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Offering Agency:	Chicago Service Center
CFDA Number:	81.049
CFDA Description:	Office of Science Financial Assistance Program
Opportunity Number:	DE-PS02-09ER09-26
Competition ID:	09-26
Opportunity Open Date:	07/02/2009
Opportunity Close Date:	09/01/2009
Agency Contact:	Lori Jernigan Grant Analyst E-mail: Lori.Jernigan@science.doe.gov Phone: 301-903-5212

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SF424 (R & R)

Research & Related Budget

Project/Performance Site Location(s)

Research And Related Other Project Information

Optional Documents

R & R Subaward Budget Attachment(s) Form Disclosure of Lobbying Activities (SF-LLL)

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**APPLICATION FOR FEDERAL ASSISTANCE
 SF 424 (R&R)**

3. DATE RECEIVED BY STATE	State Application Identifier
<input type="text"/>	<input type="text"/>

1. * TYPE OF SUBMISSION
 Pre-application Application Changed/Corrected Application

4. a. Federal Identifier
b. Agency Routing Identifier

2. DATE SUBMITTED
Applicant Identifier

5. APPLICANT INFORMATION * Organizational DUNS:

* Legal Name:

Department: Division:

* Street1:
 Street2:

* City: County / Parish:

* State: Province:

* Country: * ZIP / Postal Code:

Person to be contacted on matters involving this application

Prefix: * First Name: Middle Name:

* Last Name: Suffix:

* Phone Number: Fax Number:

Email:

6. * EMPLOYER IDENTIFICATION (EIN) or (TIN):

7. * TYPE OF APPLICANT:
 Other (Specify):

Small Business Organization Type Women Owned Socially and Economically Disadvantaged

8. * TYPE OF APPLICATION: If Revision, mark appropriate box(es).

New Resubmission A. Increase Award B. Decrease Award C. Increase Duration D. Decrease Duration

Renewal Continuation Revision E. Other (specify):

* Is this application being submitted to other agencies? Yes No What other Agencies?

9. * NAME OF FEDERAL AGENCY:

10. CATALOG OF FEDERAL DOMESTIC ASSISTANCE NUMBER:
 TITLE:

11. * DESCRIPTIVE TITLE OF APPLICANT'S PROJECT:

12. PROPOSED PROJECT:
 * Start Date * Ending Date

*** 13. CONGRESSIONAL DISTRICT OF APPLICANT**

14. PROJECT DIRECTOR/PRINCIPAL INVESTIGATOR CONTACT INFORMATION

Prefix: * First Name: Middle Name:

* Last Name: Suffix:

Position/Title:

* Organization Name:

Department: Division:

* Street1:
 Street2:

* City: County / Parish:

* State: Province:

* Country: * ZIP / Postal Code:

* Phone Number: Fax Number:

* Email:

<p>15. ESTIMATED PROJECT FUNDING</p> <p>a. Total Federal Funds Requested <input style="width:150px;" type="text" value="819,719.00"/></p> <p>b. Total Non-Federal Funds <input style="width:150px;" type="text" value="0.00"/></p> <p>c. Total Federal & Non-Federal Funds <input style="width:150px;" type="text" value="819,719.00"/></p> <p>d. Estimated Program Income <input style="width:150px;" type="text" value="0.00"/></p>	<p>16. * IS APPLICATION SUBJECT TO REVIEW BY STATE EXECUTIVE ORDER 12372 PROCESS?</p> <p>a. YES <input type="checkbox"/> THIS PREAPPLICATION/APPLICATION WAS MADE AVAILABLE TO THE STATE EXECUTIVE ORDER 12372 PROCESS FOR REVIEW ON: DATE: <input style="width:100px;" type="text"/></p> <p>b. NO <input checked="" type="checkbox"/> PROGRAM IS NOT COVERED BY E.O. 12372; OR <input type="checkbox"/> PROGRAM HAS NOT BEEN SELECTED BY STATE FOR REVIEW</p>
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17. By signing this application, I certify (1) to the statements contained in the list of certifications* and (2) that the statements herein are true, complete and accurate to the best of my knowledge. I also provide the required assurances * and agree to comply with any resulting terms if I accept an award. I am aware that any false, fictitious, or fraudulent statements or claims may subject me to criminal, civil, or administrative penalties. (U.S. Code, Title 18, Section 1001)

* I agree

* The list of certifications and assurances, or an Internet site where you may obtain this list, is contained in the announcement or agency specific instructions.

18. SFLLL or other Explanatory Documentation

19. Authorized Representative

Prefix: * First Name: Middle Name:

* Last Name: Suffix:

* Position/Title:

* Organization:

Department: Division:

* Street1:

Street2:

* City: County / Parish:

* State: Province:

* Country: * ZIP / Postal Code:

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*** Signature of Authorized Representative**

Completed on submission to Grants.gov

*** Date Signed**

Completed on submission to Grants.gov

20. Pre-application

Project/Performance Site Location(s)

Project/Performance Site Primary Location

I am submitting an application as an individual, and not on behalf of a company, state, local or tribal government, academia, or other type of organization.

Organization Name:

DUNS Number:

* Street1:

Street2:

* City: County:

* State:

Province:

* Country:

* ZIP / Postal Code: * Project/ Performance Site Congressional District:

Project/Performance Site Location 1

I am submitting an application as an individual, and not on behalf of a company, state, local or tribal government, academia, or other type of organization.

Organization Name:

DUNS Number:

* Street1:

Street2:

* City: County:

* State:

Province:

* Country:

* ZIP / Postal Code: * Project/ Performance Site Congressional District:

RESEARCH & RELATED Other Project Information

1. * Are Human Subjects Involved? Yes No

1.a If YES to Human Subjects

Is the Project Exempt from Federal regulations? Yes No

If yes, check appropriate exemption number. 1 2 3 4 5 6

If no, is the IRB review Pending? Yes No

IRB Approval Date:

Human Subject Assurance Number:

2. * Are Vertebrate Animals Used? Yes No

2.a. If YES to Vertebrate Animals

Is the IACUC review Pending? Yes No

IACUC Approval Date:

Animal Welfare Assurance Number

3. * Is proprietary/privileged information included in the application? Yes No

4.a. * Does this project have an actual or potential impact on the environment? Yes No

4.b. If yes, please explain:

4.c. If this project has an actual or potential impact on the environment, has an exemption been authorized or an environmental assessment (EA) or environmental impact statement (EIS) been performed? Yes No

4.d. If yes, please explain:

5. * Is the research performance site designated, or eligible to be designated, as a historic place? Yes No

5.a. If yes, please explain:

6. * Does this project involve activities outside of the United States or partnerships with international collaborators? Yes No

6.a. If yes, identify countries:

6.b. Optional Explanation:

7. * Project Summary/Abstract

8. * Project Narrative

9. Bibliography & References Cited

10. Facilities & Other Resources

11. Equipment

12. Other Attachments

Complexity, Dynamics, and Variability of Oxoanion Adsorption-Desorption Reactions and the Connection to Macroscopic Processes

PI: Jeffrey G. Catalano, Washington University in St. Louis

PROJECT SUMMARY

Oxoanion adsorption-desorption reactions controls the fate of environmental toxins that are released during energy production, the migration of toxic or radioactive components of nuclear waste, including waste released into the environment at DOE facilities, and the effectiveness of remediation strategies employed at these sites. Understanding the mechanisms and kinetics of these reactions is essential for credibly predicting the migration of contaminants at DOE facilities and the performance of radioactive waste disposal sites. While these aspects of oxoanion adsorption-desorption have been studied extensively, recent research has documented unexpected complexity in the behavior of the oxoanion arsenate. It is now clear that major knowledge gaps exist concerning the intrinsic complexity, dynamics, and variability of oxoanion adsorption-desorption and how these fundamental characteristics control macroscopic phenomena. Closing these gaps is essential to accomplishing the goals of the Office of Basic Energy Science's Geosciences Research Program.

The overall objectives of this proposal are to determine the fundamental complexity, dynamics, and variability of oxoanion adsorption-desorption reactions on iron and aluminum oxide surfaces at the molecular-scale and then to connect these processes to macroscopic-scale phenomena. Specific objectives are to: (1) Determine the molecular-scale reactions controlling the complexity of arsenate adsorption and evaluate which processes dominate the reactivity of complex mineral powders; (2) Identify the processes controlling arsenate adsorption-desorption rates on mineral surfaces and constrain the relative importance of surface reaction heterogeneity, particle aggregation, and diffusion in determining arsenate adsorption-desorption rates on mineral powders; and (3) Evaluate the variability among oxoanions in their molecular-scale mechanisms and kinetics of adsorption-desorption and how this is manifested at the macroscopic-scale.

The proposed research will be conducted using a two-step approach designed to obtain molecular-scale information and then apply this to explain macroscopic-scale processes. The first step involves investigating the adsorption mechanisms and adsorption-desorption rates on specific surfaces of the mineral hematite and corundum. In the second step, this fundamental information will be used to interpret the macroscale adsorption behavior displayed by hematite powder of progressively increasing surface complexity. This approach will be applied in three distinct modules designed to: (1) Assess the complexity of adsorption behavior displayed by arsenate, a well-studied model oxoanion; (2) Characterized the dynamics of arsenate adsorption-desorption; and (3) Determine the variability in adsorption mechanisms and adsorption-desorption rates display be a series of oxoanions. Synchrotron-based methods including RAXR, time-resolved X-ray reflectivity, and EXAFS spectroscopy will be combined with laboratory-based batch and flow-through reactor wet chemistry studies, atomic force microscopy, Auger electron microscopy, dynamic light scattering and zeta potential measurements.

This research will identify fundamental complexity intrinsic to mineral-water interfaces, elucidate the dynamics of oxoanion adsorption-desorption on mineral surfaces, characterize the intrinsic variability in adsorption-desorption behavior among different oxoanions, and directly test how these fundamental processes influence macroscopic oxoanion adsorption-desorption phenomena. This work will provide new insight into processes such as dynamic equilibrium between distinct surface complexes and the dynamic feedback between ion adsorption and particle aggregation. In addition, the proposed research will accomplish many of the stated goals of the Geosciences Research Program, including understanding how molecular-scale interfacial processes are related to phenomena observed at the macroscopic-scale and elucidating the roles of thermodynamics and kinetics in interfacial reactions of specific elements. This work will advance the scientific basis for predicting contaminant transport and improve our understanding of fundamental yet complex geochemical processes.

PROJECT NARRATIVE

Principal Investigator (PI): Jeffrey G. Catalano **Position Title of PI:** Assistant Professor
Mailing Address of PI: 1 Brookings Dr, Campus Box 1169, St. Louis, MO 63130
Telephone Number of PI: 314-935-6015 **Email of PI:** catalano@wustl.edu
Applicant/Institution: Washington University in St. Louis
Street Address/City/State/Zip: 1 Brookings Drive, St. Louis, MO 63130
DOE/Office of Science Program Office: Basic Energy Sciences, Geosciences
Program Office Technical Point of Contact: Dr. Nicholas B. Woodward
Year Doctorate Awarded: 2005
Is the PI in a Tenure-Track Appointment? Yes **PECASE Eligible:** Yes

I. INTRODUCTION

Geochemical processes occurring at mineral-water interfaces are important to water quality [1], contaminant transport [2], soil formation, the geologic disposal of nuclear waste [3], ore deposit formation [4], acid mine drainage [5], and biomineralization [6]. An important interfacial reaction is ion adsorption, a process that often controls the fate of environmental contaminants and the composition of natural waters [7]. Of particular concern is the adsorption-desorption behavior of oxoanions, as many of these species are environmental toxins released during energy production [8], toxic or radioactive components of nuclear waste, including waste released into the environment at DOE facilities [9,10], or essential compounds used to remediate contamination at these sites [11,12]. Understanding the mechanisms and kinetics of oxoanion adsorption-desorption is thus essential for credibly predicting the migration of contaminants at DOE facilities and the performance of radioactive waste disposal sites.

Oxoanion adsorption-desorption behavior has been investigated for over forty years; much of this work has focused on iron and aluminum (oxyhydr)oxides, the dominant sorbents of oxoanions [13-102]. While spectroscopic probes have inferred mechanistic origins for macroscopic oxoanion behavior [13-28] that can be employed in thermodynamic models [29-39], my recent studies suggest that key mechanisms, including substantial outer-sphere adsorption, have been overlooked in the case of arsenate [42, 44]. Preliminary data discussed below (Section IV) documents additional complex and unexpected arsenate adsorption behavior. Given the similarities in the adsorption behavior of oxoanions [31, 32, 36, 39, 103], it is likely that arsenate is not alone in displaying tremendous complexity at mineral-water interfaces. It is unclear how such complex behavior depends on major chemical parameters and how it manifests itself at the macroscopic-scale. Translating this complexity into thermodynamic models for linking with macroscopic systems, a goal of the Office of Basic Energy Science's Geosciences Research Program, cannot be achieved when the intrinsic complexity of mineral-water interfaces, such as the number of distinct surface complexes that occur on a single mineral, is unknown or severely underestimated.

The kinetic behavior of oxoanion adsorption-desorption is likely a critical control on the fate of these species in the environment [104]. Macroscopic rates of adsorption and desorption of oxoanions have been determined (e.g., [83, 87, 98]), but these appear to be orders of magnitude slower than intrinsic reaction rates determined from pressure-jump relaxation measurements [51, 74, 75, 95, 99-101]. While diffusional controls on reaction rates can explain the discrepancy in timescales, an added complication is that these macroscopic rates display biphasic behavior, e.g., there is often observed a rapid phase of adsorption followed by a slow phase. Bulk diffusion cannot explain such a phenomenon, and this has instead been attributed to interparticle diffusion, diffusion into mineral pores, and heterogeneous surface reaction energetics [48, 65, 87, 98]. Given the underestimated complexity of arsenate adsorption, it is possible that some oxoanion surface complexes display adsorption-desorption kinetics not yet accounted for in pressure-jump relaxation measurements. It is thus not clear how the complexity of oxoanions adsorption affects adsorption-desorption kinetics and whether macroscopic oxoanion adsorption-desorption rates are partially controlled by surface reactions rather than diffusion.

Oxoanions display a range of protonation behavior, molecular geometry, and charge. The adsorption and desorption of oxoanions are often described through generally similar mechanisms [31,

32, 36, 39, 103] and their kinetic behavior has been explained using a few general reaction formulations (e.g., **[51, 105]**). However, rarely has the mechanistic and kinetic behavior of a series of oxoanions been compared in a rigorous and systematic fashion under identical sorbent and solution conditions. The primary exception is the pressure-jump relaxation measurements by Sparks and other **[51, 74, 75, 95, 99-101]** that provided the only fundamental information available regarding intrinsic oxoanion adsorption-desorption rates. Even this work may need reanalysis as most studies were completed before the widespread use of molecular-scale probes that could identify the surface species involved; the study that did involve such probes **[51]** did not account for the range of surface complexes identified in my recent investigations. It is thus not clear what intrinsic variability exists in oxoanion adsorption-desorption behavior, what is the physical origin of this variability, and what aspects of fundamental interfacial reaction mechanisms controls the variability in the behavior displayed by oxoanions at the macroscale.

Filling the major knowledge gaps discussed above is essential to meeting the scientific challenges outlined in a recent report identifying the research priorities of the Office of Basic Energy Science's Geosciences Research Program **[106]**. The priority research direction "Mineral-Water Interface Complexity and Dynamics" sets the goals of understanding how molecular-scale interfacial processes are related to phenomena observed at the macroscopic-scale and elucidating the roles of thermodynamics and kinetics in interfacial reactions of specific elements. In addition, cross-cutting issues identified in the report document the need for a fundamental understanding of the mechanisms and rates of interfacial processes and the microscopic basis for macroscopic complexity. *Determining the fundamental complexity, dynamics, and variability of oxoanion adsorption-desorption and how these connect to macroscopic phenomena is thus essential to meeting the goals of the Geosciences Research Program.*

II. PROJECT OBJECTIVES

The overall objectives of this proposal are to determine the fundamental complexity, dynamics, and variability of oxoanion adsorption-desorption reactions at the molecular-scale and then to connect these processes to macroscopic-scale phenomena. Specific objectives are:

1. Determine the molecular-scale reactions controlling the complexity of arsenate adsorption and evaluate which processes dominate the reactivity of complex mineral powders.
2. Identify the processes controlling arsenate adsorption-desorption rates on mineral surfaces and constrain the relative importance of surface reaction heterogeneity, particle aggregation, and diffusion in determining arsenate adsorption-desorption rates on mineral powders.
3. Evaluate the variability among oxoanions in their molecular-scale mechanisms and kinetics of adsorption-desorption and how this is manifested at the macroscopic-scale.

III. SCIENTIFIC BACKGROUND

Relevant aspects of the scientific literature are reviewed below to support the major hypotheses to be tested and to motivate the experimental design. Recent results and preliminary data are discussed in Section IV and the hypotheses and proposed research follow in Section V.

A. Reactivity of Surface Functional Groups

Surface complexation models **[38, 107-118]** explicitly assume that ion adsorption occurs at specific surface sites and that these sites (on metal oxides) are oxygen surface functional groups. Many applications of such models **[33-37, 85, 89, 103, 107-111, 118-129]** are founded on the concept that surface functional group reactivity is directly related to the coordination state of these oxygen atoms, with more highly coordinated sites having less ability to bind protons and adsorbates. An additional extension of the assumptions in such models is that surface functional groups having the same coordination to the same metal cation, e.g., oxygen atoms singly coordinated by aluminum, will display similar protonation behavior and reactivity towards adsorbates. For example, $>Al-OH_2^{+1/2}$ sites on the edge of gibbsite [γ - $Al(OH)_3$] are predicted to display similar behavior as the same type of sites on the surface of corundum

[α -Al₂O₃] whereas sites in different coordination states, e.g., singly and doubly coordinated sites, on a single mineral phase are expected to display vastly different reactivity. *While minor variations are expected, most modern surface complexation models predict that surface functional group coordination state is a primary control on the reactivity of trivalent metal (oxyhydr)oxide surfaces.*

B. Oxoanion Adsorption Mechanisms

Oxoanion adsorption mechanisms have been extensively studied through macroscopic wet chemistry measurements, ATR-FTIR and EXAFS spectroscopies, and surface complexation modeling [13-102]. Most oxoanions are suggested to form inner-sphere complexes, with bridging bidentate species predominant [13,14,16-25,27,40-44,46,47,50,52,62,64,67-69,76,77,81,86,90,91,130-134]. Some oxoanions (arsenite, selenite, selenate, sulfate, chromate, and molybdate) have been suggested to also form outer-sphere species [13,19,28,50,78-81], but it is unclear if such species occur only for certain oxoanions or if the non-ubiquity suggested to date reflects a sampling bias inherent in the characterization methods used. It is difficult for ATR-FTIR or EXAFS spectroscopy to conclusively identify outer-sphere species if inner-sphere species are present [42] because outer-sphere species generally lack a diagnostic signature in such spectra. As described below, I have recently identified coexisting inner- and outer-sphere arsenate species on corundum and hematite surfaces under conditions within the range of previous studies. As preliminary measurements suggest that the coverage of arsenate outer-sphere species are not sensitive to changes in ionic strength, this traditional signature of such species in macroscopic studies is likely not applicable to arsenate. *The difficulties in detecting outer-sphere oxoanion species spectroscopically and the potential that some outer-sphere forming-oxoanions (e.g., arsenate) do not display ionic strength-dependent adsorption behavior suggest that the occurrence of such species has been underestimated in previous studies.*

C. Oxoanion Adsorption-Desorption Kinetics

The intrinsic adsorption-desorption rates of select oxoanions on goethite and γ -Al₂O₃ have been determined using pressure-jump relaxation methods [51, 74, 75, 95, 99-101]. These studies identified one or two reaction steps that occur on timescales of 10⁻³ to 10⁻¹ s involved in the adsorption-desorption of each oxoanion studied. Reaction steps thought to be associated with inner-sphere complexation, thus involving ligand exchange, occur on the slower end of this range. While it is not straightforward to assign these intrinsic rates to specific reaction steps as many rates were determined and modeled prior to the widespread application of spectroscopic methods for characterizing adsorbate species, these are clearly involved in processes related to the formation of oxoanion surface complexes. While data is sparse it is known that the exchange of oxo-ligands on oxoanions with water typically occurs on timescales (t_{1/2} ~1-600 hours) that are orders of magnitude slower than these intrinsic adsorption-desorption rates [135-143]. These intrinsic adsorption-desorption rates thus must be controlled the rate of surface functional group exchange, which are likely rapid for singly coordinated functional groups [144-151].

Macroscopic oxoanion adsorption-desorption rates are often orders of magnitude slower than the intrinsic rates and are thought to thus be primarily controlled by transport processes [48, 76, 83, 98, 152]. As an example, arsenate adsorption-desorption kinetics have been studied frequently on powder substrates, and these studies often observe what is termed “fast” and “slow” kinetic behavior [48, 65, 76, 84, 87, 98]. While the fast component is generally assumed to reflect a bulk or film diffusion rate control, there is disagreement regarding the origin of the slow component, with this feature attributed to either interparticle diffusion [48, 65, 87] or to heterogeneity in surface reaction energetics [98]. The Zhang and Stanforth [98] study is particularly insightful as they observed no relationship between particle aggregation and the slow adsorption component. Aggregation should lead to increased interparticle diffusion limitations on adsorption rates. As this work suggests the slow rate is reaction-controlled, it is thus possible that an additional adsorption reaction occurs on the timescale of minutes to hours.

Arsenate desorption rates from mineral powders are often observed to be slower overall than adsorption rates [15, 83], and have similarly displayed dual (i.e., fast and slow) release rates from goethite upon addition of phosphate [76] and from kaolinite [84]. Other oxoanions also display this behavior (e.g.,

[105]). Similar to adsorption, intrinsic desorption rates inferred from pressure-jump relaxation measurements [51, 74, 75, 95, 99-101] are orders of magnitude faster than the macroscopic rates of desorption observed in powder systems. Possible explanations for this discrepancy include bulk or film diffusion effects, interparticle diffusion effects, entrapment of arsenate because of particle aggregation [153, 154], and a secondary adsorption reaction that results in a relatively inert surface species. *The role of aggregation and possible secondary reactions on the adsorption-desorption kinetics of arsenate and other oxoanions is currently unresolved.*

IV. RECENT RESULTS AND PRELIMINARY DATA

A. Interfacial Water Ordering

I have recently made a series of measurements to investigate ordering of interfacial water near (012), (110), and (001) surfaces of hematite and corundum [155-159]. On all surfaces studied water fully coats the surface and forms a continuous network from the surface functional groups to bulk water. The degree of water ordering with respect to the fixed crystal lattice decreases with increasing distance from the surface over a length scale of approximately 1 nm. Water has a similar interfacial structure of the hematite and corundum (012) surfaces; the (110) surfaces also display similar interfacial water structure (**Fig. 1**). These measurements suggest that the structure of interfacial water is primarily controlled by the arrangement of oxygen functional groups on the surface. Each pair of surfaces also shows a similar trend with respect to the degree of ordering shown by specific water sites. The lower of the two sites of water that is directly adsorbed to surface functional groups is more ordered on hematite surfaces; the upper adsorbed water site and water further from the surface is more ordered on corundum surfaces. This may be related to difference in surface functional group exchange rates [144-146, 148, 149, 157, 158].

The corundum (001) surface displays fundamentally different interfacial water structure [hematite (001) has not been studied in this way to date]. There is a single adsorbed water site that has a broader distribution than on the (110) and (012) surfaces; more distant water has a similarly broad distribution. This likely reflects the flat topography of the (001) surface compared to the corrugated structures of (012) and (110) as well as the existence of only bridging oxygen functional groups on (001); the (110) and (012) surfaces contain singly, doubly, and triply coordinated functional groups. The structure and ordering of interfacial water on these surfaces thus appears to be controlled by the distribution, arrangement, and exchange rates of surface functional groups.

B. Complex Arsenate Adsorption

In a recent in situ resonant anomalous X-ray reflectivity (RAXR) study of arsenate adsorption on corundum and hematite (012) [42] I observed that, in a pH 5 and 0.01 M NaCl solution, arsenate adsorption was bimodal on both surface, simultaneously forming inner- and outer-sphere surface complexes (**Fig. 2**). These complexes were structurally similar on both surfaces. Arsenate adsorbed 40% inner-sphere and 60% outer-sphere on corundum (012); this distribution was 70%:30% on hematite (012). In addition, the ratio between inner- and outer-sphere species was constant on both surfaces over a wide range of arsenate solution concentrations (10^{-6} to

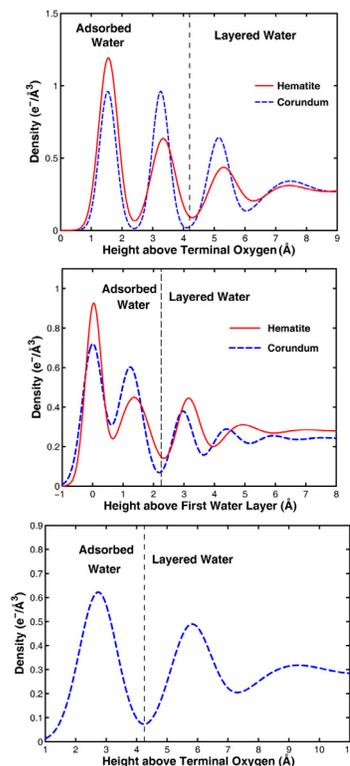


Figure 1. Interfacial water structure near hematite and corundum (012) (top), (110) (middle), and (001) (bottom).

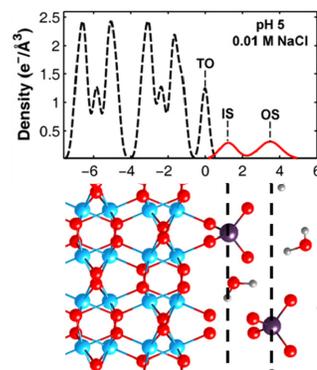


Figure 2. Inner- and outer-sphere arsenate complexes on (012) surfaces and their spatial relationship.

10^{-3} M). This demonstrates that at the pH and ionic strength condition studied these species had approximately equivalent affinity for each surface.

Unpublished RAXR measurements of the corundum (012) surface reacted with 10^{-3} M arsenate at pH 5 and substantially increased ionic strength (1.0 M NaCl) showed no significant change in the total coverage or distribution of arsenate between inner- and outer-sphere sites, in contrast to the classically expected strong ionic strength dependence of outer-sphere adsorption (**Fig. 3**).

In contrast, measurements made at 0.01 M NaCl but at pH 9 identified only an inner-sphere complex (**Fig. 3**). Together, these measurements suggest that outer-sphere arsenate adsorption is strongly pH-dependent but weakly influenced by ionic strength.

Arsenate adsorption behavior was further explored on the corundum (001) surface using RAXR. This surface is terminated exclusively in doubly coordinated oxygen groups and has a relaxed structure nearly identical to the basal plane of gibbsite [160]. Given the expected unreactivity of doubly coordinated oxygen groups [110, 161] arsenate was predicted to adsorption only as outer-sphere complexes. However, RAXR measurement identify the presence of both inner- and outer-sphere complexes (**Fig. 4**), with the inner-sphere complex at a position only consistent with tridentate binding to doubly coordinated oxygen groups.

While unexpected, the results are reproducible and cannot be explained by binding to steps or defects or to a different surface termination, as these features either exist at a low surface density or do not contribute to a RAXR signal.

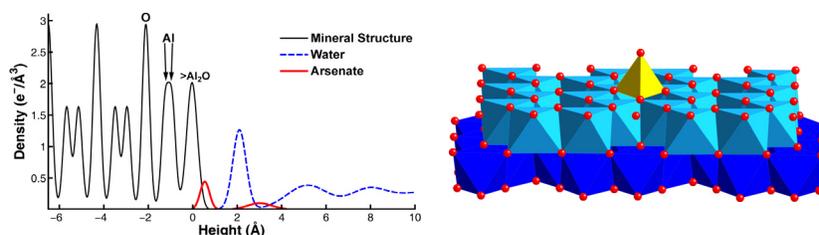


Figure 4. (left) Arsenate distribution above the corundum (001) surface. (right) Inner-sphere adsorption geometry on this surface

C. Arsenate Desorption

A corundum (012) surface reacted with 10^{-3} M total arsenate at pH 5 in 0.01 M NaCl was placed in deionized water for two hours. Arsenic K-edge RAXR spectra were then collected on this surface and the arsenate distribution was determined (**Fig. 5**). The total amount of arsenate sorbed on the surface was reduced a factor of 4. The resulting arsenate distribution still contained both inner- and outer-sphere species, but the ratio of the two types differed from the adsorption conditions, changing from 40%:60% inner- to outer-sphere ratio before desorption to 65%:35% ratio after desorption. As this was a test measurement the pH was not rigorously controlled and flow-through conditions were not employed, allowing for re-equilibration. It is thus unclear if the observed behavior reflects a kinetic phenomenon or equilibration between the mineral surface and the desorbing fluid. It does indicate that adsorption of these species is reversible and occurs on a timescale amenable to X-ray reflectivity methods.

V. RESEARCH PLAN

A. Overall Research Approach

The proposed research will be conducted using a two-step approach designed to obtain fundamental molecular-scale information and then apply this to explain macroscopic-scale processes.

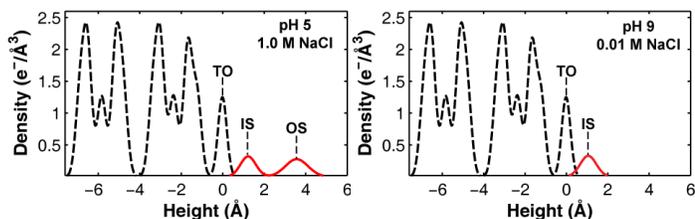


Figure 3. Distribution of arsenate surface complexes at the corundum (012) surface at pH 5 and 1 M NaCl (left) and at pH 9 and 0.01 M NaCl (right).

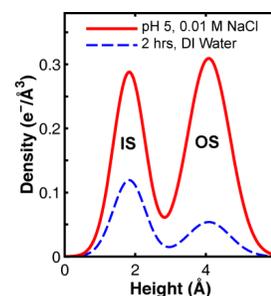


Figure 5. Arsenate distribution on the corundum (012) surface before and after desorption in DI water.

This approach is motivated by the lack of ability to directly obtain detailed, fundamental information in macroscopic systems and the uncertainty in how fundamental molecular-scale processes upscale to such systems. In the first step, measurements of oxoanion adsorption mechanisms and adsorption-desorption kinetics will be made on a series of single crystal surfaces of hematite and corundum (Fig. 6A). These measurements are designed to explore the fundamental complexity, dynamics, and variability of these reactions. Initial work will focus on the oxoanion arsenate as substantial preliminary work has been done on this molecule (see Section IV). The variability of oxoanion adsorption-desorption reactions will be explored by then also examining selenate, selenite, molybdate, phosphate, and silicate; the motivation for selecting these species is described in Module 3.

In the second step, macroscopic adsorption-desorption behavior and rates will be studied on two sets of hematite powders. One powder consists of mono-dispersed single crystal platelets (Fig. 6B) bound primarily by {001} and {012} faces. The second suspension consists of approximately spherical particles (Fig. 6C) representative of those used in previous studies. The platelets will be employed as a bridge system between the single crystal surfaces examined in the first approach and the more complex spherical particles used in most macroscopic studies.

Further comments on the selection of mineral substrates are warranted. The use of both hematite and corundum single crystals is motivated by both practical constraints and scientific interests. While the PI currently possesses a collection of hematite single crystal substrates that will be used in this project, obtaining additional substrates is difficult and expensive (\$200 -1500 per crystal). The proposed work will require employing many different crystals during a single run at the synchrotron in order to efficiently explore how arsenate adsorption-desorption mechanisms and rates vary with chemical conditions. While these crystals can be cleaned and returned to their unreacted form, this cannot be done during a single experimental run because of time constraints and lack of appropriate equipment at the synchrotron facility. Corundum crystals are inexpensive (\$5-10 per crystal) and commercially available and will be used for testing a range of conditions during an experimental run. This procedure will identify important aspects of oxoanion adsorption-desorption behavior, and then relevant conditions will be explored on hematite.

This dual-substrate procedure is justified by the almost identical arsenate adsorption behavior and interfacial water structure on isostructural surfaces of hematite and corundum [42, 155-159]. General features of arsenate adsorption behavior (e.g., the dependence of outer-sphere complexation on pH but not ionic strength, diffusion-limited adsorption rates of arsenate surface species) are thus expected to be the same on isostructural surfaces of these minerals. Previous large differences in reactivity [162-167] observed between corundum and hematite (001) surfaces are likely predominantly the result of differences in surface structure [160, 168] (i.e., the *surfaces* used in these studies were not isostructural) and not a fundamental difference in chemical affinity of these two substrates. A separate study conducted by the PI that suggested uranyl binds differently to the corundum and hematite (012) surfaces [169] is fundamentally flawed as the structural model used for the corundum (012) surface [170] included the wrong surface termination [159]. The PI hopes to revisit this work in the future. *All work to date that accurately compares the reactivity of truly isostructural surfaces of hematite and corundum demonstrates that these display fundamentally similar behavior with respect to water ordering and ion adsorption.*

The differences that do exist in the way isostructural hematite and corundum surfaces react appear to be more subtle (see Section IV). Arsenate forms the same two types of adsorption complexes on the (012) surfaces of these minerals, but the distribution of arsenate between these two complexes

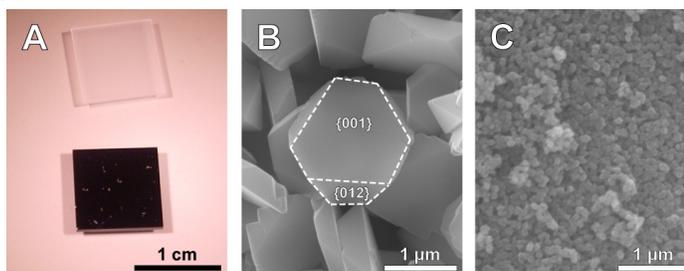


Figure 6. Size range of iron and aluminum oxide substrates. (A) Photograph of hematite (dark) and corundum single crystals. (B,C) SEM images of (B) monodispersed hematite single crystal platelets showing distinct crystallographic faces (outlined) and (C) “conventional” aqueous-synthesized hematite powder.

differs slightly. In addition, interfacial water appears to take on the same structure near isostructural hematite and corundum surfaces but the water shows greater positional disorder or vibrational motion on hematite. It is possible that these differences are related to the relative exchange rates of functional groups on these surfaces [144,146,157,158,161]. Investigating oxoanions adsorption-desorption behavior on isostructural surfaces of corundum and hematite is thus of interest as it will better characterize the intrinsic (i.e., not structurally-controlled) reactivity differences between iron and aluminum oxides. In addition, while corundum is rare in soils and sediments, its surface functional groups have comparable reactivity to similar groups on other aluminum (oxyhydr)oxides (see Section III.A.).

The use of only hematite in the powder studies reflects experimental constraints. The PI and his group have developed reproducible aqueous synthesis procedures for the hematite platelets and many synthesis procedures exist for “conventional” hematite powders [171]. Corundum cannot be synthesized directly from aqueous solution under ambient conditions, and while single crystal powders of corundum exist [172], the lack of synthesis control is a concern in using such materials in fundamental studies.

B. Research Modules

The proposed research is divided into three distinct modules designed to explore the fundamental complexity, dynamics, and variability of oxoanion adsorption-desorption. In addition, each module seeks to determine how key molecular-scale processes influence overall macroscopic-scale phenomena. Each module description contains a set of major hypotheses to be tested.

Module 1 – Complexity of Arsenate Adsorption

i. Motivation and Overview

My recently published work [42, 44] and the preliminary data discussed above (Section IV) concerning arsenate adsorption mechanisms on specific surfaces of corundum and hematite document an unexpected level of complexity. While past studies have observed a few different types of inner-sphere surface complexes, predominantly bridging bidentate complexes bound to singly coordinated functional groups [13, 15-18, 20, 24, 27, 40, 41, 47, 50, 52, 62, 64, 67, 68, 76, 86, 91, 130, 131, 133, 134], my work suggests that arsenate may bind to multiple functional group types and as both inner- and outer-sphere complexes. Further, the occurrence of outer-sphere complexes appears to be surprisingly insensitive to ionic strength but shows a strong pH-dependence. In addition, the location of outer-sphere arsenate species suggests that the oxo-ligand on this molecule occur at positions normally occupied by interfacial water molecules. This may be coincidental but it also may indicate some role of interfacial water in stabilizing such species, as has been suggested for alkaline and alkaline earth cations [173]. Finally, aggregation affects macroscopic oxoanions adsorption [153] and an understanding of the effect of this process on adsorption mechanism may thus be needed to upscale molecular-scale results. This module seeks to explore the origins of the complexity of arsenate adsorption on iron and aluminum oxide surfaces, to quantify the variability in complex adsorption behavior displayed by isostructural mineral phases, and to determine how such complexity is manifested in multi-particle systems.

ii. Major Hypotheses:

- 1. Arsenate adsorption mechanisms and the resulting surface coverage display similar dependencies on solution composition on isostructural hematite and corundum surfaces.*
- 2. Variability in arsenate adsorption behavior on different crystallographic surfaces of a single mineral reflects the type and arrangement of surface functional groups and interfacial water structure.*
- 3. This complexity extends to systems composed of mineral powders but is modified by aggregation.*

iii. Proposed Research

This module consists of a series of studies performed in two tracks. One track will explore arsenate adsorption behavior on the surfaces of single crystals of the isostructural phases corundum and hematite. The second track seeks to upscale these results to systems composed of mineral powders.

Single crystal studies. Hematite and corundum single crystals displaying the (012), (110), and (001) surfaces will be employed in this study. These surfaces were selected because they display different types of surface functional groups and interfacial water structure [157-160, 168, 174, 175]. I have extensive experience working with all of these and have determined the interfacial water structure on all but the hematite (001) surface. This surface is complicated by the typical occurrence of two co-existing surface terminations [168]. I am currently developing a preparation method, in consultation with Dr. Kevin Rosso of PNNL, to produce a surface terminated exclusively in doubly coordinated oxygen groups, isostructural with the corundum (001) surface. Once developed, interfacial water structure will be determined, and this will be used as a reference structural model to explore water structure near the more complex surface containing two distinct terminations. This work will be completed prior to the start of this project. All crystals will be prepared following previously described procedures [157-159].

The distribution and coverage of arsenate surface complexes will be determined on these surfaces over a range of pH (3 to 10) and ionic strength conditions (0.01 to 1 M) using in situ RAXR measurements. Additional uptake measurements under select fixed pH and ionic strength conditions, also using RAXR, will track how the surface coverage of individual complexes as a function of arsenate solution concentration. The RAXR method is described in detail below (Section V.C.). Single and mixed-termination hematite (001) surfaces will both be investigated as it is unclear which type dominates when such a surface is exposed on hematite powders. In effort to identify spectral signatures of outer-sphere arsenate that may be applied in the powder studies, in situ grazing incidence- extended X-ray absorption fine structure (GI-EXAFS) measurements will be attempted on select system. However, the success of such measurements is doubtful as the incident X-ray beam is typically strongly attenuated by the long path length of water it must traverse during such measurements and the required use of X-ray fluorescence to measure the EXAFS signal produces a multi-component spectrum from arsenate on the mineral surface and in solution.

These measurements are designed to determine: (1) the dependence of inner-sphere and outer-sphere complexes, and inner-sphere complexes bound to surface functional groups having different coordination states, on solution composition; (2) the variability in the behavior of similar complexes on different surfaces of each mineral; (3) the relationship between outer-sphere arsenate coverage and interfacial water ordering; (4) the intrinsic variation in reactivity towards arsenate displayed by the isostructural minerals corundum and hematite; and (5) the range of complex arsenate adsorption behavior potentially displayed by a single mineral phase.

Mineral powder studies. A combination of wet chemistry, EXAFS spectroscopy, atomic force microscopy, electron microscopy, Auger nanoprobe, dynamic light scattering, BET surface area, and zeta potential measurements will be employed to systematically investigate arsenate adsorption behavior on suspensions of hematite single crystal platelets and conventional hematite powders. These studies are designed to connect the fundamental observations made on single crystal surfaces with the behavior displayed by mineral powders having complex surface structures. This will be accomplished by first examining macroscale adsorption behavior and molecular-scale adsorption mechanisms on hematite platelets bound by {001} and {012} surfaces, with the goal of explaining the observed adsorption behavior in terms of reactions on specific surfaces plus the addition of interparticle effects such as aggregation. The second step will involve similar measurements on conventional hematite powders with the goal of using the information gleaned from the platelet studies to determine the fundamental origin of macroscopic adsorption behavior on complex mineral powders.

The platelet studies will begin with a series of wet chemical measurements to characterize their macroscopic arsenate adsorption behavior. Similar conditions will be explored as in the single crystal studies to allow for a direct comparison. Arsenic concentrations will be measured by inductively coupled plasma mass spectrometry (ICP-MS). The aggregation behavior of these platelets will be examined using in situ dynamic light scattering and atomic force microscopy. In the AFM measurements, a drop of the platelet suspension will be placed on a glass slide and in situ measurements will be made following settling. The PI's group has developed a method to determine the number of platelets in a cluster in the presence of image artifacts from the pyramidal tip. The platelets are monodispersed and thus of uniform

dimension; these constraints allow for determination of aggregate particle counts. Aggregation will also be investigated using electron microscopy [153, 154]. These platelet suspensions will be further characterized in order to facilitate an understanding of the contribution of the two primary surfaces to the overall adsorption behavior. EXAFS spectroscopy will determine the particle-averaged adsorption geometry of arsenate. These spectra will be interpreted with the aid of the speciation suggested by the single crystal studies on these surfaces. Measurements will focus on select representative conditions, including those that produce samples with and without significant outer-sphere complexation with the goal of identifying a spectral property indicative of the presence of such species.

In addition, Auger nanoprobe measurements will seek to determine the surface-specific (i.e., on {001} or {012}) arsenate concentrations. Some arsenate may be removed during sample preparation as the particles will need to be washed in DI water prior to drying to prevent precipitation of arsenate from the entrained solution. To account for this, similar measurements will be made on single crystal surfaces of the same orientation prepared using the same washing procedure, including single and mixed-termination hematite (001) surfaces. As the arsenate coverage on these surfaces will be determined in situ using RAXR, a direct correlation can be made between the arsenate coverage determined by Auger measurements and the in situ coverage existing on each surface. This analysis will aid in understanding how arsenate distributes between these surfaces and how different surface species contribute to the overall macroscopic adsorption behavior. This approach may also suggest the dominant termination displayed by the platelets {001} surfaces as each termination is expected to bind different amounts of arsenate.

The contribution of particle aggregation on macroscopic adsorption behavior will also be considered. The particles are predicted to experience the most aggregation near their pH_{pzc} (e.g., [98]); the pH_{pzc} will be determined by zeta potential measurements. Conditions that produce substantial aggregation are expected to produce the largest deviations from the macroscopic adsorption behavior and molecular scale adsorption mechanisms predicted from the single crystal studies. By systematically exploring the variation in uptake and speciation with aggregation these studies will be able to isolate how such a phenomenon influences adsorption.

A similar series of measurements will be performed on suspensions of conventional hematite powders, with the exception of the surface-specific Auger studies as these are not possible on particles of this size. Wet chemistry and EXAFS spectroscopy measurements will seek to determine if arsenate adsorption behavior and mechanisms differ from the platelet system. Arsenate speciation as a function of particle aggregation will again explore the effect of this phenomenon on arsenate adsorption mechanisms. Once constrained, remaining differences in uptake and speciation between the powder and platelet forms of hematite can be attributed to differences in surface properties, likely the distribution of surface functional group types. These measurements will thus elucidate the role of fundamental molecular-scale processes in determining the macroscopic arsenate adsorption behavior displayed by mineral powders.

Module 2 – Dynamics of Arsenate Adsorption-Desorption

i. Motivation and Overview

While understanding the overall mechanisms of adsorption is important, and is in fact required for creating thermodynamic model to describe this behavior, these processes are often temporally variable in natural systems. It is thus critical to assess not only the complexity but also the dynamics of arsenate adsorption-desorption processes. As described above (Section III.C.), the intrinsic rates of arsenate adsorption-desorption reactions are likely kinetically fast, operating on the millisecond timescale [51]. In addition, as ligand exchange between arsenate oxo-ligands and water is exceedingly slow these fast rates are likely controlled by the rate of movement of interfacial water and the exchange rate of singly-coordinated surface functional groups. While the former has not been measured to the best of my knowledge, the latter are likely occurs on the same timescale [144, 161] as the intrinsic adsorption component associated with inner-sphere arsenate adsorption. However, intrinsic arsenate adsorption-desorption rates have only to date been measured on goethite, and the interpretation of these rates was done before the possibility of outer-sphere arsenate adsorption was documented [42]. It is thus not clear

whether similar rates occur on hematite and corundum, although singly coordinated functional groups on those materials are expected to display exchange rates of similar orders of magnitude as for goethite.

In contrast, macroscopic adsorption studies observe much slower adsorption-desorption rates [48, 76, 83, 98, 152]. These macroscopic rates typically show a fast and slow component, and there is generally some fraction of arsenate that is not desorbable, even on timescale substantially longer than that of the slow adsorption process [15, 76, 83, 84]. The fast component can likely be explained by diffusion-limited adsorption occurring through the reaction(s) responsible for the observed intrinsic rates. The slow component has been attributed to interparticle diffusion, diffusion into mineral pores, and heterogeneous surface reactions. Interparticle diffusion constraints may not be realistic as slow adsorption does not depend on particle aggregation [98], although aggregation does appear to affect phosphate desorption [153]. Diffusion-controlled adsorption in pores is also an uncertain explanation as intrinsic desorption rates are rapid and desorption from pores should also be diffusion limited. Diffusion rates into and out of pores may not differ enough to explain the inability to desorb a substantial fraction of arsenate over long timescales. EXAFS studies of arsenate after aging do not indicate precipitate formation [15].

These past observations suggest a surface reaction [98] as at least a partial alternative explanation for the slow components of arsenate adsorption and desorption. The preliminary measurements discussed above suggest one possible reaction: arsenate binding to doubly coordinated surface functional groups. My observations on the corundum (001) surface clearly indicate that this can occur (Section IV). Oxo-ligand exchange between arsenate and water occurs on a timescale around 100 hours, although this has only been determined for AsO_4^{3-} and protonation may substantially increase this rate [138, 139]. μ_2 -OH groups on small aqueous clusters, analogues of doubly coordinated surface functional groups on iron and aluminum oxide surfaces, exchange with water on timescales of ~ 0.1 to 100 hours [146, 149]. However, similar groups on gibbsite appear to exchange at much slower rates [176]. It is thus unclear which exchange rate may control binding to doubly coordinated groups, although either are nominally consistent with the rate of slow adsorption-desorption and are likely too slow to be observed during pressure-jump relaxation measurements. This module thus seeks to explore the dynamics of arsenate adsorption-desorption in order to verify that inner-sphere binding to singly coordinated sites and outer-sphere binding are intrinsically fast, to explore binding to doubly coordinated functional groups as the source of slow adsorption-desorption behavior, and to determine the relative role of adsorption to/desorption from doubly coordinated surface functional groups and particle aggregation in controlling the slow component of macroscopic arsenate adsorption-desorption behavior.

ii. Major Hypotheses:

- 1. Adsorption-desorption reactions involving outer-sphere species and inner-sphere species bound to singly coordinated oxygen functional groups are rapid, with observed rates diffusion-controlled.*
- 2. Adsorption-desorption reactions involving inner-sphere complexes bound to doubly coordinated functional groups are slow and involved in the slow components of arsenate adsorption-desorption seen at the macroscopic-scale.*
- 3. Aggregation limits arsenate desorption rates and accounts for a portion of the arsenate not desorbable under relevant timescales.*

iii. Proposed Research Activities

This module consists of a series of studies performed in two tracks. One track will explore arsenate adsorption-desorption kinetics on the surfaces of single crystals of the isostructural minerals corundum and hematite in order to explore fundamental rates of these reactions. The second track seeks to upscale these results to systems composed of mineral powders and to constrain the effect of aggregation on arsenate adsorption-desorption rates.

Single crystal studies. Time-resolved X-ray reflectivity (XR) (see Section V.C.) coupled with RAXR measurements on pseudo-steady state systems will be employed to examine fundamental adsorption-desorption rates on single crystal surfaces of corundum and hematite. Time-resolved XR measurements will be performed in situ in a flow through cell that is based on designs provided by Dr.

Paul Fenter (see attached letter of support). RAXR measurements in such cells are challenging because of water attenuation at the X-ray energies needed to probe the arsenic K-edge. As these measurements will only be made on systems that display stable behavior after long reaction times, conventional in situ cells that maintain only a thin film of solution (~5-10 μm) will be employed. Such cells provide a stable solution environment but do not allow for flow through the cell during measurements [177].

Time-resolved measurements exploring adsorption-desorption rates will have three main foci. First, measurements will be made on (012) surfaces of hematite and corundum under conditions where both inner- and outer-sphere species coexist and where only inner-sphere species are present. These will seek to verify that the adsorption and desorption of both species are rapid, as expected based on a previous study [51]. Time-resolved XR measurements will primarily be able to obtain at best ~3 s time resolution by employing detector systems currently in use by my group. As this is much slower than the expected intrinsic rate of adsorption and desorption, inner- and outer-sphere species should show identical rates during both adsorption and desorption, and these rates should be controlled by diffusion. If these species are observed to form or desorb at different rates it would indicate that at least the slower rate was intrinsic as the effect of diffusion should be identical for these species.

Second, time-resolved XR measurements will be made to compare the rates of adsorption-desorption on the (110) surfaces of hematite and corundum with those on the (012) surfaces. Given the surface functional groups present on the (110) surface, similar adsorption mechanisms are expected to occur on both surface planes [158]. These measurements seek to determine if diffusion-limited adsorption and desorption rates differ among these surfaces under the same flow conditions. Any differences observed between (110) and (012) surfaces would suggest that adsorption-desorption rates are affected by film diffusion [178], and that film diffusion rates are affected by interfacial water structure, which differs on the two surfaces of each mineral (see Section IV). Consistent differences between each pair of isostructural corundum and hematite surfaces would point to not just interfacial water structure but also its disorder as affecting film diffusion rates.

Third, measurements will be made on (001) surfaces of corundum and hematite [both single and mixed-termination hematite (001)]. These will seek to determine the timescale for adsorption-desorption of inner-sphere arsenate species bound to doubly-coordinated oxygen functional groups. Given the slow exchange rates of oxo-ligands on arsenate and doubly coordinated surface functional groups, it is expected that intrinsic adsorption-desorption rates for such species will be observable using time-resolved XR. Flow rates during these measurements will be varied to ensure that diffusion is not the rate-limiting step. As the formation of outer-sphere species on these surfaces is expected to be intrinsically rapid, the rate of formation of such complexes will be used to establish the diffusion-limited rates. An inner-sphere complex bound to doubly-coordinated oxygen groups that forms slower than this rate will thus display intrinsic kinetic behavior. The measurement of outer-sphere formation rates will also provide additional constraints on the effect of film diffusion on adsorption-desorption rates because these surfaces have different interfacial water structure than (012) and (110) surfaces. As adsorption and especially desorption rates for inner-sphere complexes bound to doubly coordinated oxygen groups may be slower than can feasibility studied during an in situ time-resolved XR measurement, select systems will also be studied using RAXR measurements after extended reaction times in the laboratory to explore timescales of days to months. The mixed-termination hematite (001) surface should display multiple inner-sphere adsorption-desorption rates corresponding to a diffusion-limited reaction with singly coordinated functional groups and a surface-controlled reaction with doubly coordinated groups.

Mineral powder studies. Batch and continuous-flow stirred-tank reactor, EXAFS spectroscopy, AFM, electron microscopy, Auger nanoprobe, DLS, and zeta potential measurements will be used to investigate arsenate adsorption-desorption rates on suspensions of hematite single crystal platelets and conventional hematite powders. These studies are designed to connect the fundamental rate measurements made on single crystal surfaces and suggested by pressure-jump relaxation studies [51] with the kinetics displayed by mineral powders having complex surface structures. This will be accomplished by first examining macroscopic-scale adsorption-desorption rates on hematite platelets bound by {001} and {012} surfaces, with the goal of determining if these rates may be explained in terms

of reactions on specific surfaces plus interparticle effects such as aggregation [153]. The second step will involve similar measurements on conventional hematite powders with the goal of using the information gleaned from the platelet studies to identify the fundamental origin of macroscopic adsorption-desorption rates displayed by complex mineral powders.

The rates of adsorption of arsenate on both platelets and conventional hematite powders will be determined in batch reactors operating at constant temperature and pH. This setup is required as it is difficult to measure arsenate loss from solution in the effluent of a flow-through reactor. Similar batch reactor procedures have been employed in most past studies of arsenate adsorption kinetics for this reason [48, 76, 83, 98, 105, 152]. Dissolved arsenate concentrations will be determined using ICP-MS. Aggregation will be explored using DLS, AFM, and electron microscopy. Reaction conditions will be selected based on the results of Module 1. Select studies will be performed at a series of different mixing rates to explore diffusional control on the observed kinetic behavior. Based on the hypothesis that the slow component of arsenate adsorption is controlled by binding to doubly-coordinated oxygen groups, and thus reflects a surface reaction control and not a diffusional control, it is expected that the fast adsorption process will display a dependence on mixing rate while the slow component will not. Adsorption and desorption rates as a function of particle aggregation will also be determined in order to evaluate the role of this process in such systems.

The rates of desorption of arsenate are generally observed to be slower than for adsorption and desorption is normally determined by examining the amount of arsenic in solution after a given reaction time. These factors make desorption studies amenable to being conducted in continuous-flow stirred-tank reactors, designs for which will be provided by Prof. Daniel Giammar (see attached letter of support). Arsenate desorption rates under conditions identical to those used in the single crystal studies will be measured for both the platelet and conventional powder suspensions. Most studies will be conducted for up to 24 hours, but select studies will proceed for up to a month to examine the timescale over which the slow desorption processes occurs. Desorption of arsenate bound to doubly coordinated functional groups is expected to be substantially slower than from other groups, and characterization methods will be employed to investigate this change in relative surface speciation after desorption. EXAFS measurements will investigate possible changes in the distribution of surface species and zeta potential measurements changes in the electrokinetic behavior. DLS, AFM, and electron microscopy measurements will be used to identify changes in particle aggregation during desorption. Auger nanoprobe measurements on the platelets after desorption will be conducted to determine if the distribution of arsenate between the {012} and {001} surfaces changes.

Module 3 – Variability in Oxoanion Adsorption-Desorption

i. Motivation and Overview

Although arsenate is a widely studied oxoanion and the above modules will investigate fundamental behavior, further study is required to investigate the variability in the complexity and dynamics of oxoanion adsorption-desorption. While most oxoanions adsorb through a finite set of mechanisms, it is expected that they will distribute differently between different types of surfaces complexes (e.g., inner- versus outer-sphere species, inner-sphere species bound to singly versus doubly coordinated oxygen groups). Rates of adsorption-desorption of outer-sphere species and inner-sphere species bound to singly coordinated groups on specific surfaces are expected to be diffusion limited (see Section III) for all species, and should be similar at the macroscopic-scale [105] unless they have substantially different effects on aggregation. Adsorption-desorption rates of oxoanions reacting with doubly coordinated groups on specific surfaces should also be similar if the reaction rates are determined primarily by the rate of surface functional group exchange. A variation in rates would suggest that at least some oxoanions have oxo-ligand exchange rates faster than functional group exchange rates. In addition, if these rates are responsible for the slow component of oxoanion adsorption-desorption kinetics then the fraction of the adsorbing or desorbing species involved in this slow component should be proportional to the fraction of the adsorbed oxoanions that bind to doubly coordinated groups. This module thus seeks to explore the systematic variability of oxoanion adsorption complexity and dynamics

by identifying how different oxoanions distribute between different adsorption sites, investigating the rates of adsorption-desorption of different oxoanions, and exploring how differences in aggregation induced by oxoanions affect these rates at the macroscopic-scale.

ii. Major Hypotheses:

1. *Oxoanions occupy similar adsorption sites and their distribution between sites correlates with their charge and pKa values.*
2. *Macroscopic oxoanion adsorption-desorption rates are controlled by diffusion, the exchange rate of doubly coordinated oxygen functional groups, and aggregation.*

iii. Proposed Research Activities

This module consists of a series of studies performed in two tracks. One track will explore oxoanion adsorption mechanisms and adsorption-desorption kinetics on the surfaces of single crystals of the isostructural phases corundum and hematite. The second track explores the variability in oxoanion adsorption-desorption rates at the macroscopic-scale and seeks to relate this to fundamental processes. Similar procedures will be employed as used in Modules 1 and 2. The results obtained in this module will be compared to those obtained for arsenate.

Single crystal studies. The adsorption mechanisms of selenate, selenite, and molybdate will be determined on the (012) and (001) surfaces of hematite and corundum using RAXR as these are environmentally-relevant oxoanions with accessible X-ray adsorption edges. Test measurements will be performed on arsenite and chromate, but these are expected to suffer from X-ray beam-induced redox transformations. The adsorption sites of phosphate and silicate will also be explored using XR. As they are tetrahedral oxoanions they will likely occupy similar adsorption sites as arsenate. The XR data will thus be interpreted with the aid of information gained from XR and RAXR studies of arsenate. Time-resolved XR will be used to investigate the rates of adsorption and desorption of these oxoanions on the (001) and (012) surfaces. Only a subset of chemical conditions will be explored; these will be selected based on the results of the previous modules.

Mineral powder studies. The uptake behavior and adsorption-desorption rates of these oxoanions will be explored on both hematite platelets and conventional hematite powders. When possible, their adsorption mechanisms will be determined using EXAFS or ATR-FTIR spectroscopy. The variability in aggregation behavior induced by these species will also be determined. Auger nanoprobe measurements on hematite platelets will examine the distribution of oxoanions between different crystal faces. As in the single crystal studies only a subset of chemical conditions will be explored.

C. Unique Project Methods

Time-resolved XR. X-ray reflectivity (XR) and its three-dimensional extension crystal truncation rod (CTR) scattering have seen widespread use in studying mineral surface structure and reactivity [155-160, 168-170, 174, 175, 177, 179-187]. In situ time-resolved XR allows one to probe dynamic changes in surface structure in real time [177, 188-190]. These measurements examine the change in XR as a function of time at a fixed scattering condition sensitive to the process of interest. To date this method has been mainly employed in investigating mineral dissolution processes where the change in XR is due to changes in roughness and step density [177, 188-190]. These measurements operate at fixed X-ray beam energy and scattering condition, removing systematic errors associated with monochromator and diffractometer motion. This allows time-resolved XR measurements to have uncertainties determined by counting statistics that are much lower than the 2-5% uncertainty associated with XR measurements; 0.1-1% uncertainties are feasible for the proposed systems.

The application of time-resolved XR to probe adsorption-desorption is a straightforward extension of this method. The adsorption of one or more species alters the surface X-ray scattering structure factor, thus substantially altering the measured XR intensity. For example, the arsenate coverages examined in my recent investigation of the (012) surfaces produce up to a 50% change in measured intensity. The percent change in XR intensity induced by the adsorption of a species at a given

coverage is independent of the surface roughness, allowing direct comparison of rates between samples with different initial roughness. While time-dependent roughening of a surface will also alter the measured XR intensity, no change in roughness was observed during past in situ XR measurements of hematite and corundum surfaces, which lasted up to 24 hours [42, 155-159]. While not element-specific, all time-resolved XR measurements will be made on systems where the initial and final states have already been characterized by RAXR. Under such conditions the rate of change of individual components of the structure (e.g., adsorbates in different sites) can be determined directly. In addition, examining the time-resolved XR signal at multiple scattering conditions for a single system can also potentially identify the structural features inducing that change. This procedure will be explored to aid determination of the adsorption sites of phosphate and silicate, as these species cannot be examined by RAXR.

RAXR. RAXR is an extension of XR for obtaining element-specific structural information at a mineral-water interface, although only on the surfaces of large (>1 mm) single crystals [191]. RAXR measurements involve a standard XR measurement and a series of RAXR spectra, where the XR at fixed scattering condition is measured as a function of energy through the adsorption edge of a target element. Unlike XAFS spectroscopy where X-ray fluorescence is commonly detected, the RAXR signal comes from the scattered beam intensity. The scattering measured in XR only occurs at the mineral-water interface, and RAXR is thus only sensitive to the target element when it occurs at the interface in a form ordered with respect to the underlying substrate. Aqueous forms of the target element, and disordered interfacial forms like non-epitaxial precipitates, are effectively invisible to RAXR. RAXR has the added benefit of being a probe of the structure factor phase, allowing for direct inversion of the data into an element-specific structure [191].

D. Project Personnel

This project will involve the research activities of the PI, one postdoctoral scientist and one graduate student per year. The postdoctoral scientist will primarily be responsible for the single crystal studies as these are challenging measurements that require substantial time spent at the Advanced Photon Source. The graduate student will work primarily on the mineral powder studies as these tasks are largely laboratory-based and involve more straightforward methods.

VI. PROJECT TIMETABLE

Year 1: Single crystal studies will explore the dependence of complex arsenate adsorption on the (012) surfaces on chemical conditions as well as investigate the variation in adsorption mechanisms on different surfaces under select conditions. Powder studies will involve mineral synthesis and characterization and systematic measurements of the adsorption behavior of arsenate on the platelets.

Year 2: Single crystal studies will explore the dependence of arsenate adsorption mechanisms and surface coverage on chemical conditions on different surfaces; initial kinetic studies on the (012) surfaces will be conducted. Powder studies will involve uptake measurements and characterization of the conventional hematite powders as well as initial kinetic measurements on the platelet suspensions.

Year 3: Single crystal studies will focus on completing the remaining measurements needed for Module 1 as well as kinetic measurements on additional surfaces, with a focus on (001) surfaces. Powder studies will focus on completing uptake and characterization work for Module 1 and conducting kinetic measurements on the conventional hematite powder.

Year 4: Single crystal studies will focus on completing the remaining measurements needed for Module 2 and conducting initial mechanistic and kinetic studies of selenate and phosphate. Powder studies will focus on completing the wet chemistry and characterization work needed for Module 2 and determining the uptake behavior and rates for selenate and phosphate on the hematite powders.

Year 5: Single crystal studies will focus on structural and kinetic measurements of the full series of oxoanions to be explored. Powder studies will likewise focus on the full series of oxoanions.

These studies will require a substantial amount of beamtime. The PI has submitted more than 25 successful beamtime proposals and has annually received the equivalent of three weeks of surface scattering time and nine days of XAFS time over the last few years. This amount of time will be more

than sufficient to complete the needed work, and the PI is confident that additional time can be obtained if needed.

VII. EXPECTED SCIENTIFIC IMPACT

The proposed research seeks to systematically explore the complexity, dynamics, and variability of oxoanion adsorption-desorption. This research will identify fundamental complexity intrinsic to mineral-water interfaces. The reactivity of doubly coordinated surface functional groups, previously considered inert, will be characterized. The number of distinct surface complexes that occur on a single mineral, an unknown yet fundamental characteristic of adsorption behavior, will be constrained. In addition, the dependence on solution conditions of the coverage of specific surface complexes on specific surfaces on iron and aluminum oxides will be determined. This may be the first study to explicitly and directly obtain such information for a series of surface complexes on multiple surfaces of a single mineral. This work may provide a mechanistic explanation for any differences in reactivity seen between different morphologies of a single mineral; such changes may occur during redox cycling [192, 193].

This research will also elucidate the dynamics of oxoanion adsorption-desorption on mineral surfaces. Intrinsic rates of specific oxoanion surface complex formation and desorption on distinct mineral surfaces will be constrained when exceedingly fast and determined when experimentally accessible. Variations in diffusion rates at different mineral surfaces will be evaluated and related to interfacial water structure. By examining diffusion-limited rates on different surfaces of a mineral, this project may be able to clearly distinguish between bulk and film diffusion effects and relate film diffusion behavior to interfacial water structure, a fundamental molecular-scale property of mineral surfaces.

This research will also characterize the variability in adsorption-desorption behavior among different oxoanions. The distribution of oxoanions between inner- and outer-sphere complexes and among inner-sphere complexes bound to functional groups in different coordination states will be assessed. This information will be used to examine trends in behavior related to oxo-ligand bond valence, molecular shape [119], ionic radius of the central cation, and dielectric constant of the substrate [115, 117, 194]. The role of diffusion, oxo-ligand exchange rates, and surface functional group exchange rates in controlling the relative kinetic behavior of these species will be assessed.

Systematic upscaling of the molecular-scale results will directly test how fundamental processes operating this scale influence macroscopic oxoanion adsorption-desorption phenomena. The relative contribution of distinct surface complexes on different surfaces of a mineral to the overall macroscopic adsorption behavior and adsorption-desorption rates will be determined, likely for the first time. A new molecular-scale mechanism, adsorption to doubly coordinated surface functional groups, may be identified that is responsible for the slow component of macroscopic oxoanion adsorption-desorption rates. The effect of particle aggregation of oxoanions adsorption behavior will be constrained.

Beyond this new fundamental knowledge, this work may provide added support to the suggestion that adsorbed ions exist in a state of dynamic equilibrium between inner- and outer-sphere sites [195, 196]. In addition, this work may clearly demonstrate dynamic feedback between ion adsorption and particle aggregation, including the molecular mechanisms responsible and the impact of this process on adsorption-desorption rates [178]. Such observation may provide the foundation needed to incorporate these phenomena into thermodynamic, kinetic, and transport models.

Finally, the proposed research will accomplish many of the stated goals of the Geosciences Research Program [106]. This research “will achieve a robust understanding of the intrinsic heterogeneity of mineral-water interface chemistry at the molecular scale, including the coupling among structure, hydration,” and “interfacial dynamics.” This work “will introduce new scientific methodologies” for “characterization of mineral surfaces in ideal and complex structural and chemical environments” and will begin to “provide a bridge between laboratory studies and field studies.” In addition, these studies “will advance modern science-based predictive capability for contaminant transport models.” Ultimately, this work will “improve our fundamental understanding of a range of complex geological systems.”

APPENDIX 1: BIOGRAPHICAL SKETCH

JEFFREY G. CATALANO

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Education: B.S. Geology, 1999, University of Illinois at Urbana-Champaign; Ph.D. Geological and Environmental Sciences, 2005, Stanford University; Postdoctoral Fellow, Environmental Research and Chemistry Divisions, Argonne National Laboratory, 2004-2007.

Research and Professional Experience:

- Assistant Professor, Department of Earth and Planetary Sciences, Washington University in St. Louis (2007-present)
- Harold Urey Postdoctoral Fellow, Environmental Research and Chemistry Divisions, Argonne National Laboratory (2004-2007)
- Graduate Teaching Assistant and Graduate Research Assistant, Department of Geological and Environmental Sciences, Stanford University (1999-2004)
- Student Assistant, US Geological Survey, Water Resources Division, Illinois Water Science Center, Urbana, IL (1997-1999).

Publications:

Dr. Catalano has published 27 peer-reviewed journal articles.

1. **Catalano J.G.**, Fenter P.A., Park C. (2009) Water ordering and relaxations at the hematite (110)-water interface. *Geochimica et Cosmochimica Acta* **73**, 2242-2251.
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.
3. **Catalano J.G.**, Park C., Fenter P., Zhang Z. (2008) Simultaneous inner- and outer-sphere arsenate adsorption on corundum and hematite. *Geochimica et Cosmochimica Acta* **72**, 1986-2004.
4. **Catalano J.G.**, Fenter P., Park C. (2007) Interfacial water structure on the (012) surface of hematite: Ordering and reactivity in comparison with corundum. *Geochimica et Cosmochimica Acta* **71**, 5313-5324.
5. **Catalano J.G.**, Zhang Z., Park C., Fenter P., Bedzyk M.J. (2007) Bridging arsenate surface complexes on the hematite (012) surface. *Geochimica et Cosmochimica Acta* **71**, 1883-1897.
6. **Catalano J.G.**, Zhang Z., Fenter P., Bedzyk M.J. (2006) Inner-sphere surface complexation of Se(IV) on the hematite (100) surface. *Journal of Colloid and Interface Science* **297**, 665-671.
7. **Catalano J.G.**, Park C., Zhang Z., Fenter P. (2006) Termination and water adsorption at the α -Al₂O₃ (012)-aqueous solution interface. *Langmuir* **22**, 4668-4673.

8. **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 α -Al₂O₃ and α -Fe₂O₃ (1T02) surfaces. *Geochimica et Cosmochimica Acta* **69**, 3555-3572.
9. **Catalano J.G.**, Brown G.E., Jr. (2005) Uranyl adsorption onto montmorillonite: Evaluation of binding sites and carbonate complexation. *Geochimica et Cosmochimica Acta* **69**, 2995-3005.
10. **Catalano J.G.**, Brown G.E., Jr. (2004) Analysis of uranyl-bearing phases by EXAFS spectroscopy: Interferences, multiple scattering, accuracy of structural parameters, and spectral differences. *American Mineralogist* **89**, 1004-1021.

Synergistic Activities:

1. **Reviewer**, National Science Foundation, Geobiology and Low-Temperature Geochemistry Program (2008-Present)
2. **Reviewer**, Stanford Synchrotron Radiation Laboratory user proposals (2004-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*, *Environmental Science & Technology*, *Geochimica et Cosmochimica Acta*, *Journal of Contaminant Hydrology*, *Surface Science*).
5. **Mentor**, Students and Teachers As Research Scientists (STARS) program (2009)

Collaborators in the Last 48 Months:

Amend, J. (Washington U.)	Nagy, K.L. (U. Illinois)
Bedzyk, M.J. (Northwestern U.)	Park, C. (ANL)
Biswas, P. (Washington U.)	Pasteris, J.D. (Washington Univ.)
Brown, C.F. (PNNL)	Petitto, S.C. (U. Alaska)
Brown, G.E., Jr. (Stanford U.)	Pierce, E.M. (PNNL)
Chaka, A.M. (NIST)	Rosso, K.M. (PNNL)
Eng, P.J. (U. Chicago)	Serne, J.R. (PNNL)
Fenter, P. (ANL)	Singer D.M. (LBNL)
Giammar, D.E. (Washington Univ.)	Smith, S.C. (PNNL)
Ghose, S.K. (U. Chicago)	Sturchio, N.C. (U. Illinois)
Heald, S.M. (ANL)	Tanwar, K. (U. Alaska)
Icenhower, J.P. (PNNL)	Trainor, T.P. (U. Alaska)
Jun, Y.-S. (Washington Univ.)	Waychunas, G.A. (LBNL)
Kelly, S.D. (ANL)	Wellman, D.M. (PNNL)
Lo, C. (Washington U.)	Zachara, J.M. (PNNL)
McKinley, J.P. (PNNL)	Zhang, Z. (ANL)

Graduate and Postdoctoral Advisors: Dr. Gordon E. Brown, Jr., Stanford University; Dr. Paul Fenter, Argonne National Laboratory

Current Graduate Student Advisees: Andrew Frierdich (Ph.D. exp 2012); Bamidele Otemuyiwa (Ph.D. exp. 2013); Alison Beehr (Ph.D. exp. 2013)

APPENDIX 2: CURRENT AND PENDING SUPPORT

Investigator: Jeffrey 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: Bacterial Effects on Uranium and Technetium Incorporation into Carbonates I			
Source of Support: Department of Energy/BER-ERSP			
Total Award Amount: \$307,830		Total Award Period Covered: 1/1/10- 12/31/12	
Location of Project: Washington University			
Person-Months Per Year Committed to the Project.	0.5	Cal:	Acad: Sumr: 0.5
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			
Source of Support: American Chemical Society Petroleum Research Fund			
Total Award Amount: \$50,000		Total Award Period Covered: 9/1/08 - 8/31/10	
Location of Project: Washington University			
Person-Months Per Year Committed to the Project.		Cal:	Acad: 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: ETBC: Hidden Iron Oxide Redox Processes During Biogeochemical Iron Cycling: Control on Nanoscale Transformations and the Fate of Contaminants			
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			
Person-Months Per Year Committed to the Project.		Cal:	Acad: 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: Phosphate Controls on Subsurface Uranium Fate and Transport: Connecting Molecular-Scale and Sediment-Scale Processes			
Source of Support: Department of Energy/BER-ERSP			
Total Award Amount \$736,689		Total Award Period Covered: 1/1/10 – 12/31/12	
Location of Project: Washington University			
Person-Months Per Year Committed to the Project.		Cal:	Acad: 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: Acquisition of an Inductively-Coupled Plasma Optical Emission Spectrometer for Geoscience Research at Washington University in St. Louis			
Source of Support: NSF / I&F			
Total Award Amount \$101,547		Total Award Period Covered: 1/1/10 – 12/31/10	
Location of Project: Washington University			
Person-Months Per Year Committed to the Project.		Cal:	Acad: Sumr:

Support: Current Pending Submission Planned in Near Future *Transfer of Support

Project/Proposal Title: Complexity, Dynamics, and Variability of Oxoanion Absorption-Desorption Reactions and the Connection to Macroscopic Processes – THIS PROPOSAL

Source of Support: Department of Energy

Total Award Amount: \$819719 Total Award Period Covered: 3/1/10- 2/28/15

Location of Project: Washington University

Person-Months Per Year Committed to the Project. 1.0 Cal: Acad: Sumr: 1.0

APPENDIX 3: BIBLIOGRAPHY & REFERENCES CITED

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APPENDIX 4: FACILITIES & OTHER RESOURCES

Research will be performed at Washington University in St. Louis with additional measurements made at the Advanced Photon Source, a DOE-supported national user facility. Research facilities and other resources available are summarized below. Major equipment available is also 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 systems, centrifuges, magnetic stir plates, ultrasonicators, syringe pumps, peristaltic pumps, and fraction collectors. 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.

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-K α 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.

Department of Physics

The Department of Physics contains a number of scientific resources. The most relevant to this project is the machine shop, which will be used to construct X-ray sample cell and continuous-flow stirred-tank reactors.

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 (including ATR crystals) for the analysis of solids, liquids, and suspensions. Also available is a Malvern Zetasizer ZS instrument capable of particle size analysis by dynamic light scattering and zeta potential measurements.

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 Drs. Catalano and Giammar are members. A JEOL 2100F transmission electron microscope (TEM) equipped with an energy-dispersive X-ray spectrometer is available for analysis of composition in few-nm sized volumes. This instrument is outfitted with an electron-energy-loss spectrometer, a high resolution CCD camera, and a film camera for recording diffraction patterns. 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.

Laboratory for Space Sciences

A Cameca IMS 3f SIMS ion microprobe, a Cameca NanoSIMS 50 ion microprobe with high mass resolution multicollector, and a PHI 700 Scanning Auger Nanoprobe are available for use through collaborative agreement with the Laboratory for Space Sciences.

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 Sprit TEM, a Scanning Mobility Particle Sizer, and a gold coater is available for preparing SEM samples for analysis. The NRF will be acquiring a Malvern Zetasizer ZS and an ICP-MS within the next two to three months using funding currently in place.

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 and Surface X-ray Scattering measurements at 5-ID, 6-ID, 13-ID, 13-BM, 20-ID, and 33-ID-D. Sample preparation space is available in wet chemistry laboratories at this facility.

APPENDIX 5: EQUIPMENT

Major equipment available to this project is described in Appendix 4: Facilities & Other Resources for the sake of clarity.