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TITLE OF PROPOSED PROJECT Influence of Interfacial Water Structure and Surface Functional Group Coordination on Arsenate Absorption-Desorption Mechanisms and Rates						
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PROJECT SUMMARY

Intellectual Merit: Oxoanion adsorption-desorption reactions controls the environmental fate of common naturally-occurring surface and groundwater contaminants, toxins released during energy production, and toxic or radioactive components of nuclear waste. Understanding the mechanisms and kinetics of these reactions is essential for credibly predicting the migration of contaminants in natural and contaminated systems and for providing a fundamental basis for the development of remediation and water filtration strategies needed to protect human health. The mechanisms and kinetics of adsorption-desorption reactions are largely controlled by surface functional group reactivity and interfacial water structure. Critical knowledge gaps exist regarding how fundamental molecular-scale features of mineral-water interfaces, including interfacial water ordering and surface functional groups coordination, affect the adsorption-desorption mechanisms and rates of oxoanion contaminants.

Filling these key knowledge gaps regarding the role interfacial water ordering and surface functional group coordination play in controlling oxoanion adsorption-desorption is best accomplished through fundamental studies of arsenate interactions with iron and aluminum oxide surfaces. The overall objective of this proposal is to determine how fundamental interfacial properties affect the mechanisms and rate of arsenate adsorption-desorption on iron and aluminum oxides. Specific objectives are to: (1) determine the impact of interfacial water structure and surface functional group coordination on arsenate adsorption mechanisms on iron and aluminum oxide surfaces; (2) elucidate the relative role of bulk diffusion, film diffusion through ordered interfacial water, and the water exchange rates of surface functional groups in distinct coordination states in controlling the kinetics of arsenate adsorption-desorption on these surfaces; and (3) characterize how these processes are manifested and modified by interparticle interactions, including aggregation, in multi-particle systems.

The proposed research seeks to systematically explore how molecular-scale interfacial properties affect the mechanisms and rates of arsenate adsorption-desorption. This research will identify the mechanisms of arsenate adsorption on iron and aluminum oxide surfaces and determine how these relate to surface functional group coordination and interfacial water structure. This research will also elucidate how interfacial properties control arsenate adsorption-desorption rates on mineral surfaces. Systematic upscaling of the molecular-scale results will directly test how fundamental processes operating at this scale influence macroscopic oxoanion adsorption-desorption phenomena. Finally, this work may demonstrate dynamic equilibrium between inner- and outer-sphere adsorbates and dynamic feedback between ion adsorption and particle aggregation.

Broader Impacts: The research to be conducted under this proposal will greatly enhance the understanding of chemical processes responsible for the adsorption of a major global water contaminant. This work will provide a foundation for development of advanced water filtration systems and lead to an improved ability to predict the migration of contaminants in aquatic systems. The results of this work will be disseminated at national and international conferences and in peer-reviewed scientific journals and will also be incorporated into undergraduate and graduate courses. This project will also provide training to the next generation of scientists. A postdoctoral scientist, a graduate student, and two to three undergraduate students will receive training and conduct research associated with this project. In addition, five high school students recruited through a local science education program will serve 6-week summer internships.

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PROJECT DESCRIPTION

I. MOTIVATION

Chemical processes occurring at mineral-water interfaces are important to water quality [1], contaminant transport [2], the 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 naturally-occurring water contaminants [1], toxins released during energy production [8], or toxic or radioactive components of nuclear waste [9, 10]. Understanding the mechanisms and kinetics of oxoanion adsorption-desorption is thus essential for credibly predicting the migration of contaminants in natural and contaminated systems and for providing a fundamental basis for the development of remediation and water filtration strategies needed to protect human health. As adsorption-desorption mechanisms and kinetics are largely controlled by surface functional group reactivity and interfacial water structure [11], probing the interaction of oxoanions with molecular-scale features of mineral-water interfaces is required to meet this need.

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 in the environment [12-101]. While spectroscopic probes have inferred mechanistic origins for macroscopic oxoanion behavior [12-27] that can be employed in thermodynamic models [28-38], recent studies by the PI suggest that key mechanisms, notably outer-sphere adsorption, have been overlooked in the case of arsenate [41, 43]. Preliminary data (Section IV) documents additional unexpected complexity in the adsorption mechanisms displayed by arsenate, suggesting that the current conceptual models of oxoanion adsorption mechanisms are lacking. It is unclear how these mechanisms actually depends on fundamental properties of mineral-water interfaces, including interfacial water ordering and surface functional group coordination state, and how the effects of these molecular-scale features are manifested at the macroscopic scale.

The kinetics of oxoanion adsorption-desorption also play a critical role in controlling the fate of these species in the environment [102]. Macroscopic adsorption-desorption rates of oxoanions have been determined (e.g., [82, 86, 97]), but these appear to be orders of magnitude slower than intrinsic reaction rates determined from pressure-jump relaxation measurements [50, 73, 74, 94, 98-100]. Although 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 [47, 64, 86, 97]. While these processes are likely affected by film diffusion through ordered interfacial water and the exchange rates of surface functional groups in multiple coordination states, how such interfacial properties actually affect oxoanion adsorption-desorption kinetics is unclear.

The uncertainty in how fundamental molecular-scale features of mineral-water interfaces, including interfacial water structure and surface functional groups coordination, affect the adsorption-desorption mechanisms and rates of oxoanion contaminants is a critical knowledge gap. Of particular concern is the oxoanion arsenate as the adsorption of this species is a primary control on arsenic mobility in the environment and arsenate-sorbed iron oxides are the likely source term for arsenic-contaminated water in many locales, including Southeast Asia [1, 103-105]. Iron and aluminum oxides are important sorbents of arsenate in natural and water treatment systems [1] and are ideal materials for fundamental studies as isostructural forms of these classes of solids exist and their functional groups are expected to display similar reactivity towards arsenate adsorption [41].

Filling key knowledge gaps in the current understanding of the role interfacial water structure and surface functional group coordination play in controlling oxoanion adsorption is best accomplished through fundamental studies of arsenate interactions with iron and aluminum oxide surfaces.

II. PROJECT OBJECTIVES

The overall objective of this proposal is to determine how fundamental interfacial properties affect the mechanisms and rate of arsenate adsorption-desorption on the surfaces of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and corundum ($\alpha\text{-Al}_2\text{O}_3$). Specific objectives are:

1. Determine the impact of interfacial water structure and surface functional group coordination on arsenate adsorption mechanisms on hematite and corundum surfaces.
2. Elucidate the relative role of bulk diffusion, film diffusion through ordered interfacial water, and the water exchange rates of surface functional groups in distinct coordination states in controlling the kinetics of arsenate adsorption-desorption on these surfaces.
3. Characterize how these processes are manifested and modified by interparticle interactions, including aggregation, in multi-particle systems.

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 [37, 106-117] 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 [32-36, 84, 88, 106-110, 117-129] 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, $>\text{Al-OH}_2^{+1/2}$ sites on the edge of gibbsite [$\gamma\text{-Al(OH)}_3$] are predicted to display similar behavior as the same type of sites on the surface of corundum [$\alpha\text{-Al}_2\text{O}_3$] 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 [12-101]. Most oxoanions are suggested to form inner-sphere complexes, with bridging bidentate species predominant [12, 13, 15-24, 26, 39-43, 45, 46, 49, 51, 61, 63, 66-68, 75, 76, 80, 85, 89, 90, 130-134]. Some oxoanions (arsenite, selenite, selenate, sulfate, chromate, and molybdate) have been suggested to also form outer-sphere species [12, 18, 27, 49, 77-80], 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 [41] because outer-sphere species generally lack a diagnostic signature in such spectra. As described below, the PI has 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 [50, 73, 74, 94, 98-100]. 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. Although 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 the 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 by the rate of surface functional group exchange [144], 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 [47, 75, 82, 97, 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 [47, 64, 75, 83, 86, 97]. 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 [47, 64, 86] or to heterogeneity in surface reaction energetics [97]. The Zhang and Stanforth [97] 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 that 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 [14, 82], and have similarly displayed dual (i.e., fast and slow) release rates from goethite upon addition of phosphate [75] and from kaolinite [83]. Other oxoanions also display this behavior (e.g., [153]). Similar to adsorption, intrinsic desorption rates inferred from pressure-jump relaxation measurements [50, 73, 74, 94, 98-100] 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 [154, 155], 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

In order to obtain structural information to complement prior vibrational spectroscopy studies of water on oxide surfaces (e.g., [156, 157]), the PI has recently made a series of measurements to investigate interfacial water ordering near (012), (110), and (001) surfaces of hematite and corundum [158-162]. 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 on 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 water sites that are directly adsorbed to surface functional groups is more ordered on hematite; 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, 160, 161].

The (001) surface of corundum 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) [41] the PI 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 10^{-3} M). This demonstrates that at the pH and ionic strength condition studied these species had approximately equivalent affinity for each surface.

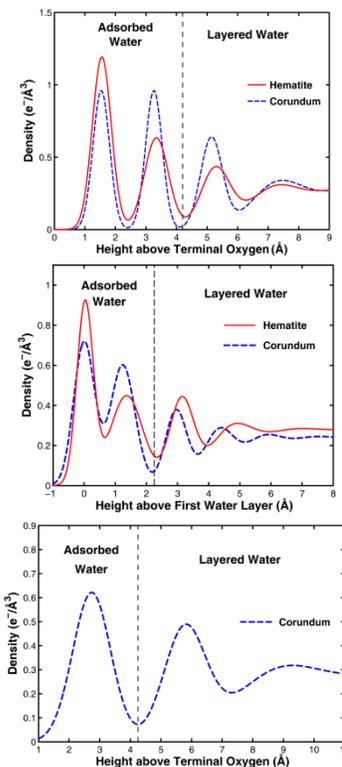


Figure 1. Interfacial water structure near hematite and corundum (012) (top), (110) (center), and (001) (bottom).

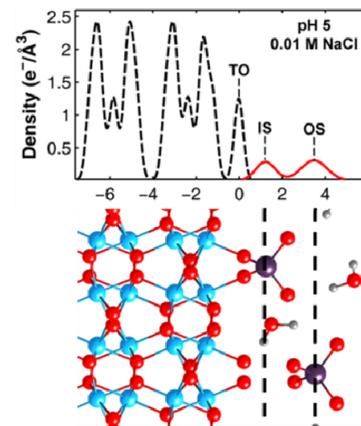


Figure 2. Inner- and outer-sphere arsenate complexes on (012) surfaces and their spatial relationship.

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. This observation conflicts with 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.

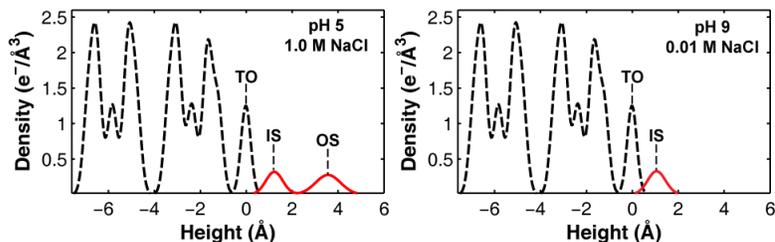


Figure 3. Distribution of arsenate surface complexes at the corundum (012) surface at pH 5 and 1 M NaCl (left) and at pH 9 and 0.01 M NaCl (right).

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 [163]. Given the expected unreactivity of doubly coordinated oxygen groups [109, 164] arsenate was predicted to adsorb 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.

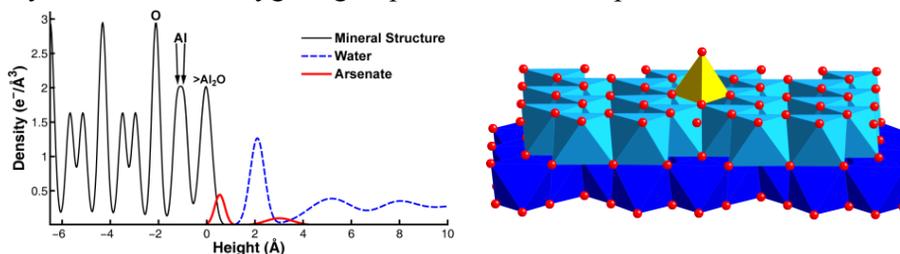


Figure 4. (left) Arsenate distribution above the corundum (001) surface. (right) Inner-sphere adsorption geometry on this surface

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.

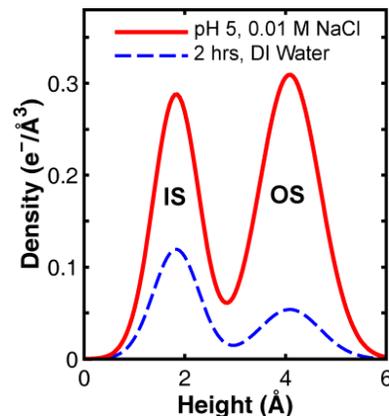


Figure 5. Arsenate distribution on the corundum (012) surface before and after desorption in DI water.

V. RESEARCH PLAN

A. Overall Research Approach

The proposed research will be conducted using a two-step approach designed to first determine how interfacial properties affect arsenate adsorption-desorption mechanisms and rates and then apply this information to explain macroscopic-scale processes. 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 arsenate 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 systematically explore how interfacial water ordering and surface functional groups of various coordination states affect and control arsenate adsorption-desorption mechanisms and kinetics. Single crystal surfaces allow for detailed characterization of interfacial reactions and method for reproducibly preparing surfaces of known structure are already established [158-162, 165]. In the second step, macroscopic adsorption-desorption behavior and rates will be studied on a powder consisting of monodispersed single crystal microplatelets (**Fig. 6B**) bound primarily by {001} and {012} faces. The reactivity of the microplatelets will be dominated by these surfaces, allowing for direct connection to the single crystal studies on these same surfaces while providing a system where the effects of interparticle interactions, especially aggregation can be examined directly.

Further comments on the selection of mineral substrates are warranted. The use of both hematite and corundum single crystals is motivated by practical constraints and scientific interests. While the PI currently possesses a small collection of hematite single crystal substrates for use in this and other projects, obtaining additional substrates is difficult (one current known supplier; only natural materials available as practical growth methods are lacking) and expensive (~\$500 per crystal). While some additional substrates will be obtained as part of this project, the number of available substrates constrains the efficiency with which single crystal studies involving hematite may be completed. This is because 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 pristine 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 in large quantities 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 [41, 158-162]. 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 [166-171] observed between corundum and hematite (001) surfaces are predominantly the result of differences in surface structure [163, 172] (i.e., the *surfaces* used in these studies were not isostructural) and not a fundamental difference in chemical affinity of these two substrates. A

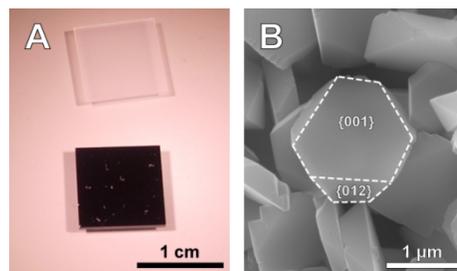


Figure 6. Size range of iron and aluminum oxide substrates: (A) Photograph of hematite (dark) and corundum single crystals. (B) SEM image of monodispersed hematite single crystal microplatelets showing distinct crystallographic faces.

separate study conducted by the PI that suggested uranyl binds differently to the corundum and hematite (012) surfaces [173] is fundamentally flawed as the structural model used for the corundum (012) surface [174] included the wrong surface termination [162]. 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 reactivity of isostructural hematite and corundum surfaces 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 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, 145, 160, 161, 164]. 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 microplatelets. Corundum cannot be synthesized directly from aqueous solution under ambient conditions, and while commercial single crystal powders of corundum exist [175], the lack of synthesis control is a concern in using such materials in fundamental studies.

B. Research Modules

The proposed research is divided into two distinct modules designed to explore how interfacial properties affect arsenate adsorption mechanisms and adsorption-desorption rates. In addition, each module seeks to determine how key molecular-scale interfacial properties influence overall macroscopic-scale phenomena. Each module description contains a set of major hypotheses to be tested.

Module 1 –Mechanisms of Arsenate Adsorption

i. Motivation and Overview

Work recently published by the PI [41, 43] 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 [12, 14-17, 19, 23, 26, 39, 40, 46, 49, 51, 61, 63, 66, 67, 75, 85, 90, 130, 131, 133, 134], prior work by the PI 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, suggesting a strong specific interaction with surface functional groups. In addition, the location of outer-sphere arsenate species suggests that the oxo-ligands 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 [176]. Finally, aggregation affects macroscopic oxoanions adsorption [154] 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 how surface functional group

coordination state and interfacial water structure control arsenate adsorption mechanisms on hematite and corundum surfaces and to determine how such effects are 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 mechanisms on different crystallographic surfaces of a single mineral reflects the type and arrangement of surface functional groups and interfacial water structure.*
3. *These effects are manifested in systems composed of mineral powders but are modified by particle aggregation.*

iii. Proposed Research

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 [160-163, 165, 172, 177]. The PI has extensive experience working with all of these and has 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 [172]. The PI is 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 [160-162].

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 varies as a function of equilibrium 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.

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 variation in reactivity towards arsenate displayed by isostructural surfaces of corundum and hematite. Together this information will establish the variability in reactivity of surface functional groups in a single coordination state towards arsenate, the difference in reactivity of surface functional groups in different coordination states, and the role of interfacial water in outer-sphere arsenate adsorption.

Mineral powder studies. A combination of laboratory-based wet chemical and analytical methods and synchrotron-based spectroscopic methods will be employed to systematically investigate arsenate adsorption behavior on monodispersed suspensions of hematite single crystal microplatelets. These studies are designed to connect the fundamental observations made on single crystal surfaces with the behavior displayed by mineral powders. This will be accomplished by examining macroscale adsorption behavior and molecular-scale adsorption mechanisms on hematite microplatelets 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 studies will begin with a series of wet chemical measurements to characterize the macroscopic arsenate adsorption behavior of the microplatelets. 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 (DLS) and atomic force microscopy (AFM). Aggregation will also be investigated ex situ using electron microscopy [154, 155]. 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. Spectroscopic 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.

Further work will seek to determine the surface-specific (i.e., on {001} or {012}) arsenate concentrations using Auger nanoprobe measurements. 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 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., [97]); 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.

Module 2 – Rates 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 models to describe this behavior, these processes are often temporally variable in environmental systems. It is thus critical to also assess the fundamental controls of the rates 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 [50]. 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 through interfacial water (i.e., film diffusion) and the exchange rate of singly-coordinated surface functional groups. While the former has not been characterized experimentally to date, the latter likely occurs on the same timescale [145, 164] 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 [41]. 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 [47, 75, 82, 97, 152]. These macroscopic rates typically show a “fast” (10s of minutes) and “slow” (10s of hours) 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 [14, 75, 82, 83]. 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 arsenate adsorption does not depend on particle aggregation [97], although aggregation does appear to affect phosphate desorption [154]. Diffusion-controlled adsorption in pores is also an uncertain explanation as intrinsic desorption rates are rapid (~100 ms) and desorption and release from pores into bulk solution should also show similar diffusion limited rates. Diffusion rates into and out of pores may not differ by the extent needed 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 [14].

These past observations suggest a surface reaction [97] 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 is dependent on protonation state (pKa values of 2.24, 6.96, and 11.50), with exchange half-lives of ~2 hours for H_2AsO_4^- , ~16 hours for HAsO_4^{2-} , and ~130 hours for AsO_4^{3-} [139, 178]. $\mu_2\text{-OH}$ 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 [144, 149]. However, similar groups on gibbsite appear to exchange at much slower rates [179]. 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 verify that intrinsic adsorption-desorption rates are fast and diffusion limited when the reactive surface site is a singly coordinated functional group, to evaluate the variability in film diffusion rates on different hematite and corundum surfaces and the connection to interfacial water structure, to explore possible surface reaction controls (i.e., adsorption onto doubly coordinated surface functional group) on the slow component of arsenate adsorption-desorption, and to characterize how these effects are modified in multi-particle systems by particle aggregation.

ii. Major Hypotheses:

- 1. Adsorption-desorption reactions involving outer-sphere species and inner-sphere species bound to singly coordinated 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

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 generally 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 [180]. RAXR measurements will only be employed under conditions where the timescale of change in surface coverage substantially exceeds the approximately 10 minutes required to obtain a RAXR spectrum [41].

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 (pH 5) and where only inner-sphere species are present (around pH 9 based on preliminary measurements; see Section IV.B.). These will seek to verify that the adsorption and desorption of both species are rapid, as expected based on a previous study [50]. Time-resolved XR measurements will primarily be able to obtain at best ~3 s time resolution by employing detector systems currently in use by the PI, and counting statistics constrains the minimum time resolution to ~100 ms. As these are generally 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 [161]. 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 [181], 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 both arsenate oxo-ligands 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. A combination of laboratory-based wet chemical and analytical methods and synchrotron-based spectroscopic methods will be used to investigate arsenate adsorption-desorption rates on suspensions of hematite single crystal platelets. These studies are designed to connect the fundamental rate measurements made on single crystal surfaces and suggested by pressure-jump relaxation studies [50] with the kinetics displayed by mineral powders. This will be accomplished by examining macroscopic-scale adsorption-desorption rates on hematite microplatelets 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 [154].

The rates of adsorption of arsenate on hematite platelets 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 [47, 75, 82, 97, 152, 153]. 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 the microplatelet suspensions. 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 microplatelets after desorption will be conducted to determine if the distribution of arsenate between the {012} and {001} surfaces changes.

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 [158-163, 165, 172-174, 177, 180, 182-190]. In situ time-resolved XR allows one to probe dynamic changes in surface structure in real time [180, 191-193]. 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 [180, 191-193]. 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. 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.

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 [194]. 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 is determined from the elastically-scattered beam intensity. The scattering measured in XR only originates 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 [194].

D. Project Personnel

This project will involve the research activities of the PI, one half-time postdoctoral researcher, one graduate student, and one undergraduate student per year. The postdoctoral researcher will primarily be responsible for the single crystal studies involving corundum, as these require exploring a broader range of conditions and will be the first to be probed using time-resolved XR. The full-time graduate student will be responsible for the hematite work, broken down into three projects: single crystal adsorption mechanisms, single crystal adsorption-desorption kinetics, mineral suspension studies. The postdoctoral researcher will assist with the single crystal and mineral suspension studies. An hourly undergraduate will work on a subset of the mineral suspension studies each year and be given the opportunity to incorporate this work into an undergraduate thesis. The PI will conduct a subset of the single crystal studies and provide overall training and project management.

In addition to these primary personnel, 1-2 local high school students will serve 6 week internships each summer. These will be recruited through the Students and Teachers as Research Scientists (STARS) program organized by the University of Missouri-St. Louis. Each student recruited through this program receives training on conducting research, including the reporting of results. The students conduct mini-research projects and then prepare research reports. Every project year one student will be recruited and supervised by the postdoctoral scientist. In years 2 and 3 a second student will be recruited and supervised by the graduate student. Both high school interns will work on small projects related to arsenate adsorption-desorption on the hematite microplatelets.

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 microplatelet synthesis and characterization and systematic measurements of the adsorption behavior of arsenate.

Year 2: Single crystal studies will explore the dependence of arsenate adsorption mechanisms and surface coverage on chemical conditions on different surfaces; kinetic studies on the

(012) surfaces will also be conducted. Powder studies will involve characterization of the arsenate-sorbed microplatelets as well as initial kinetic measurements.

Year 3: Single crystal studies will focus on kinetic measurements on additional surfaces. Powder studies will focus on conducting kinetic measurements on the microplatelet suspensions.

These studies will require a substantial amount of beamtime. The PI has annually received the equivalent of three weeks of surface scattering time and nine days of XAFS time over the last few years awarded through a peer-reviewed process. This amount of time will be more than sufficient to complete the needed work, and additional time each year will be obtained if needed.

VII. EXPECTED SCIENTIFIC IMPACTS

The proposed research seeks to systematically explore how molecular-scale interfacial properties affect the mechanisms and rates of arsenate adsorption-desorption. This research will identify the mechanisms of arsenate adsorption on iron and aluminum oxide surfaces and determine how these relate to surface functional group coordination and interfacial water structure. The reactivity of doubly coordinated surface functional groups, previously considered inert, will be characterized. In addition, the dependence on solution conditions of the coverage of specific arsenate 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 [195, 196].

This research will also elucidate how interfacial properties control arsenate adsorption-desorption rates on mineral surfaces. Intrinsic rates of formation and desorption of specific oxoanion surface complexes on distinct mineral surfaces, which are directly related to the exchange rates of surface functional groups, 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.

Systematic upscaling of the molecular-scale results will directly test how fundamental processes operating at 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 as 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 [197, 198]. 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 [181]. Such observations may provide the foundation needed to incorporate these phenomena into thermodynamic, kinetic, and transport models.

VIII. BROADER IMPACTS

The research to be conducted under this proposal will greatly enhance our understanding of the chemical processes responsible for the adsorption-desorption behavior of a major global water contaminant. This work will provide a foundation for development of advanced water filtration systems and lead to an improved ability to predict the migration of contaminants in aquatic systems. The results of this work will be disseminated at national and international conferences and through publication in peer-reviewed scientific journals. These results will also be incorporated into an undergraduate course, Environmental Geochemistry, and a graduate course, Mineral in Aqueous Environments, taken by students obtaining degrees in Environmental Studies, Earth and Planetary Sciences, Environmental Engineering, Chemical Engineering, and Chemistry.

This project will also provide training to the next generation of scientists in the broadest sense. A postdoctoral scientist involved in the project will receive advanced training in novel, synchrotron-based surface X-ray scattering methods and will learn how to access synchrotron lightsource facilities. A graduate student will gain training in similar methods and be prepared for a career in Environmental Chemical Sciences. Two to three undergraduate students will conduct research over the life of this project. 75% of the undergraduate students conducting research with the PI have been women and these activities have helped direct them to pursue graduate studies in Science, Technology, Engineering, and Mathematics (STEM) fields. A total of five high school students will serve 6-week summer internships over the life of this proposal. These students are recruited through the Students and Teachers as Research Scientists (STARS) program organized by the University of Missouri-St. Louis, and are largely pulled from the St. Louis, MO metropolitan area, which has a large population of minority groups underrepresented in STEM fields. The PI has an established relationship with the STARS program, and the STARS student that interned with the PI during the summer of 2009 received from the program an Award for Excellence in Research.

IX. RESULTS FROM PRIOR NSF SUPPORT

J.G. Catalano (PI). EAR-0818354, \$340,505, 8/15/08 – 7/31/11. *ETBC: Hidden iron oxide redox processes during biogeochemical iron cycling: Controls on nanoscale transformations and the fate of contaminants*

Biogeochemical iron cycling involves the microbially-driven alteration of iron between the ferrous (+2) and ferric (+3) oxidation states. This cycling is never instantaneous and these species often coexist and react with each other in natural systems. This project explores nanoscale surface transformations of the iron(III) oxide hematite activated by aqueous Fe(II) and how these transformations affect nutrient availability and contaminant fate. Initial findings from the first project year include: 1) Water orders near the hematite (110) surface; 2) Fe(II) induces orientation-dependent surface transformations on hematite surfaces at both acidic and neutral pH. These transformations are driven by electron transfer processes but no net Fe oxidation or reduction occurs; 3. Fe(II) adsorbs at a lower pH on nanoparticles of hematite than on larger hematite particles; 4. Fe(II) causes adsorbed Ni(II) to become incorporated into hematite but has no effect on adsorbed arsenate speciation. This project has supported the research activities of two graduate students and four undergraduate students (including three female students interested in pursuing careers in science and engineering), and also facilitated a 6-week summer internship for a high school student recruited through the STARS program. The following publications have resulted from this project:

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. Catalano J.G., Rosso K.M., Fenter P., Park C., Zhang Z. (2010) Structure and oxidation state of hematite surfaces reacted with aqueous Fe(II) at acidic and neutral pH, *submitted*.

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BIOGRAPHICAL SKETCH

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Professional Preparation: 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:

Five Related Publications:

- 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.
- 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.
- 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.
- 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.
- 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.

Five Other Significant Publications:

- 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.
- 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.

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 (1102) surfaces. *Geochimica et Cosmochimica Acta* **69**, 3555-3572.

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.

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

Collaborators in the Last 48 Months:

Amend, J. (Washington U.)

Bedzyk, M.J. (Northwestern U.)

Biswas, P. (Washington U.)

Brown, C.F. (PNNL)

Brown, G.E., Jr. (Stanford U.)

Chaka, A.M. (NIST)

Eng, P.J. (U. Chicago)

Fenter, P. (ANL)

Giammar, D.E. (Washington Univ.)

Ghose, S.K. (U. Chicago)

Heald, S.M. (ANL)

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Jun, Y.-S. (Washington Univ.)

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Park, C. (ANL)

Pasteris, J.D. (Washington Univ.)

Petitto, S.C. (U. Alaska)

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Serne, J.R. (PNNL)

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Smith, S.C. (PNNL)

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

Thesis Advisor and Postgraduate-Scholar Sponsor: Andrew Frierdich (Ph.D. exp 2012); Bamidele Otemuyiwa (M.S. exp. 2010); Alison Beehr (Ph.D. exp. 2013); Yun Luo (Post-doc 2009-Present)

BUDGET JUSTIFICATION

A. Senior Personnel.

The PI will spend substantial time managing the project and conducting experiments and requests support in the form of one month of summer salary per year.

B. Other Personnel.

Support is requested for one graduate students and one half-time postdoctoral scientist each year. The distribution of tasks for these individual is documented in the project description. The graduate student stipend is set annually by Washington University. The postdoctoral salary reflects the typical starting rate for earth science postdoctoral scientists at Washington University. Funds are also requested for support of an hourly undergraduate student.

C. Fringe Benefits.

Fringe benefits for personnel at Washington University are calculated using standard university rates.

D. Permanent Equipment.

None.

E. Travel.

Travel support is requested for:

- a. 2 person-trips in year one and 3 person-trips in years two and three (\$1000/trip) for the graduate student, postdoctoral scientist, and PI to attend technical conferences to present the results of their work.
- b. 6 person-trips per year (\$600/trip) to conduct X-ray Absorption Spectroscopy and Surface X-ray Scattering measurements at the Advanced Photon Source in Argonne, IL.

F. Trainee/Participant Costs.

None.

G. Other Direct Costs.

1. Materials and Supplies: Support is requested for the acquisition of expendables, supplies, and minor equipment associated with laboratory analyses and lab usage. Major expenses include labware, pH probes, polishing supplies, analytical equipment supplies, chemicals, DI water filtration cartridges, X-ray spectroscopy and scattering sample cell materials, and corundum single crystals. Additional support is requested in year one for the acquisition of hematite single crystals (\$2500) and construction of flow-through X-ray sample cells (\$500) and in year two for the acquisition of components for and construction of continuous-flow stirred-tank reactors (\$2000).
2. Publication Costs: None.
3. Consultant Services: None.
4. Computer Services: None.
5. Subcontracts: None.
6. Other: Support is requested for:

- a. The cover the cost of shipping hazardous materials from Washington University to the APS for measurements.
- b. Costs for other analytical methods (e.g., ICP-MS, AFM, XRD, Auger nanoprobe, DLS, zeta potential, electron microscopy) used in sample characterization. Usage of these instruments requires payment of an hourly fee (in the range of \$8-40/hour) to support the basic operation and instrument consumables. The largest cost will be the ICP-MS analyses of aqueous samples, especially from the flow-through reactor studies; these necessitate the added analytical expenses in years 2 and 3.

I. Indirect Costs.

See individual budget pages for justification.

Current and Pending Support

Investigator: Jeffrey Catalano	Other agencies (including NSF) to which this proposal has been/will be submitted.
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 Source of Support: Department of Energy 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 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/GEO-BIO 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 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:	

FACILITIES, EQUIPMENT, AND 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, and related equipment. The laboratory includes an Agilent Technologies 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, including a CCD area detector, 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 Dr. Catalano is a member. A JEOL 2100F scanning field emission transmission electron microscope (TEM) equipped with a Gatan Tridiem electron energy-imaging filter (GIF) with spectrum imaging package (STEMPack) capable of electron energy loss spectroscopy (EELS), electron energy loss spectrum imaging, and electron energy filtered (EF) imaging. The microscope is equipped with several retractable electron detectors that can be used to form STEM images: JEOL high angle annular (HAA)-dark-field (DF) detector, JEOL bright field (BF) detector, Gatan Model 805 BF/annular-DF detectors and a Gatan Model 806 HAA-DF detector. The HAA-DF detectors can measure electrons at high scattering angles (50–165 mR) where scattering is approximately incoherent, providing z-contrast images. The Gatan HAA-DF detector is located near the entrance aperture plane of the GIF Tridiem enabling concurrent acquisition of STEM DF images along with either GIF spectrum images, EELS spectra, or energy filtered images. The microscope also has a retractable Gatan Orius 2.7 x 4K pixel fiber optically coupled CCD camera mounted on-axis directly above the GIF for obtaining electron 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 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 for dynamic light scattering (DLS) and zeta potential measurements of particle suspensions and Perkin Elmer Elan DRC II ICP-MS and Optima 7300DV ICP-OES systems for determining the composition of aqueous samples by the end of 2009 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.

POSTDOCTORAL RESEARCHER MENTORING PLAN

One postdoctoral researcher will be funded half-time by this project. The postdoctoral researcher will be responsible for a subset of the proposed research as described in the project description. During this project the postdoctoral researcher will receive mentoring from the PI and provided opportunities for professional development in order to prepare the researcher for a scientific career. These mentoring and development activities will include:

- Creation of a personal development plan for the researcher. This plan, developed jointly by the PI and postdoctoral researcher, will outline the professional development goals of the researcher and establish a series of experiences, training, and development activities to be accomplished during the appointment. This plan will include a set of responsibilities for both the postdoctoral researcher and the PI.
- Enrollment in the Professional Development Program organized by the Office of Post Graduate Affairs at Washington University. This consists of an approximately monthly seminar series that covers all aspect of professional development, including obtaining funding, mentoring, communication, presentation skills, research integrity, lab management, and time management.
- Training in accessing and conducting research at national synchrotron lightsource facilities. This will include not only how to perform the methods employed in this project but also how to obtain time, the selection of beamlines to work at, and understanding the bureaucratic and organizational structure of these facilities. These are essential but underappreciated skills.
- Providing a number of opportunities to develop presentation skills. The PI's research group has bi-weekly group meetings at which members present their recent results. The postdoctoral researcher will give presentations at these meetings at least 4 times a year. The postdoctoral researcher will also be encouraged to present his or her research annually at a departmental brown bag lunch seminar as well as at the Center for Materials Innovation research forum that occurs twice a year.
- Attending at least one conference per year to present research associated with this project and to establish contacts in the field.
- Providing opportunities to meet with and/or attend dinner with scholars visiting campus to present research in the colloquia of a number of departments or the Center for Materials Innovation.
- Providing training and experience in scientific writing (including proposals). Obtaining beamtime requires submission of short (3-page) proposals that go through a peer-review process. The postdoctoral researcher will prepare 2-3 beamtime proposals per year with the assistance of the PI. The researcher will also author and co-author publications with the PI and students, receiving guidance throughout the process. The postdoctoral researcher will also participate in workshops on grant writing and publishing in scientific journals offered by the Office of Post Graduate Affairs.
- Providing opportunities to develop teaching skills. The postdoctoral researcher will be encouraged to guest lecture in undergraduate and graduate courses taught by the PI and other faculty members. The PI will attend these lectures and provide feedback on ways to improve instructional effectiveness. Following these activities the PI will assist the researcher in developing a teaching portfolio.
- Providing opportunities to develop mentoring skills. The researcher will co-mentor with the PI the undergraduate student working on the project. In addition, each summer the postdoctoral researcher will mentor a high school student during a 6-week internship organized by the Students and Teachers as Research Scientists (STARS) program of the University of Missouri at St. Louis.