

PROJECT SUMMARY

Intellectual Merit: Biogeochemical iron cycling involves primarily the alternation of iron between Fe(II) and Fe(III) oxidation states. This iron redox cycling is connected to the biogeochemical cycles of carbon, oxygen, phosphorus, and sulfur, and plays an important role controlling the fate of contaminants such as arsenic, uranium, and trichloroethylene. Aqueous Fe(II) and Fe(III) oxide minerals often coexist during biogeochemical iron cycling, and secondary abiotic reactions between these species may transform poorly crystalline iron oxides into more crystalline phases, fractionate iron isotopes, affect contaminant fate and speciation, and possibly acts as a negative feedback on microbial iron reduction. As these secondary processes have important geochemical and environmental implications, we need to obtain a mechanistic understanding of the fundamental reactions that occur between aqueous Fe(II) and Fe(III) oxides.

Recent studies have observed electron transfer and atom exchange between aqueous Fe(II) and crystalline Fe(III) oxides. Preliminary measurements reveal that the reaction of Fe(II) with hematite (α -Fe₂O₃) varies with crystallographic orientation, with the (001) surface experiencing growth and other surfaces dissolution. Similar effects were seen at pH 3 and 7. As these reactions appear to be independent of Fe(II) adsorption and do not affect the bulk mineralogy or fluid composition, they are effectively “hidden” redox processes. We hypothesize that Fe(II) serves a catalytic role, with iron atoms transferring to (001) surfaces through solution as Fe(II), and electrons transferring away from this surface through the hematite structure.

The objectives of this proposal are to: (1) characterize the nature of the dynamic hematite surface redox processes operating in the presence of Fe(II), including how they vary with solution conditions and time and whether they are continuous or self-limiting; (2) determine how this coupled growth and dissolution is affected by the presence of the common inorganic species aluminum, phosphate, and silicate, all known hematite growth modifiers; (3) determine how these processes affect the speciation of structurally compatible [Ni(II)] and incompatible [As(V)] contaminants; and (4) investigate whether these processes can be activated during reductive dissolution by sulfide, an important process in marine sediments.

These studies are expected to demonstrate a new complex abiotic interfacial redox process that occurs when biogeochemical iron cycling creates systems with coexisting Fe(II) and Fe(III) species. These studies may also provide new insight into iron biomineralization and nanoparticle synthesis. Finally, similar processes may occur for many elements that coexist in different oxidation states having different solubilities, such as S, Mn, or U; the expected results may thus serve as a guide for exploring complex redox processes in other geochemical systems.

Broader Impacts: This project will facilitate the training of two new graduate researchers in the field of biogeochemistry. It will also allow a number of undergraduate researchers (2-3 per year) to be educated in the practice of science, training them in the formulation of research questions and the use of the tools and methods needed to answer scientific questions. Each graduate researcher will be given the opportunity to mentor an undergraduate student as part of their preparation as future educators. Results of this research will be incorporated into a graduate course taught by the PI. This research also may have societal impacts, as the studies of contaminant fate during these surface redox reactions may provide the basis for future development of new remediation strategies or methods to recharge water filtration systems.

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PROJECT DESCRIPTION

1. INTRODUCTION

The biogeochemical cycling of iron in soils, sediments, and marine and lacustrine aquatic systems involves primarily the alternation of iron between the +2 (ferrous) and +3 (ferric) oxidation states (Stumm and Sulzberger, 1992). Biogeochemical iron cycling is coupled to the carbon cycle through anaerobic respiration of organic matter coupled to Fe(III) reduction (Kappler and Straub, 2005), to the oxygen cycle through abiotic and microbial reoxidation of Fe(II) (Weber et al., 2006), to the phosphorus cycle through the adsorption of phosphate onto iron oxide surfaces, limiting its bioavailability (Berner, 1973; Wheat et al., 1996, Bjerrum et al., 2002), and to the sulfur cycle through reoxidation of microbially-produced sulfide by iron oxides in marine sediments (Canfield et al., 1992; Poulton et al., 2004). Biogeochemical iron cycling in ancient systems has been implicated in the formation of banded iron formations (Konhauser et al., 2002; Johnson et al., 2008). Iron cycling also plays an important role in controlling the fate of natural and anthropogenic water contaminants, such as arsenic (Smedley and Kinniburgh, 2001), uranium (Wilkins et al., 2007), and trichloroethylene (Charlet et al., 1998a).

Conceptual iron redox cycles (**Figure 1**) have been proposed to describe key mechanisms and explore linkages with other element cycles. Common among these conceptualizations is the inherently small size of such cycles, as the processes involved happen on a local, rather than regional or global, scale. Along these lines, Stumm and Sulzberger (1992) proposed the “local” iron cycle, with Fe(III) reduced by organic molecules and Fe(II) oxidized by O₂. Iron reduction was suggested to be photocatalyzed, and iron oxidation catalyzed by mineral surfaces. While these processes are likely important in some near-surface aquatic systems, such as mountain streams (McKnight et al., 1988, 2001; McKnight and Duren, 2004), the majority of iron redox cycling likely involves microbial activity (Weber et al., 2006). A general microbial iron redox cycle involves the reduction of Fe(III) coupled to the oxidation of an electron donor (e.g., anaerobic respiration of organic matter, with Fe(III) serving as a terminal electron acceptor) and the oxidation of Fe(II) coupled to the reduction of an electron donor (e.g., anaerobic, photoautotrophic Fe(II) oxidation that fixes CO₂ into biomass). While the actual processes involved are varied and complex, microbial reactions are likely the dominant players in iron redox cycling (Weber et al., 2006). Although not a dominant component in modern systems, iron redox cycling was likely a key part of oxygenic and anoxygenic photosynthesis during the early evolution of life on Earth (e.g., Konhauser et al., 2002; Beukes, 2004).

For either conceptual model considered, this cycling never results in the instantaneous transformation of all the iron in a system from one valence state to another. Iron redox cycling frequently results in the coexistence of Fe(II) and Fe(III) species in aquatic systems, which are free to react with each other. Considering the chemical conditions often encountered in aquatic systems undergoing redox cycling, Fe(II) occurs primarily as an aqueous species and Fe(III) as solid oxide, hydroxide, and oxyhydroxide minerals (referred to collectively as iron oxides for the remainder of this proposal) or as components of aluminosilicate clay minerals. Thus, reactions between coexisting Fe(II) and Fe(III) species frequently involves dissolved ferrous iron and solid ferric iron. While Fe(III) in iron oxides and clays are both accessible to microbial reduction (Weber et al., 2006), this proposal is focused solely on iron oxides because of their widespread occurrence (Cornell and Schwertmann, 2003), including being the largest iron-bearing component of sediments supplied to the global ocean (Poulton and Raiswell, 2002). Crystalline iron oxides such as goethite and hematite are especially relevant as these are the primary iron

oxide phases in systems, such as soils, that have undergone iron redox cycling (e.g., Thompson et al., 2006).

Secondary abiotic reactions between Fe(II) and Fe(III) phases during biogeochemical iron cycling are known to modify the mineralogy of the system (e.g., Hansel et al., 2005), affect contaminant fate and speciation (e.g., Charlet et al., 1998a,b), be the source of iron isotope fractionation during microbial dissimilatory iron reduction (e.g., Crosby et al., 2005), and possibly serve as a negative feedback for microbial iron reduction (e.g., Roden and Urrutia, 2002). However, the processes occurring during the reaction of aqueous Fe(II) with solid Fe(III) oxides are still not fully understood. Fe(II) has frequently been assumed to adsorb to iron oxide surfaces, like other divalent transition metal ions (e.g., Liger et al., 1999). However, it is also known that Fe(II) may induce mineral transformations among iron oxides, primarily either a recrystallization of ferrihydrite ($\text{Fe}_{10}\text{O}_{14}(\text{OH})_2 \cdot x\text{H}_2\text{O}$, see Michel et al., 2007) to goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), or hematite ($\alpha\text{-Fe}_2\text{O}_3$), or the formation of magnetite (Fe_3O_4) at higher Fe(II) concentrations (Tronc et al., 1992; Hansel et al., 2003, 2004, 2005). Recent studies of Fe(II) reaction with well crystalline iron oxides like hematite have revealed that although obvious mineral transformations do not occur, the reaction is more complex than simple adsorption, with electron and atom exchange occurring between aqueous Fe(II) and solid Fe(II) (Williams and Scherer, 2004; Crosby et al., 2005, 2007; Larese-Casanova et al., 2007a,b).

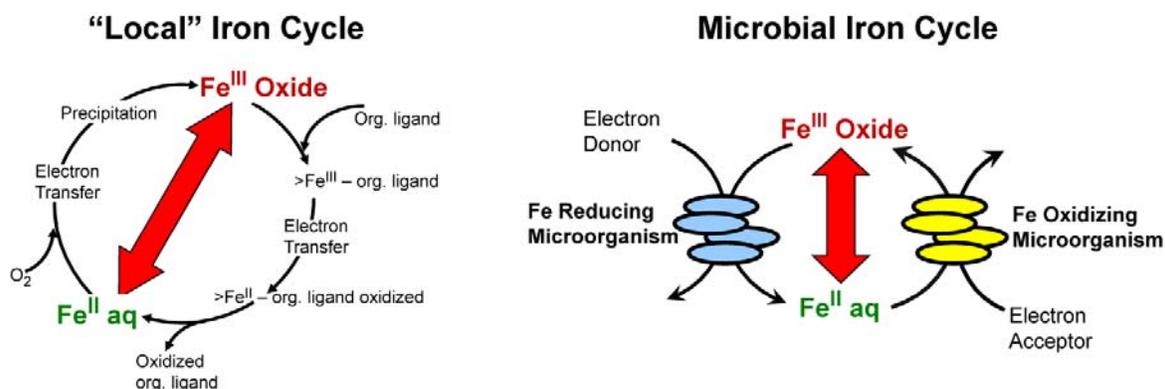


Figure 1. Two conceptual models of biogeochemical iron redox cycling: (left) The primarily abiotic “local” iron cycle from Stumm and Sulzberger (1992). Fe redox changes are suggested to be catalyzed by light [Fe(III) reduction] or surfaces [Fe(II) oxidation]. (right) The microbial iron cycle from Kappler and Straub (2005). Microorganisms couple the oxidation of Fe(II) with the reduction of electron acceptors and the reduction of Fe(III) with the oxidation of electron donors. In both conceptual models Fe(II) and Fe(III) species often coexist and may react with each other (large arrow).

I have begun exploring the processes responsible for the surprising observation of electron and atom exchange between aqueous Fe(II) and Fe(III) in hematite (see Section 3.1 for further discussion). I have observed that one crystallographic surface of hematite, (001), grows in the presence of Fe(II), while other surfaces dissolve. These growth and dissolution processes occur on the nanometer-scale at both pH 3 and 7. I hypothesize that Fe(II) accelerates the rate of dynamic dissolution and reprecipitation occurring at the hematite-water interface. As this coupled growth and dissolution process occurs with apparently little effect on the fluid composition or bulk mineralogy, I believe this is effectively a “hidden” interfacial redox process.

These observations have begun to elucidate the processes occurring during the reaction of Fe(II) with hematite, and further demonstrate that complex abiotic reactions occur in systems chemically poised by microbial activity. Here I propose to further explore these additional “hidden” redox processes that occur on iron oxides surfaces during biogeochemical iron cycling. The nature, time scale, and dependence of these processes on aqueous phase composition will be examined. Inhibitory or synergistic effects of common inorganic species (aluminum, silicate, and phosphate) will be investigated. The effect these dynamic processes have on the fate of contaminants will be studied. Finally, the potential for another naturally-occurring chemical reductant, sulfide, to activate these dynamic surface processes will be explored. Hematite was chosen for this study because it is widely-occurring, is the thermodynamically stable iron oxide under ambient conditions (Cornell and Schwertmann, 2003), does not undergo a rapid phase transformation upon reaction with Fe(II) like ferrihydrite (see Section 2.1) yet displays dynamic surface reactions (see Section 3.1), and exists in forms amenable to the detailed characterization methods needed to investigate the fundamental processes at work.

2. SCIENTIFIC BACKGROUND

Pertinent past scientific results are reviewed to provide context and guide the creation of the major hypotheses to be tested in the proposed work.

2.1. FE(II)-IRON OXIDE REACTIONS

Investigations of the reaction of aqueous Fe(II) with iron oxides historically have focused on two processes: conversion of iron oxides (primarily nanocrystalline ferrihydrite) to magnetite, and adsorption of Fe(II) on iron oxide surfaces. Research on the transformation of ferrihydrite to magnetite was motivated by the ability of other divalent transition metals (Mn, Cu, Ni, Co, and Zn) to convert ferrihydrite to a mixed-metal spinel phase (Cornell, 1988; Cornell and Giovanoli, 1988). Fe(II) was observed to have a similar effect at moderate to high Fe(II) concentrations, with conversion to goethite or related phases seen at lower Fe(II) concentrations (Jolivet et al., 1992; Tronc et al., 1992). This has been seen in later studies (e.g., Hansel et al., 2003, 2004; Jang et al., 2003), and Hansel et al. (2005) recently proposed a conceptual model describing the different conversion pathways and products for ferrihydrite reaction with Fe(II).

Fe(II) adsorption has been studied on more crystalline iron oxides, primarily hematite (e.g., Liger et al., 1999; Jeon et al., 2001, 2003a,b), goethite (e.g., Coughlin and Stone, 1995; Liger et al., 1999) and magnetite (e.g., Klausen et al., 1995). This work was primarily motivated by the enhanced reactivity of sorbed Fe(II) toward the reduction of numerous inorganic and organic contaminant species (e.g., Charlet et al., 1998a,b; Liger et al., 1999). Fe(II) displays macroscopic adsorption behavior on iron oxides similar to other divalent cations (e.g., Coughlin and Stone, 1995); it shows similar adsorption behavior on aluminum and titanium oxides as well (e.g., Nano et al., 2006). Surface complexation models have been created that successfully modeled this adsorption behavior (e.g., Liger et al., 1999; Silvester et al., 2005). However, studies have generally found that a portion of the sorbed Fe(II) is not desorbable, even in HCl at concentrations up to 0.5 M (e.g., Jeon et al., 2001), suggesting that a process more complex than simple adsorption occurs in these systems.

Other observations suggesting complex processes operate in these systems include the enhanced adsorption of Co(II), Ni(II), and Cu(II) on goethite in the presence of Fe(II), with a portion of the divalent cations not desorbable, implying they are incorporated into the mineral structure (Coughlin and Stone, 1995). These and other observations prompted recent Mössbauer

spectroscopy measurements that have revealed that electron transfer occurs between aqueous Fe(II) and Fe(III) in hematite, goethite, and ferrihydrite (Williams and Scherer, 2004). Further measurements revealed that Fe(II) adsorbed on hematite appears to result in some Fe(II) sites in the hematite structure (this Fe(II) can only be recovered upon complete dissolution of hematite) (Larese-Casanova et al., 2007a), and that at high surface coverage ($>4 \mu\text{mol}/\text{m}^2$, corresponding to initial $[\text{Fe(II)}] > 3 \text{ mM}$) a clear Fe(II) signature is present, although a portion of this may be precipitated Fe(OH)_2 (Larese-Casanova et al., 2007b). Iron isotope fractionation from microbial dissimilatory iron reduction and abiotic Fe(II) sorption onto iron oxides reveals that fractionation in these systems occurs at the mineral-water interface (and is not from any biological process) (Crosby et al., 2005, 2007; Icopini et al., 2004). These measurements also imply that atom exchange occurs between aqueous Fe(II) and Fe(III) on the surfaces of iron oxides, as otherwise there would be no fractionation.

Recent calculations provide theoretical support that electrons may be transferred from the surface of hematite into the bulk structure. Molecular dynamic (MD) simulations suggest that Fe(II) may localize near the hematite (012) surface, and that this is stabilized by the presence of hydroxyls or water molecules on the surface (Wang and Rustad, 2006), presumably because protons on these molecules serve to balance the excess negative charge created by Fe(II) in the hematite structure. Combined MD simulations and ab initio calculations of electron transfer rates from hematite (001) and (012) surfaces into the bulk structure found that the presence of water lowered the activation energy and provided a large driving force for electron diffusion towards the bulk (Kerisit and Rosso, 2006). Ab initio calculations demonstrate that electrons transport through the bulk hematite structure as small polarons, and that their transport in the (001) plane is energetically more favorable than along [001] (Rosso et al., 2003). Kinetic Monte Carlo calculations found that electrons can diffuse away from the site of interfacial electron transfer at rates consistent with measured conductivities of hematite, but that certain defects can limit electron mobility. Al(III) substitution for Fe(III) had a minimal effect as it does not alter the electrostatic potentials in the structure because it has the same charge as Fe (Kerisit and Rosso, 2007).

These recent experimental and theoretical studies suggest that complex processes are at work when Fe(II) reacts with iron oxides surfaces. It is clear that aqueous Fe(II) binds to Fe(III) oxide surfaces and transfers an electron into the substrate. It is also clear that this process results in isotopic exchange between pools of aqueous Fe(II) and solid Fe(III). These observations together suggest that the electron Fe(II) transfers to the iron oxide surface reduces an Fe(III) atom, which then desorbs, returning Fe(II) to solution. While the separation between the sites of Fe(II) adsorption and Fe(III) reductive desorption is unknown, these sites must differ for isotopic exchange to occur, and calculations demonstrate that the required electron transfer through hematite is feasible. Observation that a fraction of the “sorbed” Fe(II) cannot be recovered suggests that this process is not fully catalytic, as some Fe(II) must either remain in the hematite structure or somehow become oxidized. Further study is needed to better define the mechanisms involved in the reaction of Fe(II) with hematite and how these vary under different conditions.

2.2. DYNAMIC MINERAL SURFACE PROCESSES

The surfaces of moderately soluble mineral phases, such as calcite (CaCO_3), often display dynamic surfaces (e.g., Dove and Hochella, 1993; Stipp et al., 1994; Teng et al., 1998, 1999, 2000). Adsorbates can modify this behavior during mineral growth or dissolution (e.g., Dove and Hochella, 1993; Teng et al., 1997; Davis et al., 2000; Orme et al., 2001), which appears to be

a key control during biomineralization (De Yoreo and Dove, 2004). In certain systems chemical species that incorporate into the minerals structure can induce self-limited growth, e.g., growth stops after a molecular layer of the crystal has grown (e.g., Higgins and Hu, 2005).

Similar processes have not been observed to date on the surfaces of iron oxides. As dynamic surface changes are essentially kinetic phenomena, although thermodynamically driven, the low solubility of hematite (aqueous Fe(III) concentrations in the nanomolar to picomolar range) likely limits Fe mass transfer rates, and thus the rate at which processes can occur on hematite surfaces. However, hematite surfaces may possess a pool of surficial Fe(III) that rapidly dissolves at low pH (Samson and Eggleston, 1998; Sampson et al., 2000a). Although these active sites are transient, returning hematite to circumneutral conditions appears to regenerate the surface, recovering the initial rapid dissolution behavior (Samson and Eggleston, 2000). This demonstrates that there is some mobility of Fe(III) ions near the hematite surfaces, and suggests that hematite surfaces may potentially display dynamic growth and dissolution processes. It is likely that chemical species that enhance Fe mass transfer between different sites accelerate what are normally tremendously slow hematite surface processes.

2.3. ION ADSORPTION ON AND COPRECIPITATION WITH IRON OXIDES

A focus of many studies of iron oxides in geochemical and environmental settings has been the adsorption of contaminants, trace elements, and nutrients on to the surfaces of these phases. Adsorption has been studied extensively because it is a key process that controls the partitioning of many chemical species between mineral solids and natural waters (Brown and Parks, 2001). Iron oxides are important sorbents in geochemical and environmental systems (Brown et al., 1999). Ion adsorption behavior on iron oxide surfaces is generally pH-dependent, with cations adsorption increasing with increasing pH and oxoanion adsorption increasing with decreasing pH (**Figure 2**). Differences in the pH condition where adsorption occurs are thought to reflect differences in adsorption strength/affinity.

If present during growth, ions may also incorporate into the hematite structure, often substituting into the Fe site (Cornell and Schwertmann, 2003 and references therein). While most elements may substitute for at most a few mol% of Fe, Al can substitute at up to ~20 mol%. Al substitution in hematite is also thought to result in the formation of structural OH (Cornell and Schwertmann, 2003). Metal cations known to substitute into hematite include Cu(II), Ni(II), Mn(III), and Cr(III). Ni-, Cu-, and Cr-substituted hematite also contained structural OH (Kandori et al., 1998; Singh et al., 2000).

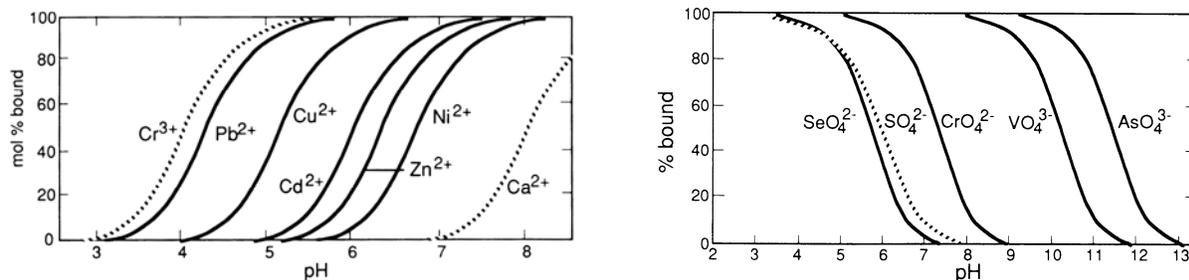


Figure 2. pH-dependent adsorption behavior of common inorganic contaminant cations and anions on ferrihydrite [from Stumm (1992) after Dzombak and Morel (1990)]. These ions show similar adsorption behavior on other iron oxides.

2.4. CONTROLS ON HEMATITE GROWTH AND MORPHOLOGY

Hematite formed in aqueous solution, often grown through transformation of fast-precipitating ferrihydrite, results in platy crystal morphologies dominated by (001) surfaces. Various organic and inorganic additives can modify this growth behavior, resulting in crystals elongated along [001] or polydomainic particles of various shapes (Cornell and Schwertmann, 2003). Phosphate leads to the formation of spindle-shaped hematite particles, often elongated along [001] (Galvez et al., 1999). Aluminum has an opposite effect, promoting the formation of thin platelets, suggesting an inhibition of growth along [001] (summarized in Cornell and Schwertmann, 2003). Unlike phosphate and many other shape modifiers, aluminum is incorporated into the hematite structure instead of primarily adsorbing on the surface. Silicate causes hematite formed from ferrihydrite to take on an ellipsoidal shape and occasionally display additional outgrowths on goethite (Cornell et al., 1987). Silicate also hinders the formation of aqueous Fe clusters in solution (Pokrovski et al., 2003) and affects the crystallinity and mineralogy of iron oxides produced during oxidation of Fe(II) solutions (Schwertmann and Cornell, 2000).

2.5. SULFIDIZATION OF IRON OXIDES

In many marine sediments the porewater distribution of sulfide is buffered by reaction with iron oxides (Canfield et al., 1992). Sulfide reductively dissolves iron oxides, frequently producing elemental sulfur (e.g., Yao and Millero, 1996; Poulton et al., 2003, 2004) and occasional sulfate, thiosulfate, and sulfite (dos Santos Afonso et al., 1992). High sulfide concentrations lead to the formation of amorphous FeS, although this phase can be transient depending on the solution conditions (Poulton et al., 2003, 2004). This appears to be purely a solubility effect (Davison et al., 1999). Only amorphous FeS appears to form on the time scales (hours to days) of these experiments; more crystalline iron sulfide phases were not identified (Poulton et al., 2003, 2004). All systems studied produced aqueous Fe(II), although a large portion was reported to be surface bound in some studies (Poulton et al., 2003, 2004).

3. PRELIMINARY RESEARCH RELEVANT TO THE PROPOSED WORK

3.1. STRUCTURAL CHANGES TO HEMATITE SURFACES AFTER REACTION WITH Fe(II)

I have made measurements in collaboration with Dr. Paul Fenter and Dr. Kevin Rosso regarding structural changes of specific surfaces of hematite after reaction with Fe(II). In these studies, oriented single crystals of hematite were reacted for ~15 hours with aqueous solution of 10^{-4} M Fe(II) at either pH 7 or 3 solutions. Changes in the molecular-scale structure of the surfaces were studied using XR, and we observed that the effects produced by Fe(II) varied with crystallographic orientation. (110) and (012) surfaces showed clear signs of dissolution over the limited duration of the experiment (**Figure 3**). Quantitative analysis of the XR data suggests that the structural changes are most consistent with the removal of a few molecular layers of each surface without a major roughening effect. This suggests dissolution occurs primarily at steps, as has been observed during XR measurements of orthoclase dissolution (Teng et al., 2001; Fenter et al., 2003). The (012) data is most striking as not only has dissolution occurred, but the resulting surface now consists of a mixture of two domain types differing in the terminating crystallographic layer [see (Catalano et al., 2007) for a description of mixed surface terminations of hematite]. This mixture of terminations manifests itself in the reversed relative intensity of

the midzone regions (large blue arrows) of the XR reflectivity (**Figure 3**). Similar effects are seen at pH 7 and 3.

In contrast, the XR data for the Fe(II)-reacted (001) surface displayed substantial oscillations (small black arrows) compared to an unreacted (001) surface in deionized water (**Figure 3**). Preliminary quantitative analysis of this data demonstrates that the surface is significantly smoother after reaction with Fe(II), and suggests the addition of a new ~ 1 nm thick hematite surface layer having increased structural disorder compared to that seen for an unreacted hematite. Fe K-edge resonant anomalous X-ray reflectivity (RAXR) measurements (not shown) confirm that this new material is not magnetite, maghemite, or green rust. Again, similar effects were seen at pH 7 and 3. The reason for the apparently more disordered structure of this hematite overgrowth is unclear, although it is possible minor Fe(II), H^+ , or both were incorporated during growth.

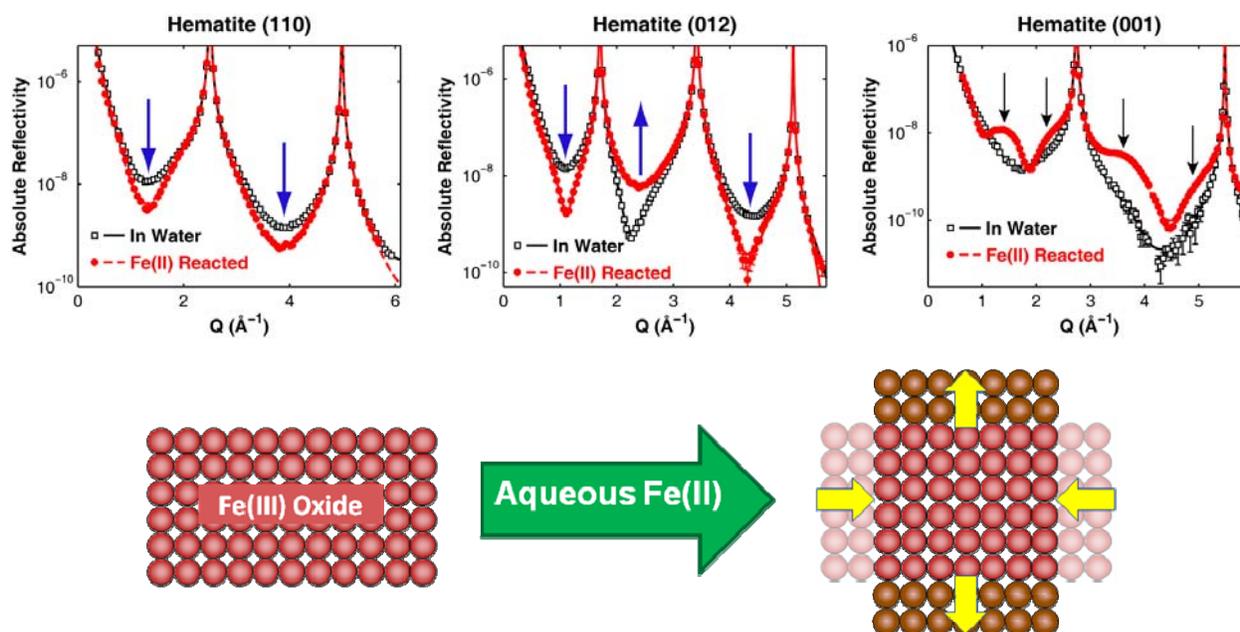


Figure 3. (top) X-ray reflectivity (XR) measurements of three hematite surfaces before and after reaction with aqueous Fe(II) at pH 7. The midzone intensity changes on the (110) and (012) surfaces after reaction (blue arrows) indicate dissolution of a few molecular layers of the surfaces. In contrast, new oscillations appear in the XR data for the (001) surface after reaction (black arrows), indicating the growth a surface film ~ 1 nm thick. (bottom) Schematic conceptual model of the simultaneous growth and dissolution process that occurs in the presence of Fe(II).

The localization of growth on (001) and dissolution on (110) and (012) surfaces suggests that electrons may transfer between surfaces through the hematite structure. A similar observation of charge migration between hematite surfaces has been seen in abiotic reductive dissolution experiments (K. Rosso, personal communication). As this nanoscale restructuring occurs at both pH 7, a condition where Fe(II) is known to adsorb to hematite surfaces, and pH 3, a condition where Fe(II) does not adsorb, the processes occurring appear to be independent of Fe(II) adsorption, and demonstrate there is still an Fe(II)-hematite surface interaction even when sorption is highly unfavorable. These observation suggests that Fe(II) serves a catalytic role, with Fe atoms transferring to (001) surfaces through solution as Fe(II), and electrons transferring away from this surface through the hematite structure. This conceptual model is consistent with

past observations of atom and electron exchange between Fe(II) and Fe(III) oxides (Williams and Scherer, 2004; Crosby et al., 2005, 2007; Larese-Casanova et al., 2007a,b).

Further study is needed to verify this conceptual model of Fe(II)-activated hematite surface transformations. Other outstanding questions include: Is this process continuous or self-limiting? What happens if common inorganic species are present that strongly bind to or incorporate into iron oxide surfaces, like aluminum, silicate, or phosphate? Do these species modify growth processes, as occurs with various inorganic and organic species on calcite? What happens to contaminant species during this process? Can this process be activated by other chemical species, such as sulfide?

4. PROPOSED RESEARCH

4.1. HYPOTHESES TO BE TESTED

The proposed research is designed to test the following main hypotheses:

- 1. Fe(II) activates simultaneous nanoscale growth and dissolution on hematite surfaces that is crystallographically controlled.*
- 2. Adsorbates modify this behavior, changing the surfaces that undergo growth and the rate of movement and morphology of steps.*
- 3. Compatible adsorbates incorporate into the new layers grown on hematite; incompatible adsorbates are released during dissolution but quickly resorb on newly grown surfaces.*
- 4. Reductive dissolution of hematite by sulfide activates these dynamic surface processes at low concentrations with additional iron sulfide precipitation at high concentrations.*

4.2. EXPERIMENTAL APPROACH

4.2.1. Materials and methods. To test the key hypotheses of this proposal, there is a need to both examine an array of reaction conditions and study fundamental processes and reaction mechanisms. These requirements will be met through the use of hematite in two forms: monodispersed powders and large single crystals of hematite. Powders consisting of monodispersed, monodomainic hematite particles that display (012) and (001) surfaces will be synthesized (Sugimoto et al., 1996). Mean particle sizes between 500 nm and 3 μm can be obtained by varying synthesis conditions; 500 nm particles will be used unless specific analysis methods require large sizes. Single crystal hematite will consist of commercially available 1 cm^2 , 1 mm thick wafers of natural hematite crystals oriented, cut, and polished to display atomically-smooth (001), (012), or (110) surfaces. Additional hematite crystals displaying natural growth faces of (001) and (012) surfaces, to be provided by Dr. Kevin Rosso (PNNL), will also be examined. The powdered hematite will allow for rapid screening of a range of chemical conditions as well as reproducible kinetic studies. The limited supply of available hematite single crystals requires that experiments on these substrates be conducted only for select conditions to elucidate the fundamental processes and mechanisms at work.

All experimental work will be conducted under strict anaerobic conditions whenever possible. Chemical work will be performed in an anaerobic chamber (Coy Laboratory Products) with a 5% H_2 /95% N_2 atmosphere and a palladium catalyst to consume any O_2 that enters the chamber by reaction with H_2 to produce water. As these chambers may still contain residual trace oxygen that can slowly oxidize aqueous Fe^{2+} , a secondary oxygen trap will be used to

remove any excess oxygen present in the system (Jeon et al., 2004). Dissolved O₂ concentrations will be monitored colorimetrically. Carbonate will be excluded from all studies to prevent the precipitation of siderite (FeCO₃).

An array of characterization tool will be utilized where appropriate. Elemental composition of the fluid phases will be determined inductively couple plasma-mass spectrometry (ICP-MS). Fe(II) concentrations will be measured spectrophotometrically (e.g., Stookey, 1970), and dissolved sulfide concentration measured either spectrophotometrically or with an ion-selective electrode. Methods to characterize the solid products in the powder studies include: powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron microprobe measurements, X-ray absorption near-edge structure (XANES) spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy, Brunauer-Emmett-Teller (BET) surface area analysis, and zeta potential measurements. Surface processes and reaction products in the single crystal studies will be characterized using: atomic force microscopy (AFM), ion microprobe measurements (NanoSIMS), Auger microscopy, X-ray reflectivity (XR), and resonant anomalous X-ray reflectivity (RAXR). Reviewers unfamiliar with XR are referred to Fenter (2002); those unfamiliar with RAXR are referred to papers by Park et al. (2006, 2007). Scanning tunneling microscopy (STM) measurements of select systems will be made with Dr. Kevin Rosso (PNNL).

4.2.2. Distribution of tasks among student researchers and the PI. As one of the goals of this proposal is to expose multiple undergraduate students to scientific research, the experiments involving powdered hematite are designed to be broken down into compact, discrete tasks. An undergraduate student can easily complete a single “mini-experiment” in a reasonable amount of time, and in this way can take part in a simple scientific experiment from start to finish. Depending on their interest level, undergraduate researchers can perform only basic wet chemical work in support of a research project being conducted by a graduate student or the PI, or also perform complimentary characterization methods, such as XRD and/or TEM. Motivated undergraduate students will be encouraged to carry out a series of intellectually-related tasks that together will form the basis of a scientific publication.

The two graduate students funded by this proposal will each work on complimentary powdered and single-crystal systems to learn to connect fundamental observation to processes occurring in more complex systems. Graduate students will be given the opportunity to mentor an undergraduate researcher when appropriate. The PI will be intimately involved in the proposed work, guiding the various research projects, training and mentoring graduate and undergraduate students, and conducting a portion of the proposed research. The graduate students will be expected to produce scientific manuscripts for publication, and the PI will involve undergraduate students in the writing process as well, with their level of involvement dependent on interest and ability.

4.3. PROJECT SYNOPSIS

4.3.1. Fe(II)-induced transformations of hematite. The first project for this proposal is focused on characterization of the transformations of hematite induced by Fe(II). As noted in Section 3.1, our observations of nanoscale dissolution on (012) and (110) surfaces of hematite and growth on (001) surfaces, combined with past studies that have identified electron transfer and atom exchange between aqueous Fe(II) and hematite, suggest that Fe(II) may act as a

catalyst, activating dynamic surface processes in the Fe(II)-H₂O-hematite system. The goal of this project is to explore this reaction in more detail to characterize the growth and dissolution processes occurring, to determine how these processes vary with pH and Fe(II) concentration, and to investigate whether these processes are continuous or self-limiting. The possibility that threshold Fe(II) concentrations are needed to activate these processes or initiate magnetite formation will be examined.

Initial experiments will examine the transformation of monodispersed, monodomainic hematite particles under a range of pH (3-7) and ferrous iron concentration (10^{-6} M to 10^{-3} M) conditions as a function of reaction time. Lower Fe(II) concentrations may also be explored but will be difficult to detect in solution because of the detection limits of spectrophotometric analysis methods. The Fe(II) and total Fe concentration in solution will be monitored over the course of reaction. Transformations of the solid phase will be monitored through a variety of methods for select representative samples. Powder XRD measurements will be used to identify the formation of other iron oxide phases (e.g., goethite, magnetite), although this is expected to occur only at the highest Fe(II) concentrations (see Section 2.1). SEM and TEM measurements will be used to determine morphologic changes in the particles after reaction, and if growth and/or dissolution are observed, electron diffraction will be used to verify the crystallographic directions these processes have occurred along. BET surface area measurements will identify systems that result in changes the particle size or shape distribution as reflected in changes in the specific surface area. Measurement of the change in zeta potential and particle size distribution of the hematite particles after reaction will also provide insight into the reaction process, and may provide additional evidence for the growth of material on the particles surfaces or a change in surface chemistry, as reflected by the measured zeta potential.

Select reaction conditions and times that display representative/unique reaction products will be further explored using single crystal hematite substrates. In situ and ex situ AFM measurements of hematite (001), (012), and (110) surfaces will be used to observe surface growth and dissolution and how these processes vary with time, pH, and Fe(II) concentration. STM measurements will be made to examine the initial nucleation of growth in select systems. XR measurements will be made to investigate how reaction conditions affect the molecular-scale surface structure. To verify growth and/or dissolution occurs on specific surfaces, select samples will be reacted in solutions spiked with ¹⁸O water to give an ¹⁸O abundance of at least 1% (compared to 0.2% natural abundance). NanoSIMS ion microprobe measurements will then be used to map the ¹⁸O distribution on the hematite crystal surfaces with ~50 nm resolution. ¹⁸O will serve as a tracer for the formation of new layers on the hematite surface, as it should be incorporated during growth. These measurements will compliment the AFM observations, provide additional confirmation that growth or dissolution occurs on specific surfaces, and will visualize the lateral extent of growth, i.e., NanoSIMS measurements help to distinguish between the formation of islands of new material versus growth of complete new layers. These investigations of powder and single crystal systems will provide new insight into the processes and mechanisms involved in the apparent dynamic surface reactions activated by ferrous iron.

4.3.2. Effects of common inorganic species. Numerous inorganic and organic molecules are ubiquitous in natural waters. Many of these are known to adsorb to or incorporate into iron oxides (see Section 2.3). Such species have the potential to affect the surface reaction between aqueous Fe(II) and hematite discussed above. In this project, I will investigate the effect three common inorganic species, aluminum, silicate, and phosphate, have on Fe(II)-induced surface

processes on iron oxides. All three of these species are known to affect the morphology of hematite, with silicate and phosphate appearing to enhance growth along [001] and aluminum hindering growth along this direction (see Section 2.4). I hypothesize these species will have a similar effect in Fe(II)-bearing systems.

Hematite powders will be reacted with Fe(II) solutions that also contain aluminum, silicate, or phosphate under a range of pH and concentration conditions similar to those used in Section 4.3.1. A subset of these studies will use hematite pre-sorbed with these additives to explore the effects of reaction sequence on surface transformations. All solutions will be designed to be undersaturated with respect to various Fe(II) solid phases (e.g., vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$). Solution concentrations of Fe(II) and the additive species will be monitored as a function of reaction time. The solid phase will be characterized after reaction to verify new phases have not precipitated, to examine morphologic changes, and to determine the relationship of any changes in particle shape to the hematite crystal structure. ATR-FTIR and/or Raman spectroscopy will be used to investigate changes in OH content of the hematite after reaction and to investigate phosphate and silicate binding modes.

Select chemical systems will be further investigated through studies using single crystal hematite. In situ and ex situ AFM measurements will be used to investigate how additives affect the processes seen in Section 4.3.1, including step movement and the nature of growth (e.g., layer by layer versus island formation), and to connect the observation from the powder studies with surface growth/dissolution mechanisms. Expected additive-induced changes in surface processes include step pinning, which phosphate is known to do on calcite surfaces (e.g., Dove and Hochella, 1993). XR measurements will be used to investigate how these additives affect the resulting molecular scale structure of the hematite-water interface. The effects of these additives on the orientation-dependence of growth and dissolution will be further investigated by NanoSIMS measurements of hematite crystals reacted in ^{18}O -spiked aqueous solutions. Auger microscopy will be used to investigate spatial distribution of near-surface Al, Si, or P after reaction. These studies will elucidate the effects strongly-sorbing aqueous species may have on these dynamic growth and dissolution processes on hematite surfaces.

4.3.3. Effect on contaminant and trace element fate and speciation. The fate of trace elements and natural and anthropogenic contaminants in aquatic systems is often affected by their adsorption onto the surfaces of minerals (e.g., Brown and Parks, 2001). The stability of such complexes is often predicated on the fact that many silicate and oxide minerals display slow dissolution kinetics (Blum and Stillings, 1995; Brantley and Chen, 1995; Dove, 1995; Nagy, 1995; Cornell and Schwertmann, 2003), providing surfaces that are effectively stable for adsorption even if the aqueous solution is undersaturated with respect to these phases. As my preliminary research suggests that Fe(II) makes hematite surfaces dynamic (and thus unstable from the perspective of an adsorbate), the presence of Fe(II) should be expected to affect the speciation of adsorbed contaminant ions.

The effect of Fe(II) on contaminant adsorption may manifest itself in multiple ways. As Fe(II) appears to induce growth of some hematite surfaces, ions compatible with the hematite structure, such as Co(II), Ni(II), and Cu(II), may be incorporated into this new material. This would be consistent with the enhanced adsorption of these elements on goethite in the presence of Fe(II) seen by Coughlin and Stone (1995). As Fe(II) induces surface transformations under pH conditions where its adsorption is expected to be both favorable (pH 7) and unfavorable (pH 3), it is likely that other divalent cations interact with hematite surfaces under these conditions,

even if they do not actually adsorb. These species might be incorporated into hematite (and thus removed from natural or industrial waters) at acidic pH values where their remediation through surface reactions has previously been considered unlikely.

Fe(II) may have a different effect on ions not compatible with the hematite structure, such as As(V). Fe(II) may induce the desorption of these species by removing the surface they are adsorbed on. Under conditions where their adsorption is still favorable, it would be expected that these species would resorb after some time, depending on their adsorption kinetics. Under conditions that favor desorption, Fe(II) may serve as a catalyst for this reaction, speeding up typically slow desorption kinetics. Although thermodynamically favorable, recent results suggest that Fe(II) does not reduce As(V) sorbed on iron oxides surfaces on time scales up to 1 month (Burnol et al., 2007), suggesting arsenic reduction is not expected in the systems described below.

This project will explore the effect Fe(II) has on the fate and speciation of two example contaminant/trace element species, Ni(II) and As(V), in the presence of hematite. Suspensions of hematite powders will be reacted with aqueous solutions containing Ni(II) or As(V) as well as Fe(II). pH values of 3 and 7 will be explored to investigate how this parameter affects Ni(II) fate, including its potential incorporation into new growth layers on hematite. These values were chosen as they represent end-member conditions where Ni(II) would be expected to adsorb or not adsorb while preventing oversaturation with respect to Fe(II) or Ni(II) hydroxide phases. As(V) adsorbs over a wide range of pH values, and while it is not possible to explore these reactions under the alkaline conditions where As(V) does not adsorb strongly because of Fe(II) solubility limits, different As(V) behavior at pH 3 and 7 may still be expected because of differences in the dominant arsenate protonation state in solution. A range of Ni(II), As(V), and Fe(II) concentrations will be examined to identify chemical trends, and select conditions at intermediate pH conditions will be explored. Based on the similar chemistry of phosphate and arsenate, the studies in Section 4.3.2 will be used as a guide as to the interesting chemical conditions to explore in the arsenate studies. The effect of Fe(II) on Ni(II) and As(V) desorption rates will also be explored.

Solution compositions, including dissolved Ni, As, and Fe(II) will be monitored as a function of reaction time to examine kinetic trends. The solid phase will be characterized after reaction to verify new phases have not precipitated and to determine the relationship of any changes in particle shape to the hematite crystal structure. BET surface area and zeta potential measurements of select samples will be made to study time-dependent changes in particle size and surface charge. Ni and As K-edge EXAFS measurements of select samples will be made to characterize possible changes in adsorption geometry after reaction, and to look for evidence of Ni incorporation onto hematite. The Ni EXAFS measurements may not be feasible because of X-ray fluorescence from the Fe in hematite; Ni K_{α} fluorescence may be difficult to observe in the presence of substantial Fe K_{β} fluorescence. RAXR measurements in the single crystal studies described below do not suffer from this problem, and thus may be essential to verifying Ni incorporation, including its location in the hematite structure.

Select systems will be further investigated using single crystal substrates. AFM measurements will investigate how these contaminants affect the growth and dissolution of specific surfaces. Ni(II) is expected to have little effect on this as it may incorporate into the structure, but As(V) is expected to have a large effect because it strongly sorbs. Similar effects as those seen in the phosphate systems described in Section 4.3.2 are expected. XR measurements will characterize the molecular-scale hematite surface structure after reaction and

RAXR measurements will determine the distribution of Ni(II) and As(V) at the hematite-water interface. If incorporated, Ni(II) will appear distributed throughout the crystal, whereas it will only appear on the surface if adsorbed. As(V) is expected to appear only on the hematite surface as it is generally incompatible with the hematite structure. NanoSIMS measurements of samples reacted in ^{18}O -spiked water will be made if unique surface features or growth behavior appear in the AFM measurements. If Ni(II) is verified to incorporate into the new growth layers, Auger Microscopy will be used to image the near-surface spatial distribution of Ni(II).

4.3.4. Transformations resulting from sulfide-hematite reaction. The final project in this proposal is focused on examining if other geochemical species can serve to activate these dynamic iron oxide surface processes, and thus affect the fractionation of iron isotopes and the fate of nutrient and contaminant species. A strong possible candidate to serve this role is sulfide. Sulfide reduction of iron oxides is an important process in marine sediments, generating Fe(II) in the process (see Section 2.5). Such a system is thus chemically poised to activate these dynamic surfaces processes. I hypothesize that sulfide does activate these processes at low concentrations (e.g., 1 to 10 μM), with the additional formation of iron sulfide precipitates at higher concentrations.

The mineral transformations that take place when sulfide is reacted with hematite powders will be studied under a range of pH conditions and as a function of reaction time and initial sulfide concentration. The ferrous iron and sulfide concentrations in solution will be monitored and the solid phase from select samples will be characterized to investigate the formation of new minerals (e.g., amorphous or crystalline FeS) and morphologic changes in iron oxides after reaction. S K-edge XANES spectroscopy will measure the solid-phase sulfur speciation after reaction to determine solid reaction products (e.g., iron sulfides, elemental sulfur). BET surface area and zeta potential measurements will also be made to provide additional constraints on particle size changes and surface modification. Sulfur speciation in solution after reaction will not be determined because of the complex array of possible reaction products make this difficult and because the focus of the proposed work is the hematite surface processes that occur in this system.

Select representative chemical systems will be further explored by reacting dissolved sulfide solutions with single crystals of hematite. AFM measurements will explore if sulfide initiates dynamic surface growth and dissolution, and will be used to look for signs of iron sulfide nucleation, which may occur well before the formation of such phases is apparent in XRD or SEM measurements in powder systems. These measurements will also determine whether any growth and dissolution processes that occur differ from those seen in sulfide-free systems. If these or other measurements suggest that the crystallographic growth direction differs in sulfide-bearing systems, select NanoSIMS measurements of samples reacted in ^{18}O -spiked water will be used for confirmation. XR measurements will elucidate the molecular-scale structure of the hematite-water interface after sulfide reaction. These studies will determine if sulfide can activate dynamic surface processes on hematite, and if these processes differ from those seen in sulfide-free systems.

5. EXPECTED SCIENTIFIC CONTRIBUTIONS

The studies contained in this proposal will provide a new understanding of nanoscale processes that occur on mineral surfaces during biogeochemical iron cycling. I will determine the mechanism likely responsible for or involved in a number of environmental processes,

including the fractionation of iron isotopes during dissimilatory iron reduction, the rapid transformation and sequestration or neutralization of environmental contaminants, and the inhibitory role of Fe(II) on microbial Fe(III) reduction. Of particular benefit to the geosciences community will be the examination of the variation of these processes with solution conditions, because if multiple processes are found to operate or if mechanisms shift with, for example, pH, then the resulting iron isotope fractionation may be expected to change as well. Obtaining an understanding of the mechanisms involved will constrain the chemical conditions where the fractionation seen in past studies (Icopini et al., 2004; Crosby et al., 2005, 2007) is applicable.

These studies will also provide insight into the effects iron cycling can have on contaminant fate and speciation and nutrient bioavailability. As I suspect the studies proposed here will detail fundamental aspects of previously unrecognized reactions that affect contaminant fate and speciation, future studies can then begin to explore more complex systems to examine their effects. Ultimately, these fundamental reactions can be built into conceptual models of contaminant fate and transport processes. In addition, these studies may suggest new ways that common inorganic species can affect iron bioavailability, and how iron redox cycling can affect phosphate bioavailability.

These studies may provide new insight into areas such as biomineralization and nanomaterial synthesis. It may be possible to control the shape of iron oxide particles by combining Fe(II), which would activate dynamic growth and dissolution, with a strongly sorbing molecule to control morphology. Aqueous Fe(II) may thus play an active role in magnetosome formation beyond the hypothesized initial transformation of ferrihydrite to magnetite (Bazylinski and Frankel, 2004). In a broader sense, the proposed research may demonstrate chemical processes that operate during the cycling of many elements. It is possible, and perhaps likely, that elements that coexist in soluble and insoluble oxidation states, such as S, Mn, and U, undergo similar dynamic surface processes driven by interfacial redox reactions. The results of the studies proposed here will thus serve as a guide for exploring complex redox processes occurring in other geochemical systems.

6. EXPECTED BROADER IMPACTS

This proposal will enhance the science education of multiple students at the undergraduate and graduate level. Two graduate students will be funded by this proposal, and their research will comprise the bulk of their Ph.D. dissertations. These students will be trained in advanced analytical techniques and will collaborate with leading scientists at two national laboratories. This proposal will also fund two to three undergraduate research positions per year. The main projects are designed to allow for small modules to be broken off that serve as undergraduate research projects (see Section 4.2.2). The PI will work with each undergraduate, walking them through the process of hypothesis formation, experimental design, data collection and analysis, and forming conclusions. This approach will serve to educate undergraduate students on how science actually works and will build their scientific confidence. In addition, an REU supplement request will be submitted for two summer undergraduate researchers if this proposal is funded. Applications for these positions will be actively sought from students at regional colleges and universities without graduate programs or that are historically attended by underrepresented minorities. Scientific results from this proposal will also be incorporated into a graduate course taught by the PI titled “Minerals in Aqueous Environments”.

The research also has potential societal impacts. These studies may reveal ways to incorporate heavy metal ions into iron oxides under acidic conditions, such as those found in

water impacted by acid mine drainage. It is possible that the addition of Fe(II) to these systems may lead to significant sequestration of many contaminant species, serving to enhance or substitute for other remediation strategies. The results of this study may also provide a scientific basis for new ways to regenerate iron oxide-based water filtration materials. If Fe(II) is found to significantly enhance desorption of contaminant species from hematite surfaces, then it may be possible to effectively clean and regenerate iron oxide sorbent materials in water filtration systems with a simple addition of Fe(II).

7. UNFUNDED COLLABORATORS

Dr. Paul Fenter of Argonne National Laboratory has agreed to participate in this research as an unfunded collaborator. Dr. Fenter is an expert on the application of advanced X-ray scattering methods to the study of fundamental aspects of mineral-water interface geochemistry, including interfacial water ordering, ion adsorption mechanisms, structure of the electrical double layer, and mineral dissolution. For the work proposed here, Dr. Fenter will contribute by assisting in the design of X-ray scattering experiments and the collection, analysis, and interpretation of X-ray scattering data.

Dr. Kevin Rosso of Pacific Northwest National Laboratory has offered to collaborate on this project and will provide assistance in the design of the atomic force microscopy measurements, make complimentary STM measurements when needed, and will conduct complimentary computational and experimental studies on related systems as part of an ongoing research project. A user proposal for the Environmental Molecular Sciences Laboratory (EMSL) at PNNL, of which Dr. Rosso is a member, will be submitted to formally establish this collaboration if this proposal is funded. Dr. Rosso is an expert in the application of scanning probe methods and *ab initio* modeling to the study of mineral surface reactions.

Dr. Frank Stadermann of the Laboratory for Space Sciences at Washington University has agreed to collaborate on this project to assist in making NanoSIMS and Auger Nanoprobe measurements. These instruments are available for use at Washington University on a collaborative basis, with users expected to contribute to the purchase of consumables; these costs are detailed in the budget justification. Dr. Stadermann is an expert in the application of NanoSIMS and Auger Nanoprobe methods to the study of geologic and extraplanetary materials.

8. RESULTS FROM PRIOR NSF SUPPORT

The PI has not previously received NSF support. This is his first submission to the NSF, as his first academic appointment began in September 2007.

9. ETBC EMPHASIS

This Emerging Topics in Biogeochemical Cycling (ETBC) emphasis proposal is intended to have the GEO/EAR program in Geobiology and Low-Temperature Geochemistry as the lead program. In line with the multidisciplinary goal of ETBC, the proposed work is also directly relevant to the following programs: the GEO/OCE program in Chemical Oceanography and the ENG/CBET program in Environmental Engineering. Parts of the proposed work may be relevant to the following programs: the GEO/OCE program in Marine Geology and Geophysics, the ENG/CBET program in Catalysis and Biocatalysis, the ENG/CBET program in Interfacial Processes and Thermodynamics, the MPS/CHE program in Analytical & Surface Chemistry, and the MPS/DNR program in Ceramics.

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BIOGRAPHICAL SKETCH

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

Five Relevant Publications:

Catalano J.G., Park C., Fenter P., Zhang Z. (2008) Simultaneous inner- and outer-sphere arsenate adsorption on corundum and hematite. *Geochim. Cosmochim. Acta*, in press.

Catalano J.G., Park C., Fenter P., Zhang Z. (2007) Interfacial water structure on the (012) surface of hematite: Ordering and reactivity in comparison with corundum. *Geochim. Cosmochim. Acta* **71**, 5313-5324.

Tanwar K., Lo C., Eng P.J., Catalano J.G., Brown G.E., Jr., Waychunas G.A., Chaka A.M., Trainor T.P. (2007) Surface diffraction study of the hydrated hematite (1 $\bar{1}$ 02) surface. *Surface Science* **601**, 460-474.

Catalano J.G., Zhang Z., Park C., Fenter P., and Bedzyk M.J. (2007) Bridging arsenate surface complexes on the hematite (012) surface. *Geochim. Cosmochim. Acta* **71**, 1883-1897.

Catalano J.G. and Brown G.E., Jr. (2005) Uranyl adsorption onto montmorillonite: Evaluation of binding sites and carbonate complexation. *Geochim. Cosmochim. Acta* **69**, 2995-3005.

Five Other Publications:

Tanwar K., Catalano J.G., Petitto S.C., Ghose S.K., Eng P.J., Trainor T.P. (2007) Hydrated α -Fe₂O₃ (1 $\bar{1}$ 02) surface structure: Role of surface preparation. *Surface Science* **601**, L59-L64.

Catalano J.G., Zhang Z., Fenter P., and 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.

Zhang Z., Fenter P., Kelly S.D., Catalano J.G., Bandura A., Kubicki J.D., Sofo J., Wesolowski D.J., Machesky M.L., Sturchio N.C., and Bedzyk M.J. (2006) Structure of Zn²⁺ at the TiO₂ (110) – aqueous solution interface: Comparison of X-ray standing wave, X-ray absorption

spectroscopy and density functional theory results. *Geochim. Cosmochim. Acta* **70**, 4039-4056.

Catalano J.G., Park C., Zhang Z., Fenter P. (2006) Termination and water adsorption at the α -Al₂O₃ (012)-aqueous solution interface. *Langmuir* **22**, 4668-4673.

Catalano J.G., Trainor T.P., Eng P.J., Waychunas G.A., and 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. *Geochim. Cosmochim. Acta* **69**, 3555-3572.

Synergistic Activities: Reviewer, U.S. Civilian Research and Development Foundation; Reviewer, Stanford Synchrotron Radiation Laboratory user proposals; Reviewer for Scholarly Journals (American Mineralogist, Chemical Geology, Environmental Science & Technology, Geochemical Journal, *Geochimica et Cosmochimica Acta*, Geology, Journal of Colloid and Interface Science, Journal of Environmental Management, Journal of Environmental Radioactivity, Journal of Hazardous Materials, Science of the Total Environment, *Thermochimica Acta*).

Collaborators in the Last 48 Months:

Bandura, A. (St. Petersburg State U.)

Bedzyk, M.J. (Northwestern U.)

Benzerara, K. (U. Paris 6-7)

Bluhm, H. (LBNL)

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

Calas, G. (U. Paris 6-7)

Cances, B. (U. Reims)

Chaka, A.M. (NIST)

Eng, P.J. (U. Chicago)

Farges, F. (Mus. Nat. d'Histoire Naturelle)

Fenter, P. (ANL)

Ghose, S.K. (U. Chicago)

Heald, S.M. (ANL)

Juillot, F. (U. Paris 6-7)

Kelly, S.D. (ANL)

Kendelewicz, T. (Stanford U.)

Kubicki, J.D. (Penn State U.)

Lo, C. (Washington U.)

Machesky, M.L. (ISWS)

McKinley, J.P. (PNNL)

Morin, G. (U. Paris 6-7)

Nagy, K.L. (U. Illinois)

Nilsson, A. (SSRL)

Ona-Nguema, G. (Stanford U.)

Park, C. (ANL)

Petitto, S.C. (U. Alaska)

Salmeron, M. (LBNL)

Smith, S.C. (PNNL)

Sofa, J. (Penn State U.)

Starr, D.E. (LBNL)

Sturchio, N.C. (U. Illinois)

Tanwar, K. (U. Alaska)

Trainor, T.P. (U. of Alaska)

Waychunas, G.A. (LBNL)

Wesolowski, D.J. (ORNL)

Yamamoto, S. (SSRL)

Yoon, T.Y. (Hanyang U.)

Zachara, J.M. (PNNL)

Zhang, Z. (ANL)

Ph.D. Advisor: Gordon E. Brown, Jr., Stanford University

Postdoctoral Advisor: Paul Fenter, Argonne National Laboratory

Former and Current Graduate and Postdoctoral Students: none

BUDGET JUSTIFICATION

The bulk of the requested funding is for personnel cost. Two graduate students will work year round on this project, and the PI will contribute substantial time conducting measurements at the Advanced Photon Source (2-3 weeks/year) and analyzing and interpreting the data back at Washington University. The graduate student support is for a 12 month salary, except in year 1 where only summer funding is requested. Additional funding is requested for undergraduate hourly research assistants (600 hours/year). The Department of Earth and Planetary Sciences (EPSc) strongly encourages undergraduate research, and majors from EPSc and the Environmental Studies Program frequently work with faculty members on research projects. A portion of the proposed work has been designed to support compact research modules that may be carried out by undergraduate students, and will lead to part or all of a scientific manuscript to be submitted for publication. Additional funding for 2 summer REU students will be requested as an REU supplement if this grant is funded.

Requested non-personnel costs include materials/supplies, analytical, and travel costs. \$4500/year in travel funding is requested to cover the cost of two trips per year (one week each) to the Advanced Photon Source by the PI and two graduate student (@ \$750 per trip per person, including \$60/night housing cost at the Argonne Guest House and per diem meal expenses of \$45/day). An additional \$3000/year in travel funding is requested to cover the cost of attending one scientific meeting per year for the PI a graduate student, and an undergraduate student. Additional travel support will be requested in the REU supplement to send summer REU students to a scientific meeting. Other direct costs include \$3000/year for the use of analytical instrumentation (ICP-MS, TEM, SEM, Raman, FTIR, XRD, BET, Zeta Potential) at Washington University. The hourly rate for such instruments runs about \$40/hour, and I anticipate using these for a total of approximately 75 hours per year. The amount requested for supplies and expendables (\$4000 year 1, \$7000 years 2 and 3) includes the cost of AFM cantilevers, single crystal substrates, reagents, anaerobic chamber gasses, and other laboratory consumables. The higher second and third year costs reflect the need to partially reimburse for consumable used during NanoSIMS measurements, such as photomultipliers, ion sources, and gas cylinders. \$5000 in equipment funding is requested in year 1 for a glovebox enclosure for the AFM to allow imaging under anaerobic conditions. \$500 in publications costs is requested in year 3.

Current and Pending Support

(See GPG Section II.C.2.h for guidance on information to include on this form.)

The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal.	
Investigator: Jeffrey Catalano	Other agencies (including NSF) to which this proposal has been/will be submitted.
Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: ETBC: Hidden Iron Oxide Redox Processes During Biogeochemical Iron Cycling: Controls on Nanscale Transformations and the Fate of Contaminants - THIS Source of Support: NSF Total Award Amount: \$ 340,505 Total Award Period Covered: 09/01/08 - 08/31/11 Location of Project: Washington University Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 1.00	
Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: Iron Oxide Morphology and Composition as Possible Indicators of Sedimentary Redox Cycling Source of Support: American Chemical Society Total Award Amount: \$ 50,000 Total Award Period Covered: 09/01/08 - 08/31/10 Location of Project: Washington University Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 0.70	
Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: Water Ordering and Complex Oxoanion Absorption Behavior at Iron and Aluminum Oxide-Water Interfaces Source of Support: Department of Energy Total Award Amount: \$ 420,863 Total Award Period Covered: 09/01/08 - 08/31/11 Location of Project: Washington University Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 1.00	
Support: <input type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: Source of Support: Total Award Amount: \$ Total Award Period Covered: Location of Project: Person-Months Per Year Committed to the Project. Cal: Acad: Sumr:	
Support: <input type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support Project/Proposal Title: Source of Support: Total Award Amount: \$ Total Award Period Covered: Location of Project: Person-Months Per Year Committed to the Project. Cal: Acad: Summ:	

*If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period.

FACILITIES, EQUIPMENT, AND OTHER RESOURCES

Experimental work specified in this proposal will be performed primarily in the laboratory of the PI at Washington University in St. Louis. This laboratory has much of the instrumentation needed for the proposed studies. Additional facilities are available on campus for an hourly usage fee. Access to synchrotron radiation facilities at the Advanced Photon Source (APS) requires the submission of short proposals and the award of beamtime is based on a competitive, peer-review process. I anticipate no difficulty in obtaining beamtime at the APS based on my success in receiving beamtime over the past five years. During this period I have been the PI on 8 successful APS proposals and co-PI on an additional 12 successful proposals. I currently have a highly rated program proposal for preliminary work on this project that expires in May 2008. A new APS program proposal for the work proposed here will be submitted in spring 2008, when the current proposal is set to expire. A new proposal cannot be submitted sooner as it would be rejected for being too similar to the still-active proposal (an APS user cannot have duplicate active proposals for a single project).

Laboratory Facilities Available for Solution Chemistry and Sample Preparation and Characterization

Catalano Laboratory, Washington University: Catalano's research facilities are located in the new Earth and Planetary Sciences building and include a general purpose wet chemical laboratory, equipped with standard equipment needed for solution chemistry and sample preparation. This equipment includes a Coy Laboratory Products anaerobic chamber, pH meters, analytical balances, UV/Vis spectrophotometer, wheel and fixture for polishing crystalline substrates, muffle and tube furnaces, deionized water system, laboratory ovens, centrifuges, etc. The laboratory also just received a new Agilent Technologies (formerly Molecular Imaging) atomic force microscope (AFM) model 5500, capable of imaging mineral surfaces under aqueous conditions. The AFM is housed in separate space from the wet chemical laboratory to provide for quiet operation. The laboratory also maintains computing facilities needed for analysis of X-ray scattering and spectroscopic data and geochemical modeling.

Fenter Laboratory, Argonne National Laboratory: Dr. Paul Fenter has offered on a collaborative basis the use of his wet chemistry laboratory facilities at Argonne National Laboratory for sample preparation prior to and during experimental runs at the Advanced Photon Source. Fenter's laboratory contains chemicals and equipment needed to prepare single crystal samples and aqueous solutions, including crystal polishing equipment, a deionized water system, and a Coy Laboratory Products anaerobic chamber. Dr. Fenter has also agreed to provide software developed by his group to process and analyze the X-ray scattering data that will be collected as part of the proposed experiments.

Department of Earth and Planetary Sciences, Washington University: Facilities available for use in sample characterization in the Department of Earth and Planetary Sciences include: a JEOL-8200 electron microprobe, a Rigaku powder X-ray diffractometer, HoloLab 5000-532 and 5000-633 Raman microprobes, and a Nicolet Nexus 670 FTIR with ATR accessories.

Jens Environmental Molecular and Nanoscale Analysis Laboratory, Washington University:

The Jens Environmental Molecular and Nanoscale Analysis Laboratory is a shared instrumentation facility and is supported by a core user group of faculty from the Department of Energy, Environmental, and Chemical Engineering. The facility is available to all Washington University and non-University researchers. Facilities available in the Jens laboratory include: a Gemini 2375 BET surface area and pore volume measurement instrument, an HP 1100 HPLC, an Agilent 7500ce ICP-MS with hydride generation for analysis of As and Se and an octopole reaction cell for removal of polyatomic interferences, a Shimadzu TOC-500 total organic carbon analyzer (also measures total inorganic carbon), a Hitachi model S-4500 Field Emission SEM-EDX, and a Nicolet Nexus 470 FTIR with ATR accessories.

Department of Energy, Environmental, and Chemical Engineering, Washington University:

A Malvern Zetasizer Nano ZS is available for zeta potential measurements and particle size analysis.

Center for Material Innovation (CMI), Washington University:

Facilities available in CMI include: a new JEOL JEM-2100F scanning field emission TEM, a Hitachi S-4500 field emission SEM, and a Quantum Design Physical Properties Measurement System.

Laboratory for Space Sciences, Washington University:

Facilities available in the Laboratory for Space Sciences through a collaborative agreement include: a Cameca IMS 3f SIMS ion microprobe, a Cameca NanoSIMS 50 ion microprobe with high mass resolution multicollector, a PHI 700 Scanning Auger Nanoprobe, a JEOL 2000FX TEM, and a JEOL 840A SEM-EDX.

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 XR and RAXR measurements described in this proposal can be performed at a number of different beamlines, including 4-ID-D, 5-ID-C, 6-ID-B, 11-ID-D, 12-BM, 13-ID-C, 20-ID-C, and 33-ID-D. XANES and EXAFS measurements can also be performed at a number of different beamlines, including 5-BM-D, 9-BM-B (S K-edge XANES only), 10-ID-B, 12-BM-B, 13-BM-C, 20-BM-B, and 20-ID-C.