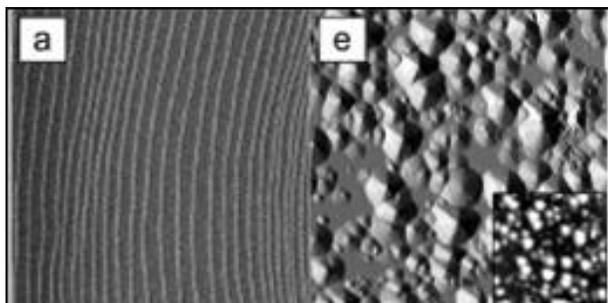
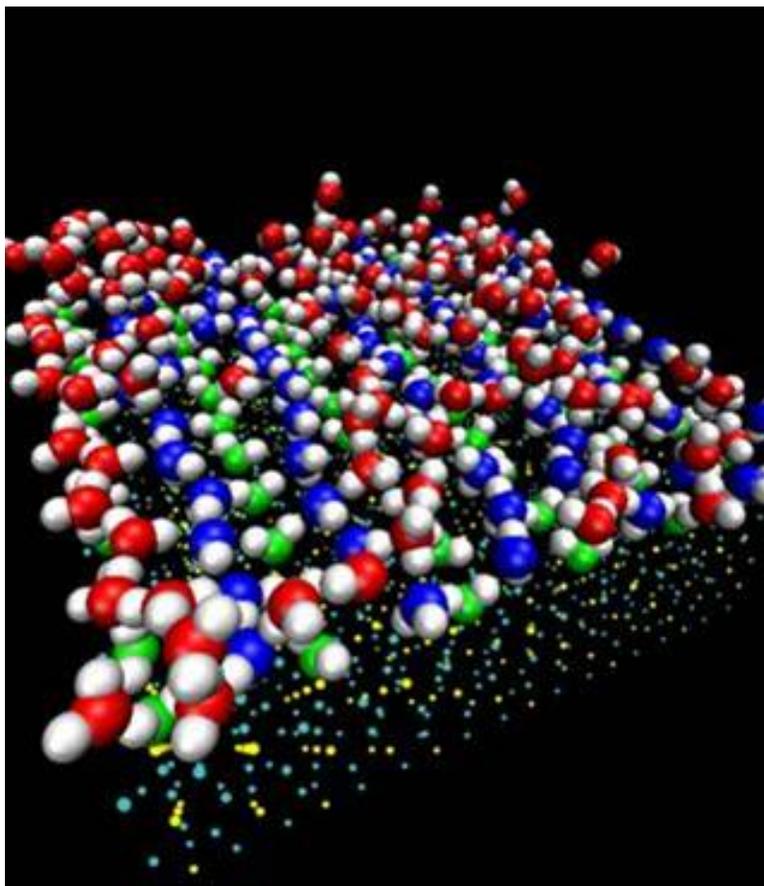


Experimental and Theoretical Geochemistry



March 12-13, 2009

Geosciences Research Program, Office of Basic Energy Sciences

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FORWARD

“Experimental and Theoretical Geochemistry” is the fifteenth 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 on their Office of Basic Energy Sciences’ supported research. 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 Prof. Patricia Maurice of the University of Notre Dame, Prof. Peggy O’Day of the University of California, Merced, Prof. Larry Edwards of the University of Minnesota, and Dr. Sonia Esperanca of the National Science Foundation. They join our Principal Investigator co-chairs Dr. Tetsu Tokunaga from Lawrence Berkeley National Laboratory, Prof. Trish Dove from Virginia Tech, Dr. Susan Carroll from Lawrence Livermore National Laboratory, and Dr. Steve Sutton from the University of Chicago. 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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Figure 1: MD snapshot of rutile hydrated surface. Titanium atoms: yellow. Oxygen atoms in rutile: cyan. Oxygen atoms in the L₁ layer: green. Oxygen atoms in the L₂ layer: blue. Oxygen atoms in the L₃ layer: red. Hydrogen: white. Image courtesy of Dave Wesolowski, ORNL.

Figure 2: Unreacted (001) hematite surface (a) – AFM image, and precipitation of large hematite pyramids (e) on reacted (001) surface. Image courtesy of Kevin Rosso, PNNL.

Experimental and Theoretical Geochemistry

-Agenda-

O'Callaghan's

Annapolis, MD

March 12-13, 2009

Thursday, March 12 (AM)

7:30 **Registration/Continental Breakfast**

8:30 **Introductions and Greetings**

Nicholas Woodward, Department of Energy

Session 1

Chairs: Patricia Maurice (Notre Dame), Tetsu Tokunaga (LBNL)

8:45 Glenn Waychunas, Lawrence Berkeley National Laboratory

The Nanogeoscience Program at LBNL/UC Berkeley: Structural, Physical, Electronic, and Kinetic Studies Combined with Computer Simulation of Important Natural Nanoparticle Reaction Pathways

9:10 Don Baer, Pacific Northwest National Laboratory

Reaction and Aging Behaviors of Iron Nanoparticles

9:35 Michael Hochella, Virginia Tech

Influence of Grain Size, Morphology and Aggregation on Galena Dissolution

10:00 Dave Wesolowski, Oak Ridge National Laboratory

Nanoscale Complexity at the Mineral-Water Interface

10:25 **Coffee/refreshments**

10:50 Jim Rustad, University of California, Davis

Carbonate in Fe- and Al- Oxide Minerals: Speciation and Isotopic Heterogeneity

11:15 Daniel Strongin, Temple University

Pyrite Surface Reactivity under Environmentally Relevant Conditions

11:40 Heather Allen, Ohio State University

Vibrational Sum Frequency Studies of Structure at Geochemical Interfaces: Water, Ions, and Silica

12:05 **Lunch** (on your own)

Thursday, March 12 (PM)

Session 2

Chairs: Peggy O'Day (UC Merced), Trish Dove (Virginia Tech)

- 1:05 Kevin Rosso, Pacific Northwest National Laboratory
Dynamics of Coupled Dissolution/Growth and Bulk Charge Transport in Fe(II)-Catalyzed Transformation of Fe(III)-oxides/oxyhydroxides
- 1:35 David Elbert, Johns Hopkins University
Investigating the Crystal Chemical Controls on Uranium Contamination in Soils
- 2:00 Randy Cygan, Sandia National Laboratories
Advances in Modeling the Mineral-Water Interface
- 2:25 Eugene Ilton, Pacific Northwest National Laboratory
The Influence of Reaction Pathways on the Reduction of U^{VI} to U^{IV} : The Role of the Intermediate U^V Species
- 2:50 **Coffee/refreshments**
- 3:10 Andrey Kalinichev, Michigan State University
Computational and Spectroscopic Studies of Molecular Structure and Dynamics at Mineral-Water Interfaces
- 3:35 Steve Sutton, University of Chicago
Synchrotron-based Geochemical Studies Involving Fluids and Melts
- 4:00 Tony Lanzirotti, University of Chicago
Applications of Hard X-ray Microprobe Techniques in Evaluating the Biogeochemistry of Metals in the Environment
- 4:25 Alexandra Navrotsky, University of California, Davis
Nanophases - Implications for Thermodynamics in the Critical Zone
- 4:50 William Casey, University of California, Davis
Isotope-Exchange Dynamics in Large Oxide Ions
- 5:15 **Adjourn**
- 6:30 **Dinner** (On your own)

Friday, March 13 (AM)

7:30 **Coffee/Continental Breakfast**

Session 3

Chairs: Larry Edwards (Minnesota), Susan Carroll (LLNL)

8:20 Nick Woodward
Introduction

8:35 Don DePaolo, Lawrence Berkeley National Laboratory
Isotopic Fractionation during Precipitation of Minerals from Aqueous Solution

9:00 John Valley, University of Wisconsin
*Ion Microprobe Analysis of Oxygen and Silicon Isotope Ratios in Authigenic Quartz:
High Precision and Accuracy*

9:25 Mike Murrell, Los Alamos National Laboratory
Uranium-Series Transport from Micron to Meter Scales and Beyond

9:50 Frank Richter, University of Chicago
Kinetic Isotope Fractionation by Transport Processes

10:15 **Coffee/refreshments**

10:35 Sally Newman, Caltech
*Experimental Study of the Dependence of Water Diffusion on Water Content in High-Al
Basalt, Haplobasalt, and Haploandesitic Melts*

11:00 Juske Horita, Oak Ridge National Laboratory
Experimental and Theoretical Study of Brucite under Pressure

11:25 Bruce Watson, Rensselaer Polytechnic Institute
Grain-Boundary Diffusion of Excluded Elements

11:50 **Lunch** (on your own)

Friday, March 13 (PM)

Session 4

Chairs: Sonia Esperanca (NSF), Steve Sutton (Chicago)

- 1:05 Henry Teng, George Washington University
Formation of Metastable CaCO₃ Polymorphs in the Presence of Oxides and Silicates
- 1:30 Carrick Eggleston, University of Wyoming
Properties of Adsorbed Cytochromes from Dissimilatory Metal Reducing Bacteria: Density and Rigidity of Periplasmic vs. Outer-Membrane Cytochromes
- 1:55 Trish Dove, Virginia Tech
Investigating the Physical Basis of Biomineralization
- 2:20 Pupa Gilbert, University of Wisconsin
Experiments and Theory of Biomineral Formation
- 2:45 **Coffee/refreshments**
- 3:05 Ray Fletcher, Penn State University
Evolution of the Size and Porosity of Corestones in the Weathering Profile
- 3:30 Carl Steefel, Lawrence Berkeley National Laboratory
Resolving the Discrepancy between Laboratory and Field Rates: A Reactive Transport Approach
- 3:55 Susan Carroll, Lawrence Livermore National Laboratory
Connecting Molecular Structure to Surface Reactivity Using NMR, XRD, and Solution Chemistry
- 4:20 Tetsu Tokunaga, Lawrence Berkeley National Laboratory
Hydraulic Properties of Adsorbed Water Films in Unsaturated Porous Media
- 4:45 Ian Bourg, Lawrence Berkeley National Laboratory
Computational Geochemistry: Applications to Mineralogy, Geochemistry, and Hydrology
- 5:10 Nick Woodward
Concluding remarks
- 6:00 **Refreshments**
- 6:30 **Awards Banquet**

The Nanogeoscience Program at LBNL/UC Berkeley: Structural, Physical, Electronic, and Kinetic Studies Combined with Computer Simulation of Important Natural Nanoparticle Reaction Pathways

Jill Banfield¹, Ben Gilbert², Dino Spagnoli¹, Glenn Waychunas², Ken Williams², and Hengzhong Zhang¹

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²*Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA*

With the aid of facilities funding from LBNL, and strong concurrent support from the Earth Sciences Division at LBNL, we have been able to unite the efforts of several PIs within one new laboratory for the study of environmentally, biologically and geochemically significant nanoparticulate systems. We illustrate some of the ongoing work here with two examples: surface structure, surface water structure and aggregation behavior of Fe oxyhydroxide nanoparticles in aqueous solution; and atomic structure measurements of nanometer amorphous TiO₂.

Oriented aggregation (OA) has been shown in a number of diverse systems, both natural and laboratory, but the details of the mechanism and the conditions under which OA is favored are not well understood, certainly for natural nanoparticles. Our studies to date have included goethite and hematite, and are being extended to maghemite, ferrihydrite and schwertmannite. MD simulations of nanohematite show ordered water layers at the nanoparticle surface that vary in character (exchange rates) according to surface topology, and also as a function of interparticle separation. The work needed to separate particles as a function of separation distance differs considerably from the vacuum case, and shows evidence of periodicity due to water structure at small separations. In the vacuum case there is also a strong dependence on particle orientation in this work function, and simulations are in progress to investigate if orientation effects in solution are as important. Surface sites near edges and corners of particles is inferred to have different acid-base character than on flat surfaces, due to bond deficit considerations, and the concept has been verified by non-linear optical spectroscopy on single crystal surfaces. Extended to nanoparticles, this should lead to variations in surface protonation according to very localized topology, and perhaps further water structure variations. Simulations that include varied protonation, and ultimately, dissociated water, are the next step in the investigation.

Amorphous titania, TiO₂, is an important precursor for synthesis of single-phase nanocrystalline anatase. We were able to synthesize 2 nm amorphous titania by hydrolysis of titanium ethoxide, with verification of the size by TEM and gas adsorption. Synchrotron high photon energy x-ray scattering was used to probe the atomic correlations in these samples via PDF analysis. Molecular-dynamics simulations were used to generate input structures for reverse Monte Carlo analysis of the PDF patterns. X-ray absorption spectroscopy (XAS) simulations were used to screen candidate structures obtained from the RMC by comparing with experimental XAS data.

The structure model that best describes both the PDF and XAS data shows that amorphous TiO₂ particles consist of a highly distorted shell and a small strained anatase-like crystalline core. The average coordination number of Ti is 5.3 and the Ti-O bond length distribution centers around 1.940 Å. Relative to bulk TiO₂, the reduction in the coordination number is primarily due to the truncation of the Ti-O octahedra at the amorphous nanoparticle surface, and the shortening of the Ti-O bond length due to bond contraction in the distorted shell. The pre-existence of the anatase-like core may be critical to the formation of single-phase nanocrystalline anatase in crystallization of amorphous TiO₂ upon heating.

Reaction and Aging Behaviors of Iron Nanoparticles

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The objective of our research is to obtain fundamental information about the physical and chemical transformations that occur on and within mineral oxide nanoparticulates due to electron transfer reactions and other interactions with their local environment. The nature of the reactive surfaces, the accessibility of reactive sites, and the structures of the surface and interface layers (or whole nanoparticles) often change significantly as particles respond to and react with their local environment (e.g., surface structure alterations, phase changes, passive layer formation ...). Although geochemically induced changes occur for bulk materials, the nature and rate for the changes can be more dramatic for nano-sized mineral phases. This project focuses on obtaining information about these geochemically mediated transformations and how they alter particle reactivity, electron availability and particle mobility. Natural particles and specially grown model particles are used to study particle transformations, interfacial reaction products and particulate reactivity. The particles examined (and to be examined) include different sizes of iron (Fe(0)) nanoparticles, magnetite particles, and iron (hydr)oxide particles that can coat the Fe(0) surface. Electron transfer initiated transformations have been studied using carbon tetrachloride, a probe molecule of surface reactivity that is not incorporated into the surface structure.

Iron and other nanoparticles (NPs) have been shown to have a greatly increased reactivity towards a variety of geochemically important solute species, including chlorinated hydrocarbons, oxyanions, and metallic cations, and to produce different reaction products than microscale iron surfaces. In recently completed work we have found that nanoparticulate iron is highly dynamic and that NP aging in solution can have significant impacts on reaction processes. Although such changes complicate full understanding of the behavior and lifecycle of NPs, to the degree that these aging processes can be understood and influenced by NP coatings, size, and composition they also provide an opportunity to predict NP behavior. Current work includes examination of the impact of organic coatings on nanoparticle properties.

The work includes four major activities: 1) synthesis of well-defined NPs, 2) characterization of their surface and bulk composition as well as physical and electronic structure (before and after reaction measurements), 3) *in situ* real-time and batch measurements of NP properties and reactivity in vacuum and solution, and 4) theory and modeling work that helps identify reaction mechanisms and reaction intermediates.

Influence of Grain Size, Morphology and Aggregation on Galena Dissolution

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24061-0420*

The acidic, non-oxidative dissolution of galena nanocrystals had been studied using both microscopic and wet-chemical methods. The effects of particle size, shape, aggregation state, and grain proximity on dissolution rates were investigated. Nearly monodisperse galena nanocrystals with an average diameter of 14.4 nm and a truncated cubic shape were synthesized. In the dissolution experiments of dispersed nanocrystals, galena nanocrystals attached on the surface of a TEM grid were exposed to deoxygenated HCl solutions (pH 3) at 25 °C. Capping groups on nanocrystals were removed via a washing process, and chemistry of nanocrystals was examined using X-ray photoelectron spectroscopy (XPS). The evolution of the size and shape of the pre- and post-dissolution nanocrystals were studied in detail using transmission electron microscopy (TEM), and the dissolution rate was calculated directly according to the size shrinking of galena nanocrystals. To assess the size effect, galena microcrystals (~ 3 μm) were synthesized and dissolved under similar conditions to the dispersed nanocrystals. The results showed that the nanocrystals dissolved at a surface area normalized rate of one order of magnitude faster than the microcrystals. In addition, dissolution rate is orientation-dependent on a single nanocrystal. High-resolution TEM (HRTEM) images indicated the {111} and {110} faces dissolve faster than {100} faces on galena nanocrystals, rationalized by the average coordination number of ions on each of these faces.

To assess the aggregation effect, dissolution experiments of aggregated galena nanocrystals were conducted using a wet-chemical method, and the results were compared with the rates of microcrystals and dispersed nanocrystals. These experiments showed that the rate of aggregated nanocrystals is in the same order of magnitude as the rate of microcrystals, but one order of magnitude smaller than that of dispersed nanocrystals.

Finally, the effect of the close proximity between nanocrystals on dissolution was observed by HRTEM. Dissolution was greatly inhibited on galena nanocrystal surfaces that were closely adjacent (1-2 nm, or less) to other nanocrystals, a direct indication of the properties of aqueous solutions and ion transport in extremely confined spaces and probably relevant to the slow dissolution of aggregated nanocrystals.

The dissolution phenomena of galena nanocrystals observed in this study is likely important for understanding the environmental fate and behavior of nanoparticles in aquatic systems.

Nanoscale Complexity at the Mineral-Water Interface

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The mineral-water interface is a complex nanoscale regime in which many of the dominant geochemical processes at the Earth's surface and in the shallow crust take place. This domain differs in structure, dynamics and reactivity from the bulk solid or fluid because of under-bonded atoms exposed at the mineral surface, disruption of the hydrogen bond network and ion hydration of the bulk solution, and electrical and chemical potential gradients at the interface. New developments in molecular level probes (e.g. synchrotron X-ray reflectivity) and computational modeling capabilities have converged to permit advances beyond purely thermodynamic descriptions of interfacial phenomena that treat the solvent as a dielectric continuum and the surface as a featureless plane of uniform charge. These molecular probes have been quantitatively linked with macroscopic studies of surface charge, ion adsorption and electrophoretic mobility of powder suspensions using unique high temperature experimental systems to provide a more comprehensive understanding of interfacial equilibrium properties. Further developments are now permitting linkage of molecular simulations with direct probes of interfacial dynamics, including inelastic neutron scattering and other surface spectroscopies. As computing power and algorithms advance, there is the promise of simulating transport and reaction rates and mechanisms over time scales relevant to mineral dissolution and precipitation kinetics.

This project has focused in recent years on a detailed comparison of the interaction of aqueous electrolytes in the system Na^+ - K^+ - Rb^+ - Ca^{2+} - Sr^{2+} - Zn^{2+} - Co^{2+} - Nd^{3+} - Y^{3+} - Cl^- - CF_3SO_3^- with the isostructural minerals rutile (α - TiO_2) and cassiterite (α - SnO_2) over wide ranges of pH, temperature and salinity. The (110) face of both phases is the most stable and best developed, but the smaller lattice spacing and higher polarizability of Ti(IV) in rutile result in significant differences in the interfacial structure and dynamics. Protonation of surface oxygens is clearly related to the nature of bonds with substrate metal atoms, but is also influenced by strong hydrogen bonds among surface species and between them and next-layer water molecules, and both are influenced by surface lattice spacing. All ions studied on these surfaces exhibit inner sphere sorption at several sites whose relative abundances change with pH and temperature and are largely dictated by sorbed ion radius and charge, and crystal surface structure. The assignment of inner sphere ions to 'Stern planes' and bond valence models of surface protonation are consistent with the atomic-scale interfacial properties, but the concept of the interfacial solvent as a dielectric continuum appears to have no molecular basis. Furthermore, water molecules near the surface exhibit a wide range of vibrational properties and diffusional dynamics that are likely to play a dominant role in surface reaction rates and mechanisms.

Carbonate in Fe- and Al- Oxide Minerals: Speciation and Isotopic Heterogeneity

James Rustad¹, Dave Dixon², and Jean-Francois Boily³

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²*Department of Chemistry, University of Alabama, Tuscaloosa, AL*

³*Pacific Northwest National Laboratory, Richland, WA*

Ab initio molecular dynamics and quantum chemistry techniques are used to calculate the structure, vibrational frequencies, and carbon-isotope fractionation factors of the carbon dioxide component [CO₂(m)] of soil (oxy)hydroxide minerals goethite, diaspore, and gibbsite. We have identified two possible pathways of incorporation of CO₂(m) into (oxy)hydroxide crystal structures: one in which the C⁴⁺ substitutes for four H⁺ [CO₂(m)_A] and another in which C⁴⁺ substitutes for (Al³⁺, Fe³⁺) + H⁺ [CO₂(m)_B]. 2-D correlation infrared spectroscopy is consistent with calculated frequencies and suggests the existence of both CO₂(m) species in synthetic goethite. Calculations of isotope fractionation factors give large differences between the two structures, with the CO₂(m)_A being isotopically lighter than CO₂(m)_B by ~10 permil in the case of gibbsite and nearly 20 permil in the case of goethite. The reduced partition function ratio of CO₂(m)_B structure in goethite differs from CO₂(g) by less than 1 permil. The predicted fractionation for gibbsite is more than 10 permil higher, close to those measured for calcite and aragonite. The surprisingly large difference in the carbon-isotope fractionation factor between the CO₂(m)_A and CO₂(m)_B structures within a given mineral suggests that the isotopic signatures of soil (oxy)hydroxide could be heterogeneous.

Pyrite Surface Reactivity under Environmentally Relevant Conditions

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Research has addressed the chemistry relevant to the environmental problem referred to as Acid mine drainage (AMD), resulting from the oxidation of metal-sulfides, primarily pyrite. This environmental impact of AMD includes acidification of rivers and streams as well as leaching of toxic metals from the metal-sulfide material. Prior studies investigated the use of phospholipid layers on pyrite to suppress the oxidation of the mineral in abiotic and biotic conditions. Even in the presence of iron oxidizing bacteria the lipid layer, which assembles into a bilayer structure, significantly suppresses the rate of pyrite oxidation (by 80% relative to pyrite without lipid). More recent studies have investigated the ability of the adsorbed lipid layers to suppress pyrite oxidation in the presence of heterotrophic bacteria that are also found in AMD environments. Studies show that heterotrophic bacteria do disrupt the lipid bilayer structure and decrease the effectiveness of the lipid layers in decreasing pyrite oxidation. We show, however, that by using lipids with specific types of functional groups and by modifying the layer *in situ* that this disruption of the bilayer can be minimized in the presence of heterotrophic bacteria.

Vibrational Sum Frequency Studies of Structure at Geochemical Interfaces: Water, Ions, and Silica

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Studies of aqueous salt, acid, silica, lipid, fatty acids, interfacial depth, and molecular organization within the air-solution interfacial region and the silica surface are presented. Water structure, hydration, ion pairing, interfacial propensity of solutes, intermolecular interaction, and interfacial organization are discussed. Vibrational sum frequency generation (VSFG), Raman, and infrared spectroscopies are used to investigate the above mentioned systems. Comment on future directions and advances in the field of aqueous interfacial structure within the VSFG field is provided.

Dynamics of Coupled Dissolution/Growth and Bulk Charge Transport in Fe(II)-Catalyzed Transformation of Fe(III)-oxides/oxyhydroxides

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The flux of ions and charge equivalents at mineral/water interfaces plays a central role in setting the composition of natural waters, soil evolution, and in determining the availability and environmental impact of adsorbed or occluded elements, such as heavy metals and radioactive contaminants. Traditionally, because most mineral surfaces in nature are structurally complex, explorations of fundamental reactions at these interfaces have attempted to reduce their description to a minimal set of individual surface site types at the molecular-scale. Key assumptions in this approach are that the bulk solid is an inactive spectator and that remote surface sites react independent of each other. Minerals that are electrical semiconductors do not fit this model and new approaches are needed. Redox transformations among the iron oxide and oxyhydroxide minerals are an important example system. Under certain anoxic conditions, Fe(II) undergoes net oxidative adsorption at hematite (001) surfaces, resulting in growth, and concurrent net reductive dissolution at crystallographic edge surfaces. This behavior appears to be controlled by surface structure, which when combined with solution conditions sets the surface potential, and is enabled by charge migration through the bulk. We report recent experimental insights towards understanding this process from molecular length scales to several tens of microns. Surface specific potentiometry and atomic force microscopy for hematite (001) in contact with various Fe(II) solutions shows that the surface termination, potential, and microtopography have a complex but systematic dependence on the pH, measurement time, and the presence of chelating ligands. At larger length scales, Mossbauer characterization of hematite grown on (001) shows a temperature dependence of the Morin transition that is similar to previous work but under significantly different solution conditions, suggesting a mechanistic link. Surface complexation modeling can fit the apparent pH dependence of the inner Helmholtz potential for the (001) surface across a wide pH range. Molecular dynamics calculations show that Fe(II) adsorption and interfacial electron transfer kinetics are facile. Calculated rate constants are being used to develop large-scale kinetic Monte Carlo simulations that allow communication between remote surface sites via bulk charge transport. The collective findings will be discussed along with implications for development of a new mechanistic framework that treats semiconducting mineral/water interfaces in terms of the global composition, structure, and morphological characteristics of whole crystals.

Investigating the Crystal Chemical Controls on Uranium Contamination in Soils

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Among the many types of environmental contaminants, the high toxicity and complex chemistry of uranium makes it particularly problematic. A critical part of understanding uranium contamination involves the identification and characterization of solid-phase sources and sinks for U including: sorption and incorporation in minerals, glasses and other amorphous materials, and organic matter. Investigation of meaningful samples is usually difficult, however, because many U hosts are fine-grained, sparsely distributed, intimately intergrown with other phases, and prone to adulteration during analysis. Further challenges arise because highly reactive grain coatings in many soils comprise micron- to nano-scale regimes that have experienced complex or even unknown contamination histories. To meet the challenges of these materials, we use focused ion-beam milling to integrate electron and light microscopies as well as associated X-ray and electron energy-loss spectroscopies at the range of scales critical to understanding soil uranium budgets.

Our recent work has included investigation of vadose zone sediments from the Hanford Site 300 Area. We have identified six classes of solid hosts. These include: 1) metatorbernite [$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$]; 2) coatings comprised mainly of phyllosilicates on sediment clasts; 3) an amorphous zirconium (oxyhydr)oxide found in clast coatings; 4) amorphous and poorly crystalline materials that line voids within basalt lithic fragments; 5) amorphous palagonite surrounding fragments of basaltic glass; and 6) Fe- and Mn-oxides. The findings highlight the complexity of U geochemistry as well as the importance of microscopic transport at the site. The discoveries also identify important crystal chemical problems needing further study. Current work is focused on two hosts in particular which contain large portions of the U at the Hanford:

1) The newly discovered, amorphous Zr-(oxyhydr)oxide contains 16% of the total uranium budget (84 - 327 ppm) in shallow samples. The oxide occurs in fine-grained coatings on lithic and mineral fragments; is intimately intergrown with the phyllosilicates and other minerals of the coatings; and in places can be seen coating individual, nano-sized phyllosilicate mineral grains. Electron energy-loss spectroscopy (EELS) reveals a P:Zr atomic ratio ~ 0.2 , suggesting it is either intergrown with minor amounts of a Zr-phosphate or has adsorbed a significant amount of phosphate. Low-temperature uptake of U by Zr-(oxyhydr)oxides and phosphates has been studied in the lab, but to our knowledge ours is the first report of such uptake in the field.

2) Uranyl phosphates, particularly those in the autunite/meta-autunite groups, are important mineral hosts for uranium in a variety of natural and contaminated environments in addition to Hanford. Using temperature-resolved synchrotron X-ray diffraction and Rietveld refinement techniques, we have begun investigating phase transformations between the variably hydrated phases of the group. Particularly exciting results show transformation from autunite-type sheets in metatorbernite to a lower hydrate containing uranophane-type sheets that allow reduced basal spacing while continuing to accommodate interlayer Cu. This discovery opens a range of new research directions and establishes a need to understand relevant phase relations.

Advances in Modeling the Mineral-Water Interface

Randy Cygan and Jeffery A. Greathouse

Geochemistry Department, Sandia National Laboratories, Albuquerque, NM

Interfaces play a critical role in many geochemical processes. Adsorption, dissolution, precipitation, nucleation, and growth mechanisms, in particular, are controlled by the dynamic interplay of structure, thermodynamics, and statistical mechanics at the mineral-water interface. These mechanism details are typically beyond the sensitivity of experimental and analytical techniques, and so require accurate models and simulation methods to understand the important molecular processes. In this effort, we have developed and used classical and electronic structure methods to investigate the complex behavior of the mineral-water interface and its significance in the environment.

Phyllosilicate minerals provide a unique opportunity to examine the behavior of water at a defined interface. Comprised of two-dimensional sheets and layers, phyllosilicates include a wide variety of multicomponent low-symmetry clay minerals having variable layer charge. Layer charge is an important characteristic of these phases, and ranges from no charge with van der Waals forces controlling the interactions between layers, to low charge clay phases like smectites that can readily expand with water or other intercalates, to relatively high-charge phases like mica having strong electrostatic forces act between layers. Outside of a few exceptions, clay minerals typically occur as nanoparticles having a grain size of less than 2 microns.

The accurate molecular simulation of many hydrated chemical systems, including clay minerals and other phyllosilicates and their interfaces with aqueous solutions, requires improved classical force field potentials to better describe structure and vibrational behavior. Improved parameterization of layer hydroxyl groups will lead to well-defined models for edge hydroxyl groups. Classical and *ab initio* molecular dynamics simulations of the bulk structure of pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), and Na-montmorillonite ($\text{Na}_x(\text{Mg}_x\text{Al}_{1-x})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$) exhibit dissimilar behavior in the hydroxyl stretch region of power spectra derived from atomic trajectories. The classical simulations, using the CLAYFF force field, include a standard harmonic potential and a new Morse potential parameterized for both dioctahedral and trioctahedral phases for the O-H bond stretch. The force field is used in large-scale molecular dynamics simulations of mineral surfaces with aqueous solutions, and provides insights on chemical speciation and adsorption phenomena.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

The Influence of Reaction Pathways on the Reduction of U^{VI} to U^{IV} : The Role of the Intermediate U^V Species

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This project is focused on the interfacial oxidation/reduction mechanisms of polyvalent metal ions important in subsurface systems. The current research is targeted at unraveling the reaction pathways involved in the reduction of U^{VI} to U^{IV} . This emphasis was sparked by our previous unexpected discovery that an intermediate oxidation state of uranium (i.e., U^V) was stabilized on the surfaces of ferrous micas after heterogeneous reduction of $U^{VI}aq$ by structural Fe^{II} . These observations were based on short term experiments and did not address fundamental issues concerning reduction mechanisms, such as whether U^{IV} is formed by two sequential one electron transfers from the mineral to sorbed uranyl, or by disproportionation of sorbed U^V . Subsequently, the solid phase reductant was changed from Fe^{II} containing micas to magnetite. The U^{VI} -magnetite system has received appreciable attention due to magnetite being a ubiquitous ferrous bearing oxide, a metabolic product of bacterial respiration, and a corrosion product of steel with ramifications for storage of nuclear waste. A major discovery during the present grant period, using a combination of XPS and XAS, is that U^V formed at the near-surface of magnetite but U^{IV} did not, despite long reaction times and sufficiently reducing conditions to stabilize $UO_2(c)$. Consequently, not only did U^V not disproportionate, but it was not reduced by a second electron transfer. In this context, it is curious that results of past studies of U^{VI} reaction with magnetite have ranged from no observed reduction at all to clear evidence for U^{IV} . In all cases, other than the present study, the possible presence of U^V was not considered. We note that identifying U^V is not a trivial task and its formation has not previously been expected due to its tendency to rapidly disproportionate in aqueous solution. With respect to the variable results of prior research, we strongly suspect that different experimental conditions and variations in starting materials altered reaction pathways which, in turn, influenced the reduction of U^{VI} to U^{IV} . The key could be the balance between the thermodynamic driving force for reduction and the creation of coordination sites for U^V that either stabilize U^V or have high activation energy barriers that prevent further reduction to U^{IV} . For example, in the present experiments, the initial pH values ranged from 3.2 to 4.7 and Fe^{II} was not added to solution. Both parameters increased due to magnetite dissolution, where pH and $Fe(aq)$ rose to ~ 7 and 200 $\mu mol/L$, respectively. Under these conditions the thermodynamically stable phase for uranium was predicted to be $UO_2(c)$. However, the calculated uranium concentration in equilibrium with $UO_2(c)$ was far lower than experimentally observed. In fact, the final pH and uranium concentration indicated equilibrium with schoepite, a phase which could rapidly form in these systems. The presence of U^{VI} on the surface was also confirmed by both EXAFS and XPS analysis. So it appears that given the dissolved Fe^{II} and U concentrations in solution the system was not in final redox equilibrium. Further, on-going analyses of EXAFS data, coupled with XPS analyses, indicated that an appreciable portion of sorbed U^V could be incorporated into an Fe (hydr)oxide phase and/or an extended U phase. Thus, U^V may be stabilized to some degree in a thermodynamically and structurally uncharacterized species which prevented further reduction.

Computational and Spectroscopic Studies of Molecular Structure and Dynamics at Mineral-Water Interfaces

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Molecular-scale knowledge of the thermodynamics, structure, transport and reactivity of aqueous solutions at mineral surfaces is crucial for quantitative understanding and prediction of many geochemical and environmental processes. We use a combination of computational and experimental methods to address fundamental questions related to the molecular-scale structure and dynamics at hydrated mineral interfaces. Experimental studies drive the continued development of better computational approaches. In turn, the computational efforts help to quantitatively interpret the experimental results and lead to new more focused experiments.

At mineral surfaces, individual water molecules and hydrated ions simultaneously participate in several dynamic processes characterized by different, but equally important time- and length-scales. On the short ~ 1 -100 ps time scale, the interfacial dynamics is dominated by molecular librational and re-orientational motions. These motions are responsible for the reformation and breaking of individual H-bonds, and the strength of these bonds is directly related to the frequencies of intra-molecular O–H vibrations. We have comprehensively investigated the librational dynamics of water at the surface and in the interlayers of the prototypical layered double hydroxide, hydrocalumite, using a combination of inelastic and quasielastic neutron scattering at several complementary instruments (HFBS, DCS and FANS at NIST; HRMECS and QENS at IPNS). Comparison of experimental data for hydrated and dehydrated samples combined with the results of MD simulations uniquely identifies the spectral peaks in three energy ranges 45-55, 65-90, and 90-120 meV as being due, respectively, to the librations of interlayer H₂O, surface-sorbed H₂O, and surface OH groups. The rotational residence time for interlayer H₂O is ~ 8 -10 ps and the rotational radius is ~ 1.2 Å.

On the longer ~ 0.1 -10 ns time scale, the surface mobility of H₂O and ions is controlled by their surface sorption and by the dynamics of reformation of the entire interfacial H-bonding network. Using MD simulations, we have quantified the slow diffusional motions of H₂O molecules on the surfaces of quartz and the Ca-silicate tobermorite by means of van Hove self-correlation functions, $G_S(r,t)$. The results clearly show a distinct characteristic time, τ , = ~ 0.8 ns for the hopping diffusion of water molecules on the surface of tobermorite, in excellent quantitative agreement with ¹H NMR field cycling relaxometry results (Korb et al., 2007a,b; Kalinichev et al., 2007). These results are also consistent with recent neutron spectroscopic data for water dynamics on rutile and cassiterite surfaces (Mamontov et al., 2007, 2008). MD simulations predict that similar hopping diffusional dynamics of H₂O is several times faster at the ideal (001) surface of quartz, but in reality it can be significantly slowed by atomic-scale roughness of the surface.

Ca²⁺ ion is a major component of many natural materials, and a ⁴³Ca proxy for ⁸⁷Sr in NMR studies may be the only way to learn about the molecular-level structure and dynamics of Sr²⁺ released from nuclear waste. We have initiated NMR investigations of Ca-bearing materials using ⁴³Ca at natural abundant levels (0.145%). Preliminary data collected at the HFMR User Facility at PNNL indicate that natural abundance ⁴³Ca NMR is a viable approach for many

complex materials and identified the facilities and approaches needed for more detailed studies. Ca^{2+} ions have also been identified in our earlier MD simulations as being the principal drivers of the supramolecular aggregation of natural organic matter (NOM) in soil and water. To quantitatively understand the structure and energetics of Ca-NOM interactions, we have recently initiated MD simulations of potentials of mean force for this and related systems.

Synchrotron-based Geochemical Studies Involving Fluids and Melts

Steve Sutton, Mark Rivers, Matt Newville and Peter Eng

University of Chicago

Synchrotron-based analytical methods have proved to be valuable in geochemical studies of the properties of fluids and melts. Such research provides information on the speciation of metals in hydrothermal fluids associated with ore-formation, the temperature and oxidation states of ancient magmas, the effects of CO₂ on low-temperature geological solutions, the structures and reactivities of hydrated mineral surfaces, and the flow properties of multi-phase fluids in soils. This presentation will describe experiments in each of these areas conducted at the GSECARS facility at the Advanced Photon Source (Argonne, IL).

Microscale x-ray absorption fine structure (XAFS) spectroscopy is being used in ore-relevant studies to establish the speciation of metals in hydrothermal fluids. These applications involve measurements on fluid inclusions (both natural and synthetic) where the samples are analyzed *in-situ* above their homogenization temperature (up to 700 °C) using a heating stage (e.g., Berry et al. 2009). A recent study of fluid inclusions from the Omsukchan Granite (Russia) indicated that [CuCl₂]⁻ is a stable speciation at magmatic temperatures.

A microXAFS study of Br in CO₂-bearing synthetic fluid inclusions revealed that Br exhibits a strong pre-edge feature at temperatures from 298 to 423 K (Evans et al. 2007). This feature has been interpreted as being due to alteration of the hydration of Br by CO₂ thereby allowing charge density changes to favor a *1s-p* bound state transition. The implication is that the presence of CO₂ causes halogen-bearing solutions to behave in ways that were previously unknown, with potentially significant consequences for the transport and deposition of metals in solution and fluid-rock interaction.

MicroXAFS can also be used to determine the valence states for multivalent elements in igneous glasses, which in turn can be used as proxies for oxygen fugacity and temperature. Recent results (Berry et al. 2008) support the identification of the Belingwe komatiite as a product of high mantle temperatures (~1,700 °C), rather than melting under hydrous conditions, confirming the existence of anomalously hot mantle in the Archean.

Mineral-water interface studies aim to establish the atomic-scale structures of mineral surfaces, the structural and reactivity changes that occur during hydration and the resultant metal sorption properties of these surfaces. These *in-situ* experiments typically involve combinations of x-ray reflectivity, crystal truncation rod, x-ray standing waves and grazing-incidence XAFS methods. A focus of this work is the determination of structural and reactivity changes of hydrated metal oxide surfaces (e.g., Tanwar et al. 2008).

Fluids can be imaged within objects using x-ray computed microtomography (CMT), for example, in determinations of the distribution and flow properties of multi-phase fluids in soils (e.g., Brusseau et al. 2008). CMT can also reveal the dynamics of bubble growth in basaltic melts providing insight into degassing mechanisms during volcanic eruption (Bai et al. 2008).

References: Berry, A. J., et al. (2009) *Chem. Geol.* 259, 1-6; Evans, K. A., et al. (2007) *J. Synch. Rad.* 14, 219-226; Berry, A. J., et al. (2008) *Nature* 455, 960-963; Tanwar, K. S., et al. (2008) *Geochim. Cosmochim. Acta* 72, 3311-3325; Brusseau, M. L., et al. (2008) *Water Resour. Res.* 44, W01411-1-W01411-9; Bai, L., et al. (2008) *Earth Planet. Sci. Lett.* 267, 533-547.

Applications of Hard X-ray Microprobe Techniques in Evaluating the Biogeochemistry of Metals in the Environment

A. Lanzirotti, S. Sutton and M. Rivers

University of Chicago

Synchrotron-based microanalytical techniques offer distinct advantages in studying biogeochemical processes in the environment by allowing analyses *in-situ* and in some cases *in-vivo*. Utilizing micrometer and sub-micrometer x-ray fluorescence, spectroscopy and scattering methods, these synchrotron-based hard x-ray microprobes offer earth and environmental scientists the ability to, for example, determine the chemical speciation of elements in moist soils, in waste-forms, and in biological specimens with little or no chemical pretreatment at detection limits that typically exceed those of conventional methods by several orders-of-magnitude. Microfocused scattering methods allow us to directly interrogate the mineralogy to which these species are bound in a spatially resolved manner simultaneously. Extensions of these methods into three dimensions through fluorescence computed microtomography allow us to image trace element distributions, speciation, and mineralogy *in-situ* without physical sectioning. This presentation will describe experiments in this area conducted at the X26A facility at the National Synchrotron Light Source (Brookhaven National Laboratory) and discuss developments in designing the next generation hard x-ray microprobe at the planned NSLS-II facility.

Synchrotron μ -XRF mapping of elemental distributions across coral skeleton micro-architecture, for example, have been used to understand the biochemical response of corals from the Great Barrier Reef to bleaching events. High resolution *in-situ* μ -XRF mapping is an ideal tool to investigate how differences in trace element partitioning correspond to the fine-scale architecture of coral skeleton. The study showed that the uptake of certain trace elements were impacted by the stress event and associated changes in skeletal growth of the coral. For example, measured Sr/Ca of skeletal structures show that they are compositionally zoned, with a strong response 6 months after the start of the bleaching event. The data also demonstrate that Br is selectively incorporated within dissepiments and that Br K-edge μ XANES can be used to identify the Br species involved.

Another example is the study of the potential health risks associated with elevated levels of arsenic, thallium, and mercury found in samples of windblown dust from abandoned gold mine tailings in Nova Scotia. Synchrotron-based μ -XRD, μ -XRF, and μ -XANES analysis at X26A were employed to characterize the solid-phase speciation of arsenic in the tailings and associated airborne particulates, finding that scorodite is the dominant secondary phase in some samples. Arsenic bioaccessibility was also characterized using an *in vitro* two-part extraction method designed to mimic the human digestion system.

We will also discuss examples of utilizing fluorescence computed microtomography to understand how organisms in the environment interact with contaminant and nutrient metal species in soils at a genetic and cellular level. In these studies we have been able to three dimensionally image the metal distribution within plants *in-vivo* with parts per million detection sensitivities that correlate with anatomical structure.

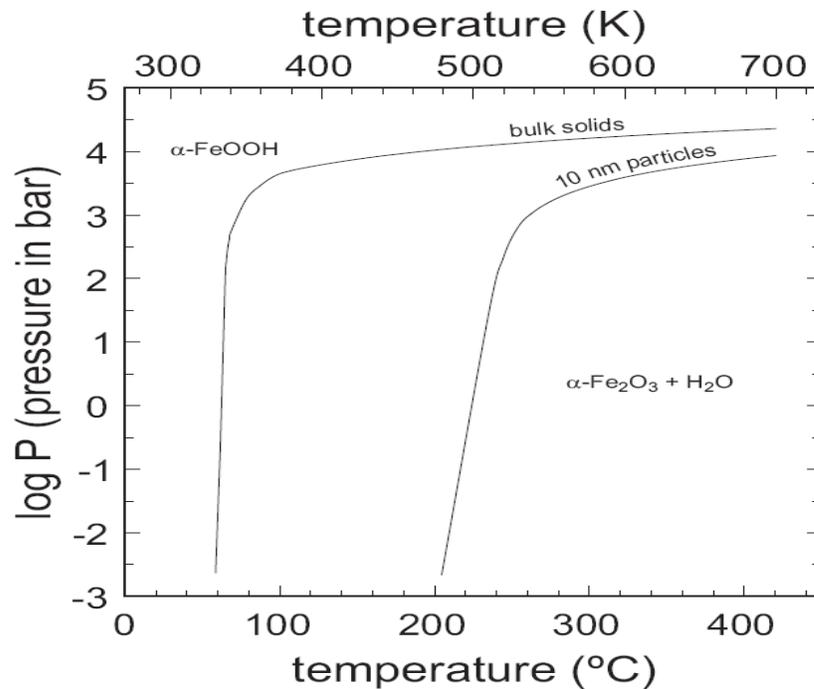
Nanophases - Implications for Thermodynamics in the Critical Zone

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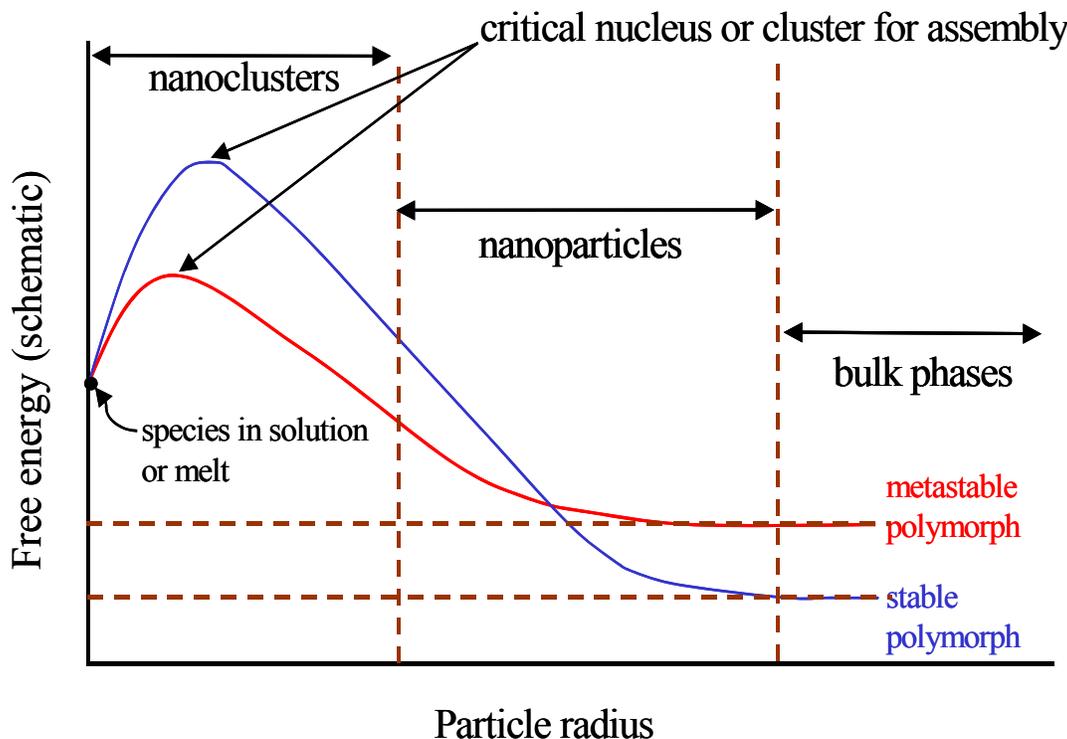
Aerosol particles, soil minerals, finely disseminated ore deposits, metal contaminants in watersheds, carbonates freshly precipitated from aqueous solution, corrosion products of nuclear fuels – all these are largely fine grained, indeed nanophase, materials. In addition to being chemically more reactive than larger crystals, nanoparticles are structurally and thermodynamically different from bulk materials. These differences affect equilibrium properties such as P-T regions of thermodynamic stability and aqueous solubility and influence kinetics of dissolution and precipitation. These effects in turn influence geochemical processes relevant to climate change, CO₂ sequestration, and resource and waste management. Here I summarize recent findings, based on solution calorimetric studies, of the stability of iron oxide minerals and some new results on amorphous calcium carbonate. Implications for kinetics, control of phases during biomineralization, and the Ostwald step rule are discussed.

Goethite = Hematite + Water
Dehydration equilibrium shifted up in temperature by as much as 150 °C
for nanophases

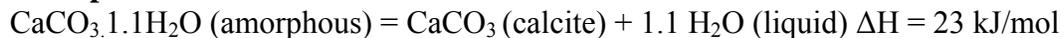


The Ostwald Step Rule

Seemingly metastable phases are first crystallized, but in fact they are thermodynamically stable as small particles



Amorphous Calcium Carbonate- new results



So amorphous hydrated calcium carbonate is much more metastable than other crystalline polymorphs (aragonite, vaterite) and any anhydrous amorphous calcium carbonate would be even more metastable.

Isotope-Exchange Dynamics in Large Oxide Ions

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We examine isotope exchanges and hydrolytic reactions in 50-100 atom oxide ions¹ because reactions at structural oxygens can be followed with unprecedented clarity and coupled directly to simulation. This work has led to important conceptual advances, such as identifying the role of highly bonded, normally inert oxygens in controlling dissociation and isotopic substitution via metastable forms¹. We have also identified classes of geochemical reactions that can be predicted reliably using simulation, including the rates of exchange of waters bound to various surface oxygen sites. These experimental data lend themselves well to 'rare-event' methods² of simulation.

We are now examining manganese-oxide clusters that are geochemically interesting and are also lead candidates for capturing photoenergy by oxidation of water to O₂. Key for design of these photocatalysts are the rates at which the structural oxygens undergo oxygen-isotope exchange with bulk solution waters and pathways for oxygen elimination. We are thus following oxygen-isotope exchanges in an intact Mn₄^{IV,IV,IV,III}O₄ cubane³ and examining whether the μ₃-oxo sites in extended structures are labilized by the extra electron at the Mn^{III} center. This work is not only directly relevant to new methods of clean energy production, but also has geochemical implications because structurally similar manganese-oxide minerals are broad oxidizing agents in nature. Also, the similarity of these clusters to common mineral structures has been suggested as key to the evolutionary development of the oxygen-evolving complex in Photosystem-II.

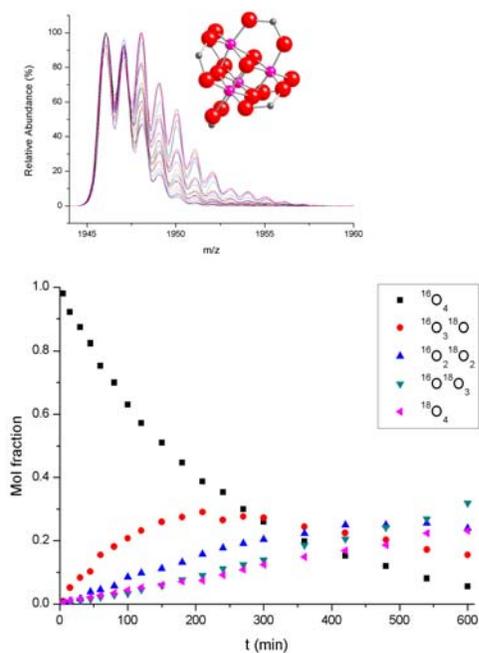


Figure - Rates of oxygen-isotope exchanges are measured in the the Mn₄^(IV,IV,IV,III)O₄ cubane structure (**left**), yielding rate coefficients for isotopic exchange of all specific oxygens. This particular cluster is a key candidate for water-oxidation photocatalysis³ and energy storage. The core Mn₄O₄ structure (**inset**) is made stable with phosphinate ligands, but the isolated μ₃-oxo are also well represented in manganese-oxide minerals. We find that the extra Mn^{III} electron is averaged over all bound oxygens at 298 K, such that they undergo ¹⁸O-substitutions at virtually equal rates (**bottom**).

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2. Wang, J., Rustad, J. R. & Casey, W. H. Calculation of water-exchange rates on aqueous polynuclear clusters and at oxide-water interfaces. *Inorganic Chemistry* 46, 2962 - 2964 (2007).
3. Brimblecombe, R., Swiegers, G. F., Dismukes, G. C. & Spiccia, L. Sustained water oxidation photocatalysis by a bioinspired manganese cluster. *Angewandte Chemie*, International Edition 47, 7335-7338 (2008).

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Isotopic Fractionation during Precipitation of Minerals from Aqueous Solution

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Recent work on mid-mass stable isotope systems like Ca, Mg, Fe, Cr, and Mo suggests that these systems have promise for understanding geochemical processes at all scales. However, because minerals precipitated from aqueous solution at low temperature do not form at isotopic equilibrium, there is a need for a better theory. For Ca isotopes in calcite, our work has produced evidence that at equilibrium there is no fractionation between aqueous Ca ions and calcite at low temperature (ca. 5°C). Collaborations with F. Richter are also serving to constrain isotopic fractionation effects due to diffusion in aqueous solution. These results make Ca isotopes more amenable to treatment than others, and we use the available information as a basis for a first cut at a general theory for isotopic fractionation during mineral precipitation from aqueous solutions.

Precipitation rates can be expressed as area-normalized fluxes (e.g. mol/m²/sec), and are understood as net rates (R_{net}), the difference between a forward rate (precipitation; R_p) and a backward rate (dissolution; R_d). Both forward and backward rates are likely to be higher for light isotopic species. Isotopic equilibrium can only be maintained if the *net* precipitation rate is much smaller than the gross precipitation-dissolution rates ($R_{\text{net}} \ll R_d$). If this condition is met, the mineral may still not form at isotopic equilibrium if there is a transport limitation in the fluid phase (which for calcite is the common situation).

Precipitation of minerals from solution can occur in four regimes. In Regime 1 (equilibrium), R_{net} is much smaller than R_d and slow enough that there are no fluid-phase transport limitations. In Regime 2 (equilibrium, transport limited), R_{net} is much smaller than R_d , but fast enough that there are transport limitations in the fluid phase. In Regime 2 the fluid phase in contact with the crystal surface is in isotopic equilibrium with the crystal surface, but the solid is not in equilibrium with the bulk aqueous reservoir due to isotopic fractionation during transport. In Regime 3 (pure kinetic) R_{net} is larger than R_d , but slow enough that there are no transport limitations in the fluid phase. In Regime 3, the isotopic composition of the solid phase is determined by the attachment-detachment kinetics of the isotopic species at the interface; in general the solid will be enriched in the light isotopic species, in excess of the equilibrium fractionation. In Regime 4 (kinetic, transport limited) R_{net} is larger than R_d and fast enough that there are transport limitations in the fluid phase.

The definition of the regime boundaries is determined by several factors – including the background exchange rate (R_d), the aqueous diffusivities of ions, and the hydrodynamics of the solution phase. The fractionation factor is likely to have temperature dependence, solution chemistry dependence, and mineral surface chemistry dependence in addition to rate dependence. Examples, implications, and problems with this model will be discussed.

*The title of the project is “Integrated isotopic studies of geochemical processes.” The grant supports radiogenic, stable, and noble gas isotopic studies. BES provides core support for labs involving 2 TIMS, 2 Noble gas and 2 stable isotope mass spectrometers, and an MC-ICPMS.

Ion Microprobe Analysis of Oxygen and Silicon Isotope Ratios in Authigenic Quartz: High Precision and Accuracy

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This project focuses on microanalysis of diagenetic quartz cements and secondary silica. New procedures employing a CAMECA ims-1280 ion microprobe permit study of oxygen isotope ratio in ultra-small samples. We have contoured $\delta^{18}\text{O}$ across single crystals and within individual overgrowths at all scales down to sub-one-micron. Mineral zonation patterns provide new insights into timing and processes of water/rock interaction, and migration of fluids through sandstone aquifers.

Careful tuning of the ims-1280, sample preparation, and standardization are critical for obtaining accurate and precise results. Repeated analysis of an appropriate standard monitors precision and stability of the instrument, and can be the basis of a correction for bias. However, there are additional confounding effects and careful standardization alone does not necessarily guarantee accuracy. The best results are obtained if samples and standards are mounted together within 5 mm of the center of each sample: $\pm 0.3\%$ (2SD) for $10\mu\text{m}$ pits, $\pm 1\%$ for sub- $1\mu\text{m}$ pits. Sample relief, inclined surfaces, or proximity to edges are also important and can be monitored at sub-micron scale by profilometer. For instance, polishing relief of $30\mu\text{m}$ can degrade precision from ± 0.3 to $\pm 3\%$ and cause errors of up to 4% in $\delta^{18}\text{O}$ (Figure 1).

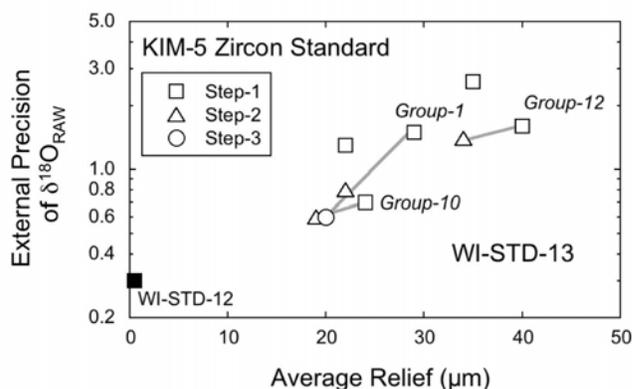


Figure 1. Spot-to-spot reproducibility (2 SD) for measurements of $\delta^{18}\text{O}$ with $10\mu\text{m}$ diameter spots in KIM-5 standard grains at WiscSIMS. The amounts of polishing relief were reduced in three repolishing steps of the same grain mount. Note that the reproducibility of analyses is shown on the Y-axis as a logarithmic scale. The filled square ($\pm 0.3\%$) is from a second mount of KIM-5 with minimized relief ($\leq 0.5\mu\text{m}$), analyzed during the same session. (Kita, Valley et al. 2009 Chem. Geol.)

We are investigating applications of the new analytical technology to paleoclimate studies, fossil fuel reservoirs, and groundwater and hydrothermal systems. We are applying experience gained in microanalysis of syntaxial quartz overgrowths in the St. Peter sandstone (Kelly et al. 2007, GCA) to quartz cements in the Mount Simon sandstone (Trzaskus et al. 2008, GSA); Potsdam sandstone, New York; the Brent group, North Sea; and Carboniferous to Jurassic eolian sandstones of the western U.S.

Thin syntaxial quartz overgrowths and detrital quartz grains have been studied optically and by SEM-CL from the St. Peter and Mount Simon sandstones, and analyzed for $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ with small spot size ($10\mu\text{m}$), and high accuracy and precision (0.1 - 0.2%). These studies have

investigated mineral zonation and exchange kinetics to distinguish the effects of pedogenesis and vadose zone precipitation vs. low temperature hydrothermal precipitation. The small variability of $\delta^{18}\text{O}$ (Qt overgrowth) values rules out a systematic regional temperature variation that is predicted by groundwater flow modeling for MVT brines in SW Wisconsin and suggests that these syntaxial quartz overgrowths formed as groundwater silcretes at 10-40°C with $\delta^{18}\text{O}$ (meteoric water) = -2 and -9‰. These results suggest that $\delta^{18}\text{O}$ of overgrowths may be a proxy for $\delta^{18}\text{O}$ (meteoric water) and paleoclimate.

Uranium-Series Transport from Micron to Meter Scales and Beyond

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Uranium-series geochemistry and geochronology have a wide range of applications in paleoclimatology, volcanology, and other disciplines. To further explore these applications, the geoanalytical community has begun to exploit recent advances for *in situ*, micron-scale sampling via laser ablation-ICPMS. Unfortunately, improvements in instrumentation have outpaced development of the appropriate geologic reference materials generally required for *in situ* U-series work. Our current project represents new efforts to characterize reference materials for *in situ*, high spatial resolution analyses of U-series isotopes. The scientific problem to be addressed is the transport of uranium in fractures near uranium ore deposits, and well-characterized standards will be used with LA-MC-ICPMS to obtain U-series data for these fractures.

We are currently measuring U-Th concentrations and isotopics from a suite of naturally sourced glass reference materials from the USGS and the Max Plank Institute. Our initial results are shown in the Table. We find that the glass versions of existing powdered standards (BCR-2 and BHVO-2) maintain similar U and Th ratios; those, along with the other USGS standard NKT-1G, are nominally in secular equilibrium. In contrast, neither MPI-DING standard (ATHO-G, T1-G) is in secular equilibrium with respect to ^{234}U - ^{230}Th . These are the first reported U-series results for these solid standards, and the data will benefit the greater earth science community by enabling more accurate and precise reporting for a broad range of U-series work. The scientific problem addressed will provide information on the fate of actinides in the environment, contaminant transport, fracture flow, and the stability of natural analogs for the long term storage of high level radioactive waste.

TABLE 1. LANL U and Th concentration and activity ratios for glass reference materials. Uranium data are averages of MC-ICPMS and TIMS results. Thorium data are currently from TIMS only. Errors are 2σ (%).

Reference Glass	[U] (ppm)	[Th] (ppm)	(^{234}U)/(^{238}U)	(^{230}Th)/(^{232}Th)	(^{230}Th)/(^{238}U)
BCR-2G (basalt)	1.722 ± 0.13	5.96 ± 0.40	1.000 ± 0.17	0.875 ± 0.70	0.992 ± 0.75
BHVO-2G (basalt)	0.431 ± 0.13	1.21 ± 0.51	1.000 ± 0.12	1.085 ± 0.60	1.001 ± 0.65
NKT-1G (nephelinite)	2.275 ± 0.12	7.39 ± 0.48	0.999 ± 0.14	0.930 ± 0.54	0.992 ± 0.60
ATHO-G (rhyolite)	2.390 ± 0.14	7.83 ± 0.42	0.999 ± 0.12	1.021 ± 1.10	1.100 ± 1.1
T1-G (quartz diorite)	1.670 ± 0.12	30.3 ± 0.50	1.001 ± 0.13	0.185 ± 0.88	1.106 ± 0.90

Kinetic Isotope Fractionation by Transport Processes

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Our recent experiments have documented large kinetic isotope fractionations by transport processes between phases (e.g., by evaporation) and within a single phase (e.g., chemical diffusion in both water and in molten silicates). We will also show that Soret diffusion (i.e., molecular-scale chemical transport driven by differences in temperature) is an extremely effective mechanism for fractionating the isotopes of all the major elements of a molten silicate. While we now have highly quantitative data on the parameters governing these various transport-related isotopic fractionating mechanisms, we have, with one notable exception, very little by way of a basic understanding of what determines the values of these key parameters.

In the case of evaporation of a silicate melt into vacuum, the key empirical parameter is the

evaporation coefficient γ in the Hertz-Knudsen equation $J_i = \frac{\gamma P_i^{sat}}{\sqrt{2\pi m_i RT}}$ for the flux J_i of species i

The saturation vapor pressure P_i^{sat} of the dominant gas species of mass m_i containing i is in many cases easily calculated from thermodynamic data. There is, however, as yet no theoretical understanding of what determines the value of γ . Our experiments show that γ is in some cases the same for isotopes of a given element as is the case for Fe isotopes evaporating from molten FeO but different for the Fe isotopes when they evaporate from a silicate liquid. Can molecular calculations help us understand the magnitude and mass dependence of evaporation coefficients?

The experimental data for isotopic fractionation by diffusion is summarized by a kinetic fractionation exponent β in the relationship $D_i/D_j = (m_j/m_i)^\beta$ between the self-diffusion coefficient D_i , D_j and mass of isotopes i and j . Our experimentally determined values for β in silicate liquids vary from 0.215 for lithium (very fractionating given this β and the large mass ratio), 0.075 for Ca, 0.05 for Mg, down to zero for Ge used as a silicon analogue. We can measure, but do not yet understand in any generalizable sense what determines the value of β for isotopic fractionation in a silicate liquid. Surprisingly, the situation is quite a bit better in the case of water where we have also measured isotopic fractionations during diffusion of dissolved salts. The recent molecular calculations by Ian Bourg are in excellent agreement with our experimental data for isotopic fractionations in water and represent a good example of how such calculations give insight into what determines the degree of isotopic fractionation during diffusion.

For us the most exciting recent development is our demonstration of extraordinarily large steady state isotopic fractionations of all the major elements of molten basalt when a temperature difference of 100°C is imposed. These fractionations are the result of a balance between the chemical diffusive flux and the thermally driven flux. And as we will show, the thermally driven flux is much more mass dependent (i.e., isotopically fractionating) than the flux due to concentration differences.

Experimental Study of the Dependence of Water Diffusion on Water Content in High-Al Basalt, Haplobasalt, and Haploandesitic Melts

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There have been many studies of the diffusivity of water ($D_{\text{H}_2\text{O}}$) in silicate liquids and its dependence on the concentration of water ($C_{\text{H}_2\text{O}}$), but a definitive determination of the functional dependence of $D_{\text{H}_2\text{O}}$ on $C_{\text{H}_2\text{O}}$ has not been available. Diffusive concentration profiles generated experimentally usually span a large range in $C_{\text{H}_2\text{O}}$ and extraction of accurate and precise $D_{\text{H}_2\text{O}}$ vs. $C_{\text{H}_2\text{O}}$ relationships from such profiles is difficult since the derived relationships are sensitive to the numerical methods used to analyze the data. For example, when the Boltzmann-Matano method of analyzing the profiles is used to extract the dependence of $D_{\text{H}_2\text{O}}$ on $C_{\text{H}_2\text{O}}$, the results are typically unreliable at the extremes of the concentration profiles where the concentration gradients may be low, so that the derived $D_{\text{H}_2\text{O}}$ vs. $C_{\text{H}_2\text{O}}$ relationships do not provide useful information over the full range of water content in a given experiment [1].

In this study we used a “small gradient” methodology to avoid the difficulties experienced in most previous studies. Diffusion couple or hydration experiments were run in which the water contents at the two ends of the concentration profile differed by no more than ~ 1.0 wt. % H_2O . As a consequence of the small range in water content, $D_{\text{H}_2\text{O}}$ varied little across the concentration profiles, and thus artifacts or uncertainties associated with the strong concentration dependence of $D_{\text{H}_2\text{O}}$ were minimized. By doing a series of such experiments, each of which was used to determine $D_{\text{H}_2\text{O}}$ for a different (but small) range of $C_{\text{H}_2\text{O}}$ we were able to build up the $D_{\text{H}_2\text{O}}$ vs. $C_{\text{H}_2\text{O}}$ relationship over a wide range of $C_{\text{H}_2\text{O}}$ without having to assume the functional form of this relationship or any of the problems associated with precise and accurate determination of the relationship from a single experiment spanning a wide range of $C_{\text{H}_2\text{O}}$.

We report here the results of such a study on a high-Al basalt, a haplobasalt ($\text{Ab}_{45}\text{Di}_{37}\text{Wo}_{18}$, in mol. %), and a haploandesite melt ($\text{Ab}_{77}\text{Di}_{19.5}\text{Wo}_{3.5}$) at 1300 °C with water contents of 4, 6, and 6 wt.%, respectively, and pressure up to 100, 160, and 200 MPa, respectively. $D_{\text{H}_2\text{O}}$ increases by at least an order of magnitude with $C_{\text{H}_2\text{O}}$ over this water concentration range. Our data suggest that $D_{\text{H}_2\text{O}}$ can generally be described as a linear function of $C_{\text{H}_2\text{O}}$ over this range. The haploandesite result is inconsistent with the data suggesting that $D_{\text{H}_2\text{O}}$ is independent of $C_{\text{H}_2\text{O}}$ in andesite melts, as presented in the single published study [1]. However, our new data are consistent with the many investigations of the dependence of the $D_{\text{H}_2\text{O}}$ on $C_{\text{H}_2\text{O}}$ in the literature for silicate melts (basalt, rhyolite, dacite) (summarized in [2]).

Acknowledgements: This work was supported by the U.S. Department of Energy (DE-FGO2-06ER15773) and by the Russian Foundation for Basic Research (RFBR, grant 06-05-64631).

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Experimental and Theoretical Study of Brucite under Pressure

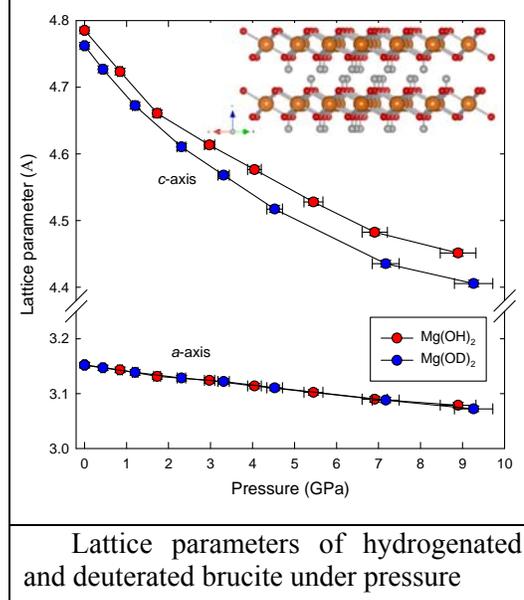
Juske Horita

Chemical Sciences Division, Oak Ridge National Laboratory

The mineral brucite, $\text{Mg}(\text{OH})_2$, belongs to the group of the CdI_2 -type minerals with a simple hexagonal layered structure with the hydroxide ion directed along the layer stacking direction and bonded to three magnesium atoms (see Figure). The high-pressure behavior of brucite and other brucite-type minerals with alkaline-earth and transition metals is of great geochemical and geophysical interest, because these brucite-type minerals serve as a simple, yet useful analog for more complex, hydrogen-bearing oxide and silicate minerals in the deep-earth. In addition, the brucite “layer” is a fundamental building unit in a great variety of hydrous sheet silicates, which include micas and clays. For these reasons, the structure and dynamics of brucite-type minerals, in particular the position of hydrogen atoms and the nature of the interlayer bond, under high pressures and/or temperatures have been extensively investigated as a model system for understanding hydrous minerals under compression.

We have been conducting systematic experimental and theoretical study for investigating structural changes of brucite under pressure, particularly the effect of H-D substitution and isotope fractionation. A neutron powder diffraction study of hydrogenated and deuterated brucite was conducted at ambient temperature and at pressures to 9 GPa, using a Paris-Edinburgh high-pressure cell at the WAND instrument of ORNL High Flux Isotope Reactor. The two materials were synthesized by the same method and companion measurements of neutron diffraction were conducted under the same conditions. Our refinement results show that the lattice-parameters of the a axis, parallel to the sheets of Mg-O octahedra, decreases only slightly with pressure with no effect of H-D substitution (Figure). However, the c axis of $\text{Mg}(\text{OD})_2$ is shorter and decreases more rapidly than that of $\text{Mg}(\text{OH})_2$ with increasing pressure (Figure). Consequently, the unit-cell volume of deuterated brucite is slightly, but systematically smaller than that of normal brucite. Our results suggest that H-D substitution of brucite and other hydrous minerals with H-bonding likely influences their structural and dynamic properties under pressure, including the position of hydrogen atoms. The measured effect of H-D substitution on the unit-cell volume also demonstrates that brucite (and other hydrous minerals) preferentially incorporate deuterium over hydrogen under pressure via

the relationship: $\left(\frac{\partial \ln \beta}{\partial P}\right)_T = -\frac{\Delta V}{nRT}$, where β is the reduced partition function ratio and $\Delta V = V^* - V$ is the unit-cell volume isotope effect. In addition, we have extended our theoretical calculations to 10 GPa, based on a Kieffer-type mineral model (Einstein-Debye hybrid density of



state model) with the Born-Mayer potential function and quasi-harmonic approximation. Our neutron diffraction data and theoretical calculations show that the value of $10^3 \ln \beta$ increases to 368 and 127 ‰, respectively, at 10 GPa, suggesting that the distribution of hydrogen isotopes of hydrous minerals in deep-earth conditions may differ significantly from that in near-surface environments.

Grain-Boundary Diffusion of Excluded Elements

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It is well known that grain boundaries can serve as a significant host ‘phase’ for impurities (trace elements) in a polycrystalline system. Less well understood is the extent to which these impurities are mobile in grain boundaries under circumstances where they are highly incompatible the crystal lattice. Indeed, traditional methods of characterizing grain boundary diffusion rely upon lattice compatibility to make the measurements possible: it is ‘leakage’ from the boundaries into the grains that provides a detectable concentration in the bulk material.

We have been developing a technique for measuring grain-boundary transport under circumstances when the elements of interest are hosted entirely in the grain boundaries, as is likely to be the case for some high field-strength and large-ion lithophile elements in rocks of Earth’s crust and upper mantle. This technique involves the use of ‘detector’ or ‘sink’ particles (phases) dispersed through the rock of interest that are much smaller than the grains of the major phase. A phase makes a suitable detector if it forms a solid solution with the diffusant of interest, so ions migrating through the grain boundaries of the major phase are ‘scavenged’ by the detector particles, allowing grain boundary fluxes to be computed.

Most of our efforts to date have focused on constraining transport in the grain boundaries of synthetic quartzites, with Fe and Mg as the diffusants of interest. The quartzites are synthesized in a solid-media pressure apparatus at 1.5 GPa and 1125°C with ~5 vol% of a sink phase (e.g., fayalite – Fe₂SiO₄). Upon recovery from the apparatus, the pre-synthesized quartzite is placed against a source of Mg ions (e.g., MgF₂) and returned to high P-T conditions. This juxtaposition of an Mg source against a quartzite containing dispersed Fe₂SiO₄ particles drives Fe↔Mg exchange along the quartz grain boundaries, which is detected and quantified by EPMA analysis of the initially Mg-free fayalite particles. A time series set of experiments was conducted at 1125°C for durations ranging from 2 hours to 8 days to evaluate the ‘sustainability’ of the grain-boundary diffusive flux. A marked diminution of the flux with time is observed, which is believed to be due to rate-limitation by lattice diffusion in the source and/or sink phases.

Other experimental configurations aimed at measuring grain-boundary fluxes of excluded elements are under development, including approaches that allow us to isolate the role of individual grain boundaries of pre-determined misorientation. We will report the results of these experiments, in addition to our preliminary findings on rare-earth mobility in quartzite.

Formation of Metastable CaCO₃ Polymorphs in the Presence of Oxides and Silicates

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Carbonate polymorphs occur widely in geological and biological environments. A number of external factors, particularly the presence of organic and biological molecules and templates, are known to be able to effectively direct the crystallization of specific carbonate polymorphs. Here, we conducted crystallization experiments to explore whether minerals through the presence of surface functional groups can selectively induce the crystallization of metastable carbonate polymorphs. Three types of minerals, simple oxide, framework aluminosilicate, and phyllosilicate, were used in this study. Experimental results demonstrate that minerals indeed have the ability to influence carbonate polymorphic formation. For simple metal oxides, it appears that their polymorphic selectivity is related to the minerals' surface charge conditions. Specifically, negatively charged surfaces favor the formation of metastable polymorphs while zero or positive charges are more selective for calcite. The charge-polymorph relationship is supported by the results of phyllosilicate experiments, but does not fit to interpret the behavior of silicon oxides. Whereas the presence of permanent structural charges on phyllosilicates may have facilitated the crystallization of non-calcite polymorphs, calcite is the dominant polymorph in silicon oxide experiments despite the negatively charged substrate surfaces. We suspect the discrepancy may be related to the more significant dissolution of SiO₂ at alkaline conditions under which carbonate crystallization take place. Additional results from experiments using pre-treated complex oxide (potassium feldspar) on which hydrated amorphous silica surface coating is generated by acid leaching support the dissolution hypothesis. These findings suggest that inorganic surface functional groups may have the similar ability with organic ones to selectively induce metastable carbonate polymorph crystallization. These results may have implications for subsurface geological carbon sequestration processes considering that carbonate precipitation in underground CO₂ storage sites is essentially an interface induced mineralization and majority of the interfaces are the surfaces of existing silicate and oxide minerals.

Properties of Adsorbed Cytochromes from Dissimilatory Metal Reducing Bacteria: Density and Rigidity of Periplasmic vs. Outer-Membrane Cytochromes

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Cytochromes are heme proteins with a role in biochemical electron transport and redox catalysis. Many cytochromes utilize conformation change as part of catalytic cycling. Outer membrane cytochromes from dissimilatory metal reducing bacteria (DMRB) such as *Shewanella oneidensis* MR-1 and *Geobacter sulfurreducens* are thought to be terminal reductases in enzymatic electron transfer from cell to solid-phase ferric minerals or other metals. We hypothesize that outer membrane cytochromes from DMRB undergo conformation change as part of their catalytic cycle, whereas periplasmic cytochromes with a different biochemical role have different conformational properties. Such redox-linked conformation change is key to understanding the operation of these “nanodevices”.

Although we do not yet know the structures of key outer-membrane cytochromes, and are not likely to know the structures at many of the key points in the catalytic cycle in the near future, it is still possible to detect conformation change by monitoring protein density. Here, we present results from the use of two related protein adsorption techniques, Optical Waveguide Lightmode Spectroscopy (OWLS) and Quartz Crystal Microbalance with Dissipation (QCM-D). OWLS provides data on the mass of adsorbed polypeptide (protein) and excludes accompanying solvent; QCM-D gives the total mass, including solvent. The difference in adsorbed mass between the two techniques allows quantification of the amount of solvent that “sorbs” to oxide surfaces by virtue of accompanying protein molecules, and allows estimation of protein density in the sorbed state. In addition, the dissipation technique in QCM-D provides information on the shear modulus of adsorbed protein.

We conducted OWLS/QCM-D measurements on horse heart cytochrome *c* (Cyt *c*), on OmcA, MtrC and Stc from *S. oneidensis* MR-1, on OmcB and PpcA from *G. sulfurreducens*, and on ApcA from *Acidiphilium cryptum* in the oxidized form. Without exception, periplasmic cytochromes are compact, high density, high rigidity proteins. In contrast, the outer-membrane cytochromes are all unusually low density, low rigidity proteins. This implies a fundamental difference in enzymatic role. The low density of outer-membrane cytochromes implies relative conformational flexibility and likely solvent exposure of hemes. Experiments with reduced cytochromes are underway.

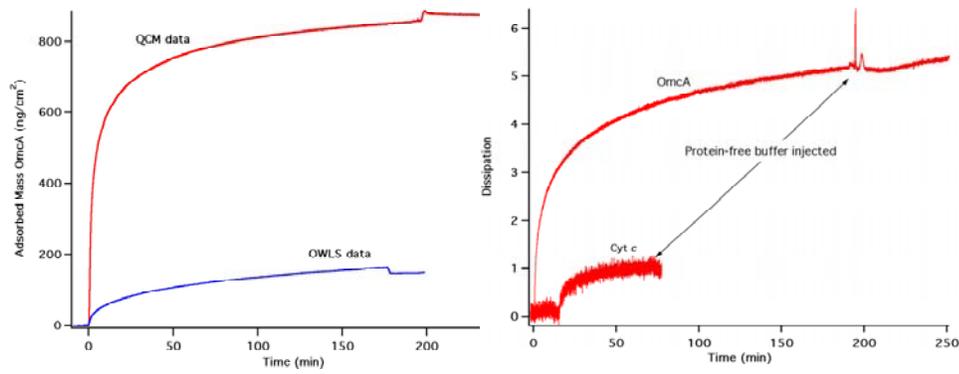


Figure: Left- QCM and OWLS data for OmcA adsorbed to alumina at pH 7; OmcA is the least dense protein we have observed, with only 18% protein in the total adsorbed mass. Right-dissipation data showing that Cyt c has much lower dissipation than OmcA, reflecting higher rigidity.

Investigating the Physical Basis of Biomineralization

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At the intersection of earth and life, the carbonate skeletons of marine invertebrates and carbonate cements hold clues for deciphering earth history. For more than 50 years, studies documented that these calcification environments, biological and inorganic, are typically enriched in proteins and a remarkable variety of other complex macromolecules. Researchers have long-postulated that biomolecules must regulate mineralization in these systems, yet a mechanistic basis has never been well established. Here we summarize recent findings from our efforts to establish a better understanding of biomolecule influences on carbonate formation and the signatures contained therein.

From amino acids to proteins: Role of molecular charge and hydrophilicity in regulating the kinetics of crystal growth (Elhadj et al., 2006, PNAS). This study uncovered a systematic relationship between the ability of biomolecules to promote the kinetics of calcite (CaCO_3) growth and their hydrophilicity, or ability to restructure local water. Growth rates are dependent on peptide composition, but not on sequence. Data analysis shows that the rate enhancement arises from an increase in the kinetic coefficient. We interpret the mechanism to be a catalytic process whereby biomolecules reduce the magnitude of the diffusive barrier, E_k , by perturbations that displace water molecules. The result is a decrease in the repulsive barrier for attachment of solutes to the solid phase. These findings demonstrate that the growth-modifying properties of the small amino acids and peptides may be scaled up to better understand mineralization processes that are mediated by complex proteins. The new insights suggest enhancement of calcite growth may be estimated *a priori* from the composition of peptide sequences and the calculated values of hydrophilicity and net molecular charge.

Peptides enhance magnesium signature in calcite: New insights into origins of vital effects (Stephenson, et al., 2008, Science). Studies relating the magnesium content of calcified skeletons to temperature often report unexplained deviations from the signature expected for inorganically precipitated calcite. These ‘vital effects’ are believed to have biological origins but mechanistic bases for measured offsets remain unclear. Building upon our findings from Elhadj et al. (2006), we hypothesized that because 1) cation incorporation is the rate-limiting step to growth and 2) Mg is more strongly solvated than Ca, then rate-modifying peptides could also lower the desolvation barrier to Mg incorporation relative to Ca, and thereby alter magnesium signature. Indeed we found that a simple hydrophilic peptide, sharing the same carboxyl-rich character as macromolecules isolated from sites of calcification, increases calcite magnesium content up to 3 mol%. Comparisons to previous studies that correlated Mg content of carbonate minerals with temperature show that the Mg enhancement due to peptides results in offsets equivalent to 7-14°C. The insights also provide a physical basis for anecdotal evidence that organic chemistry modulates the mineralization of inorganic carbonates and suggest a novel approach to tuning impurity levels in controlled materials synthesis.

Systematic control of biomolecules on magnesium contents in amorphous calcium carbonate: Insights for nonclassical calcification (Wang et al., 2009, in prep.). Many calcified skeletons form by processes that involve a transient precursor of amorphous calcium carbonate (ACC) (e.g. Beniash et al., 1997, *PRIS Lon. B*). This nonclassical type of mineralization begins by stabilizing ACC as a reactive intermediate that later transforms to a crystalline polymorph, such as calcite or aragonite. The process raises the question of whether mineralization by this pathway is the explanation for why biogenic carbonates contain much more Mg than is possible by classical step growth processes (Mackenzie et al., 1983, *RiMG*). There is anecdotal evidence biomolecules could modulate the Mg signatures reported in biogenic ACC. For example, Levi et al., (1998, *Chm.EurJ.*) noted that the amino acid sequence and conformation of glycoproteins may affect new shell chemistry and Raz et al. (2000, *Adv.Mat.*) found that proteinaceous extracts from coralline algae and acidic polymers induce a 50% increase in Mg content in carbonates formed via ACC. Building from these insights, we investigated calcification by this alternative pathway to test the hypothesis that ACC compositions are regulated by biomolecule chemistry. We postulated that unlike the ion-by-ion addition to the step edge of a crystal, ACC compositions reflect the competition of Ca and Mg ions for interactions with carboxyl groups of the biomolecules to modulate the aqueous chemistry of the local mineralization environment.

By measuring the Mg:Ca of the amorphous calcium carbonate that forms in the presence of simple carboxylated molecules, we find that the Mg content of ACC is controlled by the ability of the biomolecules to bind Mg versus Ca. That is, experiments conducted at three solution ratios of Mg:Ca show a predictable relationship whereby biomolecules which have stronger affinity to Ca than to Mg induce the formation of ACC with higher Mg signatures. Looking ahead, these findings may pose new questions regarding controls on Mg signatures in some biominerals, the origins of some cements and Mg-rich carbonates in the sedimentary record, while also suggesting a chemical basis for using/tuning biomolecules to promote more efficient cementation during geological storage of carbon.

Experiments and Theory of Biomineral Formation

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The ultrastructure of biominerals is one of the most fascinating aspects of these minerals, attracting the attention of geochemists, materials scientists, chemists, physicists and engineers. Typically, the ultrastructure is revealed and analyzed at multiple scales by electron microscopies. Another experimental method, only recently introduced into the study of biominerals, is synchrotron spectromicroscopy. As this method detects both the organic and mineral components, the bonds at their interface, and crystal orientation at the nano-scale, it revealed several biomineral formation and transformation mechanisms (1,2). Here we discuss recent results on the biomineral formation and ultrastructure in three distinct biomineral systems:

(i) Spicules in the sea urchin larval embryos are triradiate, as the Mercedes-Benz symbol, yet they are formed by a single crystal of calcite. The unusual crystal habit was explained by the initial aggregation of a transient amorphous calcium carbonate (ACC) phase, which subsequently transforms into crystalline calcite. We recently revealed that there are in fact two ACC precursors, and that crystallinity propagates through the amorphous phase via secondary nucleation, following a fractal network pattern (3).

(ii) The sea urchin tooth is composed of calcitic plates, needles and polycrystalline matrix. According to the conventional wisdom all these elements are aligned and diffract as a single crystal. We revealed instead that they are arranged into two distinct and alternating blocks of crystals A and B, stacked as ABABAB. The angle between A and B crystal blocks is less than 6°. This ultrastructure may explain how the tooth grinds limestone, thus far a puzzle in biomineral research (4).

(iii) Columnar and sheet nacre are formed by a variety of mollusk shells, and differ from one another. In gastropod columnar nacre we observed gradually ordering tablet crystal orientation with distance from the prismatic-nacre boundary. This was not observed either in cephalopod columnar nacre or in bivalve sheet nacre. A theoretical model explains the kinetics of this ordering mechanism with distance in terms of competition for space (5,6).

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Evolution of the Size and Porosity of Corestones in the Weathering Profile

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Evolution of surface roughness and porosity within it, and the mechanisms operative in maintaining these, are basic to an understanding of critical zone dynamics. We report on two studies, one at the ~ 100 m scale of an entire weathering profile within a catchment, the other at the $\sim 10^{-2}$ m scale across individual corestones. The former bridges scales between a box model of weathering and erosion for an entire catchment and the detailed study of a weathering profile segment accessed by an augured hole. Data from a ~ 100 m weathering profile exposed by later erosion in volcaniclastic rock within two catchments within the Luquillo National Forest, Puerto Rico are interpreted using a one-dimensional, steady-state model to treat a profile containing corestones. A second, ongoing study measures fractal distributions of micro-scale surface roughness and porosity distribution across the weathering front of a corestone by neutron scattering.

In each catchment, a \sim stratified weathering profile is exposed, albeit poorly, by erosion. In the uppermost elevations of the Bisley catchment, only saprolite is exposed on slopes above a first-order stream channel. Down-channel, corestones a few decimeters in dimension first appear, and maximum geometric mean size (S) increases downward, until where the channel assumes a constant slope $\sim 6^\circ$, the largest corestones thereafter maintaining constant S . The constant-slope interval is interpreted as developed parallel to a sub-planar bedrock surface at the base of a tilted weathering profile of thickness ~ 100 m, and the observed smooth, monotonic variation in maximum S with elevation is modeled. Corestones initiate as joint-bounded bedrock blocks of dimension S_0 . As these “cells” move towards the erosional surface, corestones are reduced in size, the remaining volume filled within saprolite. Model geometry consists of a profile-normal stack of equant, cubical volumes. Corestone-to-saprolite conversion is described by the single reaction albite to kaolinite. Within each cell, reactant concentration (H^+ , buffering capacity β) is assigned a single value, c . The process changes the current values of S and c in cells, and the weathering profile is described by the sequences of their values. The model is closed by rules for: (i) the rate of reduction, dS/dt , within a cell by reaction and grain disaggregation; and (ii) the condition on mass conservation on c applied between cells. Long-term corestone weathering rate is \sim independent of diffusive transport because access of fresh corestone to reactants is provided by intermittent fracture or disaggregation at a shorter time-scale.

The rate of profile advance into bedrock, W = erosion rate, is tied to the buffer capacity-modified influx of reactant by a relation expressing gross mass conservation. The model yields a corestone reaction rate at the input reactant concentration c_R :
$$K(\gamma c_R)^N = (W/6)(S_0/L^*) \cong 0.66 - 6.6 \times 10^{-12} \text{ cm/s}$$
, where $S_0/L^* = 0.13$, S_0 and L^* , a model length scale, are provided by the data fit, and $W = 0.1 - 1 \text{ cm/100 a}$. This rate may be related to laboratory rates of albite dissolution. The model fit provides an estimate of $\beta \approx 100 - 1000 < 10^5 - 10^7$ obtained by Brantley et al. (2008).

Resolving the Discrepancy between Laboratory and Field Rates: A Reactive Transport Approach

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The precipitation of clay minerals during water-rock interaction exerts an important control on solution composition, and thus the rate of dissolution of primary phases (Maher et al., 2009). In this regard, it is essential to quantify the precipitation kinetics of the clays, and particularly those of kaolinite. Dissolution and precipitation rates of low defect Georgia kaolinite (KGa-1b) as a function of Gibbs free energy of reaction were measured at 22°C and pH 4 in continuously stirred flow through reactors (Yang and Steefel, 2008). Dissolution and precipitation rates determined at steady state could not be described with the same rate law—dissolution was described well by a Transition State Theory (TST) rate formulation with a Temkin coefficient of 2, while precipitation rates at steady state followed a distinct trend that was not reversible with the dissolution rates (Figure 1).

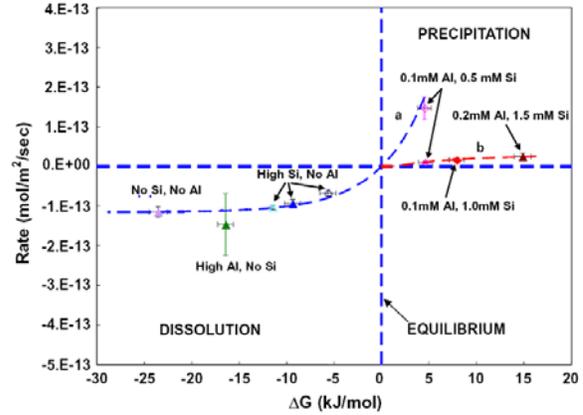


Figure 1: Dependence of the kaolinite dissolution and precipitation rates as a function of Gibbs free energy.

Reactive transport calculations of coupled albite dissolution and kaolinite precipitation using the code *CrunchFlow* were carried out for conditions broadly similar to those investigated by Maher et al. (2009) at the Santa Cruz chronosequences in an attempt to constrain kaolinite precipitation rates at a pH of about 7. Using the kaolinite precipitation rate determined in this study at pH 4 along with a nonlinear, parallel rate law for albite, the reactive transport calculations predict that the pore water composition will remain close to equilibrium with respect to kaolinite ($\log Q/K_{eq} \sim 0.1$), while albite remains far from equilibrium (Figure 2). However, the results at circumneutral pH (6-8) depend critically on the pH dependence of kaolinite precipitation rates, or on the solubility of the specific kaolinite group mineral that forms as a function of time and space in the weathering profile. As the kaolinite precipitation rate constant decreases from 10^{-15} mol/m²/s ($\log k = -15$) to 10^{-16} mol/m²/s ($\log k = -16$), the simulations predict that the kaolinite supersaturation will rise substantially (in

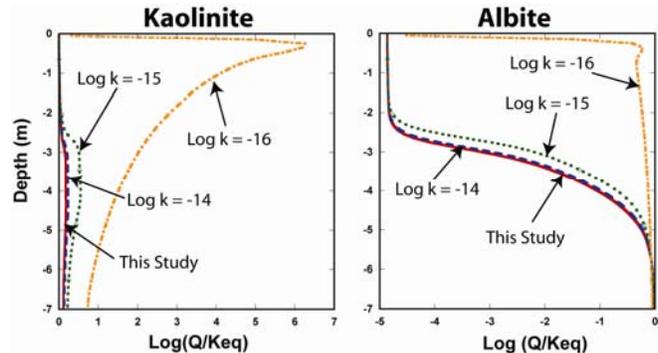


Figure 2: Saturation state of kaolinite and albite as a function of the rate constant of kaolinite. Similar results may be obtained by considering a more soluble kaolinite.

agreement with pore water data from the site), while the feldspar approaches equilibrium more closely (Figure 2). Data from the Santa Cruz site suggests that the solubility of the kaolinite decreased over time. Reactive transport modeling is currently focusing on incorporating this “aging” of the kaolinite.

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Connecting Molecular Structure to Surface Reactivity Using NMR, XRD, and Solution Chemistry

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We have studied the reaction mechanisms for the uptake of dissolved Al on amorphous silica and the crystallization of tobermorite by combining bulk-solution chemistry experiments with solid-state Nuclear Magnetic Resonance and X-ray diffraction techniques.

We find that reaction of dissolved Al with amorphous silica consists of at least three reaction pathways; (1) adsorption of Al to surface silanol sites, (2) surface-enhanced precipitation of an aluminium hydroxide, and (3) bulk precipitation of an aluminosilicate phase. From the NMR speciation and water chemistry data, we calculate that $0.2 (\pm 0.04)$ tetrahedral Al atoms nm^{-2} sorb to the silica surface and that this amount is nearly constant from pH 4.3-8.2. Once the surface has sorbed roughly half of the total dissolved Al ($\sim 8\%$ site coverage), aluminium hydroxides and aluminosilicates precipitate from solution. These precipitation reactions are dependent upon solution pH and total dissolved silica concentration. We find that the Si:Al stoichiometry of the aluminosilicate precipitate is roughly 1:1 and suggest a chemical formula of NaAlSiO_4 in which Na^+ acts as the charge compensating cation. For the adsorption of Al, we propose a surface-controlled reaction mechanism where Al sorbs as an inner-sphere coordination complex at the silica surface. Analogous to the hydrolysis of $\text{Al}(\text{OH})_6^{3+}$, we suggest that rapid deprotonation by surface hydroxyls followed by dehydration of ligated waters results in four-coordinate $(>\text{SiOH})_2\text{Al}(\text{OH})_2$ sites at the surface of amorphous silica.

We investigated reaction rates and mechanistic pathways for cement mineral growth coupling water chemistry with XRD and NMR spectroscopic data. We find that semi-crystalline Al-CSH forms as a precursor solid to the cement mineral tobermorite. Rate constants for tobermorite growth are faster when the solution volume is reduced by half, suggesting that rates are dependent on solution saturation and that the Gibbs free energy is the reaction driver. However, calculated solution saturation indexes for Al-CSH and tobermorite differ by less than one log unit, which is within the measured uncertainty. Based on this data, we consider both heterogeneous nucleation as the thermodynamic driver and internal restructuring as possible mechanistic pathways for growth. NMR spectroscopy show two [4]Al coordination structures at 59.9 ppm and 66.3 ppm with quadrupolar product parameters (PQ) of 0.21MHz and 0.10 MHz (± 0.08) from ^{27}Al 3Q-MAS NMR and speculate on the Al occupancy of framework sites by probing the protonation environment of Al metal centers using $^{27}\text{Al}\{^1\text{H}\}$ CP-MAS NMR.

Hydraulic Properties of Adsorbed Water Films in Unsaturated Porous Media

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Properties of adsorbed aqueous films determine conditions for residual water saturation in porous and fractured geologic media, and influence the dynamics of pore scale water displacement that ultimately determine macroscale distributions of immiscible fluids in the subsurface. For this reason, the distribution of water relative to other immiscible fluids is of interest in hydrogeology, subsurface waste isolation, petroleum engineering, and geologic carbon sequestration. However, hydraulic properties of adsorbed films are difficult to characterize because of their high viscous resistance and extremely low flow rates. In this study, hydraulic properties of thin films are being explored through calculations based on interfacial chemistry and scaling, and through direct measurements.

Hydraulic properties of adsorbed water films in unsaturated porous media were predicted through combining Langmuir's film model with scaling analysis, without use of any adjustable parameters. Diffuse double layer influences are predicted to be important because of the strong dependence of adsorbed water film thickness (f) on ion charge (z). Film thickness, film velocity, and unsaturated hydraulic conductivity are predicted to vary with z^{-1} , z^{-2} , and z^{-3} , respectively. In monodisperse granular media, the characteristic grain size (λ) controls film hydraulics through λ^{-1} scaling of (1) the perimeter length per unit cross sectional area over which films occur, (2) the critical matric (capillary) potential (ψ_c) below which films control flow, and (3) the magnitude of the unsaturated hydraulic conductivity when $\psi < \psi_c$. While it is recognized that finer textured sediments have higher unsaturated hydraulic conductivities than coarser sands at intermediate ψ , the λ^{-1} scaling of hydraulic conductivity predicted here extends this understanding to very low saturations where all pores are drained. Extremely low unsaturated hydraulic conductivities are predicted under film-controlled conditions (generally $< 0.1 \text{ mm y}^{-1}$). On flat surfaces, the film hydraulic diffusivity is shown to be constant (invariant with respect to ψ).

Predictions of thin film hydraulic properties are being tested through experiments on quartz glass surfaces of known surface roughness (root mean square roughness $< \text{nm}$, up to $10 \text{ }\mu\text{m}$). Samples are contained in a chamber and equilibrated through a porous ceramic containing aqueous solutions of either mono- or divalent ions, with ψ controlled at the ceramic boundary. The chamber is placed in front of a monochromatic X-ray beam (National Synchrotron Light Source X26A, and Advanced Photon Source 13-ID-C) used to determine film thicknesses through X-ray fluorescence of monovalent (Rb^+ and Br^-) and divalent (Mg^{2+} and SeO_4^{2-}) ion tracers in the water films. The monochromatic, hard X-ray beam permits efficient characterization of local average water film thickness through X-ray fluorescence monitoring of ionic solutes. With a 0.1 mm^2 beam, fluorescence intensity scaled linearly with film thicknesses over the range of 10 to 400 nm for the tested solution concentration of 300 mM. Applying the Langmuir film equation, the lower range of measureable thicknesses corresponds to matric potentials in the range of -20 to -30 kPa. The ability to resolve film thicknesses over this range demonstrates that our approach is suitable for conditions commonly occurring in nature, and that the technique can be a useful complement to synchrotron X-ray computed tomography for

studying aqueous phase distributions in unsaturated porous media. A new sample chamber design is currently being tested to partially circumvent the problem of long experimental times required for thin film flow equilibration.

Computational Geochemistry: Applications to Mineralogy, Geochemistry, and Hydrology

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Molecular dynamics (MD) simulations are well established in geochemistry as complements of experimental probes of molecular-scale structure (EXAFS, X-ray and neutron diffraction) and sub-nanosecond dynamics (IR, neutron scattering). However, thanks to recent major increases in computational power, MD simulation techniques can now probe length and time scales that approach those at which natural earth materials have been routinely modeled as continua, thus offering a means to test existing continuum-scale models. We illustrate this innovation with two examples in which continuum-scale hydrologic parameters were successfully determined by MD simulation: (1) use of MD simulations of noble gas isotopic fractionation by diffusion in liquid water to reinterpret continuum-scale hydrologic models of solute transport in aquifers and lacustrine sediments (Bourg and Sposito, 2008) and (2) use of MD simulations of diffusion in smectite interlayer nanopores to model the continuum-scale diffusion of water and cations (Na^+ , Sr^{2+} , Cs^+) in clay barriers (Bourg and Sposito, 2009). First-principles quantum mechanical geometry optimizations also have made great progress recently, thanks to improved computational codes and MPP hardware. We illustrate these advances in geometry optimizations based on quantum mechanics with the examples of trace metal sorption (Kwon et al., 2009a) and photochemical reactivity (Kwon et al., 2009b) of layer type Mn oxides, which are important both environmentally and in materials science. Our calculations provide new insight into the well-known conundrum of trace metal sorption on Mn oxide vacancies vs. direct metal incorporation into the Mn oxide structure, and they reveal how the vacancies can enhance the photoreductive dissolution of Mn oxides by sunlight.

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