

Surficial Geochemical Processes



**Advanced Photon Source Conference Center
Argonne National Laboratory
March 7-8, 2003**

FORWARD

“Surficial Geochemical Processes” is the tenth in a series of Geosciences Research Program Symposia dating from 1995. These symposia are topically focused meetings for principal investigators in the program and provide opportunities for our investigators to give presentations to one another and to discuss their Office of Basic Energy Sciences’ supported research. Dr. Paul A. Fenter of Argonne National Laboratory has kindly agreed to serve as host of the meeting using the excellent facilities here at the Advanced Photon Source. I would like to thank Paul for his hard work in making this meeting possible. In addition to the recognition the symposium gives to all of the investigators, we traditionally also recognize one outstanding contribution from a DOE Laboratory Project and one from a University Project. The outstanding contributions are selected by our session chairpersons. We are fortunate to have as guest session co-chairs Professor Richard Reeder from the State University of New York at Stony Brook, Prof. Udo Becker from the University of Michigan, Professor Samuel Traina from the University of California at Merced and Dr. William C. Luth, Basic Energy Sciences emeritus. They join our Principal Investigator co-chairs Dr. David Veblen of the Johns Hopkins University, Dr. John Tossell of the University of Maryland, Dr. David Weslowski of Oak Ridge National Laboratory, and Dr. John Zachara of Pacific Northwest National Laboratory. For their efforts on behalf of the investigators I thank them all. We are looking forward to an outstanding series of presentations.

Nicholas B. Woodward
Geosciences Research Program
Office of Basic Energy Sciences
U.S. Department of Energy

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Surficial Geochemical Processes
-Agenda-
Advanced Photon Source Conference Center
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Friday, March 7 (AM)

- 7:45 **Registration** (APS Conference Center Atrium)
Coffee (APS Gallery, lower level)
- 8:15 **Introductions and Greetings** (APS Conference Center Auditorium)
Nicholas Woodward, Department of Energy
Beverly Hartline, Deputy Laboratory Director, Argonne National Laboratory

Interfacial Reactions: Imaging and Theory

Chairs: Udo Becker and David Wesolowski

- 8:30 Don Baer, Pacific Northwest National Laboratory
Solution Effects on Growth and Dissolution Processes at the Calcite Surface
- 8:55 Steven Higgins, Wright State University
Surface Kinetics, Step Dynamics, and the Growth and Dissolution Of Minerals
- 9:20 Henry Teng, George Washington University
Controls Of Undersaturation On Etch Pit Formation
- 9:45 William Casey, University of California, Davis
Tailored Crystal Growth And Impurity Control Using Adsorbates
- 10:10 **Coffee/refreshments** (APS Gallery, lower level)
- 10:40 David Veblen, Johns Hopkins University
TEM Studies of Mineral Coatings, 'Surface' Reactions, and Uranium Sorption in Soils
- 11:05 Eugene Ilton, Pacific Northwest National Laboratory
Heterogeneous Reduction of Uranyl by Micas: Crystal Chemical and Solution Controls
- 11:30 Dimitri Sverjensky, Johns Hopkins University
Prediction of Chemical Reactions at the Solid-Water Interface
- 11:50 **Lunch** (APS Gallery, lower level)

Friday, March 7 (PM)

Interfacial Reactions: Experiment and Simulation

Chairs: Rich Reeder and David Veblen

- 1:00 David Wesolowski, Oak Ridge National Laboratory
Nanoscale Complexity at the Oxide/Water Interface
- 1:25 Neil Sturchio, University of Illinois at Chicago/ANL
Revelations at the Mineral-Fluid Interface
- 1:50 Randy Cygan, Sandia National Laboratory
Molecular Simulations of Layered Minerals and Their Interactions with Hazardous Waste
- 2:15 Kathryn Nagy, University of Illinois at Chicago
Sorption and Precipitation Reactions at the Mica-Water and Quartz-Water Interfaces
- 2:40 **Coffee/refreshments** (APS Gallery, lower level)
- 3:10 R. James Kirkpatrick, University of Illinois, Urbana-Champaign
Molecular Modeling of Aqueous Fluids in Nanospaces and at Fluid-Mineral Interfaces
- 3:35 Glenn Waychunas, Lawrence Berkeley National Laboratory
Surface Complexation and Precipitate Geometry for Aqueous Zn(II) Sorption on Ferrihydrite: Complementary EXAFS and Multiple-Scattering Analysis
- 4:00 Gordon Brown, Stanford University
Sorption Reactions At Mineral-Water Interfaces: X-Ray Spectroscopic/Scattering Studies Of Sorption Complex Geometries, Surface Structure And Reactivity, Effects Of Organic And Inorganic Ligands, And Complex Natural Samples
- 4:25 Satish Myneni, Princeton University
X-ray Spectroscopy of Natural Organic Molecules: Functional Group Chemistry of Molecules in Aqueous Solutions and at Mineral-Water Interfaces
- 4:50 **Discussion**
- 5:30 **Adjourn**
- 6:00 **Dinner** (Argonne Guest House dining room)

Saturday, March 8 (AM)

8:00 **Coffee/refreshments** (APS Gallery, lower level)

Reactions, Oxidation and Thermodynamics

Chairs: William Luth and John Zachara

8:30 Daniel Strongin, Temple University

Investigations of The Mechanism and Inhibition of Pyrite Oxidation

8:55 John Tossell, University of Maryland

Calculation of the Energetics for Oxidation of Sb(III) to Sb(V) Sulfides by Polysulfides

9:20 Jim Rustad, Pacific Northwest National Laboratory

Ultrascale Simulation of Surface Charging in Heterogeneous Oxide Systems: The Importance of the Crystal Chemical Characteristics of Edge Regions

9:45 Steve Sutton, University of Chicago

Synchrotron-based Surface and Microscale Geochemical Studies at GSECARS and NSLS X26A

10:10 **Coffee/refreshments** (APS Gallery, lower level)

10:45 Peter Rock, University of California, Davis

Electrochemical Measurements and Theoretical Predictions of the Thermodynamics of Carbonate and Oxide Minerals

11:10 Alexandra Navrotsky, University of California, Davis

Thermodynamics of Minerals Stable Near the Earth's Surface

11:35 Carlo Pantano, Pennsylvania State University

Interface Reactions and Dissolution of Glass in Aqueous and (Bio)Organic Media

12:00 **Lunch** (APS Gallery, lower level)

Saturday, March 8 (PM)

Microbe-Mediated Geochemical Reactions

Chairs: Samuel Traina and John Tossell

- 1:15 John Zachara, Pacific Northwest National Laboratory
Mineral Transformations Resulting from Bacterial Interfacial Electron Transfer to Fe(III) Oxides
- 1:40 Jillian Banfield, University of California, Berkeley
Nanoparticle Products of Microbial Biomineralization of U, Fe, and Zn
- 2:05 Steven Lower, University of Maryland
Mineral Specific Biological Interactions: Nanoscale Force-Distance Measurements Between Iron Oxyhydroxides And Shewanella Or Siderophores
- 2:30 Tjerk Straatsma, Pacific Northwest National Laboratory
Molecular Basis for Microbial Adhesion to Geochemical Surfaces: Computer Simulation of Pseudomonas aeruginosa Adhesion to Goethite
- 2:55 **Coffee/refreshments** (APS Gallery, lower level)

NanoScience Project Reports:

- 3:25 Jillian Banfield, University of California, Berkeley
Size, Structure, and Aggregation of Nanoparticles
- 3:50 Don Baer, Pacific Northwest National Laboratory
The Reaction Specificity of Nanoparticles in Solution: Characteristics and Properties of Iron Nanoparticles
- 4:15 Alexandra Navrotsky, University of California, Davis
Thermochemistry of Nanomaterials
- 4:40 **Discussion**
- 5:30 **Adjourn**
- 6:30 **Refreshments** (Argonne Guest House dining room)
- 7:00 **Banquet** (Argonne Guest House dining room)

Solution Effects on Growth and Dissolution Processes at the Calcite Surface

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Experimental and theoretical studies of how solution impurities and other solution changes impact dissolution and growth processes at the calcite cleavage surface have been a major theme of our recent work. Using atomic force microscopy as our primary tool, we have measured the step velocity, pit shape, and, in a few cases, secondary phase formation while varying solution components (Ca^{2+} , Mn^{2+} , Sr^{2+} , Co^{2+} , Mg^{2+} , and CO_3^{2-}) in a controlled fashion. In most cases, adding ions to the solution slows step motions. However, in contrast to all other impurities we have studied, Mg^{2+} enhances dissolution rather than retarding it. Of the impurities that retard dissolution, Sr^{2+} and CO_3^{2-} demonstrate selective sorption to the most sterically accessible step site resulting in a substantial slowing of dissolution of this type of step. Mn^{2+} and Co^{2+} retard dissolution relatively uniformly due to non-selective step sorption. Mn^{2+} , Sr^{2+} , Co^{2+} , and Ca^{2+} additions to the solution have little impact on dissolution rate until a threshold concentration is reached, whereupon near complete frustration of dissolution occurs upon further increase in impurity concentration. These results have been explained using a simple terrace-ledge-kink model that incorporates site-blocking and works equally well with metal ion or carbonate ion pair concentrations. This site-blocking model cannot explain the enhanced dissolution behavior of calcite in the presence of Mg^{2+} . In calcite growth processes, Ca^{2+} ions demonstrate preferred kink sorption sites, manifested by the unique pit shape observed during pit fill-in. Heteroepitaxy of a manganese carbonate phase has been observed in solution when the ion activity product of Mn^{2+} and CO_3^{2-} exceeds the solubility limit of MnCO_3 . Thermodynamic data indicates that the resulting phase is most likely a $\text{Mn}_{0.5}\text{Ca}_{0.5}\text{CO}_3$ phase, consistent with our XPS and EPR measurements. These islands, while growing many microns in length along the [221] direction, have a uniform width of 150-220 nm and a uniform height of only 2.5 nm, corresponding to eight atomic layers. The islands cease growing when they encounter a step edge and have been observed to dissolve when undercut by a growing etch pit. A glued wetting layer model with conditions of constant surface chemical potential has been used to model the observed morphology of the heteroepitaxial layer. Although not all the required parameters are accurately known, the model accurately depicts the measured cross-sectional profiles of the islands. In this case, models and considerations associated with nano-phase formation on surfaces in vacuum apply to structure grown in solution.

This work was supported by the Office of Basic Energy Science, Geosciences Research Program, U.S. Department of Energy. The work was conducted in the Environmental Molecular Sciences Laboratory, a U.S. Department of Energy user facility located at Pacific Northwest National Laboratory.

Surface kinetics, step dynamics, and the growth and dissolution of minerals

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Carbon sequestration by CO₂ injection into deep saline aquifers may result in long-term chemical alteration of host phases and eventual growth of carbonate minerals. To advance our understanding of microscopic dissolution and growth kinetics of minerals (in particular, carbonate minerals) we have made significant modifications to the Hydrothermal AFM (HAFM) that was constructed under previous BES funding. These modifications included incorporation of a precision fluid inlet nozzle into the fluid cell, enabling modeling of the fluid cell hydrodynamics. This modification is particularly important for the study of fast surface reactions where the rate of deposition or dissolution is significantly limited by bulk fluid mass transport. We have utilized this experimental apparatus in studies of dissolution on the (104) surfaces of magnesite (MgCO₃) and calcite (CaCO₃) using *in-situ* atomic force microscopy (AFM) at elevated temperature. Analysis of experimental AFM data suggests that magnesite dissolution is kinetically hindered due to very slow exchange along step edges. The dissolution flux was found to vary nonlinearly with the concentration of H⁺, which was best represented by a Langmuir isotherm for proton adsorption. The apparent surface kinetic detachment coefficient, k'_n , for the surface complex was determined to be 5×10^{-12} mol cm⁻² s⁻¹, but this coefficient is morphology dependent. The velocity of dissolving + steps was constant, within error, over the entire experimental pH range while the dissolution flux varied by over an order of magnitude in this same range. AFM imaging revealed a dramatic increase in step density associated with a large increase in dissolution flux that was attributed to the protonation of terrace-adsorbed carbonate sites (*i.e.*, adions). We propose that the intrinsic protonation constant, K_{int} , differs for adions, kink, step and terrace sites based on the observations of surface and step morphology as a function of pH.

Calcite dissolution generally occurs in the mixed transport-kinetics controlled regime (even at high fluid velocities) where quantitative surface kinetics can be obtained by accounting for the transport components. Our studies of calcite dissolution as a function of fluid flow rate show the importance of controlled hydrodynamics in this system. When more complicated conditions are examined such as the dissolution of calcite in the presence of other divalent cations such as Sr²⁺ and Mg²⁺, it becomes increasingly important to account for mass transport and the heterogeneous consumption/production of these species. This work demonstrates the importance of elementary surface kinetic studies and the role of fundamental reactions in determining macroscale behavior.

In parallel to these microscopic experiments, we have conducted closed system hydrothermal experiments assessing the chemical alteration of calcic plagioclase minerals in high P_{CO₂} systems. These experiments were designed to simulate various conditions that may be encountered in deep aquifers targeted for CO₂ sequestration. EQ3/6 was used to model alteration scenarios with available kinetic data. Calculation predictions were tested in four experiments to determine if carbonate minerals would form under specific laboratory conditions as predicted by calculation. Each experiment used Dickson-type rocking gold bag autoclaves running for 3 to 5 months with 75-100 μm-sized An₆₀ plagioclase grains at

150° C and pressures of 100 bars. Variables include initial CO₂ fugacity (from 0.15 to 70 bars), supporting electrolyte, alkalinity and pH. Calculations suggest that enough alkalinity could be produced by reaction with plagioclase to reach saturation with respect to carbonate minerals; higher CO₂ fugacity led to saturation with respect to dawsonite [NaAlCO₃(OH)₂] at pH 3.6, and lower CO₂ fugacity led to saturation with respect to calcite at pH 5.9 and at pH 6.9 (with and without 0.01 m initial alkalinity, respectively). The reacted plagioclase grains were analyzed by petrography, XRD, SEM/EDS, CO₂ analysis, and AFM. Petrography and powder XRD did not reveal any carbonate precipitate. SEM and AFM images showed no evidence for secondary carbonate mineral precipitation, and analysis of the grains for CO₂ exsolution after acidification revealed no carbonate source. The plagioclase dissolution rates were highest initially then progressively slowed as the solutions became more saturated with respect to the feldspar. Because of the complex initial aqueous conditions, dissolution congruency could not be precisely established. We are now using open system (flow through) reactors to study these mineral growth/dissolution processes under conditions where chemical affinity is held constant. This work highlights the need for longer-term field and laboratory experiments to test geochemical aspects of CO₂ sequestration, as well as for evolution of codes to better account for dissolution/growth inhibition, nucleation, and other processes.

Controls Of Undersaturation On Etch Pit Formation

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Mineral dissolution is a vital component of natural weathering processes and controls various geochemical processes at both local and global scales. It is one of the intensively studied topics in the broad area of mineral-fluid interfacial geochemistry. To date it is widely recognized that overall dissolution at the Earth surface or near-surface conditions may be a surface reaction controlled process for many minerals. This conclusion arrives from a plethora of observations. Among them, the nearly ubiquitous occurrence of etch pits on dissolved surfaces stands the most noticeable.

Viewing surface etching in a bigger picture, however, the dislocation theories predict a saturation-dependent nature for pit formation. Observations on crystal faces of simple salt compounds, metals, and even laboratory dissolved and field weathered quartz grains corroborate the prediction. Yet, the controls of undersaturation on pit formation have not been literally incorporated into our knowledge base for mineral dissolution, for conventional approaches either treat dissolution as independent of undersaturation or attempt to extrapolate dissolution rate to near equilibrium conditions based upon the linear dependence of kinetics on chemical affinity. Thus, it seems that what we understand so far may only represent certain extreme cases at high under-saturation conditions, or may over-estimate the actual dissolution kinetics since little dissolution can occur on flat surfaces when pits do not nucleate.

This study attempts to look into the controls of solution undersaturation on etch pit formation using calcite as a model system. Experiments were conducted on $\{10\bar{1}4\}$ cleavage faces at various undersaturations to study the behavior of surfaces and the response of defects exposed at the surfaces. Observations were made using *in situ* fluid cell Atomic Force Microscope. The goal is to determine the undersaturation ranges where pit-induced and step-induced dissolution dominate. Three dissolution modes were observed. When saturation index $\Omega > 0.541$, no etch pits form and dissolution primarily occurs at existing steps. Upon the appearance of the first visible pits when Ω decreases to $\Omega_c = 0.541 - 0.410$, continuous reduction in saturation states thereafter slowly increases the pit density on terraces while step dissolution simultaneously proceeds. Finally, when undersaturation reaches beyond $\Omega_{max} = \sim 0.007$, a precipitous increase in pit density takes place, sharply contrasted to the ordered fashion of pit formation observed at conditions above this level. These observations are explained as two-dimensional and unassisted pit nucleation at $\Omega < \sim 0.007$, defect- and step-assisted dissolution in between $\Omega = 0.541$ and 0.007 , and step-induced dissolution for $\Omega > 0.541$.

The values of Ω_c come in good agreement with the predicted critical undersaturations for pit nucleation at line defects by the dislocation theories. The occurrence of Ω_{max} is not directly predicted but is a logical implication of the dissolution thermodynamics. These findings suggest that (1) dissolution at near and far from equilibrium (i.e., $\Omega > \Omega_c$, $\Omega < \Omega_{max}$) is not controlled by dislocations, therefore (2) dislocation density should only have significant effect on dissolution rates in the saturation range of $\Omega_{max} < \Omega < \Omega_c$; (3) dissolution kinetics should be nonlinearly related to the chemical affinity of dissolution reactions: at sufficiently close to equilibrium when dislocations cannot open up, dissolution rate will be limited by the number of existing steps; at too far from equilibrium when pits are able to spontaneously nucleate in defect-free regions, dissolution kinetics will be dictated by the number of the

maximally achievable steps.

These findings may provide explanations for several well-observed geochemical relationships, including the insignificant dependence of dissolution rates upon dislocation densities in distilled water, and the ‘plateau’ behavior of dissolution kinetics at both close to and far from equilibrium. The explosive occurrence of unassisted pit nucleation at $\Omega \sim \Omega_{\max}$ is not indicated by the current expressions of dissolution rate equations. This suggests that a ‘general’ rate law remains to be developed to describe the overall dissolution processes.

Tailored Crystal Growth and Impurity Control using Adsorbates

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The morphologies, growth rates and properties of crystals grown from solution are dramatically affected by adsorbates that poison highly reactive steps. Even in simple model systems, the interaction of the adsorbate with the surface depends strongly on subtle differences in adsorbate-step geometry. These subtleties affect the equilibrium crystal morphology despite the fact that the adsorbate may actually be acting only as a surfactant to alter the interfacial energy; it may be entirely excluded from the bulk of the crystal. Although there have been many studies of adsorbate-crystal interactions, most suffer from a lack of precise knowledge about the molecular structure of the adsorbate in solution and at the surface; the solutes added to the growth solutions are *labile* and convert rapidly into different molecular forms. The *lability* of the adsorbate is defined relative to the lifetime of a typical growth terrace on the crystal surface. For imaging via Atomic Force Microscopy growth terraces typically move at rates of $R \approx 1\text{-}2 \mu\text{m/s}$ and have lateral dimensions of $L \approx 100\text{-}200 \text{ nm}$. In order to identify the actual molecule affecting growth, the molecule must not disproportionate on a time scale defined by: $\frac{L}{R} \approx 0.1 \text{ s}^{-1}$.

We are using inert solutes to modify the growth kinetics and morphologies of potassium-dihydrogen-phosphate (KDP) growth steps. This KDP crystal is arguably the canonical system for understanding crystal growth from aqueous solution. We prepared a series of inert-metal complexes that exchange ligands on timescales that are much, much larger than the movement of steps on the growing KDP surface and that differ dramatically in charge, structure and size. For example, anionic $[\text{Fe}(\text{CN})_6(\text{aq})]^{3-}$ and cationic $[\text{Co}(\text{NH}_3)_6(\text{aq})]^{3+}$ inert octahedral complexes affect the kinetics of step migration differently, yet cannot form strong covalent bonds to the surface. Uptake of these adsorbates requires charge-compensation by protons or by formation of vacancies or interstitials and, surprisingly, we find that the anion influences the KDP (100) step velocity dramatically, but not the cation. Conversely, complexes containing phosphate ligands, which we expect to strongly influence the surface by substituting for the H_2PO_4^- moiety at the KDP growth surface, may give rise to an empirical relation between the unit cell size of a crystalline solid, the steric properties of the exposed growth surface, and the size, shape and charge of the incoming adsorbate. Correspondingly, we find that monodentate phosphate groups $[\text{Co}(\mu_2\text{-O})\text{HPO}_3(\text{NH}_3)_5(\text{aq})]^+$ causes a dead zone of no reaction by pinning elementary steps on the (001) surface of KDP. A similar complex with bidentate phosphate: $[\text{Co}(\mu_2\text{-O})_2\text{HPO}_2(\text{NH}_3)_4(\text{aq})]^+$ apparently has no effect. New data will also be shown for complexes with biphasphate and triphosphosphate ligands organized into both chains and rings. The ultimate goal of this research is definition of a set of rules that relate the electrostatic and steric properties of adsorbates to the growth processes at the KDP surface.

TEM Studies of Mineral Coatings, “Surface” Reactions, and Uranium Sorption in Soils

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Although theoretical and modeling approaches are becoming increasingly common in the earth sciences, microscopic observations still play an important role. This is especially true for complex systems such as soils and mineral coatings, where chemical behavior can be difficult, if not impossible, to predict. This presentation will explore examples where transmission electron microscopy (TEM) studies have revealed such unexpected phenomena.

It is commonly assumed that U(VI) in soils sorbs primarily to Fe and Al oxides and oxyhydroxides. TEM observations on soils from the Field Research Center at the DOE Oak Ridge Reservation show conclusively that uranium sorbs strongly to goethite, as expected, possibly as complexes involving phosphorus. However, uranium occurs in even higher concentrations in particles that have unusually complex chemical compositions with substantial C, O, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, and U. We predict that future studies using energy-filtered TEM (EFTEM) will show these particles to be mixtures of carbonate, phosphate, sulfate, and silicate phases.

So-called iron-oxide coated sands are so common in aquifers and other geological environments that they have been accorded the acronym IOCS. Their abundance accounts in part for the numerous studies on sorption of metals by goethite and other oxyhydroxides and oxides. Yet, there have been only a few studies aimed at determining the true makeup of such coatings on natural sands. In effect, the *status quo* has been analysis by color: if a sample of sand is brown or red, it's assumed to be coated by goethite or hematite. The few TEM studies of IOCS show that this is not generally the case, as exemplified by observations on sands from an Atlantic coastal plain aquifer at Oyster, Virginia. The coatings on these sands, which were assumed to be Fe oxide or oxyhydroxide, are instead predominantly amorphous and poorly crystalline aluminosilicate materials. Although it imparts strong color to the sands, goethite typically accounts for less than 10% of the coating material. The geochemical behavior of such sands and their interactions with bacteria may be quite different from those of pure goethite.

The fact that laboratory and natural weathering rates can differ by factors up to 10,000 has been a long-standing puzzle in geochemistry. We suggest that this discrepancy has arisen because laboratory dissolution experiments intended to represent weathering are different from most actual, natural weathering mechanisms. Both light and electron petrography show that weathering commonly occurs predominantly in the interiors of crystals, rather than by dissolution along grain boundaries. Dissolution rates probably do not accurately reflect weathering rates, because they do not take into account intracrystalline diffusion. Examples of interior weathering reactions include micas interacting with acidic, metal-bearing solutions. Such reactions demonstrate the complex interplay among solution chemistry, redox and ion exchange capacities of the mineral, and the valence state of the attacking metal.

Heterogeneous Reduction of Uranyl by Micas: Crystal Chemical and Solution Controls

Eugene Ilton
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This contribution primarily uses X-ray photoelectron spectroscopy (XPS) to better understand mechanisms for coupled sorption-reduction of aqueous U(VI) by ferrous micas. Additional information was obtained with X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM). The research highlights the importance of heterogeneous pathways for reducing U(VI) to sparingly soluble U(IV).

Three micas (high, medium and low Fe/Mg biotite), prepared as thin centimeter-sized books, were reacted with UVI solutions that contained 0-25 mM Na⁺ or K⁺, at pH = 4.5, 5.0, 6.0, and 9.5. All the experiments were performed under argon at one bar and 25°C. Samples were extracted at timed intervals for up to 20 hours. Both mica edge and basal plane orientations were analyzed by XPS. Analyses of peak positions, core satellites, and the 5f valence band indicate that U(VI) can be reduced by biotite and that heterogeneous reduction depends on the type and concentration of alkali cation in solution, crystallography, and mica composition. We conclude that ferrous micas can reduce U(VI) on edge sites, not exposed basal plane surfaces, and that Na⁺ and that K⁺ facilitate and hinder the reaction, respectively. These observations pertain over a broad range of pH.

X-Ray absorption near edge spectroscopy (XANES) of annite thick-sections indicate that the interlayer region, as opposed to external basal surfaces, are also possible sites for heterogeneous reduction of U(VI). TEM of annites with high uranium provide additional evidence for interlayer uranium; interestingly, this uranium is concentrated in U/Fe-rich nano-scale zones. However, neither XAS nor XPS found correlations between U and Fe. Each technique may be sampling different aspects of the reaction between uranyl and mica due to their different scales of observation.

One of our more intriguing discoveries was evidence for sorbed pentavalent uranium. This was a surprising result because U(V) is unstable under most conditions, including those of our experiments, and readily disproportionates to U(IV) and U(VI). However, the relevance of U(V), beyond its interest as a reaction intermediate, was made manifest by the recent discovery of Wyartite, the first U(V)-containing mineral (Burns and Finch, 1999). Sorption itself may inhibit the disproportionation of U(V) either by restricting U(V) mobility or by ligand field/bonding effects. We will discuss this and other factors that could affect the probability of a one or two electron transfer from Fe(II) to U(VI).

Burns and Finch (1999) Wyartite: Crystallographic evidence for the first pentavalent-uranium mineral. American Mineralogist, 84, 1456-1460.

Prediction of chemical reactions at the solid-water interface

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Surface complexation plays an important role in the equilibria and kinetics of processes controlling the compositions of soilwaters and groundwaters, the scavenging of metals in the ocean, the chemical evolution of low-temperature and deep high-temperature fluids, and the fate of contaminants in groundwaters. However, there is no currently-available model of surface complexation that can be used to analyze these processes by predicting surface charge and adsorption of metals and anions for the wide range of fluid compositions, solids and temperatures of interest for both natural and industrial processes. Recent progress in developing a predictive triple-layer model for surface protonation, and metal and anion adsorption in electrolyte solutions will be summarized. By analyzing extensive sets of experimental data, it has been possible to develop internally-consistent sets of the parameters characteristic of surface complexation models such as site-densities, surface protonation constants, electrolyte adsorption constants, and integral capacitances. Crystal chemical and Born solvation theory can be used to rationalize and explain how these parameters vary from one solid to another. In addition, it becomes possible to make predictions of surface charge for oxides immersed in electrolyte solutions, including predictions for many systems that have not yet been experimentally studied, and to establish general trends of surface charge development. This type of surface complexation and theoretical analysis has been extended to a study of the dependence of metal and anion adsorption on ionic strength and surface loading. Such analysis of the adsorption of alkaline earths and divalent transition and other heavy metals adsorbing to powders of oxide minerals immersed in electrolyte solutions can reveal the likely stoichiometry of adsorption reactions and the extent to which protons and hydroxyl ions participate in surface complexation. Such information should be regarded as complementary to that derived from the results of X-ray studies. The results of analysis of alkaline earth and divalent transition and heavy metal adsorption emphasize the importance of multiple surface reactions occurring under different conditions of pH, ionic strength and surface loading. Some reactions seem common to a wide range of adsorbing metal types and mineral surfaces. Crystal chemical and Born solvation theory can be used to extend our predictive capabilities for such reactions.

Nanoscale Complexity at the Oxide-Water Interface

David J. Wesolowski, Ariel Chialvo, Pascale Bénézeth, Donald A. Palmer, Baohua Gu,
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Michael L. Machesky, Moira K. Ridley, Peter T. Cummings, Milan Predota
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Serguei N. Lvov, James D. Kubicki, Xiangyang X. Zhou, Mark V. Fedkin, Andrei V. Bandura
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An integrated, multidisciplinary approach is taken to develop a quantitative, molecular-level understanding of the electrical double layer (EDL) between aqueous solutions and metal oxide surfaces. Oxide powder pH and ion adsorption titrations and microelectrophoresis measurements are conducted at temperatures ranging from 10 to 290°C. These thermodynamic data are augmented by X-ray standing wave (XSW) and reflectivity (XR) studies conducted *in situ* at solution/single crystal interfaces, currently at room temperature, but eventually at elevated temperatures as well. In parallel with these experimental studies, ab initio molecular modeling is employed to test the stabilities of postulated surface species and to develop pair-wise potentials for input into large scale molecular dynamics simulations of the EDL. These experiments and calculations provide molecular-level constraints for classical EDL and site-specific sorption models. Rutile (α -TiO₂) has been the focus of efforts thus far, due to its very low solubility, intensively studied surface properties, and great practical importance as a catalyst and industrial material. Future efforts will target oxides with lower bulk dielectric constants and lower/higher pH_{pzc}'s, such as quartz, with which were currently performing neutron scattering and reflectivity studies to elucidate the adsorption mechanisms and geometries of organic molecules.

Ti-O bond lengths at the submerged <110> and <100> surfaces determined by XR and ab initio calculations were coupled with powder pH titration and microelectrophoresis data in water and 0.001-1.0 molal NaCl and RbCl solutions to develop a high temperature extrapolation of the MUSIC surface protonation model, which also adequately rationalizes the pH_{pzc} of magnetite and nickel ferrite to 300°C. XSW and XR studies for rutile <110> single crystal surfaces coupled with molecular dynamics simulations demonstrate that water molecules, Na⁺, Rb⁺, Ca²⁺, Sr²⁺, Y³⁺ and Nd³⁺ bind at a “tetradentate” site involving two terminal and two bridged oxygens, with no intervening hydration waters, even for the monovalent cations. Water diffusivity estimates suggest that the “shear plane” at which the zeta potential is established lies within 5-7 angstroms of the surface. The displacement of sorption isotherms of the alkaline earth cations with increasing ionic strength is shown to be due to competition with the background electrolyte cations for the same binding site, rather than “outer sphere” sorption. Zn²⁺ is shown to bind to rutile <110> at monodentate bridged oxygen and bidentate terminal oxygen sites, in registry with bulk Ti positions, as postulated for Co²⁺ by Towle et al. (1999) from GI-EXAFS studies. The binding of all cations becomes stronger with increasing temperature, with pH's of 50% adsorption of dilute solutions of the multivalent cations paralleling their first hydrolysis constants, but at a much lower pH, and with temperature dependences much stronger than that of the pH_{pzc}. Surface hydrolysis is required in order to rationalize proton release associated with adsorption of transition metal and trivalent ions, given the constraints imposed by the X-ray data.

Revelations at the Mineral-Water Interface

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Synchrotron X-ray reflectivity (Fenter, 2002) and X-ray standing wave techniques (Bedzyk and Cheng, 2002) are being applied to gain new insights and understanding of processes occurring at mineral-fluid interfaces. Issues that we have addressed with these techniques during the past few years include the structures of adsorbed and near-surface water at mineral-fluid interfaces, the kinetics and mechanisms of alkali feldspar dissolution, and the three-dimensional “imaging” of bulk impurity and surface adsorbed ions.

The structure and behavior of water at interfaces is fundamental to all solid-liquid interfacial phenomena. Using high-resolution specular X-ray reflectivity (up to momentum transfer of $>6 \text{ \AA}^{-1}$), we and our collaborators have examined the following mineral-water interfaces: calcite (Fenter et al., 2000a), barite (Fenter et al., 2001), orthoclase (Fenter et al., 2000b, 2003), muscovite (Cheng et al., 2001), rutile (Z. Zhang et al., unpublished data), quartz (Schlegel et al., 2002), and apatite (C. Park et al., unpublished data). On calcite, barite, rutile, and quartz, exposed surface metal ions are chemically bonded with oxygens of water species (hydroxyl, water, or hydronium). On orthoclase and apatite, in addition to this effect, incipient ordering of water above the surface was observed, perhaps indicating hydrogen bonding of bulk water molecules with the chemisorbed water species. On muscovite, more distinct oscillations in water oxygen density were measured, giving evidence of extended water ordering. The spacings between neighboring water layers in the near-surface, strongly oscillatory region ($\sim 2.5 \text{ \AA}$) were approximately the size of the water molecule. The density oscillations extended to about 10 \AA above the surface, and were interpreted as being due to adsorbed water (as H_3O^+) at the ditrigonal K^+ site and to a “hard-wall” effect whereby a periodic hydrogen-bonded water structure develops near the interface (Cheng et al., 2001).

By monitoring X-ray reflectivity at the anti-Bragg condition during dissolution of gem-quality orthoclase we are able to measure precise dissolution rates on specific crystal faces (prepared by cleaving) as a function of temperature, pH and solution composition (Teng et al., 2001; Fenter et al., 2003). This work has led to insights on the reaction mechanisms involved in alkali feldspar dissolution and may lead to an improved general rate law relating pH, temperature, and crystal structure.

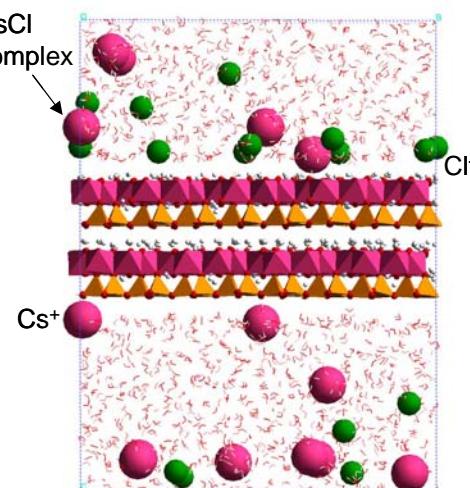
The Bragg X-ray standing wave method has been applied in a number of studies of metal ion incorporation at the surface and within the bulk of calcite and rutile (reviewed by Bedzyk and Cheng, 2002; Fenter 2000c). We recently have extended this technique to include a new model-independent approach to image atom distributions with $\sim \text{\AA ngstrom}$ resolution. This approach was demonstrated with the elemental distribution in bulk muscovite mica for both major and impurity elements (Cheng et al., 2001). We also demonstrate its use as a means to reveal ion distributions at mineral-water interfaces with using data obtained at the rutile-water interface in a separate collaborative project (D. Wesolowski, ORNL). This approach shows clearly that that Sr^{2+} , and Y^{3+} occupy a tetradsdentate site with a height determined by their ionic radii, whereas Zn^{2+} primarily occupies a monodentate site at the rutile(110)-water interface (Z. Zhang et al., unpublished data).

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Molecular Simulations of Layered Minerals and Their Interaction with Hazardous Waste

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The fate of chemical and radioactive wastes in the environment is related to the ability of natural phases to attenuate and immobilize contaminants through chemical sorption and precipitation processes. Our ability to understand the molecular control of these processes is provided by a few experimental and analytical methods such as X-ray absorption, vibrational, and NMR spectroscopies. However, due to complexities in the structure and composition of clay and other hydrated minerals, and the inherent uncertainties of the experimental methods, it is important to apply theoretical molecular models for a fundamental understanding and interpretation of these phenomena. In this effort, we have developed a general forcefield suitable for the simulation of hydrated and multicomponent mineral systems. Interatomic potentials were derived from parameterizations incorporating structural and spectroscopic data from a variety of simple hydrated compounds. A flexible water model is used to describe the water and hydroxyl behavior. Bulk structures, relaxed surface structures, and intercalation processes are evaluated and compared to experimental and spectroscopic findings for validation. Simulations of clay, hydroxide, oxyhydroxide, and layered double hydroxide phases combine energy minimization and molecular dynamics methods to describe the structure and behavior of water, hydroxyl, surface species, and intercalates in these systems. The dynamics of the water-clay interlayer can be determined with atomic density profiles and surface maps derived from molecular dynamics trajectories. We have used molecular dynamics methods to simulate the swelling behavior of various clays, the intercalation of trichloroethene in smectite, the sorption of radionuclides onto the basal surfaces of clays (see figure), and the complex structure of antigorite.



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Sorption and Precipitation Reactions at the Mica-Water and Quartz-Water Interfaces

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In order to understand how secondary minerals nucleate heterogeneously on mineral substrates, accurate pictures of the substrate mineral-water interface must first be obtained. This picture involves discernment of the behavior of both sorbates and water at the interface. To this end we have investigated the structures of the interfaces between quartz and water as well as between muscovite and aqueous salt solutions. In contrast to X-ray Absorption Spectroscopic techniques, synchrotron-based X-ray reflectivity provides specific information concerning the distribution of water. This unique ability to characterize water structure illuminates the character of the charged mineral surface as well as the inner-sphere or outer-sphere nature of sorbates.

We used high-resolution in-situ X-ray reflectivity measurements at BESSRC-CAT, Advanced Photon Source, to characterize the sorption of K, Cs, Ca, and Ba from chloride solutions onto the basal surface of muscovite. X-ray reflectivity data were collected and converted to electron density profiles perpendicular to the interface. Cations were attached to the basal surface dominantly in the first adsorbed layer, which has the highest electron density of the solution phase. Derived heights above basal oxygens for K (1.67(6) Å) and Cs (2.15(9) Å) differ by the difference in their crystallographic radii and correspond closely to values in bulk K- and Cs-micas. Heights for Ca (2.5(1) Å) and Ba (2.04(5) Å) follow the trend for hydrated radii and deviate from the trend for crystallographic radii. All derived heights imply that no separate water layer exists between the sorbates and mineral surface. Interpretations of electron density profiles indicate the presence of cosorbed water or possibly, for divalent cations, cosorbed chloride. Water layering above the sorbed cation layer and minimal relaxation of the bulk muscovite were observed.

The structures of prismatic and pyramidal growth faces of natural quartz crystals were investigated ex situ by atomic force microscopy (AFM) and in water by high-resolution X-ray reflectivity. AFM images revealed ~ 0.1 to 1 μm-wide flat terraces delimited by steps of one to several unit cells in height. These steps follow approximately directions given by the intersection of growth faces. Modeling of X-ray reflectivity data indicates that surface silica groups on flat terraces have only one free Si-O bond each (presumably hydroxylated), except for some having two free Si-O bonds observed on a single prismatic surface. Vertical relaxation of atomic positions (< 0.4 Å for terminal oxygens and < 0.2 Å for silicon and oxygen atoms fully coordinated to structural tetrahedra) is limited to a depth of 14 Å. Electron density profiles for all measured interfaces are consistent with a single layer of adsorbed water, with no evidence for additional organization of water molecules into distinct layers extending into the bulk solution.

Molecular Modeling of Aqueous Fluids in Nanospaces and at Fluid-Mineral Interfaces

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Molecular dynamics (MD) modeling provides unique insight into the structure and molecular scale dynamical behavior of geochemically important aqueous fluids at fluid-mineral interfaces and in nano-pores confined between mineral phases. We describe here a series of MD simulations designed to critically test the capabilities of the CLAYFF force field (developed by Randall T. Cygan of the Sandia National Laboratories in collaboration with us) and the SPC water model to satisfactorily simulate these situations and to explore the effects of mineral surfaces and of nano-confinement on the properties and behavior of aqueous fluids. Previous work has shown that classical MD methods that allow for energy and momentum transfer between the solid and fluid using the CLAYFF force field effectively reproduce the structure of a wide variety of hydrous, low-temperature minerals and also effectively explain NMR observations of the dynamics of interlayer water and anions in layered double hydroxides (LDHs). We describe here recent computations of the power spectra (density of states) of interlayer water and anions in a variety of Mg/Al, Ca/Al and Li/Al LDHs that reproduce well the experimentally observed relatively low frequency, far infrared spectra of these phases (collected in collaboration with James E. Amonette of the Pacific Northwest National Laboratory). Even though CLAYFF was not optimized to reproduce either the structures of LDHs or their vibrational spectra, the frequencies of the observed and computed modes are in surprisingly good agreement. These modes include those related to torsional motions of the metal-hydroxide layer structure, librational motions of water and OH-groups, and cooperative translational vibrations of interlayer H₂O and anions. The latter are related to distortion of the H-bonding network and include separate bands for water motion dominantly parallel and dominantly perpendicular to the layers. The frequencies of these modes, near 75 and 150 cm⁻¹, respectively, are very similar to those for bending and stretching of O···O···O linkages in the H-bonded network of bulk water, despite the differences in local structure. The good agreement of the computed and observed modes for interlayer species is a stringent test of the computational techniques and indicates that similar calculations for fluid-mineral interfaces and nano-confined fluids are likely to provide useful insight. MD computation of atomic density profiles perpendicular to mineral surfaces is also providing detailed molecular and nano-scale structure of the near-surface fluid that can be compared to results from in-situ synchrotron-based X-ray scattering studies. Recently initiated MD simulations for bulk water and water confined in nano-scale mineral pores and analysis of the computed results in terms of multi-species radial distribution functions, translational and orientational order parameters, and power spectra is providing new insight into the effects of confinement scale on fluid structure, dynamics and energetics. Simulations provide structural and dynamical insight into the origin of the disruption of the tetrahedral H-bonding network of water by hydroxide surfaces. Long-term objectives include developing the ability to provide predictive and interpretive molecular- and nano-scale models to compliment traditional macroscopic multi-layer models for mineral-fluid interfaces and to better understand the complexation of dissolved organic species with inorganic cations and anions.

Surface Complexation and Precipitate Geometry for Aqueous Zn(II) Sorption on Ferrihydrite: Complementary EXAFS and Multiple Scattering analysis

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Zn and a few other cations show non-linear sorption characteristics on ferrihydrite as a function of surface coverage which have not been explained on a molecular level, and thus cannot be modeled realistically. We examined “Two-line” ferrihydrite samples precipitated and then exposed to a range of aqueous Zn solutions (10^{-5} - 10^{-3} M), and also coprecipitated in similar Zn solutions (pH 6.5), with Zn K-edge EXAFS and full multiple-scattering XANES analysis. Typical Zn complexes on the surface have Zn-O distances of 1.97(.02) Å and coordination numbers of about 4.0(0.5), consistent with tetrahedral oxygen coordination. This contrasts with Zn-O distances of 2.11(.02) Å and coordination numbers of 6-7 in the aqueous Zn solutions used in sample preparation. Second neighbor information is less precise, but EXAFS fits indicate as many as 4 Zn-Fe neighbors at 3.44(.04) Å in coprecipitated samples, and about 2 Zn-Fe neighbors at the same distance in adsorption samples. In both sets of samples the fitted coordination number of second shell cations decreases as sorption density increases, indicating changes in the number and type of available complexing sites or the onset of competitive precipitation processes. Our analyses suggest that the Zn sorption complexes are inner-sphere and at lowest sorption densities are bidentate, sharing apical oxygens with adjacent edge-sharing $\text{Fe}(\text{O},\text{OH})_6$ octahedra. Coprecipitation samples show similar geometry, but these are polydentate, sharing apices with more than two adjacent edge-sharing $\text{Fe}(\text{O},\text{OH})_6$ polyhedra, in an arrangement somewhat like the local geometry of Zn in franklinite. Results are inconsistent with Zn entering the ferrihydrite structure, or formation of other Zn-Fe precipitates. The fitted Zn-Fe coordination numbers drop with increasing Zn density with a minimum of about 1.0 (0.2). This change appears due to the onset of precipitation of zinc hydroxide polymers with mainly tetrahedral Zn coordination. At still higher Zn surface loading a second type of precipitate forms. This has a structure based on a layer topology, with mainly octahedral Zn coordination. Rationalization of these structural changes can be made via bond valence considerations. The formation of Zn-containing precipitates at solution conditions two or more orders of magnitude below their nominal solubility limits is discussed with respect to other systems showing related behavior.

Calculations of the XANES for 50-200 atom clusters of structure from Zn model compounds using the full multiple-scattering code Feff 8.0 accurately replicate experimental near-edge spectra, and display features characteristic of specific first neighbor anion coordination geometry and second neighbor cation geometry and number. Analogous calculations of the XANES for small molecular clusters indicative of precipitation and sorption geometries for Zn on ferrihydrite, as suggested by the EXAFS analysis, are in good agreement with trends with sample composition, Zn-oxygen coordination, second neighbor cation coordination. An analysis of the multiple scattering paths contributing to the XANES demonstrates the importance of scattering paths involving the anion sublattice. The specific advantages of complementary quantitative XANES and EXAFS analysis are considered, and limits on the extent of structural information obtainable from XANES analysis discussed.

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Sorption Reactions at Mineral-Water Interfaces: X-ray Spectroscopic/Scattering Studies of Sorption Complex Geometries, Surface Structure and Reactivity, Effects of Organic and Inorganic Ligands, and Complex Natural Samples

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Sorption reactions at mineral-water interfaces have been the subject of intensive study for many years because of their importance in sequestering trace metals in aquatic systems and soils, which impacts the biogeochemical cycles of these metals and the composition of natural waters as well as crystal growth and dissolution processes. Such interfaces in natural systems are very complex and require a reductionist approach in which carefully controlled model systems of increasing complexity are examined using molecular-scale probes in order to characterize surface sites, reaction products, and the effects of time, ligands, and surface coatings on sorption reactions. Complex natural samples are studied in parallel to provide constraints on sorbent types and the types of precipitates formed. As discussed below, molecular-level speciation of heavy metals and metalloids in such samples can be determined in favorable cases using an approach similar to that used in the model system studies. In addition, the geochemical processes responsible for metal(loid) sequestration reactions in natural systems can be unraveled based on simplified model system results.

Synchrotron X-ray methods are playing an increasingly important role in such studies because of their ability to probe local bonding environments of selected metal(loid)s in complex, multiphase systems. We have used synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy methods to determine the geometry, composition, and mode of attachment of selected metal-ion complexes (Cr^{3+} , Co^{2+} , Cu^{2+} , Zn^{2+} , As^{5+} , Se^{4+} , Sr^{2+} , Pb^{2+} , and U^{6+}) at a variety of mineral/aqueous solution interfaces, including $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, TiO_2 (rutile), TiO_2 (anatase), hydrous Mn-oxides, am- SiO_2 , and $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolinite). One major conclusion from this body of work is that metal complexes at mineral/water interfaces are often different from those in aqueous solutions. These differences include higher degrees of hydrolysis, different first-shell coordination environments, and a higher proportion of multinuclear complexes for surface vs. solution complexes. Another conclusion is that sorbent dissolution reactions can play a very important role in determining the types of “surface” precipitates in which a trace-metal ion may be sequestered. For example, time-dependent studies of Co^{2+} and Zn^{2+} sorption products at the kaolinite/water interface showed that a combination of adsorption and dissolution reactions resulted in the formation of Co- and Zn-layered double hydroxide (LDH) phases that effectively sequester these divalent ions. Similar studies of Cr^{3+} and Cu^{2+} found no evidence for these LDH’s, presumably due to the fact that

Cr^{3+} and Cu^{2+} cannot be stably accommodated in LDH structures. Instead, hydroxides of Cr^{3+} and Cu^{2+} were found with increasing aging. Such information is essential for accurate modeling of metal ion uptake using macroscopic uptake data and surface complexation models.

In order to help constrain the types of binding sites on mineral surfaces involved in true adsorption reactions, we have also carried out grazing-incidence XAFS studies of Co^{2+} adsorption on $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 (rutile) single crystal surfaces and of Cu^{2+} and Zn^{2+} adsorption on $\alpha\text{-Al}_2\text{O}_3$ surfaces. Simple local bonding principles incorporated in Pauling's rules for complex ionic crystals were used to help constrain plausible local bonding configurations of these metal ions at mineral/water interfaces. To place additional constraints on the types of sites on mineral surfaces available for metal-ion binding, we have also undertaken crystal truncation rod (CTR) diffraction studies of hydrated $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ surfaces, finding significant structural differences between different crystallographic surfaces of $\alpha\text{-Al}_2\text{O}_3$ [(0001) vs. (1-102)] and between the (0001) surfaces of $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$. These studies also clearly show that the hydrated surfaces have structures significantly different from simple terminations of the bulk structures. These structural differences help explain the greater reactivity of Pb^{2+} on $\alpha\text{-Fe}_2\text{O}_3$ (0001) vs. $\alpha\text{-Al}_2\text{O}_3$ (0001) as well as its greater reactivity on $\alpha\text{-Al}_2\text{O}_3$ (1-102) vs. $\alpha\text{-Al}_2\text{O}_3$ (0001). In-situ long-period X-ray standing wave studies of Pb^{2+} sorption at the $\alpha\text{-Al}_2\text{O}_3$ (0001)/ and (1-102)/solution interfaces (pH 4.5), in the presence and absence of SeO_4^{2-} , confirmed the greater reactivity of the (1-102) surface. The presence of 600 μM SeO_4^{2-} results in a significant diffuse-layer accumulation of Pb at the $\alpha\text{-Al}_2\text{O}_3$ (1-102)/water interface, but has almost no influence at the (0001) surface, presumably due to the weak affinity of SeO_4^{2-} for this surface.

We have also investigated the effects of selected inorganic (Cl^- , CO_3^{2-} , and SO_4^{2-}) and organic (EDTA) ligands on Pb^{2+} sorption reactions on goethite, finding that ternary surface complexes form and significantly enhance Pb^{2+} uptake relative to ligand-free systems. Parallel XAFS studies of the effects of bipyridine and glutamate on Cu^{2+} uptake on alumina and am-SiO₂ found that Type-A ternary complexes formed on these surfaces and that in some cases (e.g., Cu^{2+} sorption on am-SiO₂) uptake is inhibited.

Additional complexity in the form of microbial biofilms was added to the $\text{Pb}^{2+}/\alpha\text{-Al}_2\text{O}_3$ (0001) and related interfacial systems. Although this particular project was supported primarily by funding from NSF, the long-period X-ray standing wave experimental protocols were developed with DOE-BES support and applied to studies of the partitioning of Pb^{2+} between *Berkholderia cepacia* biofilm coatings and the underlying $\alpha\text{-Al}_2\text{O}_3$ or $\alpha\text{-Fe}_2\text{O}_3$ substrates. Our results showed that these coatings had little effect on the intrinsic reactivity differences among the alumina and hematite surfaces, with Pb^{2+} adsorbing preferentially to the substrates at μM concentrations and partially partitioning into the biofilm coating at higher concentrations.

The speciation of Zn^{2+} and Pb^{2+} in complex natural samples from the U.S. and France was studied using a combination of methods, including XAFS spectroscopy, transmission electron microscopy, electron microprobe analysis, inductively coupled plasma-mass spectrometry, X-ray photoelectron spectroscopy, and selective chemical extractions. These studies made use of the extensive model system studies of Zn^{2+} and Pb^{2+} described above and succeeded in demonstrating that adsorption of Zn^{2+} and Pb^{2+} to iron and manganese oxides and humic materials is an important process in Zn- and Pb-contaminated soils. Also consistent with our model system studies, we found that Zn-containing layered double hydroxides form in natural systems, effectively sequestering Zn^{2+} prior to transformation of these Zn-LDH phases into Zn-containing phyllosilicates. In a soil developed over a period of 10,000+ years on Pb-rich sandstone in central France, we found that the extremely insoluble ($K_{\text{sp}} = 10^{-99}$) mineral plumbogummite ($\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) is the main host for Pb^{2+} in this soil profile.

X-ray Spectroscopy of Natural Organic Molecules: Functional Group Chemistry of Molecules in Aqueous Solutions and at Mineral-Water Interfaces

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Humic substances, produced from the biochemical alteration of plant and other biological material, are ubiquitous in the environment. Their functional group chemistry and macromolecular structures dictate mineral weathering and biogeochemical cycling of elements and contaminants in soils, sediments and aquatic systems. We developed soft X-ray synchrotron end station to facilitate the studies of C-, N-, and O-functional groups of organic molecules in aqueous solutions and at the mineral-water interfaces. Using this instrument we examined the functional group chemistry (C, N, P, S, halogens) and metal complexation of model organic molecules, biological macromolecules and humic substances. While X-ray studies on C-, N-, and P-functional groups are complementary to and supportive of the corresponding NMR studies, unique information on organosulfur and organohalogen moieties associated with humics and their metal and mineral surface interactions can only be obtained using X-ray spectroscopy and spectromicroscopy methods. In addition organic molecules in soils can be examined directly using x-rays without any sample isolation. Using the spectral signatures of model molecules, we are probing mineral-humic interactions and organic molecule dynamics in soil systems, and the chemistry of organic molecules associated with aerosols. Details of these investigations will be presented.

Investigations of the Mechanism and Inhibition of Pyrite Oxidation

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Earlier work in our groups has shown that the reaction between pyrite and water leads to the formation of hydrogen peroxide in solution. Recently we have conducted a series of batch pyrite oxidation experiments in which for the first time the production of hydrogen peroxide as well as OH radical was monitored as a function of time. The results of these experiments indicate that the OH radical is formed immediately as water interacts with the pyrite surface. There are three reaction pathways for this surface-generated OH radical: a) reaction with disulfide; b) release into solution and formation of H₂O₂; and 3) release to solution and reaction with any electron donor (radical scavenger). Results of the experiments show a immediate increase of sulfate in the solution, indicating that pathway (a) is fast. Pathway b leads to the hydrogen peroxide reported earlier. The hydrogen peroxide thus formed persists for many days and appears to be rather unreactive. Pathway c is of interest because this leads to the decomposition of compounds such as oxalate, a proposed oxidation inhibitor.

In an effort to inhibit Pyrite, FeS₂, oxidation, which has severe environmental implications, the adsorption of two-tail phospholipids on the mineral has been investigated as a means to suppress the oxidation chemistry. Spectroscopic studies suggest that the binding of long-chain, two-tail lipids, such as L-¹⁴-Phosphatidylcholine and 1,2-bis(10,12-tricosadiynoyl)-*sn*-Glycero-3-Phosphocholine, occurs primarily through the phosphate group of the lipid head group. The adsorption of this type of lipid on pyrite results in a strong suppression of the oxidation of the mineral under oxic conditions down to a pH of 1. Experimental observations suggest that the long-chain, two-tail lipids form protective bilayer lipid coatings on the pyrite surface.

Calculation of the energetics for oxidation of Sb(III) to Sb(V) sulfides by polysulfides

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Recent experimental studies (Helz, et al., *Environ. Sci. Technol.*, **36**, 943-948, 2002) have reported the existence of two new Sb sulfide species, $\text{Sb}_2\text{S}_5^{-2}$ and $\text{Sb}_2\text{S}_6^{-2}$, in alkaline sulfidic solutions in equilibrium with stibnite, Sb_2S_3 , and orthorhombic S. These species contain Sb(V), which has also recently been identified in similar solutions using EXAFS by other researchers. This represents a significant change from the consensus a decade ago that sulfidic solutions of Sb contained only Sb(III) species. I have calculated from first principles of quantum mechanics the energetics for the oxidation of the Sb(III) sulfide dimer $\text{Sb}_2\text{S}_4^{-2}$ to the mixed Sb(III,V) dimer $\text{Sb}_2\text{S}_5^{-2}$ and then to the all Sb(V) dimer, $\text{Sb}_2\text{S}_6^{-2}$. Gas-phase reaction energies have been evaluated using polarized valence double zeta effective core potential basis sets and Moller-Plesset 2nd order treatments of electron correlation. All translational, rotational and vibrational contributions to the gas-phase reaction free energy have been calculated. Hydration energies have been obtained using the COSMO version of the self-consistent reaction field polarizable continuum method. Negative free energy changes are calculated for the oxidation of the dianion of the III,III dimer to the III,V dimer by both small polysulfides, like S_4H^{-1} , and elemental S, modeled as S_8 . For the further oxidation of the III,V dimer to the V,V dimer the reaction free energies are calculated to be close to zero. The partially protonated Sb III,III dimer monoanion $\text{HSb}_2\text{S}_4^{-1}$ can also be oxidized, but the reaction is not so favorable as for the dianion. Comparison of the calculated aqueous deprotonation energies of $\text{H}_2\text{Sb}_2\text{S}_4$, $\text{H}_2\text{Sb}_2\text{S}_5$ and $\text{H}_2\text{Sb}_2\text{S}_6$ and their dianions with values calculated for various oxyacids indicates that the III,V and V,V dimers will have $\text{pK}_{\text{a}2}$ values below 5, so that their dianions will be the dominant species in alkaline solutions. These results are thus consistent with the recent identification of $\text{Sb}_2\text{S}_5^{-2}$ and $\text{Sb}_2\text{S}_6^{-2}$ species. I have also calculated the Raman spectra of $\text{Sb}_2\text{S}_5^{-2}$ and $\text{Sb}_2\text{S}_6^{-2}$ to assist in their identification. The calculated vibrational frequencies of the III,V and V,V dimers are characteristically higher than those of the III,III dimer I previously studied. The III,V dimer may contribute shoulders to the Raman spectrum. Calculations of the visible-UV spectra of these dianions also yield results consistent with the experimental observations.

Ultrascale Simulation of Surface Charging in Heterogeneous Oxide Systems: The Importance of the Crystal Chemical Characteristics of Edge Regions

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Protonation reactions oxide at the oxide-water interface exert a strong influence on surface complexation between the oxide and charged solutes in the vicinity of the interface. Over the last decade, attention has been focused on incorporating molecular-level detail into surface protonation models, often through introduction of hypothetical or calculated surface structures. Behind much of this effort there is a tacit assumption that the chemical behavior of a given mineral can be represented as a composite of its participating surfaces.

Little explicit attention has been focused on the role of more complex structural controls on chemical reactivity such as edge regions of intersecting surfaces. It is generally accepted that such regions may have enhanced reactivity, however, in many ideal laboratory systems, the proportion of these types of sites is small relative to terraces. However, this may not be the case in more complex natural systems. It is increasingly being recognized that pervasive kinetic roughening can yield highly complex surface morphologies on nanometer length scales. Recent advances in molecular simulation of oxide-water interfaces have made it possible to investigate these more complex surface structures.

This presentation describes a series of computer experiments on idealized model systems designed to yield insight into how protons are distributed in oxide-water environments that are heterogeneous on nanometer length scales. It is shown that in small systems, the surface charge distribution cannot be predicted by the charging of the individual crystal faces, and is instead dominated by unique crystal chemical characteristics of edge regions. Because of the morphological complexity inherent in low-temperature geological materials, edge effects are proposed to have a significant influence on the thermodynamics and kinetics of acid-base, complexation, and redox reactions in these systems.

Synchrotron-based Surface and Microscale Geochemical Studies at GSECARS and NSLS X26A.

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GeoSoilEnviroCARS (GSECARS) is a national user facility for frontier research in the earth sciences using synchrotron radiation at the Advanced Photon Source, Argonne National Laboratory. GSECARS provides earth scientists with access to the high-brilliance hard x-rays from this third-generation synchrotron light source. X-ray-based analytical techniques of utility to geoscientists have been implemented including: (1) x-ray absorption fine structure (XAFS) spectroscopy; (2) x-ray fluorescence microprobe analysis; (3) microtomography; (4) powder, single crystal and interface diffraction; (5) high-pressure/high-temperature crystallography and spectroscopy using the diamond anvil cell; (6) high-pressure/high-temperature crystallography using the large-volume press; and (7) inelastic x-ray scattering. A wide range of research is being conducted covering topics from the chemistry, nature, and dynamics of Earth's core and mantle to processes at work in the Earth's crust that control the transport and bioavailability of toxic species. X26A, the only high-energy microprobe beamline at NSLS, is utilized for microXRF, microXAFS, and microXRD research on problems in low temperature geochemistry, environmental science and related topics. This science is driven by the requirement for determination of the compositions, structures, oxidation states, and bonding characteristics of chemical species in earth materials with trace element sensitivity and micrometer spatial resolution.

Recent results from surface and microscale geochemical studies include: (1) structure determination of the hydrated α -Al₂O₃ (0001) surface (Eng et al. 2000); (2) observation of partial Fe occupancy on the hydrated α -Fe₂O₃ (0001) surface helping to explain the large reactivity difference between α -Al₂O₃ (0001) and α -Fe₂O₃ (0001) (Trainor et al. 2002); (3) Pb speciation at the biofilm-metal oxide interface (Templeton et al. 2003); (4) observed oxidation of Mn(II) during surface reaction of rhodonite, suggesting Mn mobility retardation via precipitation and/or hydrolysis (Farquhar et al. 2002); (5) identification of chloride complexes as the Cu species in hydrothermal fluid inclusions from an ore-forming region in Australia (Mavrogenes et al. 2002); (6) confirmation of strong arsenic sequestration by iron hydroxide plaques on plant roots from a Superfund site (Keon et al. 2002); (7) discovery of As³⁺ co-existing with As⁵⁺ in oxidized rims of roaster iron oxide grains in mine tailings from gold mining activities in the Yellowknife area (Canada) (Walker et al. 2003); (8) observation of sharply terminated Cr diffusion fronts in soil aggregates caused by locally rapid Cr(VI) reduction by microbial activity (Tokunaga et al. 2003), (9) heterogeneous uptake of hexavalent chromium and uranium by calcite during crystallization (Reeder et al. 2001) (10) observation of heterogeneous incorporation of Sr into coral aragonite (Allison et al. 2001; Finch et al. 2003) and (11) evidence of dynamic effects on fluid distribution in porous media (Wildenschild et al. 2002).

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Electrochemical Measurements and Theoretical Predictions of the Thermodynamic Properties of Carbonate and Oxide Minerals

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Assessment of two of the proposed strategies for reducing the flow of carbon dioxide into the atmosphere, namely, disposal of CO₂ in geological media and acceleration of the carbon cycle in soil or oceans requires a detailed knowledge of the Gibbs energies of carbonate minerals. Carbonate mineral solubilities vary considerably with composition and sound thermodynamic data is the starting point for estimating the fate of carbonate in geologic strata.

We have devised an electrochemical double-cell technique that can be used for the direct determination of the Gibbs energies of formation of metal carbonate solid solutions (e.g., Ca_xM_{1-x}CO₃(ss)), mixed-metal carbonate minerals (e.g., dolomite), hydroxycarbonates (e.g., hydrocerussite), disordered metal carbonates (e.g., protodolomites), and metal oxides (e.g., the hematite-to-geothite conversion).

We have developed new theoretical method based on electrostatics for calculating lattice energies of calcite-structure metal carbonates, which we have extended to calcite-structure metal-carbonate solid solutions. The method has also been applied to metal oxides of the type M₂O₃ with the corundum structure.

Our lattice-energy calculation model for calcite-structure metal carbonates treats the lattice energy (ΔU) as a sum of electrostatic, polarization, and repulsive components. The electrostatic contribution is evaluated by summing the energies of all pairwise point-charge interactions throughout the crystal, while the polarization contribution is determined via computation of all ion/dipole and dipole/dipole interactions in the crystal. The repulsive energy contribution to ΔU is evaluated by using the Slater potential. Before the three components of ΔU can be evaluated, the parallel and perpendicular components of the oxygen polarizability in MCO₃(s) must be determined along with the charge distribution of CO₃²⁻ in MCO₃(s). The calculation of the polarizabilities is accomplished by using the Lorentz Local Field Method which requires experimentally determined crystal refractive indices as input.

Thermodynamics of Minerals Stable Near the Earth's Surface

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The interaction of solid phases in rocks, sediments, and soils near the Earth's surface with the atmosphere, hydrosphere, and biosphere determines the inorganic environment in which we live. Mineral reactivity (dissolution and precipitation) determines the amounts and distances of transport of inorganic constituents by aqueous solutions. Such transport may lead to desirable consequences (e.g.: available nutrients, ore deposits) or to undesirable effects (e.g.: heavy metal, nitrate, sulfate, or radionuclide contamination). These contaminants are of concern to the Department of Energy because of the legacy of nuclear weapons production and related problems. But the underlying scientific questions are similar whether the end result is favorable or unfavorable from the human perspective. (1) What are the thermodynamic driving forces for mineral-water interactions, and what equilibrium conditions or steady states can be achieved? (2) What are the rates of such reactions, and what are the controlling mechanisms, especially those involving the rate-determining steps, which frequently occur at the mineral-water interface? To attack the second set of questions, one has to have answered the first; to assess the rate of approach to equilibrium, one has to know which way is downhill. The focus of this research project has been to determine the thermodynamic properties of minerals stable near the Earth's surface. High temperature reaction calorimetry has been the major technique used to determine enthalpies of formation of mineral phases from the oxides. The data have been combined with available or estimated entropies of formation to calculate free energies and phase equilibria. The reasons for phase stability, in terms of structure, bonding, order-disorder, and other factors, have been sought in order to provide a systematic picture and predictive capability.

Low temperature minerals have complexities less frequently encountered in high temperature metamorphic, igneous, and ultra-high-pressure phases. (1) They are often hydrated, with structural water, structural hydroxyl, and adsorbed or loosely bound water playing major roles. (2) They sometimes contain other anions (e.g. carbonate, sulfate, nitrate...) which also produce gases on decomposition. (3) Metastability and polymorphism are common. (4) Poorly crystalline, fine-grained (nanophase), and disordered materials are often seen. Having high surface area, such materials may dominate kinetics, contaminant adsorption, and physical properties. Thus the ability to define compositional and structural complexities and the development of appropriate thermodynamic cycles for calorimetry of volatile-bearing continue to be crucial aspects of our work.

Our ongoing projects span a variety of minerals: sulfates including the jarosite group, acid mine drainage minerals, hydrotalcites, uranium minerals, and the development of calorimetric techniques for sulfides. Here I focus on examples taken from jarosites, hydrotalcites and uranium (VI) minerals. In each case, enthalpies of formation were measured for the first time. The energetics of formation from properly selected simple end-members were close to zero in several cases and could be used to make predictions for wider classes of materials. We are beginning to develop calorimetric methods for minerals in acid mine drainage and for sulfides.

Interface Reactions and Dissolution of Glass in Aqueous and (Bio)Organic Media

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To investigate the release of (trace) elements from silicates and phosphates at the surface of the earth, we have been engaged in the laboratory study of mineral dissolution in the presence and absence of microbial life. We have performed many of the experiments using glasses because they can be synthesized over a wide and controlled range of composition without the complicating effects of crystallographic defects; this provides for a focus on the trace-metal chemical effects. Moreover, the ability to prepare smooth surfaces on glass permits the use of surface science techniques to probe the adsorption of metal-chelates and their morphologic effects. We have used a variety of different microorganisms: e.g., *Azotobacter vinelandii*, *Shewanella putrefaciens*, and *Methanobacterium thermoautotrophicum*; these were selected because they are dominant in soils, and have evolved to live under aerobic, either aerobic or anaerobic, and anaerobic conditions, respectively. In this presentation, our understanding of the surface reactions on simple and complex oxides will be briefly reviewed. Subsequently, the specific effects of microbial species upon the release and utilization of phosphate, iron and molybdenum from oxide minerals and glass will be described. It will be shown that when stressed by environmental conditions, the soil microbes produce and secrete organic ligands and polymers that alter the local pH and/or provide a chemical sink that enhances the mineral solubility. The study of these biological effects not only expands our understanding of metal-ion transport and mineral weathering in soil, but also provides some explanation for the observed discrepancy between laboratory and field weathering rates.

Mineral Transformations Resulting from Bacterial Electron Transfer to Fe(III) Oxides

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Ferrous iron in various forms is a facile heterogeneous reductant of both inorganic and organic solutes in subsurface materials and sediments. Ferrous iron exists in these materials within primary, rock forming minerals such biotite and ilmenite and in a biogeochemically active pool. The biogeochemical Fe(II) pool is low in concentration, controlled by microbiologic activity (iron reducing and oxidizing bacteria), exhibits temporal dynamics and microscopic heterogeneity, is comprised of adsorbed and bioprecipitated Fe(II) forms, and is poorly characterized and understood. We discuss the biogenesis of unique and reactive ferrous containing solids through the action of dissimilatory iron reducing bacteria on poorly crystalline Fe(III) oxides under anoxic conditions. Silica and phosphate-containing 2-line ferrihydrite and a mixture of ferrihydrite/akaganeite were incubated with the facultative iron reducer *S. putrefaciens* and an electron donor for time periods in excess of one year. Si and P are known to retard the crystallization of ferrihydrite under oxic conditions. The aqueous phase composition was monitored and solid samples removed at various time points. The solid phases were studied in detail using x-ray diffraction, variable temperature transmission Mossbauer spectroscopy, and scanning and transmission electron microscopy. In the absence of P, ferrihydrite and ferrihydrite/akaganeite were transformed into biogenic magnetite rapidly within one day. The biogenic magnetite, believed to form through topotaxis, exhibited 10 nm domain size and contained excess Fe(II) [$\text{Fe(II)/Fe(III)} > .5$]. With increasing incubation time, a rare ferrous rosasite mineral phase $[\text{Fe}_2(\text{OH})_2\text{CO}_3]$ evolved from the excess Fe(II) associated with magnetite. In contrast, the presence of P inhibited magnetite formation, and bacterial reduction yielded an unusual “Fe(II)-sorbed ferrihydrite” with Fe(II) concentration well in excess of hydroxyl surface site density. This phase gradually recrystallized into carbonate-intercalated green rust with further bacterial electron transfer. Green rusts of variable Fe(II)/Fe(III) ratio were obtained depending on P concentration. The formation of both of these phases was made possible by the presence of carbonate resulting from the microbial oxidation of the electron donor (lactate). The formation mechanisms and environmental implications of these solids will be further described.

Nanoparticle products of microbial biomimetic mineralization of U, Fe, and Zn

Yohey Suzuki, Clara Chan, John Moreau, Heng Zhang, Jill Banfield

Microbial biomimetic mineralization can dramatically modify the distribution of metals in the environment. The goals of this research are to determine the mechanisms by which cell surfaces, enzymatic activity, and microbial byproducts induce mineral precipitation and the factors that determine the fate of these products. Our work focuses on biogeochemical processes in metal-contaminated environments associated with two abandoned mines. Field work has been carried out at the Midnite Mine in Washington, where uranium contamination of soils and sediments has occurred, and in a flooded underground mine tunnel in SW Wisconsin, where Zn, Pb, and U contaminants are cycled across a redox boundary. Microbial activity in oxic and anoxic zones results in formation of metal oxide, metal sulfide, and phosphate biominerals in proximity to, and within, cells. Precipitation reactions occur as the result of enzymatic reactions involved in energy generation, sequestration of toxic ions, and adsorption onto cell polymers.

We have combined molecular biological characterization of the microbial communities, experiments involving cultured microorganisms, and high-resolution mineralogical and geochemical analyses (in situ and in the laboratory) to understand biogeochemical metal cycling. We have redesigned oligonucleotide probes used for detection of sulfate-reducing bacteria (SRB) to show that SRB are more important in natural samples than previously recognized. The size, form, and distribution of nanometer-scale ZnS products of SRB were determined. Results revealing the presence of both hexagonal and cubic polymorphs have been rationalized by thermodynamic analysis of the dependence of phase stability on particle size.

Our results show that mechanisms by which organisms are resistant to the chemical toxicity of uranium include formation of extracellular and intracellular nanoparticles of uranium phosphate and oxide. Uranium is also associated with ferric iron oxyhydroxide nanoparticles formed in microaerophilic zones, and is cycled as these minerals dissolve, either through biological reductive or acid-promoted dissolution.

Our work has highlighted the ultra-small size of many biomimetic products. A combination of synchrotron- and electron microscopic studies revealed that the average size of UO_2 products is $< 2 \text{ nm}$, that they are terminated with highly reactive surfaces not found on macroscopic oxides, and that they grow via oriented aggregation processes (in some cases, mediated by organic polymers). Measurement of structural characteristics has been used to evaluate the size-dependent solubility of uranium oxide. In combination, results indicate enhanced potential for transport due to particle sizes that form a continuum with clusters, and for redissolution, due to high surface reactivity and solubility (Suzuki et al. 2002).

Some iron-oxidizing bacteria manufacture polymeric compounds to localize mineral precipitation. Mineralization of polymer strands yields remarkable micron-scale long, nanometer-wide crystals of akageneite that are coated with nanometer-scale ferrihydrite aggregates. The high aspect ratio of akageneite is accomplished by end-to-end assembly of nanoparticles. A scheme by which cells optimize energy generation by utilizing enhanced proton motive force due to oxide precipitation is proposed.

Mineral specific biological interactions: Nanoscale force-distance measurements between iron oxyhydroxides and *Shewanella* or siderophores

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The bacterium-mineral interface is ubiquitous near the surface of the Earth. Fundamental forces governing interactions at this interface are very different than those that dominate the macroscale world. Whereas the force of gravity dominates the interactions between macroscopic bodies (e.g., plants and animals) and the Earth, intermolecular forces (e.g., van der Waals, electrostatic, solvation interactions) are the prevailing forces with which microscopic bacteria must contend. For comparison, the force of gravitational attraction between the Earth and a bacterium ($\sim 10^{-12}$ g) is $\sim 10^{-14}$ N (Newtons). This stands in contrast to the magnitude of the forces we have quantitatively measured at the bacterium-mineral (or biomolecule-mineral) interface, which are greater by three to five orders of magnitude. In nature, these latter forces—so-called “nanoforces” because of their magnitude and the nanometer scale of space over which they exist—are at the heart of all interactions between biologically produced polymers and mineral surfaces. These nanoscale forces control, for example, (1) electron transfer pathways between reductases in the cell wall of dissimilatory iron reducing bacteria and reactive iron centers in the crystal structure of oxyhydroxides, and (2) iron oxyhydroxide dissolution mediated by siderophore ligands that complex iron from mineral surfaces.

In one investigation, living cells of *Shewanella oneidensis* were linked to a force-sensing cantilever used in a biological force microscope, to measure force interactions as a function of the distance between a bacterium and goethite (FeOOH) or diaspore (AlOOH), under aerobic versus anaerobic conditions. Energy values (in attoJoules; 10^{-18} Joules) derived from these measurements show that the affinity between *S. oneidensis* and goethite rapidly increases by 2-5 times under anaerobic conditions where electron transfer from bacterium to mineral is expected. A unique signature in the force curves suggest that under anaerobic conditions an ~ 150 kDa putative iron reductase is localized and/or mobilized within the outer membrane of *S. oneidensis*, and specifically interacts with the goethite surface. No such observations were made for experiments with diaspore, or for measurements using nonviable cells.

In another investigation, a protein coupling technique was used to covalently attach the siderophore azotobactin to a force-sensing cantilever. A force microscope was used to probe the activated cantilever against goethite and its isostructural Al-equivalent diaspore, under aerated conditions. Upon contact with each mineral surface, average adhesion forces between azotobactin and goethite were 2-3 times greater than the force value associated with diaspore under identical solution conditions. The relative force affinity for the iron containing mineral (versus aluminum) qualitatively correlates with the difference between the aqueous complex formation constants estimated for azotobactin and Fe(III)(aq) ($K_f=1028$) and Al(III)(aq) ($K_f\sim 1016$). Further, the adhesion force between azotobactin and goethite significantly decreases when small amounts of soluble iron ($FeCl_3 \cdot 6H_2O$) are added, suggesting the azotobactin’s chelating groups specifically interact with the goethite surface. Plateau features in the force data generated upon tip retraction from the surface indicate these chelating groups are associated with azotobactin’s carboxyl-terminal hydroxamate moiety.

Ongoing investigations are aimed at identifying if and how membrane-associated proteins are involved in interactions with metal oxyhydroxides (e.g., mineral recognition, cellular adhesion, electron

transfer). A proteomic approach is being used to map the physical and functional architecture of membrane-associated proteins involved in anaerobic respiration of *S. oneidensis*. Expression profiles of proteins will be examined under aerobic versus anaerobic conditions using two-dimensional gel electrophoresis in combination with mass spectrometry to identify membrane-associated proteins specifically involved in adhesion and/or anaerobic respiration. The completed genome sequence of *S. oneidensis* MR-1 will be probed with sequence analysis techniques (genomics) to identify likely candidate proteins. Additionally, polypeptide phage display libraries will be used to identify polypeptide “motifs” involved in mineral recognition and binding. Upon completion, these “motifs” can be used to search the genome of *S. oneidensis* for putative membrane-associated proteins that may be involved in mineral-microbe adhesion. The genes encoding these putative proteins will be cloned, expressed, and purified and their functional properties evaluated *in vitro*. The specific interactions between an individual recombinant protein and a mineral surface can then be probed with force microscopy. We believe that the resulting protein force signature, when compared to the whole-cell force measurements, can be used to correlate individual membrane-bound proteins with specific feature(s) of the whole-cell force trace. This research may allow us to design bacteria that exhibit a selective affinity for particular inorganic phases or crystallographic surfaces by exploiting the exquisite control bacteria have over the expression of certain cell wall macromolecules.

**Molecular Basis for Microbial Adhesion to Geochemical Surfaces:
Computer Simulation of *Pseudomonas aeruginosa* Adhesion to Goethite**

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The adhesion of bacteria to mineral surfaces plays a central role in characterizing their contribution to the fate of contaminants in complex environmental systems by effecting microbial transport through soils, respiration redox chemistry, and ion mobility. Bacteria growing on a surface may reduce metal transport, whereas free-living bacteria that constitute mobile suspended particles may have a higher sorbing capacity and increase metal transport. They may reduce mineral metal ions through direct contact or by reducing complexed ions. The adhesion of the outer membrane of *Pseudomonas aeruginosa* to the mineral goethite was investigated using classical molecular dynamics simulation. A fragment model for goethite was developed and has been integrated into a fully atomistic membrane model. Properties for the resulting system were collected from a 1.5 ns simulation in the isothermal-isobaric ensemble. The response of the membrane to the presence of the mineral is investigated by analysis of radial distribution functions representing an average picture of the hydrogen bonding, as well as distribution of orientational vectors defined for each saccharide group that show the extent of the mineral's perturbations on the membrane. Significant structural changes were observed for the outermost saccharide groups, several of which rotate to form hydrogen bonds with the mineral surface. The structure of the inner core, and the corresponding integrity of the membrane, is attained. The mineral surface dehydrates slightly in the presence of the membrane as saccharide hydroxyl groups compete with water molecules for hydrogen bonding sites on its surface.

Size, Structure, and Aggregation of Nanoparticles

Benjamin Gilbert, Hengzhong Zhang, Forrest Gilbert, Jillian F. Banfield
Jim Rustad, Glenn Waychunas

Very fine nanoparticles are chemically distinct from the bulk materials of the same stoichiometry. The high proportion of underbonded surface atoms causes internal strain, the consequence of which can be modified phase stability. Strain-induced atomic rearrangement and loss of crystal symmetry alters the electronic density distribution, affecting reactivity. Quantum confinement imposes a further electronic perturbation not present in bulk materials, which can strongly change electrooptic properties.

Reconstruction, reaction and aggregation occur at nanoparticle surfaces. The concepts and results of classical thermodynamics for bulk samples are a limited guide to reactivity on a nanoscale if the surface structure differs from bulk materials. The present research is aimed at obtaining atomic models of nanoparticle structure, from which thermodynamic values can be calculated and integrated with theory and data from mesoscopic and macroscopic regimes. The specific goals are: 1) to develop and verify molecular dynamics (MD) force potentials within nanoparticles to allow description of nanoparticles and their interactions with other particles and surface ligands; 2) to use the verified potentials to extract absolute and relative thermodynamic parameters. The integration of MD simulations with thermodynamic principles allows prediction of structures and trends in behavior with size as an independent variable. Data and calculations performed to date show the considerable potential of this approach.

MD simulations indicated that surface ligands could have a substantial impact on nanoparticle structure. Experimentally, it is possible to reversibly transform 3 nm ZnS between sphalerite and wurtzite phases by switching the nanoparticle environment between methanol and moist air. Furthermore, we have shown that the binding of water causes a profound structural modification in nanocrystalline ZnS. The data indicate a surface-driven disorder/order transition, consistent with the MD structures. MD simulations also show that water adsorption can invert the relative phase stability of the two nanophases. It is experimentally observed that water binding stabilizes the sphalerite structure. We have now begun to follow the kinetics of the structural transitions, experimentally, and in the simulations.

In addition to ligand binding, aggregation state can have an effect on nanoparticle structure through particle-particle interactions, and it is possible to induce structure switching by changing the aggregation state. Reversible transformations in 3 nm ZnS nanoparticles between distorted and more ordered structures are achieved by ultrasonically induced disaggregation and vacuum reaggregation.

Large-scale MD calculations have been carried out on 2-216 1-2 nm sized particles of hematite and goethite. These particles are fully solvated by dissociable water molecules. We have developed a method for accelerating time scales that preferentially puts spectral power into low-frequency modes, accentuating transition state path sampling. In the small goethite systems, we have observed attachment events involving edge-face interaction governed by inhomogeneous charge surface charge development. The spherical hematite particles undergo very few attachment events.

The Reaction Specificity of Nanoparticles in Solution: Characteristics and Properties of Iron Nanoparticles

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The general objectives and current progress for a new nanoscience program based at PNNL will be described. The reactivity of nanometer-sized materials is often quite different from that of either the bulk material or the individual atoms and molecules that comprise it. Much of this size-dependent reactivity stems from the development of unique electronic structures intermediate between those of bulk materials and free atoms.

Zero-valent iron (Fe) represents one system whose chemistry exhibits intrinsic nanoscale reactivity as well as the transition from metallic to semiconducting behavior. Iron and iron bimetallic nanoparticles have been shown to have a greatly increased reactivity towards a variety of environmentally important solute species including chlorinated hydrocarbons and reducible oxyanions. Furthermore, the products of these reactions differ, often in an environmentally friendly manner, from those obtained when 0.1 to 1 mm particles of Fe are used. These changes occur for particles of the size range where significant variations in electronic and magnetic properties are induced for pure metal particles. However, the Fe particles have the additional complication of a reaction layer that forms on the surface in solution. The differences in selectivity may be induced by the changes in the electronic structure of the nano-sized particles or changes in the structure of the coatings formed on the particles in solution. This program involves a coupled experimental and modeling research effort for studying reactive metal, bimetallic, and oxide nanoparticles, using chlorinated hydrocarbons and inorganic oxyanions as model compounds.

Current theory and understanding of oxide surface chemistry and the ability to create nanoparticles in a controlled fashion provide an excellent starting point that makes this challenging problem tractable. The program integrates: 1) synthesis of well defined particles, 2) characterization of their surface and bulk composition as well as physical and electronic structure, 3) measurements of reactivity in vacuum and solution, and 4) theory and modeling efforts to help explain the oxide structures and reactivity of specific sites. Quasi-continuum (QC) and molecular dynamics (MD) simulations provide formation and structure information and are being used in conjunction with simulations of surface reactivity using linked quantum mechanical/molecular dynamics (QM/MD) of solute binding energies, electron reduction potentials, and reaction transition states.

The talk will examine the nanoscience nature of the questions being addressed, aspects of the growth and characterization of Fe and Fe-Oxide nanoparticles, initial electrochemical based reaction studies and the first products of the QC model for Fe-oxide clusters.

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Thermochemistry of Nanomaterials

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The goal of this project is to use calorimetry as a tool to study the differences between nano and bulk materials, focusing on both heat capacities and enthalpies of formation and phase transition. Reaction calorimetry at UCD, adiabatic low temperature calorimetry at BYU, and “calorimetry on a chip” at UCS form a powerful combination. We are focusing in several areas: the energetics and heat capacities of nanophase titania and zirconia; a comparison of bulk, nanophase, thin film, and multilayer materials in CoO-MgO, and the energetics and entropies and heat capacities of hydration of nanoparticles. The instrumentation, approaches, and some preliminary results for ZrO₂, TiO₂, and CoO are presented.

Participants:

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