

PROJECT SUMMARY

Intellectual Merit: The availability and speciation of phosphate and trace elements in sediments, soils, and aquatic systems are strongly affected by biogeochemical cycling involving iron and manganese oxide minerals. These phases are commonly thought to affect the fate of such elements through passive means such as adsorption and coprecipitation. However, recent studies, including by the PI, have demonstrated that in systems where aqueous Fe(II) and solid Fe(III) oxides coexist, active secondary abiotic interfacial atom exchange and electron transfer reactions drive nanoscale surface transformations of the mineral phase during biogeochemical cycling. We have shown that these interfacial self-exchange processes between aqueous Fe(II) and Fe(III) oxides may lead to both trace element incorporation and release. Although less well studied, similar processes appear to occur for common manganese oxides.

While mineral structural transformations during biogeochemical cycling and their impact on trace element and nutrient fate are well studied for the iron oxides, analogous studies are generally lacking for the Mn system. Similar to iron, environments where active biogeochemical Mn cycling is occurring often contain coexisting aqueous Mn(II) and solid Mn(III/IV) oxides. However, the lamellar structure and complex composition of these manganese minerals, which are in many ways analogous to smectites, and the ability of Mn to undergo comproportionation and disproportionation reactions, suggest that interfacial atom exchange and electron transfer reactions will be more complex for Mn oxides than for Fe oxides and likely lead to bulk structural transformations. Such chemical and structural modification of Mn oxides may have a substantial impact on the fate of trace elements and phosphate in biogeochemical systems. In addition, for neither the Fe nor Mn system has the impact of organic ligands on structural transformation induced by interfacial electron transfer and atom exchange processes been adequately studied.

The primary research objective of this proposal is to expand our understanding of how atom exchange and electron transfer reactions drive nanoscale mineral transformations and affect trace element and nutrient fate. Specific objectives are to: (1) establish how such reactions affect the structure and composition of Mn oxides; (2) characterize the impact of these reactions on the fate of structurally compatible and incompatible trace elements and phosphate; and (3) determine how small organic ligands modify Fe and Mn secondary abiotic atom exchange and electron transfer reactions and how this then affects trace element and nutrient fate. These objectives will be accomplished through a series of systematic studies that combine laboratory-based wet chemistry with advanced chemical and structural characterization of the solid bulk and surface structures and the speciation of associated trace elements and phosphate. The proposed research activities will demonstrate the operation of a new class of mineral transformations and trace element and nutrient reactions during biogeochemical cycling. This work will improve our understanding of how Fe and Mn cycling in sediments, soils, and aquatic systems affect phosphate and micronutrient availability and the fate of contaminants.

Broader Impacts: The proposed research will provide potential societal benefits in the form of identifying new processes affecting contaminant fate and transport, suggesting new remediation approaches, and serving as inspiration for novel synthesis routes for battery materials. More importantly, the research described in this CAREER proposal will be leveraged to enhance a number of educational activities. These activities are organized around a theme of inquiry-based learning at the undergraduate and high school level. The proposed research activities will be actively used as learning activities for both undergraduate and high school students. These research-based educational activities will be improved and optimized in the PI's research group, department, and for a local program providing research opportunities to high school students through the development and implementation of assessment plans. A new undergraduate course on Geology and Human Health that incorporates inquiry-based learning and inquiry-based learning modules for an aqueous geochemistry course will be developed. Course materials, pedagogical approaches, and research results will be widely disseminated through websites, blogs, and publication in scientific and education journals.

TABLE OF CONTENTS

For font size and page formatting specifications, see GPG section II.B.2.

	Total No. of Pages	Page No.* (Optional)*
Cover Sheet for Proposal to the National Science Foundation		
Project Summary (not to exceed 1 page)	1	_____
Table of Contents	1	_____
Project Description (Including Results from Prior NSF Support) (not to exceed 15 pages) (Exceed only if allowed by a specific program announcement/solicitation or if approved in advance by the appropriate NSF Assistant Director or designee)	15	_____
References Cited	6	_____
Biographical Sketches (Not to exceed 2 pages each)	2	_____
Budget (Plus up to 3 pages of budget justification)	8	_____
Current and Pending Support	1	_____
Facilities, Equipment and Other Resources	2	_____
Special Information/Other Supplementary Docs/Mentoring Plan	3	_____
Appendix (List below.) (Include only if allowed by a specific program announcement/ solicitation or if approved in advance by the appropriate NSF Assistant Director or designee)	_____	_____
Appendix Items:		

*Proposers may select any numbering mechanism for the proposal. The entire proposal however, must be paginated. Complete both columns only if the proposal is numbered consecutively.

I. INTRODUCTION

The proposed CAREER project involves substantial research and educational components. The research activities investigating mineral transformations during biogeochemical cycling and their impact on trace element and nutrient fate will be leveraged to enhanced the educational activities, which are organized around the theme of inquiry-based learning. In an attempt to provide a coherent discussion of the proposed research and underlying scientific issues, the research activities are presented first, followed by the educational plan. Integration of the proposed research and educational activities is described in Section IX.

II. SCIENTIFIC MOTIVATION

The concentrations of phosphate and trace elements in sediments, soils, and aquatic systems are strongly affected by reactions occurring at the surfaces of iron and manganese oxide minerals. These processes are of great importance to biological activity as they affect the availability of both macro- and micronutrients (e.g., P, Co, Ni, Cu, Zn, Se, Mo) [1-3]. Mineral surface have been shown to control nutrient bioavailability occur in both modern and paleoenvironments [4-10]. In addition to playing essential roles in enzymes, many trace elements are also water contaminants (e.g., Co, Ni, Cu, Zn, As, Se) whose fate is often controlled by mineral-water interface reactions [1]. Iron and manganese oxides are commonly considered to affect the fate of such elements are adsorption and coprecipitation.

This view concerning the major processes controlling element fate does not account for the involvement of solid iron and manganese oxide phases in active biogeochemical cycling. It is well established that microorganisms and, in the case of Mn, fungi can mediate the oxidative precipitation and reductive dissolution of these oxide minerals. However, recent work has identified substantial secondary abiotic reactions that occur between the reduced dissolved forms and oxidized solid oxide forms of Fe and Mn. Aqueous Fe(II) and solid Fe(III) oxides undergo coupled atom exchange and electron transfer (AE-ET) reactions, where Fe(II) oxidatively adsorbs on crystalline iron oxides [11-15], transferring an electron either into the bulk or to a different surface site, where reductive dissolution occurs [16, 17]. These reactions occur under a range of acidic to alkaline pH conditions [11, 14, 17-22]; while reactions at acidic conditions are enhanced by the Fe complexant oxalate [17], they occur at low pH even in simple systems lacking complexants [18]. Coupled AE-ET reactions between aqueous Fe(II) and solid Fe(III) oxides results in structural transformations of iron oxide minerals [23-25] and their surfaces [12, 13, 18] and iron isotope equilibration and fractionation [19-21, 26-28]. AE-ET reactions in the aqueous Mn(II) – solid Mn(III/IV) oxide system have not been clearly identify, although Mn(II) does appear to oxidatively adsorb to biogenic phyllosulfates such as vernadite and birnessite [29, 30].

Substantially less is known regarding the effect these secondary abiotic reactions have on elements, including phosphate and trace elements, which adsorb to or incorporate into Fe and Mn oxides. Clearly oxidative precipitation and reductive dissolution of iron and manganese oxides by microbial metabolic processes will affect the available surface sites and thus the capacity of a given system to adsorb or coprecipitate elements. Catalyzed redox transformations on Fe and Mn oxide surfaces [31-40] will also affect the fate of some trace elements. However, more subtle processes involving nanoscale mineral transformation driven by secondary abiotic reactions may also occur even when net mineral precipitation or dissolution and trace element redox changes do not. For example, in studies from our current NSF project (Section V), it was found that Fe(II) can suppress Ni(II) adsorption onto Ni-free iron oxides through competition for surface sites but also drive mineral transformations that leads to partial Ni incorporation into the oxide structure. Furthermore, Fe(II) induces the release of Ni from the bulk structure of Ni-rich iron oxides. AE-ET reactions on iron oxide surfaces thus lead to Ni incorporation into and release from the structure of iron oxides without leaving a clear macroscopic indicator that substantial reactions driven by iron cycling have occurred.

These observations suggest that biogeochemical Fe and Mn cycling creates systems where secondary abiotic AE-ET reactions drive nanoscale mineral transformations. Such dynamic processes likely leads to substantial changes in the lability and availability of adsorbed or incorporated trace

elements and phosphate. While published and our ongoing studies have well characterized AE-ET processes in the Fe system, including their impact on the fate of other elements, analogous information is lacking for the Mn system. In addition, little is known regarding how these AE-ET reactions are affected by organic ligands for either the Fe or Mn system. Such information is essential for establishing how minerals evolve during biogeochemical cycling and the resulting impact on the availability and fate of trace elements and nutrients.

III. RESEARCH OBJECTIVES

The primary research objective of this proposal is *to expand our understanding of how AE-ET reactions drive nanoscale mineral transformations and affect trace element and nutrient fate*. Specific objective include:

1. *Establish how AE-ET reactions affect the structure and composition of common Mn oxides.*
2. *Characterize the impact of these reactions on the fate of structurally compatible and incompatible trace elements and phosphate.*
3. *Determine how small organic ligands modify Fe and Mn secondary abiotic AE-ET reactions and how this then affects trace element and nutrient fate.*

IV. SCIENTIFIC BACKGROUND

Fe(II)-Fe(III) Oxide Reactions

Beginning with the isotope-labeled Mössbauer study by Williams and Scherer [11] in 2004, recent work has provided a new understanding of the nature of the reaction between aqueous Fe(II) and solid Fe(III) oxides. These studies have demonstrated that Fe(II) oxidatively adsorbs onto goethite and hematite [11-15, 18]. In addition, aqueous Fe(II) undergoes atom exchange with goethite that leads to nearly full isotopic equilibration on time scales of about a month [21]. This oxidative adsorption and atom exchange is likely the primary source of Fe isotope fractionation during microbial iron reduction [19, 20]. More fundamental, Yanina and Rosso [17] demonstrated that with the addition of a complexing organic ligand at low pH electrochemical potentials may be established between distinct mineral surfaces of a mineral and that oxidative adsorption of Fe(II) can be coupled with electron conduction through the bulk mineral to a distinct surface, where reductive desorption of an Fe(III) atom occurs. Our recent work, describe below, suggests that in the absence of a strong complexant and at both pH 3 and 7 Fe(II) induces structural transformations of hematite surfaces that are dependent on crystallographic orientation [18]. These were attributed to potential differences between distinct sites on a particular surface rather than reactions between surfaces. *These observations demonstrate that reactions between aqueous Fe(II) and solid Fe(III) oxides involve the substantial cycling of electrons through the solid and result in atom exchange and modification of surface structure.*

Mn Oxide Mineral Phases and Nomenclature

The Mn oxides addressed in this proposal are all considered phyllosulfates (Fig. 1). These minerals are composed on Mn octahedral sheets with hydrated interlayers. The sheets develop negative charge from either vacancies or Mn(III) substituting for Mn(IV). Depending on hydration state these phases may have a 7 Å or 10 Å interlayer spacing. Vernadite $[(\text{Na,Ca,K})(\text{Mn}^{4+}, \square)\text{O}_2 \cdot n\text{H}_2\text{O}]$ contains no sheet Mn(III) and a small vacancy content. It generally occurs as nanoparticles comprised of only 2-3 stacked sheets having lateral dimensions of around 5 nm; the sheet stacking is turbostratic. Hexagonal birnessite $[(\text{Na,Ca,K})(\text{Mn}^{4+}, \text{Mn}^{3+}, \square)\text{O}_2 \cdot n\text{H}_2\text{O}]$ contains Mn(III) distributed in the sheet as well as above and below sheet vacancies; its stacking is often turbostratic but ordered stacking is possible [41-44]. Triclinic birnessite $[(\text{Na,Ca,K})(\text{Mn}^{4+}_x \text{Mn}^{3+}_{1-x})\text{O} \cdot n\text{H}_2\text{O}]$ contains ordered rows of Mn(III) in the structure and generally displays ordered stacking [43, 45, 46]. Most natural Mn oxides are turbostratic with vernadite-like to hexagonal birnessite-like sheet structures. Historically 10 Å phyllosulfates have

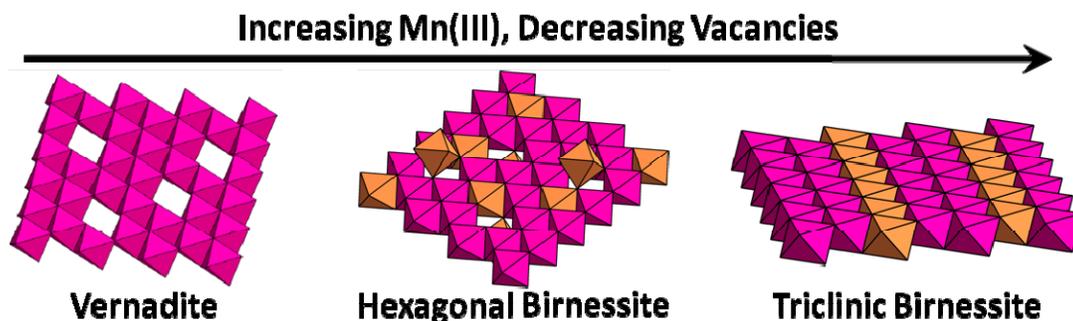


Figure 1. General classification of the phylломanganate minerals by their sheet structure. The primary octahedra contain Mn(IV) and the orange (lighter) octahedra contain Mn(III).

been called “buserite” but there is no structural justification for this nomenclature [47]; all materials considered in this proposal will be classified based only on the characteristic of the phylломanganate sheets and not their interlayer spacing. It should be noted that natural phylломanganates have a varied composition with substantial isomorphous substitution, analogous to smectites.

Reaction between Mn(II) and Mn(III/IV) Oxides

In contrast to the well-studied Fe system, work investigating analogous reactions between aqueous Mn(II) and solid Mn(III/IV) oxides has focused on transformations of Mn biooxides and not been the primary focus of any study [29, 30, 48]. These biooxides, and most natural Mn oxides, are phylломanganates consisting of octahedral sheets of manganese cation with hydrated interlayers [29, 30, 47-57]. The initial Mn oxide formed during microbial Mn(II) oxidation is similar to vernadite, with the octahedral sheet comprised essentially completely of Mn(IV) and charge development primarily from vacancies in the sheet. In the laboratory, high Mn(II) concentration may convert this initial phase to a Mn^{III}OOH solid, such as feiticnechtite [30]. This is likely of low importance in nature as MnOOH phases are not reported to occur in areas of active Mn oxide biomineralization [29, 47, 50, 51]. In the presence of moderate concentrations of Mn(II) the initial biogenic Mn oxide converts into the mixed Mn(III/IV) phylломanganate hexagonal birnessite [30, 48]. This is likely driven by oxidative adsorption of Mn(II) onto the vacancies in the vernadite sheet, producing Mn(III) both in the sheet and bound to the sheet surface on top of vacancy sites [30]. Unfortunately, systematic studies of the Mn oxides transformations by aqueous Mn(II) and the effects of solution composition on these transformations are lacking. *The current understanding of AE-ET reactions in low-temperature Mn systems is thus substantial inferior to what is known for analogous Fe systems.*

Effect of Simple Organic Ligands on AE-ET Reactions

Small organic ligands readily complex Fe(II), Fe(III), Mn(II), and Mn(III); Mn(IV) generally does not occur in solution [58]. A combination of oxalate and aqueous Fe(II) is known to catalyze the dissolution of iron oxides [59, 60]. It has recently been demonstrated that oxalate adsorption alters surface potentials in a way that favors Fe(II) oxidative adsorption on one surface coupled with electron conduction through the bulk iron oxides and reductive desorption of Fe(III) on a separate surface [17]. In the absence of oxalate this cycling may be more localized, such as between steps and terrace sites on a single surface [18]. Organic ligands are known to reductively dissolve manganese oxides [61-63]; this process has been shown to release adsorbed Cu(II) [64]. Recent work has shown that citrate initially induces slow reductive dissolution but that rates then increase substantially as dissolved Mn(II) increases, indicating an autocatalytic process [65]. Such autocatalysis was not observed during birnessite reductive dissolution by a number of other aliphatic organic acids, including oxalate [63]. *Organic ligands may thus strongly affect both Fe and Mn AE-ET reactions and impact the fate of nutrients and trace elements.*

V. RESULTS FROM PRIOR NSF SUPPORT

ETBC: Hidden iron oxide redox processes during biogeochemical iron cycling: Controls on nanoscale transformations and the fate of contaminants (EAR-0818354, 8/15/08 – 7/31/11)

This single-PI project explores nanoscale surface transformations of the iron(III) oxide hematite activated by aqueous Fe(II) and how these transformation affect nutrient availability and contaminant fate. The current submission to the CAREER program is intended to build on work completed and ongoing in this NSF project. ***The start date of the current submission (August 1, 2011) was selected to begin after this existing grant expires.*** Major findings of this continuing project include:

Fe(II)-Induced Hematite Surface Transformations

We have used surface X-ray scattering to characterize three different surfaces of hematite reacted Fe(II) at both pH 3 and 7 [18]. We find that this reaction induces surface transformations on the scale of a few monolayers in size (<1 nm in scale) that are orientation-dependent (Fig. 2) yet pH independent. The surface transformations are orders of magnitude smaller in scale than that seen in the substantially more aggressive system probed by Yanina and Rosso [17], which were conducted at elevated temperature in the presence of substantial (10 mM) oxalate. While that study clearly demonstrated a fundamental process of widespread importance, the present work is focused on systems more directly relevant to environmental biogeochemical systems.

We have coupled these studies with resonant anomalous X-ray reflectivity (RAXR) measurements of Fe(II)-reacted hematite. This method is capable of observing Fe(II) on Fe(III)-oxide surface because of crystallographic effects that make most of the Fe(III) invisible. However, no Fe(II) was observed on any surface. While previous researchers have observed adsorption and oxidation of Fe(II) on iron oxides, it had not been clear to date that the lost electron did not reduce a neighboring Fe(III) on the surface, i.e., that this liberated electron does not reside somewhere on the surface. Ongoing work to be completed before the end of the project will determine how the observed growth and dissolution is modified by adsorbed aluminum, silicate, and phosphate. The ongoing work is expected to produce one publication that builds on our published study:

- Catalano J.G., Fenter P., Park C., Zhang Z., Rosso K.M. (2010) Structure and oxidation state of hematite surfaces reacted with aqueous Fe(II) at acidic and neutral pH. *Geochimica et Cosmochimica Acta* **74**, 1498-1512.

Interfacial Water Ordering on Iron Oxide Surfaces

The structure of interfacial water affects the rates and mechanisms of reaction at mineral surfaces, including electron transfer from aqueous Fe(II) and bacterial cytochromes [66-69]. The arrangement and dynamics of interfacial water is expected to vary with the crystallographic orientation of the surface. This in turn could affect the rate and mechanisms of Fe(II) adsorption and thus potentially play a role in the orientation-dependence of Fe(II)-induced structural transformations. Prior to this proposal the water structure on only the hematite (012) surface had been characterized in situ. I have extended these measurements to the (110) and (001) surfaces; the corundum (001) surface was also studied for

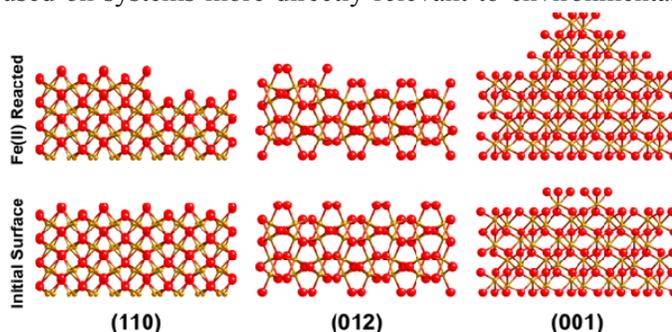


Figure 2. Schematic models of the transformations to the (110), (012), and (001) surfaces of hematite induced by reaction with Fe(II).

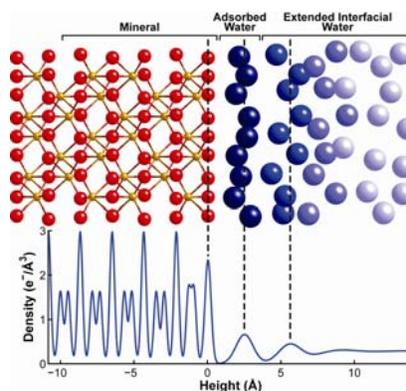


Figure 3. Schematic model of interfacial water structure near the hematite (001) surface.

comparison. As for Fe(II)-induced transformations, the (110) and (012) surfaces display similar water ordering while the structure of water near the (001) surface differs (**Fig. 3**). Whether water structure and surface transformation have a causal relationship or are both simply the result of fundamental variations in the properties of hematite surfaces is under investigation. This work has resulted in one publication and a manuscript under review:

- 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. (2010) Weak interfacial water ordering on isostructural hematite and corundum (001) surfaces. *Geochimica et Cosmochimica Acta*, submitted.

Fe(II)-Promoted Cation Incorporation into and Release from Iron Oxide Surfaces

Fe(II)-induced transformations of iron oxide surfaces through AE-ET reactions may affect the speciation of sorbing contaminant species. Adsorbed elements structurally compatible with iron oxide structures, such as Ni [70], could potentially be incorporated, providing a long-term sink for contaminants but also reducing bioavailability the micronutrients. While a tenfold-excess of Fe(II) was found to reduce the extent of Ni(II) adsorption, presumably through a competitive adsorption process, EXAFS spectra suggest that Fe(II) does alter Ni(II) surface speciation, causing partial incorporation into hematite and goethite.

AE-ET reactions may also potentially cause elements substituted into these mineral phases to be released as the solid undergoes structural recrystallization during atom exchange. We have demonstrated this effect for goethite (**Fig. 4**) and hematite doped with Ni. For goethite, Fe(II) induces the release of roughly 10% of the structural Ni in a 7-day period; 3% was released from hematite over a 3-day period. Longer-term studies over a range of conditions are ongoing.

These two seemingly contradictory observations of Fe(II)-induced incorporation and release may reflect a thermodynamic equilibration between the solid, surface, and aqueous solution. We hypothesize that the equilibrium distribution between this states is normally kinetically inhibited because of the low solubility and dissolution rate of iron oxides. Recrystallization promoted by AE-ET reactions allows this equilibration to go forward. This may lead to Ni incorporation when Ni speciation is dominantly in an adsorbed form, but Ni release when it mostly occurs substituted in the structure. The latter phenomenon may suggests that organisms such as methanogens that require trace elements as micronutrients benefit from Fe(II)-rich environments or association with iron-reducing bacteria. This work is expected to result in two publications.

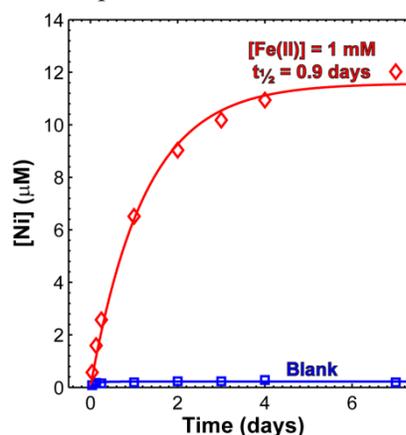


Figure 4. Ni release from Ni-doped goethite in the presence of Fe(II) and in a simple NaCl electrolyte solution at pH 7.

Fe(II) Effects on Oxoanion Adsorption

In contrast to metals like Ni, oxoanions are generally structurally incompatible with iron oxides. There is some evidence of P and Si incorporation into hematite through forced coprecipitation [71, 72], but such incorporation appears to be uncommon in nature [73]. We investigated the effect of Fe(II) on arsenate adsorption and found little observable difference in the macroscopic uptake behavior of As(V) onto both hematite and goethite over a range of pH conditions (3 to 9). We also explored this system using As K-edge EXAFS spectroscopy (**Fig. 5**). In contrast to the Ni studies, the EXAFS spectra showed no change in the coordination environment of As(V) when Fe(II) was added to the system at pH 4 or 7, even at Fe(II) concentrations as high as 1 mM. This suggests that either As(V) inhibits Fe(II)-induced surface transformations or that As(V) adsorption is not effected by such a process. Follow-up work on phosphate and sulfate are ongoing and will be completed before the end of the project; similar results are expected based on the current data we have collected. The sulfate work to date included the unexpected

finding that sulfate has no effect on macroscopic Fe(II) adsorption, in conflict with a past study [22] which found enhanced Fe(II) adsorption between pH 4 and 7.5 in the presence of sulfate. We had thus originally hypothesized the promotion of macroscopic Fe(II) adsorption by sulfate would lead to enhanced AE-ET reactions under acidic to circumneutral pH conditions. Our work to date thus shows that sulfate likely has a negligible effect, suggesting that AE-ET processes likely do not show unique behavior in sulfate-rich marine system. We are also currently investigating the effect of Fe(II) on arsenate and phosphate desorption kinetics. One paper is expected from the sulfate and phosphate adsorption work, one from the desorption kinetics study, and a paper is currently in preparation describing the arsenate adsorption results:

- Luo Y., Catalano J.G., Otemuyiwa B.T. (2010) Effect of Aqueous Fe(II) on Arsenate Adsorption to Goethite and Hematite, *in preparation*.

Characterization of Natural Biogenic Manganese Oxides

During the course of this project an opportunity presented itself to examine a shallow karst cave environment where active Fe and Mn biomineralization was occurring. We felt that this would be a natural laboratory to investigate Fe(II)-induced iron oxide transformations and their effect on trace elements. Unfortunately, the Fe oxide deposits were rare and transient and not suitable for study, but widespread areas of active Mn oxide deposition provided an opportunity to explore similar processes for the Mn system. We have found a substantial variation in Mn oxide mineral structure at different sites in the cave. Specifically, while all samples appeared to have layer stacking intermediate between vernadite and hexagonal birnessite, those from groundwater seeps, which contain elevated sustained Mn(II) concentrations, having a more birnessite-like character. Vernadite-like materials occur in the cave stream, where aqueous Mn(II) concentrations are lower, but contain trace elements (Co, Ni, Zn, Ba) at concentrations 10 to 500 times greater than at the groundwater seeps. There is a clear inverse relationship between solid phase trace element concentration and both aqueous Mn(II) concentration and Mn oxide structure. These structural variations with local Mn(II) concentrations agree with past studies of biogenic Mn oxides [29, 30]. The relationship between structure and trace element content may reflect difference in water chemistry at the different sampling sites but also may result from differences in the inherent reactivity of phyllosulfates having different structures. This work will result in one publication:

- Frierdich, A. J., Hasenmueller, E., and Catalano, J. G. (2010) Nanocrystalline Fe and Mn Oxide Deposits in Pautler Cave, Illinois. *Chemical Geology*, in preparation.

Education and Public Outreach

This project has supported the training of two graduate students (one current), five undergraduate students (including three female students interested in pursuing careers in science and engineering and one Iraq War veteran), and a postdoctoral researcher. This project also facilitated 6-week summer internships for two local high school students. One graduate student and the postdoctoral researcher gained experience serving as research mentors for undergraduate and high school students. This proposal has also supported the training of two graduate students in synchrotron-based analytical methods.

The PI has also conducted three outreach activities associated with this proposal. A presentation was given at the Synchrotron Environmental Sciences IV meeting in December 2008 on applications of resonant X-ray scattering in molecular environmental sciences. This meeting was heavily attended by geosciences graduate students, and the goal of the talk was to reach out to this group to make them aware of new techniques they could use in biogeochemical research to probe interfacial redox reactions. A similar talk was given by the PI at the 2010 Advanced Photon Source Users Meeting to a group of

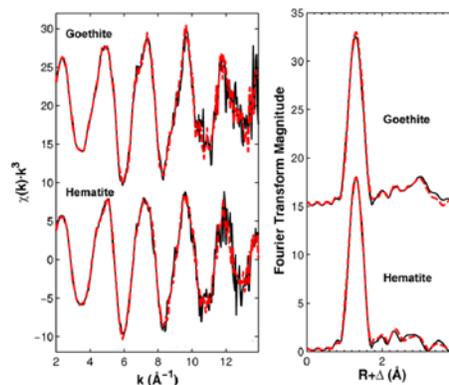


Figure 5. EXAFS spectra of As(V) adsorption to goethite and hematite at pH 7 in the presence (dashed) and absence (solid) of Fe(II).

actinide scientists. The PI also served on a panel discussion on nuclear energy in October 2008 that was organized by undergraduate students at Washington University and attended by both students and members of the general public. The PI discussed how natural and stimulated biogeochemical processes can affect the migration of nuclear waste in the environment.

VI. RESEARCH PLAN

The research objectives of this proposal will be met through a series of activities spread through three major focus areas. The first focus area addresses the fundamental nature of coupled AE-ET reactions occurring between aqueous Mn(II) and the solid Mn(III/IV) phylломanganates vernadite and hexagonal birnessite. The goal is to bring our understanding of secondary abiotic reactions in the Mn oxide system to a level comparable to what has been achieved for the Fe oxide system. The second focus area will address how these coupled secondary AE-ET reactions occurring on Mn oxides impact the fate of adsorbed and incorporated trace elements and phosphate. These studies will complement the work being completed under our current NSF grant that expires in July 2011. The third and final focus area will encompass both the Fe and Mn systems in order to explore how simple organic ligands modify secondary AE-ET reactions and how this then ultimately affects the fate of trace elements and phosphate.

These activities will be accomplished through a series of systematic studies that combine laboratory-based wet chemistry with advanced chemical and structural characterization of the solid bulk and surface structures. The PI's past work has identified a clear relationship between chemical processes and the resulting structural features [18, 74-78]. Directly relating bulk and surface structural transformations to interfacial electron transfer processes and elemental adsorption-desorption and incorporation-release provides fundamental insight into the ways in which secondary abiotic reactions modify biogeochemical systems. The major focus areas are described below:

Focus Area 1: Mn(II)-Driven Nanoscale Mn Oxide Transformations

Birnessite and related phylломanganates dominated the manganese oxides found in systems of active microbial Mn(II) oxidation [29, 47, 51]. The interlayers of these phases allow for exchange of charge-balancing cations, including Mn(II). Therefore, unlike for Fe oxides, the entire structure of these materials is accessible to AE-ET reactions as all sites in the structure are exposed at platelet edges of in hydrated interlayers. Probing how Mn(II) alters the structure of phylломanganates, including vacancy concentrations, particle size, average oxidation state, and layer stacking, can provide insight into Mn AE-ET reactions in biogeochemical systems. Characterizing the variability of these processes with the chemical composition of the aqueous phase, including the pH and electrolyte composition and concentration, will provide additional insight into the underlying controls on Mn AE-ET reactions. pH can affect the density of interlayer Mn(III) bound on top of sheet vacancies [79]. Electrolyte cations are known to affect the structure of biogenic Mn oxides [48, 57] and thus could affect the structural transformations resulting from AE-ET reactions. While Mössbauer spectroscopy [11, 14, 15, 80], surface X-ray scattering [12, 13, 18], single crystal surface potential [17], and iron stable isotope [19-21, 27, 81] studies have provided great insight into the atom exchange and electron transfer processes occurring between aqueous Fe(II) and solid Fe(III) oxides, such methods cannot be applied to the Mn system. Mn is monoisotopic, the sole stable isotope (^{55}Mn) is not Mössbauer active, and macroscopic single crystals of the relevant phylломanganates needed for X-ray scattering and surface potential measurements do not exist as these phases are nanocrystalline. Probing structural and chemical properties of the solid Mn oxides after reaction thus provides the best way through which Mn AE-ET reactions can be evaluated.

Major Hypotheses:

1. AE-ET reactions drive structural transformations that convert vernadite to hexagonal birnessite.
2. These transformations results in a reduced large change and vacancy population and an increased lateral particle size.

3. *Hexagonal birnessite undergoes continuous cycling in the presence of Mn(II), as indicated by changes in particle size and morphology.*
4. *AE-ET reactions vary with pH because of the pH-dependence of Mn(II) adsorption to edges and interlayer Mn(III) stability.*
5. *Electrolyte cations affect Mn AE-ET reactions by competing for interlayer sites, altering the distribution between Mn(II) reacting at the edges and in the interlayer.*

Proposed Research Activities:

Synthetic verndatite and hexagonal birnessite will be reacted with aqueous Mn(II) and then characterized. A range of Mn(II) concentrations (1 μ M to 10 mM), pH conditions (3 to 9), and competing electrolyte concentrations (1 mM to 1 M) and compositions (NaCl, KCl, MgCl₂, CaCl₂, BaCl₂) will be explored; the effect of sample aging time will also be investigated. Ba²⁺ is included in the list of electrolyte cations as phyllo-manganates have a strong affinity for this cation. The evolution of the solution will be monitored using inductively coupled plasma optical emission spectroscopy (ICP-OES) and mass spectrometry (ICP-MS) and spectrophotometry. The structure of the solid phases before and after reaction will be characterized using a number of methods. Both laboratory- and synchrotron-based powder X-ray diffraction (XRD) measurements will be collected. These data will be analyzed using the formalism of Drits [82, 83] to assess the Mn oxide structure for vacancies, interlayer cation positions and occupancies (e.g., Mn(III) often occurs “sorbed” to the basal surface over vacancies), and layer symmetry. Such analyses have previously been used to investigate the structure of phyllo-manganates [41, 79, 84-90]. The layer structure will also be probed by extended X-ray absorption fine structure (EXAFS) spectroscopy and analyzed using the model developed by Webb et al. [91]. These studies will be complemented for select samples by high-energy total X-ray scattering data analyzed through pair distribution function (PDF) methods to further constrain the structure. Average oxidation state will be determined through chemical means and by X-ray absorption near-edge structure (XANES) spectroscopy. The cation exchange capacity and exchangeable Mn(II) content will also be determined.

It should be noted that the exchangeable Mn(II) measurement poses a challenge but also a unique opportunity. Mn has a well known ability to undergo disproportionation and comproportionation reactions. Much of these occur in the solid phase, with Mn(II) oxidative adsorption really being a comproportionation process with a sheet Mn(IV) reduced to Mn(III). It is possible that under conditions where true interlayer Mn(II) can be exchanged for another cation, interlayer Mn(III) reductively desorbs as Mn(II), with a sheet Mn(III) site oxidizing to Mn(IV) to provide the electron. The Mn oxide sheet structure may thus show a response to Mn(II) desorption, a process with no clear analogue among phyllosilicate clays. Measurements of exchangeable Mn(II) will thus be coupled to structural measurements of the solid before and after the exchange process to assess possible disproportionation-induced structural changes.

Further characterization of the solid will investigate the effect of AE-ET reactions on Mn oxide lateral particle size and morphology. Mn(II) oxidative adsorption at the edges of the platelets would lead to an increase in particle size. Electron conduction to a different edge site followed by reductive dissolution could also lead to morphology changes. Such processes may be especially relevant to hexagonal birnessite which lacks substantial vacancies for Mn(II) adsorption. The width of the (hk0) XRD reflections will be used to constrain the coherent scattering domain (CSD) size of the platelets after reaction. In addition, transmission electron microscopy (TEM) and atomic force microscopy (AFM) will be used to assess particle size and morphology directly.

Focus Area 2: Effect of Mn AE-ET Reactions on Trace Element and Phosphate Fate

Our work has shown that, for structurally compatible elements, Fe(II) leads to element release from iron oxides but also incorporation, depending on solid, surface, and solution concentrations of the element. Adsorbed elements incompatible with the sorbent mineral structure were found to be substantially less affected Fe AE-ET reactions. Alternatively, these species may inhibit such

transformations by altering surface potentials [17] and step pinning [92]. The structure of phyllophanes suggests that these phases will display both similarities and differences during Mn AE-ET reactions to the Fe system. The shift in mineral structure toward that of hexagonal birnessite with increasing Mn(II) concentration seen in our cave studies (Section V) coupled with the observation of the conversion of initial vernadite-like biogenic precipitates to birnessite-like phases in the presence of Mn(II) [30] clearly documents that Mn(II) induces changes in the sheet structure. The inverse correlation of trace element content and aqueous Mn(II) concentration in our cave studies (Section V) raises the possibility that Mn(II)-induced transformations of biogenic Mn oxides leads to the loss of sorbed and incorporated elements, possibly because of a reduction in sheet vacancies or layer charge.

Mn(II) may thus be reasonably expected to lead to trace element release from manganese oxides, analogous to the Ni release we observed from hematite and goethite in the presence of Fe(II). However, the mechanistic reasons for this will likely differ. Fe(II) drives recrystallization that allow elements in the bulk iron oxide structure to be released. Phyllophanes are effectively 2-D crystals, with single sheets separated by hydrated interlayer accessible to Mn(II) and cationic trace elements. Any trace element release induced by Mn AE-ET reaction on phyllophanes may thus be promoted by equilibration of the solid with the solution but also from Mn competitive adsorption and in response to structural changes (e.g., site distortion from incorporation of Jahn-Teller distorted Mn(III), loss of vacancies). Structurally incompatible oxoanions may also display unique behavior as they cannot access the phyllophanate interlayer because of their negative charge. They thus have less ability to potentially inhibit electron transfer reactions than for the Fe system, although their edge adsorption may inhibit lateral growth.

Major Hypotheses:

- 1. Mn AE-ET reactions leads to a release of adsorbed and incorporated structurally compatible elements from vernadite because of a reduction in reactive vacancy sites.*
- 2. Element release from birnessite will also be observed, even at its maximum Mn(III) content, as AE-ET reactions will still drive particle recrystallization.*
- 3. Mn(II) will lead to enhanced release of structurally incompatible species such as arsenate and phosphate as Mn(II) will promote structural disruption; because of re-adsorption this will only show a macroscopic effect in system where net desorption is favorable.*

Proposed Research Activities:

To test these hypotheses we will investigate the effect of Mn(II)-induced phyllophanate transformations on trace element and phosphate speciation, binding, and release. These studies will involve reacting aqueous Mn(II) with vernadite and birnessite coprecipitated with Co, Ni, and Zn or pre-adsorbed with these same metals. We will also investigate co-adsorption of Mn(II) and these metals. These metals were selected for their affinity for phyllophanes [38, 47, 93] and structural compatibility. In addition, Co may occur in multiple valence states (II/III) and Zn in multiple coordination states (octahedral, tetrahedral). This set thus probes various aspects of transition metal coordination chemistry. The effect of Mn(II) on arsenate, selenate, and phosphate adsorption-desorption and surface speciation will also be investigated.

These studies will combine solution-phase analyses with solid-phase characterization to identify the mechanisms through which Mn(II) affects trace element and phosphate speciation. ICP-OES and ICP-MS will be used to determine dissolved element concentrations after reaction. EXAFS spectroscopy will be used to examine the speciation of trace elements associated with the solid phase in the absence and presence of Mn(II) to assess if their distribution between sites on the surface and in the phyllophanate sheets changes after AE-ET reactions. Attenuated total fluorescence Fourier transform infrared (ATR-FTIR) spectroscopy will be used to provide information on phosphate speciation. XANES will be used to track the oxidation state of Co, which typically occurs as Co^{3+} in Mn oxides [38], as well as the average oxidation state of the solid; this also will be measured separately through chemical means. Powder XRD and EXAFS will be used to evaluate the structure of the Mn oxide after reaction, and TEM and AFM measurements will evaluate particle size and morphology. These structural properties will be compared

to the properties observed in Focus Area 1 to determine if trace elements alter modify the reaction my inhibiting Mn(II) adsorption, limiting lateral growth, or altering the conductivity of the solid.

Focus Area 3: Modification of Fe and Mn AE-ET Reactions by Small Organic Acids

Past studies have shown that small organic ligands such as oxalate and citrate may enhance the interaction of reduced aqueous Fe and Mn with their oxidized solid forms [16, 17, 59-65]. However, the effect of these species on iron oxide surface transformations at circumneutral pH or the impact of organic ligand-induced reductive dissolution on the structure of the remaining Mn oxide is unknown. More importantly, the effect of organic ligand alteration of Fe and Mn AE-ET reactions on sorbed or incorporated trace metals and phosphate has not been examined. Common small organic ligands may enhance [16, 17], or, for Mn oxides, even activate [65] mineral transformations that may potentially alter the availability of these elements.

Major Hypotheses:

1. *Polycarboxylic acids have a greater impact on Fe and Mn AE-ET reactions than monocarboxylic acids.*
2. *Carboxylic acids enhanced both the incorporation and release of trace elements and phosphate during Fe and Mn AE-ET reactions.*

Proposed Research Activities:

Effect of organic ligands on hematite surface transformations. Fe(II) induces nanoscale structural transformations of hematite surfaces [12, 13, 18], with more extensive growth and dissolution features formed in the presence of substantial oxalate at pH 2 and elevated temperature (75°C) [16, 17]. Surprisingly, the combined effects of Fe(II) and organic ligands on iron oxide surface structure and composition has not been adequately explored to date under circumneutral conditions at ambient temperature and concentrations of Fe(II) and ligands more representative of natural systems. Measurements from our published study on the orientation-dependence of hematite surface structural transformations caused by aqueous Fe(II) [18] will be extended to systems containing acetic, oxalic and citric acid in order to probe the effects of mono-, di-, and tricarboxylic acids, respectively; all complex Fe(II) and Fe(III). Surface X-ray scattering measurements will characterize the structural transformations produced by the combined action of Fe(II) and these organic ligands. In addition, in situ time-resolved X-ray reflectivity and AFM measurements will be made to assess the rate and mechanism of the resulting growth or dissolution processes. This series of experiments will provide a fundamental understanding of how aqueous Fe(II) and organic ligands act cooperatively at iron oxide surfaces during AE-ET reactions.

Effect of ligand-enhanced Fe(II)-surface reactions on trace element and phosphate fate. Surface chemical and structural changes caused by the combined action of aqueous Fe(II) and carboxylic acids likely impacts adsorbed and incorporated trace elements and phosphate. We have already demonstrated that aqueous Fe(II) alone liberates substantial structural Ni(II) from Ni-substituted goethite and hematite but appears to lead to minor Ni incorporation into Ni-free iron oxides. The addition of organic ligands to such systems is expected to promote net dissolution [59, 60] but also enhance localized surface growth [16, 17, 94].

This may result in unique changes in trace element and phosphate availability and speciation depending on the element and its initial chemical form. First, in systems containing adsorbed structurally-compatible elements, net dissolution would nominally be expected to cause desorption, although this might be masked by re-adsorption if conditions are favorable. However, localized growth may potentially lead to incorporation or adsorbed species. Under the right conditions net dissolution promoted by the addition of organic ligands may thus have the counterintuitive effect of enhancing element incorporation into the structure. Second, iron oxides containing incorporated structurally-compatible elements may show enhanced trace element release in the presence of organic ligands compared to a system containing only Fe(II). Element release may occur through both net dissolution and ejection during recrystallization. Third, adsorbed structurally-incompatible elements, such as arsenate

and phosphate, are expected to either hinder the Fe(II)-ligand surface reactions by blocking surface sites or desorb and immediately resorb if conditions are favorable. However, if these species do not block sites then enhanced release may be observed when desorption is favorable, with the combined action of Fe(II) and organic ligands increasing desorption rates.

The impact of these multiple competing phenomena on trace element and phosphate fate during Fe AE-ET reactions will be unraveled through a series of systematic studies of systems containing hematite or goethite, Fe(II), an organic acid, and the element of interest. ICP-OES, ICP-MS, and spectrophotometry will characterize the solution phase. Ion chromatography (IC) will be used to measure the concentrations of the organic acids. Element speciation will be characterized using EXAFS and ATR-FTIR spectroscopy. Particle morphology and size will be determined by scanning electron microscopy.

Effect of organic ligands on Mn oxide structure. Organic ligands cause the reductive dissolution of Mn oxides [61-63]; a clear catalytic process has been observed when citrate and Mn(II) are both present [65]. However, the effect this has on the structure of the remaining solids has not been determined. The production of aqueous Mn(II) during reductive dissolution should lead to solid-phase structural transformations similar to those inferred from studies of biogenic Mn oxides. The relationship between transformations of vernadite and hexagonal birnessite and carboxylic acid concentration, Mn(II) concentration, pH, and electrolyte composition and concentration will be determined. Organic acid concentrations will be determined by IC and Mn(II) concentrations by ICP-OES; production of aqueous Mn(III), which may occur in a complexed form [65], will be determined by spectrophotometric methods. The Mn oxide structure will be characterized by powder XRD and by EXAFS spectroscopy. Select samples will be examined by PDF analysis of total X-ray scattering data.

Effect of ligand-enhanced Mn(II)-surface reactions on trace element and phosphate fate. The modification of Mn AE-ET reactions likely affects the fate of adsorbed and incorporated elements. Reductive dissolution may occur (depending on the ligand [63, 65]) which would favor the release of associated elements [64]. The interaction of Mn(II) with the solid oxide, and the hypothesized enhancement of this interaction by polycarboxylic acids, is expected to affect the release and incorporation of other elements. Comparison to ligand-free systems will help identify the specific effect of carboxylic acids on the fate of trace elements and phosphate. EXAFS and ATR-FTIR spectroscopy will be used to determine trace element and phosphate speciation. EXAFS and XRD will be used to characterize the Mn oxide structure after reaction. IC, ICP-OES, and ICP-MS will be used to characterize the solution phase.

VII. EXPECTED SCIENTIFIC IMPACTS

The proposed research activities will demonstrate the operation of a new class of mineral transformations and trace element and nutrient reactions during biogeochemical cycling. This work will improve our understanding of how Fe and Mn cycling in sediments, soils, and aquatic systems affect phosphate and micronutrient availability. The expected results will also be of relevance to the study of paleoenvironments where surface processes have been suggested to control nutrient availability [5, 7-9]. These studies may identify ways in which dissimilatory metal reduction may aid entire microbial communities by increasing the availability of essential macro and micronutrients. These studies will identify new processes through which trace element concentrations may be altered during sediment redox perturbations, such as from hydrocarbon migration [95], and diagenesis. Finally, the proposed investigations will demonstrate additional processes that need to be considered when evaluating contaminant fate and transport in active biogeochemical systems.

VIII. EDUCATIONAL PLAN

There is a broad need for an increased supply of workers well-trained in STEM fields if America is to maintain leadership in technology and sustain (or perhaps more accurately reinvigorate) economic growth [96]. As a component of this science fields need to increase diversity at the highest levels [97].

To address these issues, changes in science education have been recommended, most notably for research-based learning to become the new standard at both the undergraduate and K-12 levels [98, 99]. Unfortunately, implementation of inquiry-based learning has been slow at major research universities [100, 101]. Perhaps the largest effort in this area has been the increase in undergraduate research experiences [102]. However, unlike course-based activities, the outcomes and educational benefits of undergraduate research at the institutional or department level are rarely assessed, and it was only recently that the overall benefits of this activity were actually verified through empirical study [103].

This education plan seeks to increase the availability of inquiry-based educational activities at the undergraduate and high school level and to improve assessment of their outcomes. This will be accomplished through the development of a new inquiry-based introductory course for undergraduate non-majors, the addition of inquiry-based learning modules in an undergraduate major aqueous geochemistry course, and authentic research experiences for both undergraduate and local high school students. In addition, assessment plans will be developed and implemented at the department level for undergraduate research. A similar assessment plan will be developed and implemented for a local program that places high school students in 6-week summer internships in St. Louis-area research universities and non-profit and corporate research institutions. Individual components of this plan are described below.

Course Development

Inquiry-Based Introductory Undergraduate Course on Geology and Human Health. Interest in the connection between our health and the environment we live in has been growing over recent decades. This has led to valid, or sometimes irrational, concerns about how certain industrial or mining activities may impact the health of nearby residents. Many of these health concerns stem from geologic processes, such as natural groundwater contamination, asbestos in the atmosphere, or radon seeping into basements. It is the responsibility of earth scientists to educate the public about these processes so that informed, scientifically-justified decisions regarding the protection of human health are made by our political leaders. There has been a substantial increase in interest among earth scientists in the field of Medical Geology in recent years [104]. However, education in this area is generally lacking, especially at the undergraduate non-major level. A course offered at such a level addressing the connection between Geology and Human Health would potentially educate a substantial number of students that would otherwise never be exposed to this area of science.

I propose to develop an introductory undergraduate course for non-majors that connects Geology and Human Health and incorporates inquiry-based learning activities. This topic is amenable to inquiry-based learning as there are substantial datasets covering the properties and occurrence of toxic substances, disease occurrence, and geologic features. I am unaware of any existing course with this content being taught at this level; an upper-level undergraduate major course in this area is taught at Emory University, and aspects of this topic are addressed in some other courses. There is also the lack of a reasonable textbook as all available books on this topic are written for trained scientists (e.g., [105-108]). Other textbooks, such as those used for courses like “Environmental Geology” or “Natural Disasters” have at most one to two chapters that are relevant. The “On the Cutting Edge” website sponsored by the National Association of Geoscience Teachers does have a topic area covering Geology and Human Health, but nearly all of the teaching activities are inappropriate for an undergraduate non-major course, with many targeted to hydrogeology courses. Creation of this course thus involves substantially more effort than is associated with a traditional, lecture-based course with existing precedents. In addition, the integration of inquiry-based activities requires additional effort and the development of novel teaching approaches.

Development will occur in years 1 and 2, the course will be taught as a freshman seminar in year 3, it will be refined in year 4, and fully implemented in year 5 of the proposed project. The course development will result in a collection of lecture material, reading assignments, in class activities, and homework problems. All course materials that are not copyrighted, including the inquiry-based learning activities, will be made available to the earth science community by the creation and maintenance of a website for interested instructors. The course information will also be posted on the On the Cutting Edge

site, including a link to the site hosting the entire course content. If the course proves successful an article summarizing this course will be submitted to the Journal of Geoscience Education.

Inquiry-Based Learning Activities for a Course on Aqueous Geochemistry. An upper-level undergraduate course on Aqueous Geochemistry taught by the PI will be modified to include inquiry-based learning activities involving geochemical modeling. The course covers topics such as carbonate equilibria, acid-base chemistry, including buffers, complexation, mineral solubility, and the evaporation of natural waters. The course already includes basic training in geochemical modeling software, specifically The Geochemist's Workbench, but this is simply introduced as a technique rather than used as an educational tool. A series of activities will be created where students are asked to conduct virtual experiments to investigate major topics in aqueous geochemistry, such as how P_{CO_2} and temperature affects calcite solubility, how the common ion effect modifies mineral solubility, how organic and inorganic ligands can buffer the pH of natural waters, and the nature of chemical divides during evaporation processes. Such computational experimentation is impractical to do (or at least cruel) in homework assignments involving calculations by hand. The goal of these activities is to provide students with an improved conceptual understanding of aqueous geochemistry. These activities will be made publically available on a university-hosted website, and an overview will be uploaded to the On the Cutting Edge site. These course improvements will be implemented in year 2 of the project.

Authentic Research Experiences

Beyond the course creation and enhancement, intensive inquiry-based learning opportunities will be provided to undergraduate and high school students through **authentic** research experiences. Student learning during such activities is optimized if the experience is real [103]; positions simply as technicians prevent opportunities for intellectual contributions to the project, whereas activities with known outcomes demoralize students when they find out that their work did not actually contribute to science.

Undergraduate Research Experiences. The proposal will provide authentic independent research experiences for two undergraduate students annually. Such experiences are essential if research is to provide substantial educational benefits as these will train students to tackle complex and open-ended problems. These experiences will be designed as true educational activities. In order to accomplish the dual educational and scientific purposes of this activity, the PI will develop and optimize a pedagogical approach through trial-and-error and in response to the assessment activities proposed below. The goal is to design a sustainable undergraduate research program in laboratory-based biogeochemistry operating at the group level that provides that maximum possible educational benefit while still conducting real science. The metrics for evaluating success are the production of high-quality science, student gains in skills, and most importantly, participants acquiring an understanding of the complexity, uncertainty, and challenges associated with research and that the only "right answer" is conducting good science. The latter are the most difficult to obtain because in many ways they are counter to what students have been conditioned to expect during their education. The PI will create a blog to share his experience and insight gained from developing a robust pedagogy for undergraduate research in biogeochemistry; novel pedagogical approaches may be summarized in an article in an education journal.

Summer High School Research Internships. Each summer two high school students recruited through the St. Louis-based Students and Teachers as Researchers (STARS) program will be provided authentic research experiences. The STARS program places high school students from the St. Louis metropolitan area in six-week summer internships in local research universities. Each student is mentored by a faculty member and typically co-mentored by a graduate student or postdoctoral researcher. The program provides training in the conduct of research, laboratory safety, and the presentation of results. Each student completes a small research project and then prepares a report and oral presentation. This program provides early opportunities for students interested in STEM fields to conduct research. It also provides students exposure to fields of science and engineering not represented in high school curriculum.

Assessment of Research Experiences

All activities proposed below have been discussed with the Institutional Review Board at Washington University.

Undergraduate Research. While assessments of student learning are intimately built into coursework, even though they are sometimes of questionable effectiveness [109], an assessment of the outcomes and educational benefits of undergraduate research occurring in a department or institution are generally rare. As undergraduate research is becoming an integral component of undergraduate education in STEM fields, including earth science, it is essential that assessment tools be implemented to evaluate the effect this has on our students and to make improvements in the way in which such activities are conducted. These tools can also potentially identify benefits and challenges unique to undergraduate research conducted in specific sub-field of earth science, as laboratory-based geochemical research may have different benefits than activities like geologic mapping or seismic data processing.

This project will support the development and implementation of a plan to assess undergraduate research in the Department of Earth & Planetary Sciences at Washington University. The goals of this activity are to determine the educational benefits provided to students, characterize variations in outcomes among disciplinary areas, and to identify ways in which the undergraduate research conducted in the department can be improved. This will be accomplished through the use of student self-assessment, faculty surveys, and small group interviews. The largest component of the assessment activities will be implementation of the Undergraduate Research Student Self-Assessment (URSSA) tool in the department. URSSA was developed at the University of Colorado through support from the NSF. URSSA is an online survey instrument for measuring student's self-reported gains from their research experiences; it is focused on what students learn from their experience, not whether they enjoyed it. It measures outcomes of undergraduate research such as the influence on career decisions and growth in confidence that can only be provided by students. URSSA will be available for use for this project (see attached letter from Ms. Anne-Barrie Hunter).

URSSA survey results will be supplemented with faculty surveys to obtain input from research advisors into the educational benefits they have observed in working with their students. In addition, the PI will conduct small group interviews with undergraduate to discuss in person how undergraduate research has affected their education and career choices. Goals for the outcomes of undergraduate research in the department, which are currently lacking, will be established and these assessment activities will be used to determine which of these goals are being met. The assessment results will then be used to guide the refinement of undergraduate research in the department. New access modes will be explored to address any issues regarding the diversity of students conducting research. The connection between specific training and mentoring activities and educational outcomes will be determined and those that are most successful will be encouraged. After the initial round of assessment and program refinement a long-term assessment plan will be developed to ensure that this educational activity is optimized to provide the greatest benefits to students. The results of this activity and the specific recommendations it generates will be reported in the Journal of Geoscience Education.

High School Internships. The St. Louis area STARS program pairs high school students, typically just having completed their junior year, with a faculty member at a local research university or a scientist at local non-profit or corporate research facility. Often the students are co-mentored by a graduate student or postdoctoral scientist, especially when working at a research university. The program last conducted surveys of student to assess the benefits they received from participation between 1995 and 1998. The focus of this assessment was how the program's effect on career choice varied with student gender and to investigate the "splashdown effect", where student gains are at times offset by the letdown of their return to high school in the fall. However, no long-term, continuous assessment of the impact of the program on student participants is conducted because of program resource limitations.

The program has changed substantially since 1998 with the addition of science participants at a major non-profit plant science research center and a related corporate research facility. Additional

corporate research partners may join the program in the next few years. In addition, students and the high schools they attend have changed since 1998 with the increase of technology. Finally, the program annually receives more applicants than it has positions available. Routine assessments of the benefits of the program to student participants and the benefits to faculty, postdoc, and graduate students that serve as mentors are needed to ensure the program meets its goals of enhancing students' understanding of science and the process of inquiry and discovery.

I proposed to develop and implement a sustainable annual assessment plan for the STARS program to evaluate the impact of this activity on the students that participate. This will build on existing survey-based instruments available to the program and will include pre- and post-program surveys as well as follow-up surveys during the academic year and of recent alumni currently enrolled in college. Related to this, the success of this program strongly depends on the involvement of individual faculty and scientists. In many cases, Ph.D. students and postdoctoral scholars play substantial, active roles in mentoring the high school interns. This is expected to be beneficial to these mentors' career development, as they often receive little training in educational activities from their home institution. Documentation of clear benefits to graduate students and postdoctoral scholars would demonstrate a benefit to university participants and aid in increasing faculty involvement. As the program often has to turn away at least 30% of its applicants each year, activities that increase faculty involvement would directly result in increased opportunities for students. These assessment activities are strongly supported by the STARS program director, Dr. Ken Mares (see attached letter of support).

IX. INTEGRATING RESEARCH AND EDUCATIONAL ACTIVITIES

The proposed research activities are focused on biogeochemical processes that affect the fate and availability of contaminants and nutrients. The educational activities will be integrated with these research activities in a number of ways. First, the research experience and training of high school and undergraduate students will occur directly through the proposed research. Second, the research results will be integrated into the inquiry-based learning activities in the course development activities. Third, high school and undergraduate students conducting research on this project will participate in the student assessment activities, and although their participation will be anonymous the results will be used to improve the conduct of undergraduate research in the PI's group.

X. EXPECTED BROADER IMPACTS

The proposed research and educational activities will advance discovery and understanding, produce widely disseminated research and educational products, and provide potential societal benefits. Research activities will be actively used as learning activities for both undergraduate and high school students. These activities will be improved and optimized in the PI's research group, department, and for a local program providing research opportunities to high school students through the development and implementation of assessment plans. A new undergraduate course on Geology and Human Health that incorporates inquiry-based learning and inquiry-based learning modules for an aqueous geochemistry course will be developed. Course materials, pedagogical approaches, and research results will be widely disseminated through websites, blogs, and publication in scientific and education journals. The research will also produce potential societal benefits in the form of identifying new processes affecting contaminant fate and transport, suggesting new remediation approaches, and serving as inspiration for novel synthesis route for battery materials, which are often made of birnessite-like materials [110-113].

REFERENCES CITED

- [1] Brown, G. E., Jr.; Parks, G. A., Sorption of trace elements on mineral surfaces: Modern perspectives from spectroscopic studies, and comments on sorption in the marine environment. *International Geology Review* **2001**, *43*, 963-1073.
- [2] Bruland, K. W.; Lohan, M. C., Controls of Trace Metals in Seawater. In *Treatise on Geochemistry*, Heinrich, D. H.; Karl, K. T., Eds. Pergamon: Oxford, 2003; pp 23-47.
- [3] Morel, F. M. M.; Milligan, A. J.; Saito, M. A., Marine Bioinorganic Chemistry: The Role of Trace Metals in the Oceanic Cycles of Major Nutrients. In *Treatise on Geochemistry*, Heinrich, D. H.; Karl, K. T., Eds. Pergamon: Oxford, 2003; pp 113-143.
- [4] Berner, R. A., Phosphate removal from sea water by adsorption on volcanogenic ferric oxides. *Earth and Planetary Science Letters* **1973**, *18*, 77-86.
- [5] Bjerrum, C. J.; Canfield, D. E., Ocean productivity before about 1.9 Gyr ago limited by phosphorus adsorption onto iron oxides. *Nature* **2002**, *417*, 159-162.
- [6] Wheat, C. G.; Feely, R. A.; Mottl, M. J., Phosphate removal by oceanic hydrothermal processes: An update of the phosphorus budget in the oceans. *Geochimica et Cosmochimica Acta* **1996**, *60*, 3593-3608.
- [7] Konhauser, K. O.; Hamade, T.; Raiswell, R.; Morris, R. C.; Ferris, F. G.; Southam, G.; Canfield, D. E., Could bacteria have formed the Precambrian banded iron formations? *Geology* **2002**, *30*, 1079-1082.
- [8] Konhauser, K. O.; Pecoits, E.; Lalonde, S. V.; Papineau, D.; Nisbet, E. G.; Barley, M. E.; Arndt, N. T.; Zahnle, K.; Kamber, B. S., Oceanic nickel depletion and a methanogen famine before the Great Oxidation Event. *Nature* **2009**, *458*, 750-U85.
- [9] Poulson, R. L.; Siebert, C.; McManus, J.; Berelson, W. M., Authigenic molybdenum isotope signatures in marine sediments. *Geology* **2006**, *34*, 617-620.
- [10] Wasylenki, L. E.; Rolfe, B. A.; Weeks, C. L.; Spiro, T. G.; Anbar, A. D., Experimental investigation of the effects of temperature and ionic strength on Mo isotope fractionation during adsorption to manganese oxides. *Geochimica et Cosmochimica Acta* **2008**, *72*, 5997-6005.
- [11] Williams, A. G. B.; Scherer, M. M., Spectroscopic evidence for Fe(II)-Fe(III) electron transfer at the iron oxide-water interface. *Environmental Science & Technology* **2004**, *38*, 4782-4790.
- [12] Tanwar, K. S.; Petitto, S. C.; Ghose, S. K.; Eng, P. J.; Trainor, T. P., Structural study of Fe(II) adsorption on hematite(1-102). *Geochimica et Cosmochimica Acta* **2008**, *72*, 3311-3325.
- [13] Tanwar, K. S.; Petitto, S. C.; Ghose, S. K.; Eng, P. J.; Trainor, T. P., Fe(II) adsorption on hematite (0 0 0 1). *Geochimica et Cosmochimica Acta* **2009**, *73*, 4346-4365.
- [14] Larese-Casanova, P.; Scherer, M. M., Fe(II) sorption on hematite: New insights based on spectroscopic measurements. *Environmental Science & Technology* **2007**, *41*, 471-477.
- [15] Larese-Casanova, P.; Scherer, M. M., Morin transition suppression in polycrystalline ⁵⁷Hematite (α -Fe₂O₃) exposed to ⁵⁶Fe(II). *Hyperfine Interactions* **2007**, *174*, 111-119.
- [16] Rosso, K. M.; Yanina, S. V.; Gorski, C. A.; Larese-Casanova, P.; Scherer, M. M., Connecting Observations of Hematite (α -Fe₂O₃) Growth Catalyzed by Fe(II). *Environmental Science & Technology* **2010**, *44*, 61-67.
- [17] Yanina, S. V.; Rosso, K. M., Linked reactivity at mineral-water interfaces through bulk crystal conduction. *Science* **2008**, *320*, 218-222.
- [18] Catalano, J. G.; Fenter, P.; Park, C.; Zhang, Z.; Rosso, K. M., Structure and oxidation state of hematite surfaces reacted with aqueous Fe(II) at acidic and neutral pH. *Geochimica Et Cosmochimica Acta* **2010**, *74*, 1498-1512.
- [19] Crosby, H. A.; Johnson, C. M.; Roden, E. E.; Beard, B. L., Coupled Fe(II)-Fe(III) electron and atom exchange as a mechanism for Fe isotope fractionation during dissimilatory iron oxide reduction. *Environmental Science & Technology* **2005**, *39*, 6698-6704.

- [20] Crosby, H. A.; Roden, E. E.; Johnson, C. M.; Beard, B. L., The mechanisms of iron isotope fractionation produced during dissimilatory Fe(III) reduction by *Shewanella putrefaciens* and *Geobacter sulfurreducens*. *Geobiology* **2007**, *5*, 169-189.
- [21] Handler, R. M.; Beard, B. L.; Johnson, C. M.; Scherer, M. M., Atom exchange between aqueous Fe(II) and goethite: An Fe isotope tracer study. *Environmental Science & Technology* **2009**, *43*, 1102-1107.
- [22] Jeon, B. H.; Dempsey, B. A.; Burgos, W. D.; Royer, R. A., Reactions of ferrous iron with hematite. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* **2001**, *191*, 41-55.
- [23] Hansel, C. M.; Benner, S. G.; Fendorf, S., Competing Fe(II)-induced mineralization pathways of ferrihydrite. *Environmental Science & Technology* **2005**, *39*, 7147-7153.
- [24] Hansel, C. M.; Benner, S. G.; Neiss, J.; Dohnalkova, A.; Kukkadapu, R. K.; Fendorf, S., Secondary mineralization pathways induced by dissimilatory iron reduction of ferrihydrite under advective flow. *Geochimica et Cosmochimica Acta* **2003**, *67*, 2977-2992.
- [25] Hansel, C. M.; Benner, S. G.; Nico, P.; Fendorf, S., Structural constraints of ferric (hydr)oxides on dissimilatory iron reduction and the fate of Fe(II). *Geochimica et Cosmochimica Acta* **2004**, *68*, 3217-3229.
- [26] Beard, B. L.; Handler, R. M.; Scherer, M. M.; Wu, L. L.; Czaja, A. D.; Heimann, A.; Johnson, C. M., Iron isotope fractionation between aqueous ferrous iron and goethite. *Earth and Planetary Science Letters* **2010**, *295*, 241-250.
- [27] Icopini, G. A.; Anbar, A. D.; Ruebush, S. S.; Tien, M.; Brantley, S. L., Iron isotope fractionation during microbial reduction of iron: The importance of adsorption. *Geology* **2004**, *32*, 205-208.
- [28] Wu, L. L.; Beard, B. L.; Roden, E. E.; Kennedy, C. B.; Johnson, C. M., Stable Fe isotope fractionations produced by aqueous Fe(II)-hematite surface interactions. *Geochimica Et Cosmochimica Acta* **2010**, *74*, 4249-4265.
- [29] Bargar, J. R.; Fuller, C. C.; Marcus, M. A.; Brearley, A. J.; De la Rosa, M. P.; Webb, S. M.; Caldwell, W. A., Structural characterization of terrestrial microbial Mn oxides from Pinal Creek, AZ. *Geochimica Et Cosmochimica Acta* **2009**, *73*, 889-910.
- [30] Bargar, J. R.; Tebo, B. M.; Bergmann, U.; Webb, S. M.; Glatzel, P.; Chiu, V. Q.; Villalobos, M., Biotic and abiotic products of Mn(II) oxidation by spores of the marine *Bacillus* sp. strain SG-1. *American Mineralogist* **2005**, *90*, 143-154.
- [31] Parikh, S. J.; Lafeerty, B. J.; Meade, T. G.; Sparks, D. L., Evaluating Environmental Influences on As-III Oxidation Kinetics by a Poorly Crystalline Mn-Oxide. *Environmental Science & Technology* **2010**, *44*, 3772-3778.
- [32] Amstaetter, K.; Borch, T.; Larese-Casanova, P.; Kappler, A., Redox Transformation of Arsenic by Fe(II)-Activated Goethite (α -FeOOH). *Environmental Science & Technology* **2010**, *44*, 102-108.
- [33] Ginder-Vogel, M.; Landrot, G.; Fischel, J. S.; Sparks, D. L., Quantification of rapid environmental redox processes with quick-scanning x-ray absorption spectroscopy (Q-XAS). *Proceedings of the National Academy of Sciences of the United States of America* **2009**, *106*, 16124-16128.
- [34] Bisceglia, K. J.; Rader, K. J.; Carbonaro, R. F.; Farley, K. J.; Mahony, J. D.; Di Toro, D. M., Iron(II)-catalyzed oxidation of arsenic(III) in a sediment column. *Environmental Science & Technology* **2005**, *39*, 9217-9222.
- [35] Manning, B. A.; Fendorf, S. E.; Bostick, B.; Suarez, D. L., Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environmental Science & Technology* **2002**, *36*, 976-981.
- [36] Tournassat, C.; Charlet, L.; Bosbach, D.; Manceau, A., Arsenic(III) oxidation by birnessite and precipitation of manganese(II) arsenate. *Environmental Science & Technology* **2002**, *36*, 493-500.
- [37] Banerjee, D.; Nesbitt, H. W., XPS study of reductive dissolution of birnessite by H_2SeO_3 with constraints on reaction mechanism. *American Mineralogist* **2000**, *85*, 817-825.

- [38] Manceau, A.; Drits, V. A.; Silvester, E.; Bartoli, C.; Lanson, B., Structural mechanism of Co^{2+} oxidation by the phyllosulfate buserite. *American Mineralogist* **1997**, *82*, 1150-1175.
- [39] Scott, M. J.; Morgan, J. J., Reactions at oxide surfaces. 2. Oxidation of Se(IV) by synthetic birnessite. *Environmental Science & Technology* **1996**, *30*, 1990-1996.
- [40] Scott, M. J.; Morgan, J. J., Reactions at Oxide Surfaces. 1. Oxidation of As(III) by Synthetic Birnessite. *Environmental Science & Technology* **1995**, *29*, 1898-1905.
- [41] Lanson, B.; Drits, V. A.; Silvester, E.; Manceau, A., Structure of H-exchanged hexagonal birnessite and its mechanism of formation from Na-rich monoclinic buserite at low pH. *American Mineralogist* **2000**, *85*, 826-838.
- [42] Drits, V. A.; Silvester, E.; Gorshkov, A. I.; Manceau, A., Structure of synthetic monoclinic Na-rich birnessite and hexagonal birnessite .1. Results from X-ray diffraction and selected-area electron diffraction. *American Mineralogist* **1997**, *82*, 946-961.
- [43] Drits, V. A.; Lanson, B.; Gaillot, A. C., Birnessite polytype systematics and identification by powder X-ray diffraction. *American Mineralogist* **2007**, *92*, 771-788.
- [44] Silvester, E.; Manceau, A.; Drits, V. A., Structure of synthetic monoclinic Na-rich birnessite and hexagonal birnessite: II. Results from chemical studies and EXAFS spectroscopy. *American Mineralogist* **1997**, *82*, 962-978.
- [45] Post, J. E.; Heaney, P. J.; Hanson, J., Rietveld refinement of a triclinic structure for synthetic Na-birnessite using synchrotron powder diffraction data. *Powder Diffraction* **2002**, *17*, 218-221.
- [46] Post, J. E.; Veblen, D. R., Crystal-Structure Determinations of Synthetic Sodium, Magnesium, and Potassium Birnessite Using Tem and the Rietveld Method. *American Mineralogist* **1990**, *75*, 477-489.
- [47] Manceau, A.; Lanson, M.; Geoffroy, N., Natural speciation of Ni, Zn, Ba, and As in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction. *Geochimica et Cosmochimica Acta* **2007**, *71*, 95-128.
- [48] Zhu, M. Q.; Ginder-Vogel, M.; Parikh, S. J.; Feng, X. H.; Sparks, D. L., Cation Effects on the Layer Structure of Biogenic Mn-Oxides. *Environmental Science & Technology* **2010**, *44*, 4465-4471.
- [49] Bargar, J. R.; Tebo, B. M.; Villinski, J. E., In situ characterization of Mn(II) oxidation by spores of the marine *Bacillus* sp strain SG-1. *Geochimica Et Cosmochimica Acta* **2000**, *64*, 2775-2778.
- [50] Dick, G. J.; Clement, B. G.; Webb, S. M.; Fodrie, F. J.; Bargar, J. R.; Tebo, B. M., Enzymatic microbial Mn(II) oxidation and Mn biooxide production in the Guaymas Basin deep-sea hydrothermal plume. *Geochimica Et Cosmochimica Acta* **2009**, *73*, 6517-6530.
- [51] Manceau, A.; Kersten, M.; Marcus, M. A.; Geoffroy, N.; Granina, L., Ba and Ni speciation in a nodule of binary Mn oxide phase composition from Lake Baikal. *Geochimica et Cosmochimica Acta* **2007**, *71*, 1967-1981.
- [52] Saratovsky, I.; Gurr, S. J.; Hayward, M. A., The Structure of manganese oxide formed by the fungus *Acremonium* sp. strain KR21-2. *Geochimica et Cosmochimica Acta* **2009**, *73*, 3291-3300.
- [53] Saratovsky, I.; Wightman, P. G.; Pasten, P. A.; Gaillard, J. F.; Poepelmeier, K. R., Manganese oxides: Parallels between abiotic and biotic structures. *Journal of the American Chemical Society* **2006**, *128*, 11188-11198.
- [54] Tan, H.; Zhang, G. X.; Heaney, P. J.; Webb, S. M.; Burgos, W. D., Characterization of manganese oxide precipitates from Appalachian coal mine drainage treatment systems. *Applied Geochemistry* **2010**, *25*, 389-399.
- [55] Villalobos, M.; Bargar, J.; Sposito, G., Mechanisms of Pb(II) sorption on a biogenic manganese oxide. *Environmental Science & Technology* **2005**, *39*, 569-576.
- [56] Villalobos, M.; Toner, B.; Bargar, J.; Sposito, G., Characterization of the manganese oxide produced by *Pseudomonas putida* strain MnB1. *Geochimica Et Cosmochimica Acta* **2003**, *67*, 2649-2662.

- [57] Webb, S. M.; Tebo, B. M.; Bargar, J. R., Structural influences of sodium and calcium ions on the biogenic manganese oxides produced by the marine *Bacillus* sp., strain SG-1. *Geomicrobiology Journal* **2005**, *22*, 181-193.
- [58] Baes, C. F.; Mesmer, R. E., *The hydrolysis of cations*. Wiley: 1976.
- [59] Suter, D.; Siffert, C.; Sulzberger, B.; Stumm, W., Catalytic dissolution of iron(III)(hydr)oxides by oxalic acid in the presence of Fe(II). *Naturwissenschaften* **1988**, *75*, 571-573.
- [60] Zinder, B.; Furrer, G.; Stumm, W., The coordination chemistry of weathering: II. Dissolution of Fe(III) oxides. *Geochimica et Cosmochimica Acta* **1986**, *50*, 1861-1869.
- [61] Stone, A. T., Reductive Dissolution of Manganese(III/IV) Oxides by Substituted Phenols. *Environmental Science & Technology* **1987**, *21*, 979-988.
- [62] Stone, A. T.; Morgan, J. J., Reduction and Dissolution of Manganese(III) and Manganese(IV) Oxides by Organics. 2. Survey of the Reactivity of Organics. *Environmental Science & Technology* **1984**, *18*, 617-624.
- [63] Wang, Y.; Stone, A. T., Reaction of Mn^{III,IV} (hydr)oxides with oxalic acid, glyoxylic acid, phosphonoformic acid, and structurally-related organic compounds. *Geochimica et Cosmochimica Acta* **2006**, *70*, 4477-4490.
- [64] Godtfredsen, K. L.; Stone, A. T., Solubilization of Manganese Dioxide-Bound Copper by Naturally-Occurring Organic-Compounds. *Environmental Science & Technology* **1994**, *28*, 1450-1458.
- [65] Wang, Y.; Stone, A. T., The citric acid-Mn^{III,IV}O₂(birnessite) reaction. Electron transfer, complex formation, and autocatalytic feedback. *Geochimica et Cosmochimica Acta* **2006**, *70*, 4463-4476.
- [66] Kerisit, S.; Rosso, K. M., Oxidative adsorption of iron(II) at the hematite-water interface. *Geochimica Et Cosmochimica Acta* **2009**, *73*, A642-A642.
- [67] Kerisit, S.; Rosso, K. M.; Dupuis, M.; Valiev, M., Molecular computational investigation of electron-transfer kinetics across cytochrome-iron oxide interfaces. *Journal of Physical Chemistry C* **2007**, *111*, 11363-11375.
- [68] Lin, J. P.; Balabin, I. A.; Beratan, D. N., The nature of aqueous tunneling pathways between electron-transfer proteins. *Science* **2005**, *310*, 1311-1313.
- [69] Wigginton, N. S.; Rosso, K. M.; Stack, A. G.; Hochella, M. F., Jr., Long-range electron transfer across cytochrome-hematite (α -Fe₂O₃) interfaces. *Journal of Physical Chemistry C* **2009**, *113*, 2096-2103.
- [70] Singh, B.; Sherman, D. M.; Gilkes, R. J.; Wells, M.; Mosselmans, J. F. W., Structural chemistry of Fe, Mn, and Ni in synthetic hematites as determined by extended X-ray absorption fine structure spectroscopy. *Clays and Clay Minerals* **2000**, *48*, 521-527.
- [71] Campbell, A. S.; Schwertmann, U.; Stanjek, H.; Friedl, J.; Kyek, A.; Campbell, P. A., Si incorporation into hematite by heating Si-ferrihydrite. *Langmuir* **2002**, *18*, 7804-7809.
- [72] Galvez, N.; Barron, V.; Torrent, J., Preparation and properties of hematite with structural phosphorus. *Clays and Clay Minerals* **1999**, *47*, 375-385.
- [73] Cornell, R. M.; Schwertmann, U., *The Iron Oxides: Structure, Properties, Reactions, Occurrences, and Uses*. 2nd ed.; Wiley-VCH: Weinheim, 2003; p 664.
- [74] Catalano, J. G.; Brown, G. E., Jr., Uranyl adsorption onto montmorillonite: Evaluation of binding sites and carbonate complexation. *Geochimica et Cosmochimica Acta* **2005**, *69*, 2995-3005.
- [75] Catalano, J. G.; Park, C.; Fenter, P.; Zhang, Z., Simultaneous inner- and outer-sphere arsenate complexation on corundum and hematite. *Geochimica et Cosmochimica Acta* **2008**, *72*, 1986-2004.
- [76] Catalano, J. G.; Trainor, T. P.; Eng, P. J.; Waychunas, G. A.; Brown, G. E., Jr., CTR diffraction and grazing-incidence EXAFS study of U(VI) adsorption onto α -Al₂O₃ and α -Fe₂O₃ (1-102) surfaces. *Geochimica et Cosmochimica Acta* **2005**, *69*, 3555-3572.
- [77] Catalano, J. G.; Zhang, Z.; Fenter, P.; Bedzyk, M. J., Inner-sphere adsorption geometry of Se(IV) at the hematite (100)-water interface. *Journal of Colloid and Interface Science* **2006**, *297*, 665-671.

- [78] Catalano, J. G.; Zhang, Z.; Park, C.; Fenter, P.; Bedzyk, M. J., Bridging arsenate surface complexes on the hematite (012) surface. *Geochimica et Cosmochimica Acta* **2007**, *71*, 1883-1897.
- [79] Villalobos, M.; Lanson, B.; Manceau, A.; Toner, B.; Sposito, G., Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*. *American Mineralogist* **2006**, *91*, 489-502.
- [80] Silvester, E.; Charlet, L.; Tournassat, C.; Gehin, A.; Greneche, J. M.; Liger, E., Redox potential measurements and Mossbauer spectrometry of Fe^{II} adsorbed onto Fe^{III} (oxyhydr)oxides. *Geochimica et Cosmochimica Acta* **2005**, *69*, 4801-4815.
- [81] Pedersen, H. D.; Postma, D.; Jakobsen, R.; Larsen, O., Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). *Geochimica et Cosmochimica Acta* **2005**, *69*, 3967-3977.
- [82] Drits, V. A.; Tchoubar, C., *X-ray diffraction by disordered lamellar structures: Theory and applications to microdivided silicates and carbons*. Springer: 1990.
- [83] Plançon, A., CALCIPOW: a program for calculating the diffraction by disordered lamellar structures. *Journal of Applied Crystallography* **2002**, *35*, 377.
- [84] Chukhrov, F.; Sakharov, B.; Gorshkov, A.; Drits, V.; Dikov, Y., Crystal structure of birnessite from the Pacific Ocean. *International Geology Review* **1985**, *27*, 1082-1088.
- [85] Lanson, B.; Drits, V. A.; Feng, Q.; Manceau, A., Structure of synthetic Na-birnessite: Evidence for a triclinic one-layer unit cell. *American Mineralogist* **2002**, *87*, 1662-1671.
- [86] Lanson, B.; Drits, V. A.; Gaillot, A. C.; Silvester, E.; Plançon, A.; Manceau, A., Structure of heavy-metal sorbed birnessite: Part 1. Results from X-ray diffraction. *American Mineralogist* **2002**, *87*, 1631-1645.
- [87] Lanson, B.; Marcus, M. A.; Fakra, S.; Panfili, F.; Geoffroy, N.; Manceau, A., Formation of Zn-Ca phyllo-manganate nanoparticles in grass roots. *Geochimica Et Cosmochimica Acta* **2008**, *72*, 2478-2490.
- [88] Gaillot, A. C.; Drits, V. A.; Manceau, A.; Lanson, B., Structure of the synthetic K-rich phyllo-manganate birnessite obtained by high-temperature decomposition of KMnO₄: Substructures of K-rich birnessite from 1000 °C experiment. *Microporous and Mesoporous Materials* **2007**, *98*, 267-282.
- [89] Gaillot, A. C.; Flot, D.; Drits, V. A.; Manceau, A.; Burghammer, M.; Lanson, B., Structure of synthetic K-rich birnessite obtained by high-temperature decomposition of KMnO₄. I. Two-layer polytype from 800 °C experiment. *Chemistry of Materials* **2003**, *15*, 4666-4678.
- [90] Gaillot, A. C.; Lanson, B.; Drits, V. A., Structure of birnessite obtained from decomposition of permanganate under soft hydrothermal conditions. 1. Chemical and structural evolution as a function of temperature. *Chemistry of Materials* **2005**, *17*, 2959-2975.
- [91] Webb, S. M.; Tebo, B. M.; Bargar, J. R., Structural characterization of biogenic Mn oxides produced in seawater by the marine *Bacillus* sp. strain SG-1. *American Mineralogist* **2005**, *90*, 1342.
- [92] Dove, P. M.; Hochella, M. F., Jr., Calcite precipitation mechanisms and inhibition by orthophosphate: In situ observations by Scanning Force Microscopy. *Geochimica et Cosmochimica Acta* **1993**, *57*, 705-714.
- [93] Manceau, A.; Lanson, B.; Drits, V. A., Structure of heavy metal sorbed birnessite. Part III: Results from powder and polarized extended X-ray absorption fine structure spectroscopy. *Geochimica Et Cosmochimica Acta* **2002**, *66*, 2639-2663.
- [94] Loring, J. S.; Simanova, A. A.; Persson, P., Highly mobile iron pool from a dissolution-readsorption process. *Langmuir* **2008**, *24*, 7054-7057.
- [95] Beitler, B.; Chan, M. A.; Parry, W. T., Bleaching of Jurassic Navajo sandstone on Colorado Plateau Laramide highs: Evidence of exhumed hydrocarbon supergiants? *Geology* **2003**, *31*, 1041.

- [96] Committee on Prospering in the Global Economy of the 21st Century, *Rising Above the Gathering Storm: Energizing and Employing America for a Brighter Economic Future*. National Academies Press: Washington, DC, 2007.
- [97] The Congressional Commission on the Advancement of Women and Minorities in Science, E. a. T. D., *Land of Plenty: Diversity as America's Competitive Edge in Science, Engineering and Technology*. National Science Foundation: Washington, DC, 2000.
- [98] The Boyer Commission on Educating Undergraduates in the Research University, *Reinventing Undergraduate Education: A Blueprint for America's Research Universities*. Carnegie Foundation for the Advancement of Teaching: New York, NY, 1998.
- [99] Handelsman, J.; Ebert-May, D.; Beichner, R.; Bruns, P.; Chang, A.; DeHaan, R.; Gentile, J.; Lauffer, S.; Stewart, J.; Tilghman, S. M.; Wood, W. B., Scientific Teaching. *Science* **2004**, *304*, 521-522.
- [100] Kuh, G. D., *High-Impact Educational Practices: What They Are, Who Has Access to Them, and Why They Matter*. Association of American Colleges and Universities: Washington, DC, 2008.
- [101] The Boyer Commission on Educating Undergraduates in the Research University, *Reinventing Undergraduate Education: Three Years after the Boyer Report*. Carnegie Foundation for the Advancement of Teaching: New York, NY, 2002.
- [102] Karukstis, K. K.; Elgren, T. E., *Developing and Sustaining a Research-Supportive Curriculum: A Compendium of Successful Practices*. Council on Undergraduate Research: Washington, DC, 2007.
- [103] Laursen, S.; Hunter, A.-B.; Seymour, E.; Thiry, H.; Ginger, M., *Undergraduate Research in the Sciences: Engaging Students in Real Science*. Josey-Bass: San Francisco, CA, 2010.
- [104] Bunnell, J., Medical Geology: Emerging Discipline on the Ecosystem–Human Health Interface. *EcoHealth* **2004**, *1*, 15-18.
- [105] Selinus, O.; Alloway, B. J., *Essentials of medical geology: impacts of the natural environment on public health*. Academic Press: 2005.
- [106] Skinner, H. C. W.; Berger, A. R., *Geology and Health: closing the gap*. Oxford University Press: 2003.
- [107] Sahai, N.; Schoonen, M. A. A., *Medical mineralogy and geochemistry*. Mineralogical Society of America: Washington, DC, 2006; Vol. 64, p 332.
- [108] Liddell, D.; Miller, K., *Mineral fibers and health*. CRC: 1991.
- [109] Huba, M. E.; Freed, J. E., Learner-centered assessment on college campuses: Shifting the focus from teaching to learning. *Community College Journal of Research and Practice* **2000**, *24*, 759-766.
- [110] Kim, S. H.; Kim, S. J.; Oh, S. M., Preparation of layered MnO₂ via thermal decomposition of KMnO₄ and its electrochemical characterizations. *Chemistry of Materials* **1999**, *11*, 557-563.
- [111] Renuka, R.; Ramamurthy, S., An investigation on layered birnessite type manganese oxides for battery applications. *Journal of Power Sources* **2000**, *87*, 144-152.
- [112] Nakayama, M.; Kanaya, T.; Lee, J. W.; Popov, B. N., Electrochemical synthesis of birnessite-type layered manganese oxides for rechargeable lithium batteries. *Journal of Power Sources* **2008**, *179*, 361-366.
- [113] Kim, Y.; Hong, Y.; Kim, M. G.; Cho, J., Li_{0.93}[Li_{0.21}Co_{0.28}Mn_{0.51}]O₂ nanoparticles for lithium battery cathode material made by cationic exchange from K-birnessite. *Electrochemistry Communications* **2007**, *9*, 1041-1046.

BIOGRAPHICAL SKETCH

JEFFREY G. CATALANO

Department of Earth and Planetary Sciences
Center for Materials Innovation
Washington University in St. Louis
Saint Louis MO 63130-4862

Tel.: (314) 935-6015
Fax.: (314) 935-7361
E-mail: catalano@wustl.edu
<http://envgeochem.wustl.edu/>

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).

Publications:

Five Related Publications:

Catalano J.G., Fenter P., Park C., Zhang Z., Rosso K.M. (2010) Structure and oxidation state of hematite surfaces reacted with aqueous Fe(II) at acidic and neutral pH. *Geochimica et Cosmochimica Acta* **74**, 1498-1512.

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., 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., 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.

Five Other Significant Publications:

Catalano J.G. (2010) Relaxations and interfacial water ordering at the corundum (110) surface. *The Journal of Physical Chemistry C* **114**, 6624-6630.

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., 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 (1 $\bar{1}$ 02) 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.

Synergistic Activities:

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

Collaborators in the Last 48 Months:

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

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); Alison Beehr (Ph.D. exp. 2013); Yun Luo (Post-doc 2009-Present)

BUDGET JUSTIFICATION

Senior Personnel:

1.0 month per year support for Catalano (PI). Catalano is responsible for project management, proposal submission to national user facilities, and training of the graduate student in laboratory and analytical methods. In addition, Catalano shares co-responsibility for data acquisition, data analysis, and preparation of publications with the graduate student.

Other Personnel:

12.0 months per year support for a graduate student except in year 1, when support for two graduate students is requested. Support is requested in years 1 and 2 for current graduate student Andrew J. Frierdich to complete his Ph.D. degree. Support is requested in years 2 to 5 for new graduate student Margaret Anne Gray, who has university and other support available in her first and second year. Support in the final year of this 5-year project may go to a new graduate student if Ms. Gray has completed her degree.

In addition, support is requested for two undergraduate student researchers per year (\$4000 per student). The funding provided will allow the PI to provide hourly pay for summer research positions. Hourly pay is essential to providing these opportunities to students lacking substantial family wealth as such students need to support themselves in summer.

Travel:

Costs were estimated based on previous trips, current airfare, federal per-diem and standard mileage rates.

Travel to Technical Conferences

\$2000 per year for the PI and a graduate student to attend a scientific conference such as GSA, AGU, ACS, or Goldschmidt (when in the United States).

Travel to Advanced Photon Source to Conduct Measurements

This project requires travel to the Advanced Photon Source to conduct X-ray spectroscopic and scattering measurements. 6 person-trips per year are required at a cost of \$600 per trip.

Materials and Supplies:

\$4000 per year for consumable supplies. Expenses estimated based on current usage and projected needs and calculated from Washington University contract prices with major vendors (e.g., Fisher Scientific, Airgas, Ted Pella) include: \$700 for laboratory gases for anaerobic chambers and water deoxygenation; \$3000 for laboratory consumables, including plasticware, syringes and syringe filters, tubing, centrifuge tubes, water purification supplies, and sample holders and supplies for analytical methods; and \$300 for chemicals

Publication Costs:

\$500 per year for page charges for publications in journals.

Shipping and Faxes:

\$250 per year for shipping samples to and from national user facilities and for faxing access and safety forms to these facilities.

Analyses:

\$4000 per year to pay hourly instrument usage fees. These are determined based on the estimated number of hours of use per year and the current rates for instrument time. Major annual expenses include powder XRD, TEM, ICP-OES, and ICP-MS measurements. Other expenses may include SEM-EDS, AFM, and BET surface area measurements.

Current and Pending Support

Other agencies (including NSF) to which this proposal has been/will be submitted

Investigator: Jeffrey Catalano

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

Project/Proposal Title:

Iron Oxide Morphology and Composition as Possible Indicators of Sedimentary Redox Cycling (Single PI)

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: Current Pending Submission Planned in Near Future *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 (Single PI)

Source of Support: NSF/GEO-EAR

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

Project/Proposal Title: Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments

[Catalano PI; co-PIs Giammar (Wash. U.) and Wang (PNNL)]

Source of Support: DOE/SBR

Total Award Amount: \$624,385 (WU portion)

Total Award Period Covered: 06/01/11 – 05/31/14

Location of Project: Washington University

Person-Months Per Year Committed to the Project.

Cal:

Acad:

Sumr: 1

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

Project/Proposal Title: Bacterial Effects on Uranium and Technetium Incorporation into Carbonate Minerals

[co-PI Catalano; PI Lüttge (Rice); co-PIs Arvidson (Rice), Icenhower (Rice)Burgos (Penn St.), Wu (PNNL), Um (PNNL)]

Source of Support: DOE/SBR

Total Award Amount: \$312,807 (WU portion)

Total Award Period Covered: 10/01/10 – 9/30/13

Location of Project: Washington University

Person-Months Per Year Committed to the Project.

Cal:

Acad:

Sumr: 0.5

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

Project/Proposal Title:

Iron-Bearing Phyllosilicate Clay Formation Pathways: Mineralogical Constraints on Past Martian Environmental Conditions (Single PI)

Source of Support: NASA/MFRP

Total Award Amount: \$236,743

Total Award Period Covered: 06/01/11 – 05/31/12

Location of Project: Washington University

Person-Months Per Year Committed to the Project.

Cal:

Acad:

Sumr: 1

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

Project/Proposal Title:

Nanoscale Mineral Transformations During Biogeochemical Cycling and the Fate of Trace Elements and Nutrients

THIS PROPOSAL

Source of Support: NSF/CAREER

Total Award Amount: \$523,891

Total Award Period Covered: 08/01/11 – 07/31/16

Location of Project: Washington University

Person-Months Per Year Committed to the Project.

Cal:

Acad:

Sumr: 1.0

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. A Dionex DX 500 ion chromatograph and a TOC analyzer are also available.

Department of Energy, Environmental, and Chemical Engineering

Shared analytical facilities in the Department of Energy, Environmental and Chemical Engineering include the Environmental Nanoscale Analysis Laboratory and the Jens Environmental Engineering Laboratory. These laboratories are common, centralized facilities maintained by full time technicians. Analytical equipment housed in these laboratories include a BET surface area analyzer, an inductively coupled plasma mass spectrometer (ICP-MS), a 96-well plate reader, an atomic absorbance spectrophotometer, a UV-visible spectrophotometer, a gas chromatograph mass spectrometer (GC-MS), three gas chromatographs (equipped with

flame-ionization, photo-ionization, electron-capture, and thermal-conductivity detectors), a high-performance liquid chromatograph (HPLC) with diode array detector, and a Fourier transform infrared spectrometer with accessories (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, and a Labconco freeze drier.

Center for Material Innovation (CMI)

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

Nano Research Facility (NRF)

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

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, Surface X-ray Scattering measurements at 5-ID, 6-ID, 13-ID, 20-ID, and 33-ID-D, powder X-ray diffraction at 5-BM, 11-BM, and 13-BM, and total X-ray scattering measurements for PDF analysis at 1-ID, 11-ID-B, and 11-ID-C. Sample preparation space is available in wet chemistry laboratories at this facility.