C.

Stanford Synchrotron Radiation Lightsource (SSRL), Stanford Linear Accelerator Center

SSRL is a DOE-supported national user facility for the study of matter using brilliant X-ray beams. Users may access this facility at no cost through a competitive, peer-reviewed proposal system. The X-ray absorption spectroscopy measurements described in this proposal can be performed at a numbers of different beamlines, including 4-1, 10-2, and 11-2; X-ray microprobe measurements may be performed at beamline 2-3 and 10-2. A 100-element segmented monolithic Ge energy-dispersive fluorescence detector will become available at beamline 11-2 starting in summer 2011, corresponding to the start date of this proposal. EXAFS spectra of low-concentration samples will be measured at beamline 11-2. Powder XRD measurements can be conducted at beamlines 2-1 and 11-3.

Environmental Molecular Science Laboratory (EMSL), Pacific Northwest National Laboratory

EMSL is funded by DOE's Office of Biological and Environmental Research and supports world-class research in the biological, chemical, and environmental sciences to provide innovative solutions to the nation's environmental challenges as well as those related to energy production. Instrumentation may be accessed through a proposal submission system. For the current work, the primary instrumentation of interest is a FEI Helios Nanolab dual-beam focused ion beam/scanning electron microscopy (FIB/SEM) microscope for preparing electron transparent samples for TEM analysis. A JEOL 2010 high-resolution transmission electron microscope (TEM) with an energy dispersive spectrometer (EDS) is available for the post-FIB TEM measurements.

APPENDIX D: CURRENT AND PENDING SUPPORT

Investigator: Jeffrey G. Catalano	Other agencies to which this proposal has been/will be submitted. None
Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: ETBC: Hidden Iron Oxide Redox Processes During Biogeochemical Iron Cycling: Control on Nanoscale Transformations and the Fate of Contaminants (Catalano is sole PI)	
Source of Support: NSF/EAR-GEO	
Total Award Amount: \$340,505	Total Award Period Covered: 8/15/08 - 7/31/11
Location of Project: Washington University in St. Louis	
Person-Months Per Year Committed to the Project. 1.0 Cal: 0 Acad: 0 Sumr: 1.0	
Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: Iron Oxide Morphology and Composition as Possible Indicators of Sedimentary Redox Cycling (Catalano is sole PI)	
Source of Support: ACS-PRF	
Total Award Amount: \$50,000	Total Award Period Covered: 9/1/08 - 8/31/10
Location of Project: Washington University in St. Louis	
Person-Months Per Year Committed to the Project. 0.7 Cal: 0 Acad: 0 Sumr: 0.7	
Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: Life cycles of metals in coal combustion: metal release and capture, speciation in fly ash, and transformations during ash reuse and storage (Catalano is co-PI)	
Source of Support: Washington University Consortium for Clean Coal Utilization	
Total Award Amount: \$21,005 (Catalano Portion)	Total Award Period Covered: 9/1/08 - 6/31/09
Location of Project: Washington University in St. Louis	
Person-Months Per Year Committed to the Project. 0.25 Cal: 0 Acad: 0 Sumr: 0.25	
Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments (Catalano is PI; Giammar and Wang co-PIs)	
Source of Support: DOE-BER: SBR (current proposal)	
Total Award Amount: \$624385 (Washington U. Portion)	Total Award Period Covered: 6/1/2011 – 5/31/2014
Location of Project: Washington University in St. Louis	
Person-Months Per Year Committed to the Project. 1.0 Cal: 0 Acad: 0 Sumr: 1.0	
Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: Bacterial Effects on Uranium and Technetium Incorporation into Carbonates (Catalano is co-PI; PI Luttge; co-PIs: Arvidson, Icenhower, Burgos)	
Source of Support: DOE-BER: SBR	
Total Award Amount: \$312,807 (Washington U. Portion)	Total Award Period Covered: 10/1/2010-9/30/2013
Location of Project: Washington University in St. Louis	
Person-Months Per Year Committed to the Project. 0.5 Cal: Acad: Sumr: 0.5	

Investigator: Jeffrey G. Catalano	Other agencies to which this proposal has been/will be submitted. None		
Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support			
Project/Proposal Title: Iron-Bearing Phyllosilicate Clay Formation Pathways: Mineralogical Constraints on Past Martian Environmental Conditions			
Source of Support: NASA: Mars Fundamental Research Program			
Total Award Amount: \$236,743		Total Award Period Covered: 6/1/2011 – 5/30/2014	
Location of Project: Washington University in St. Louis			
Person-Months Per Year Committed to the Project.	1.0	Cal: 0	Acad: 0 Sumr: 1.0
Support: <input type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support			
Project/Proposal Title:			
Source of Support:			
Total Award Amount: \$		Total Award Period Covered:	
Location of Project: Washington University in St. Louis			
Person-Months Per Year Committed to the Project.		Cal: 0	Acad: 0 Sumr:
Support: <input type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support			
Project/Proposal Title:			
Source of Support:			
Total Award Amount: \$		Total Award Period Covered:	
Location of Project: Washington University in St. Louis			
Person-Months Per Year Committed to the Project.		Cal: 0	Acad: 0 Sumr:
Support: <input type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support			
Project/Proposal Title:			
Source of Support:			
Total Award Amount: \$		Total Award Period Covered:	
Location of Project:			
Person-Months Per Year Committed to the Project.		Cal: 0	Acad: 0 Sumr:
Support: <input type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support			
Project/Proposal Title:			
Source of Support: DOE-BER: SBR			
Total Award Amount: \$		Total Award Period Covered:	
Location of Project:			
Person-Months Per Year Committed to the Project.		Cal:	Acad: Sumr: