



G

THE PETROLEUM RESEARCH FUND
TYPE G PROPOSAL

(Please refer to statement of eligibility, terms, and conditions.)

PRIVILEGED COMMUNICATION

This proposal is intended for review exclusively by ACS PRF staff, members of the PRF Advisory Board, and outside reviewers officially asked to furnish scientific comments. It may not be transmitted to other parties, copied, or retained for future reference. Please return to the PRF office, or destroy, in accordance with instructions.

Jeffrey G. Catalano
(Principal Investigator)

September 1, 2007
(Date of First Faculty Appointment)

Washington University in St. Louis
(Institution)

Earth & Planetary Sciences
(Department)

Saint Louis
(City)

MO
(State)

Title of Proposed Research: Iron Oxide Morphology and Composition as Possible Indicators of Sedimentary Redox Cycling

The ACS Petroleum Research Fund has a "zero-tolerance" policy for scientific misconduct. Scientific misconduct includes, but is not limited to, fabrication, falsification, and plagiarism. Instances of alleged or suspected scientific misconduct will be referred to a committee of the PRF Advisory Board for investigation. Upon the PRF Advisory Board's determination of scientific misconduct, the Board may, in its discretion, take any actions it deems appropriate. Such actions may include: disqualifying proposals from consideration; disqualifying individuals or institutions from submitting future proposals; revoking grant awards; contacting appropriate Officers of the relevant institution(s), such as the Dean, and/or Department Head of the investigator(s); and other such actions that the Board feels are appropriate.

By signing below, we acknowledge that we have read and understand this scientific misconduct policy.

Principal Investigator: [Signature]
(Signature)

11/27/2007
(Date)

Officer of the Institution

Endorsing the Proposal: [Signature]
(Signature)

11/28/2007
(Date)

Payment Schedule Requested: \$ 25000 (First Year) + \$ 25000 (Second Year) = Total \$50,000

I. EDUCATION AND EXPERIENCE. Indicate all degrees, when and where received. List postdoctoral appointments, previous faculty positions, and other principal positions, when and where, in chronological order.

B.S. Geology, University of Illinois at Urbana-Champaign, (1995-1999)
Ph.D. Geological and Environmental Sciences, Stanford University, (1999-2004)
Harold Urey Postdoctoral Fellow, Chemistry Division, Argonne National Laboratory (2004-2007)
Assistant Professor, Earth & Planetary Sciences, Washington University in St. Louis, (2007-present)

Ph.D. thesis title and supervisor with current mailing address, including email:

Ph.D. Dissertation Title: Molecular Scale Studies of Uranium Speciation in Contaminated Hanford, Washington Sediments and Related Model Systems.

Advisor: Prof. Gordon E. Brown, Jr., Department of Geological and Environmental Sciences, Bldg. 320, Rm. 118, Stanford University, Stanford, CA 94305-2115, E-mail: Gordon.Brown@stanford.edu

Postdoctoral research topic and research supervisor with current mailing address, including email:

Topic: Research focused on fundamental aspects of geochemical processes occurring at mineral-water interfaces.

Advisor: Dr. Paul Fenter, Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, E-mail: fenter@anl.gov

Is your position at the institution of record for this proposal a tenure-track position? yes

If not, please explain the nature of your position and attach your Department Chair's letter as page 3a stating that you meet PRF eligibility requirements.

II. STATEMENT OF OPPORTUNITY TO CONDUCT RESEARCH AT GRANTEE INSTITUTION.

A. Highest academic degree awarded to students in your department: Ph.D.

B. Available facilities - space, equipment, and supplies.

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 an anaerobic chamber, pH meters, analytical balances, UV/Vis spectrophotometer, deionized water system, 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 laboratory also maintains computing facilities needed for analysis of spectroscopic and diffraction data and geochemical modeling. Other facilities available at Washington University include three SEMs, two TEMs, two ICP-MS systems, two FTIRs with ATR attachments, two Raman microprobes, an electron microprobe, a BET surface area and pore volume measurement instrument, a total organic carbon analyzer (also measures total inorganic carbon), a SIMS ion microprobe, a NanoSIMS ion microprobe, a Scanning Auger Nanoprobe, and a powder X-ray diffractometer.

C. Research support by or to be expected from the department or institution, including startup funds.

Startup package: \$100,000 for setting up an aqueous geochemistry laboratory, \$180,000 for an atomic force microscope, \$49,000 for a CCD X-ray detector, \$25,000 for research travel support, \$20,000 for computer hardware and software, and summer salary support for June, July, and August 2008.

D. Teaching duties - list the courses you are expected to teach next year and give contact hours per week for lectures, recitations, and laboratory.

Fall 2008: EPSc 444 Environmental Geochemistry, estimated contact hours: 4/week

Spring 2009: EPSC 413 Introduction to Soil Science, estimated contact hours: 4/week

Percentage of time devoted to research during academic year: 50%.

Percentage of time devoted to research during summer: 100%.

III. PUBLICATIONS. Include titles, co-authors, and literature references. Use separate page(s) if necessary.

1. **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*, submitted.
2. **Catalano J.G.**, Park C., Fenter P. (2007) Interfacial water structure on the (012) surface of hematite: Ordering and reactivity in comparison with corundum. *Geochimica et Cosmochimica Acta* **71**, 5313-5324.
3. 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.
4. **Catalano J.G.**, Zhang Z., Park C., Fenter P., and Bedzyk M.J. (2007) Bridging arsenate surface complexes on the hematite (012) surface. *Geochimica et Cosmochimica Acta* **71**, 1883-1897.
5. 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.
6. 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. *Geochimica et Cosmochimica Acta* **70**, 4039-4056.
7. Fenter P., **Catalano J.G.**, Park C., Zhang Z. (2006) On the use of CCD area detectors for high resolution specular X-ray reflectivity. *Journal of Synchrotron Radiation* **13**, 293-303.
8. **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.
9. **Catalano J.G.**, McKinley J.P., Zachara J.M., Heald S.M., Smith S.C., and Brown G.E., Jr. (2006) Changes in uranium speciation through a depth sequence of contaminated Hanford sediments. *Environmental Science & Technology* **40**, 2517-2524.
10. **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.
11. Waychunas G.A., Trainor T.P., Eng P.J., **Catalano J.G.**, Brown G.E., Jr., Davis J.A., Rogers J., and Bargar J.R. (2005) Surface complexation studied via combined grazing-incidence EXAFS and surface diffraction: Arsenate on hematite (0001) and (10 $\bar{1}$ 2). *Analytical and Bioanalytical Chemistry* **383**, 12-27.
12. Pierce E.M., Icenhower J.P., Serne R.J., and **Catalano J.G.** (2005) Experimental determination of UO₂ (cr) dissolution kinetics: effects of solution saturation state and pH. *Journal of Nuclear Materials* **345**, 206-218.
13. Wellman D.M., **Catalano J.G.**, Icenhower J.P., and Gamerding A.P. (2005) Synthesis and characterization of sodium meta-autunite, Na₂[(UO₂(PO₄))₂ · 3H₂O. *Radiochimica Acta* **93**, 393-399.
14. **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. *Geochimica et Cosmochimica Acta* **69**, 3555-3572.
15. **Catalano J.G.**, and Brown G.E., Jr. (2005) Uranyl adsorption onto montmorillonite: Evaluation of binding sites and carbonate complexation. *Geochimica et Cosmochimica Acta* **69**, 2995-3005.
16. Wang Z., Zachara J.M., Gassman P.L., Liu C., Qafoku O., Yantasee W., and Catalano, J.G. (2005) Fluorescence spectroscopy of U(VI)-silicates and U(VI)-contaminated Hanford sediment. *Geochimica et Cosmochimica Acta* **69**, 1391-1403.
17. **Catalano J.G.**, Warner J.A., and Brown G.E., Jr. (2005) Sorption and precipitation of Co(II) in Hanford sediments and alkaline aluminate solutions. *Applied Geochemistry* **20**, 193-205.
18. Trainor T.P., Chaka A.M., Eng P.J., Newville M., Waychunas G.A., **Catalano J.G.**, and Brown G.E., Jr. (2004) Structure and reactivity of the hydrated hematite (0001) surface. *Surface Science* **573**, 204-224.
19. **Catalano J.G.**, and 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.
20. **Catalano J.G.**, Heald S.M., Zachara J.M., and Brown G.E., Jr. (2004) Spectroscopic and diffraction study of uranium speciation in contaminated vadose zone sediments from the Hanford Site, Washington State. *Environmental Science & Technology* **38**, 2822-2828.
21. Zachara J.M., Ainsworth C.C., Brown G.E., Jr., **Catalano J.G.**, McKinley J.P., Qafoku O., Smith S.C., Szecsody J.E., Traina S.J., and Warner J.A. (2004) Chromium speciation and mobility in a high level nuclear waste vadose zone plume. *Geochimica et Cosmochimica Acta* **68**, 13-30.
22. Helean K.B., Navrotsky A., Lumpkin G.R., Colella M., Lian J., Ewing R.C., Ebbinghaus B., and **Catalano J.G.** (2003) Enthalpies of formation of U-, Th-, Ce-brannerite: implications for plutonium immobilization. *Journal of Nuclear Materials* **320**, 231-244.
23. Helean K.B., Navrotsky A., Vance E.R., Carter M.L., Ebbinghaus B., Krikorian O., Lian J., Wang L.M., and **Catalano J.G.** (2002) Enthalpies of formation of Ce-pyrochlore, Ca_{0.93}Ce_{1.00}Ti_{2.035}O_{7.00}, U-pyrochlore, Ca_{1.46}U⁴⁺_{0.23}U⁶⁺_{0.46}Ti_{1.85}O_{7.00} and Gd-pyrochlore, Gd₂Ti₂O₇: Three materials relevant to the proposed waste form for excess weapons plutonium. *Journal of Nuclear Materials* **303**, 226-239.
24. Chambers S.A., Farrow R.F.C., Maat S., Toney M.F., Folks L., **Catalano J.G.**, Trainor T.P. and Brown G.E., Jr. (2002) Molecular beam epitaxial growth and properties of CoFe₂O₄ on MgO(001). *Journal of Magnetism and Magnetic Materials* **246**, 124-139.

IV. OTHER RESEARCH GRANTS. Include titles, amounts (*annual direct costs*), sources, time periods of awards, and *relationship to this PRF proposal*. Use separate page if necessary; indicate “none” if applicable.

A. List any previous or current financial support received for research.

1. Startup package from Washington University, \$373,000, no time limit. Supports the establishment of the laboratory facilities the proposed work will be conducted in, including the purchase of major equipment.

B. List any other applications pending.

1. “Water Ordering and Complex Oxoanion Adsorption behavior at Iron and Aluminum Oxide-Water Interfaces”, \$276,884, September 1, 2008 to August 31, 2011. No clear relationship to proposed work, although some results will be useful for interpreting observations made in studies funded by this proposal.

V. SUGGESTED REVIEWERS.

Provide the names and addresses of at least four suggested reviewers who are experts in the field of the proposed research. *Do not include former research mentors, collaborators, or colleagues at your current or former institutions.* It is suggested that you include the names of experts residing in the United States. Also, please do not list names of any reviewers whom you have suggested in any proposal previously submitted to ACS PRF within the past five years. Include the first name, middle initial (if any), full current mailing address with zip code, *and email address* of all suggested reviewers.

1. Prof. Michelle M. Scherer, Department of Civil and Environmental Engineering, University of Iowa, Iowa City, IA 52242-1527, Email: michelle-scherer@uiowa.edu
2. Dr. Richard V. Morris, NASA Johnson Space Center, Houston, TX 77058, Email: richard.v.morris@nasa.gov
3. Prof. William D. Burgos, 212 Sackett, Dept. of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA 16802, Email: wdb3@psu.edu
4. Prof. Marjorie A. Chan, Department of Geology & Geophysics, University of Utah, Salt Lake City, UT 84112, Email: Email: chan@earth.utah.edu

NOTE: This information must also be entered as part of your ACS PRF Type G application, on the Electronic Proposal Submission web page.

VI. PROPOSED RESEARCH.

Iron Oxide Morphology and Composition as Possible Indicators of Sedimentary Redox Cycling

ABSTRACT

Iron oxides commonly occur in sedimentary deposits, having both detrital and authigenic origins. These phases have been thought to undergo either complete reductive dissolution or phase transformation during sedimentary redox cycling, which often generates aqueous Fe(II) as a byproduct. Recent measurements indicate that iron oxides are chemically active in the presence of Fe(II) even when no obvious phase transformations or dissolution is occurring. My collaborators and I have recently observed that Fe(II) activates dynamic surface processes for one common iron oxide, hematite. These observations of coupled dissolution and growth of different crystallographic surfaces, along with the known ability of iron oxides to incorporate other trace elements, like Ni, into their structure, suggest that morphologic and compositional changes in hematite may occur during sedimentary redox cycling. These changes may potentially be useful indicators of past redox conditions in sedimentary systems, including as indicators of past flow of hydrocarbon-bearing fluids. I propose to further investigate the effects Fe(II) has on hematite morphology and the incorporation of trace elements. Studies of both monodispersed hematite particles and specific crystallographic surfaces will be investigated to connect molecular scale surface processes with observable growth and zonation features. The proposed work may lead to new methods for identifying paleoredox conditions in sedimentary systems.

PROJECT NARRATIVE

Sediments frequently contain detrital and authigenic iron oxides, occurring as primary grains, overgrowths, cements, ooids, and concretions (Cornell and Schwertmann, 2003). Sediments often experience variable redox conditions during early diagenesis (e.g., Van Cappellen and Wang, 1996) or later migration of hydrocarbon-bearing fluids (e.g., Beitler et al., 2003), and these conditions may affect iron oxides in a number of ways. Iron oxides may undergo complete reduction (e.g., sandstone bleaching, pyritization), poorly ordered forms may recrystallize to highly ordered forms (e.g., ferrihydrite conversion to goethite and/or hematite), and neof ormation of iron oxides may occur (e.g., iron oxide cementation). All of these processes involve either complete dissolution, sometimes followed by reprecipitation, or solid state transformations, and the products of these reactions provide information about the redox conditions experienced by sediments and sedimentary rocks.

My collaborators and I have recently investigated the interaction of aqueous Fe(II), a common byproduct of sedimentary redox cycling, with iron oxide surfaces. This work was initially motivated by the known ability of “sorbed” Fe(II) to rapidly chemically reduce many environmental contaminants (Charlet et al., 1998; Liger et al., 1999; Chun et al., 2006) as well as the apparent fractionation of iron isotopes that occurs during microbial dissimilatory iron reduction and Fe(II) adsorption (Crosby et al., 2005; Icopini et al., 2004). Our studies, along with other recent measurements (Williams and Scherer, 2004; Pedersen et al., 2005; Silvester et al., 2005; Larese-Casanova and Scherer, 2007), indicate that Fe(II) activates dynamic surface processes on iron oxide surfaces. On hematite ($\alpha\text{-Fe}_2\text{O}_3$) dissolution occurs on the (110) and (012) surfaces along with simultaneous growth on the (001) surface, with Fe(II) likely serving a catalytic role (**Figure 1**). This appears to indicate that a previously unrecognized iron oxide transformation process may occur during sedimentary redox cycling: Fe(II)-catalyzed dynamic reshaping of existing iron oxides through coupled growth and dissolution.

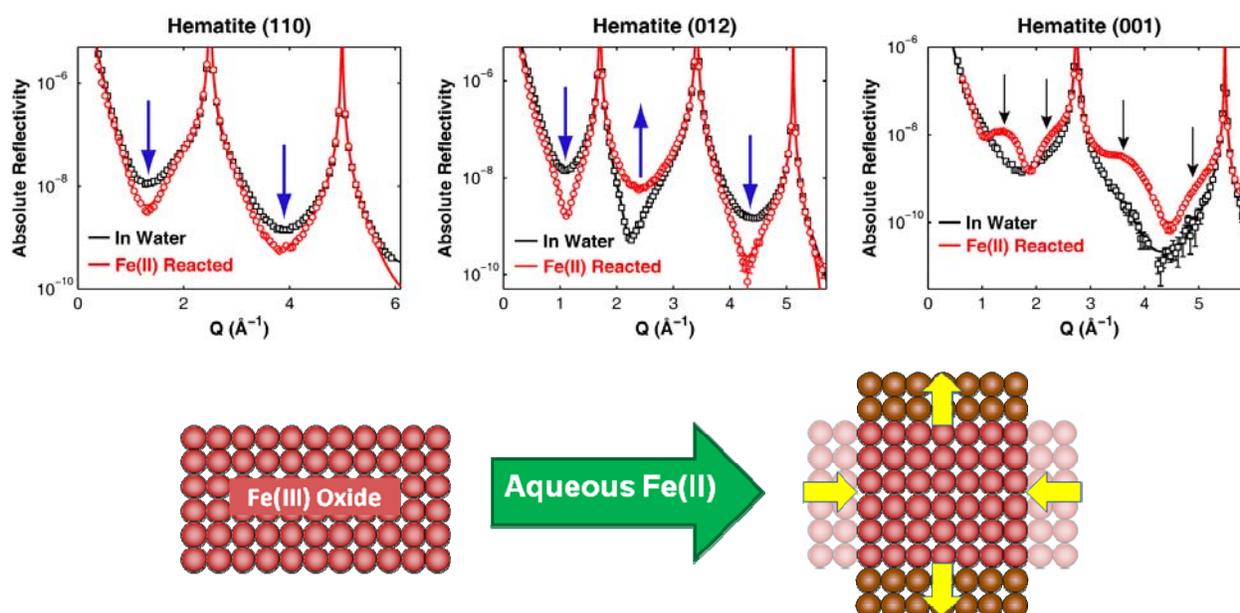


Figure 1. (top) X-ray reflectivity (XR) measurements of three hematite surfaces before and after reaction with aqueous Fe(II). The midzone intensity changes on the (110) and (012) surfaces after reaction (blue arrows) indicate dissolution of a few molecular layers of the surfaces. In contrast, new oscillations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

Our measurements to date have focused on the early stages of this behavior, with dissolution and/or growth being limited to a few molecular layers on the surface. However, I believe that this behavior continues as long as Fe(II) remains in solution, and that the rate of transformation may vary with Fe(II) concentration, temperature, or other factors. If this behavior does continue then hematite should take on an acicular morphology, elongated along the *c*-axis. Similar lengthening along one crystallographic direction has been observed for goethite after Fe(II) reaction (Chun et al., 2006). This suggests that if the couple growth and dissolution processes that reshape iron oxides can be understood then it may be possible to gain insight into

past redox conditions experienced by sediments through examination of iron oxide crystal morphology.

An additional consideration is the effect this dynamic growth and dissolution process has on other elements in the system. Trace elements compatible with the hematite structure, such as V, Mn, Co and Ni, would be expected to incorporate into the growing surface if contained in the fluid phase present during redox cycling. These and other elements are known to incorporate during synthesis of iron oxides (Cornell and Schwertmann, 2003). A past study of Ni(II), Co(II), and Cu(II) adsorption onto goethite in the presence of Fe(II) observed increased uptake compared to Fe(II)-free systems (Coughlin and Stone, 1995), suggesting that trace element incorporation during coupled dynamic growth and dissolution of iron oxides is likely. Incorporation of such elements in iron oxides may thus serve as an indicator of the type(s) of fluids present during sedimentary redox cycling. This process would be expected to result in compositional zonation of iron oxides along the growth direction. Multiple redox cycles occurring in fluids of different trace element compositions should produce multiple compositional zones in an iron oxide crystal. Incorporation of Ni and V are of particular relevance to the energy community as many forms of crude oil and bitumen contain elevated concentrations of these elements (Mossman, 1999).

I propose to investigate possible morphologic changes and composition zonation in iron oxides after reaction with aqueous Fe(II) in controlled laboratory experiments. Ni(II) will be used as an example trace element to study compositional zonation and also serve as a tracer of growth, as it readily incorporates into the hematite structure (Cornell and Schwertmann, 2003). These studies will be comprised of two separate set of experiments: (1) Fe(II) reaction with monodispersed hematite particles of known size and morphology, and (2) Fe(II) reaction on specific single crystal surfaces. Both sets of experiments will be performed under strict anaerobic conditions to ensure Fe(II) oxidation by dissolved oxygen does not occur.

Monodispersed hematite particles will be used in the first set of experiments as they have a uniform morphology and size distributions, making detecting changes in these properties straightforward. The starting size and morphology will be characterized before reactions using transmission electron microscopy (TEM), and these parameters will be determined again after reaction to characterize the morphological effects of Fe(II) reaction, including the crystallographic directions along which growth and/or dissolution occurred. The concentration of Ni in the fluid phase, measured by inductively coupled plasma-mass spectrometry (ICP-MS), will be used to monitor whether hematite growth processes results in its incorporation into the solid phase. Extended X-ray absorption fine structure (EXAFS) spectroscopy will be used to determine the local coordination environment of Ni after reaction to identify the mechanism through which incorporation occurs. Powder X-ray diffraction (XRD) measurements will be used to verify that other mineral phases do not form during these experiments.

More fundamental information on the mechanisms involved in this process will be gained by studying reactions

occurring on specific surfaces of hematite. Oriented single crystal surfaces will be studied by *in situ* atomic force microscopy (AFM) to watch changes in the surface morphology and to confirm whether growth and/or dissolution occur. Multiple crystallographic surfaces will be examined to investigate how these effects vary with orientation. AFM measurements will also identify the formation of any nanoscale precipitates and/or films. I will use nanometer-scale secondary ion mass spectrometry (NanoSIMS) to measure the composition of surfaces that display growth in AFM measurements and to verify the incorporation of compatible trace metals. NanoSIMS has improved sensitivity, compared to electron microscopy methods, to the composition of growth layers that may be only a few monolayers thick on samples that cannot be thinned for TEM measurements. Surface structural transformations and trace element incorporation will be further investigated using synchrotron-based X-ray reflectivity (Fenter, 2002) and resonant anomalous X-ray reflectivity (Park et al., 2006). These studies of single crystal surfaces will help explain the features observed in the monodispersed powder systems and provide a fundamental understanding of the processes involved in these dynamic iron oxide surface processes.

The studies proposed here will improve our understanding of new possible iron oxide transformation processes that occurs during sedimentary redox cycling. These couple dissolution and growth processes in the presence of Fe(II) may result in clear morphologic changes and compositional zonation. These features of iron oxides grains in sedimentary system may serve as additional indicators of past redox cycling. Possible applications include examining marine sediments undergoing early diagenesis, as iron oxides may record past redox states that are not reflected in current pore water compositions, or tracing the past migration and trace element composition of sedimentary fluids.

A grant received for the proposed work will fund personnel and research expenses. Over the two years of the proposal, funds will be used to support a graduate student researcher during the summer as well as two undergraduate students as part-time hourly assistants during the school year and full-time research assistants during summer. Remaining funds will be used to cover laboratory expenses, including TEM, AFM, NanoSIMS, and ICP-MS costs, and will fund one trip per year to the Advanced Photon Source for EXAFS and X-ray reflectivity measurements for the PI and one to two students (within the \$2000 annual limit on travel expenses).

REFERENCES

- 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, 1041-1044.
- Charlet, L.; Silvester, E.; Liger, E., N-compound reduction and actinide immobilisation in surficial fluids by Fe(II): the surface

- $\equiv\text{Fe}^{\text{III}}\text{OFe}^{\text{II}}\text{OH}^\circ$ species, as major reductant. *Chemical Geology* **1998**, 151, 85-93.
- Chun, C. L.; Penn, R. L.; Arnold, W. A., Kinetic and microscopic studies of reductive transformations of organic contaminants on goethite. *Environmental Science & Technology* **2006**, 40, 3299-3304.
- Cornell, R. M.; Schwertmann, U., *The Iron Oxides: Structure, Properties, Reactions, Occurrences, and Uses*. 2nd ed.; Wiley-VCH: Weinheim, 2003; p 664.
- Coughlin, B. R.; Stone, A. T., Nonreversible adsorption of divalent metal-Ions (Mn^{II} , Co^{II} , Ni^{II} , Cu^{II} , and Pb^{II}) onto goethite: Effects of acidification, Fe^{II} addition, and picolinic acid addition. *Environmental Science & Technology* **1995**, 29, 2445-2455.
- 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.
- Fenter, P., X-ray reflectivity as a probe of mineral-fluid interfaces: A user guide. *Reviews in Mineralogy and Geochemistry* **2002**, 49, 149-220.
- 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.
- Larese-Casanova, P.; Scherer, M. M., Fe(II) sorption on hematite: New insights based on spectroscopic measurements. *Environmental Science & Technology* **2007**, 41, 471-477.
- Liger, E.; Charlet, L.; Van Cappellen, P., Surface catalysis of uranium(VI) reduction by iron(II). *Geochimica et Cosmochimica Acta* **1999**, 63, 2939-2955.
- Mossman, D. J., Carbonaceous substances in mineral deposits: implications for geochemical exploration. *Journal of Geochemical Exploration* **1999**, 66, 241-247.
- Park, C.; Fenter, P. A.; Nagy, K. L.; Sturchio, N. C., Hydration and distribution of ions at the mica-water interface. *Physical Review Letters* **2006**, 97, 016101.
- 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.
- 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.
- Van Cappellen, P.; Wang, Y. F., Cycling of iron and manganese in surface sediments: A general theory for the coupled

transport and reaction of carbon, oxygen, nitrogen, sulfur, iron, and manganese. *American Journal of Science* **1996**, 296, 197-243.

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.