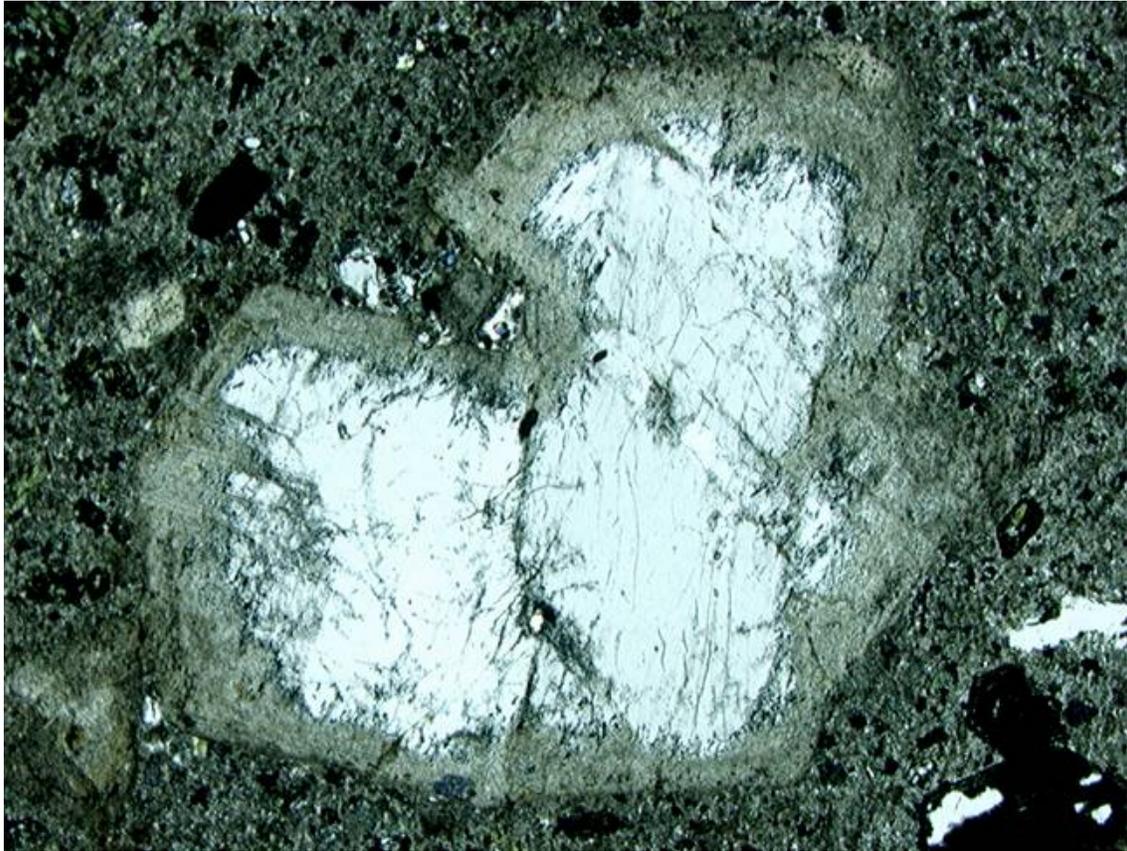


Analytical and Isotopic Geochemistry



Picture of Andesine being replaced by Albite from Lee Riciputi, Oak Ridge National Laboratory from Rico, CO.

Gaithersburg Marriott Washingtonian Center
Gaithersburg, MD
June 5-6, 2005

FORWARD

“Analytical and Isotopic Geochemistry” is the twelfth 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 Professor William McDonough from the University of Maryland at College Park, Professor Joel Blum from the University of Michigan, Professor John Hanchar from the Memorial University of Newfoundland and Professor Louis Derry from Cornell University. They join our Principal Investigator co-chairs Professor Patricia Dove of Virginia Tech, Professor R. James Kirkpatrick from the University of Illinois, Professor Satish Myneni from Princeton University and Dr. Jeffrey Seewald from Woods Hole Oceanographic Institution. 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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Table of Contents

| | |
|---|----|
| Agenda..... | 3 |
| Abstracts (listed in chronological order) | |
| Session 1 (June 5, A.M.)..... | 7 |
| Session 2 (June 5, P.M.)..... | 17 |
| Session 3 (June 6, A.M.)..... | 24 |
| Session 4 (June 6, P.M.)..... | 35 |
| Participants..... | 47 |

Analytical and Isotopic Geochemistry
-Agenda-
Gaithersburg Marriott Washingtonian Center
Gaithersburg, MD
June 5-6, 2005

Sunday, June 5 (AM)

7:30 **Registration/Continental Breakfast**

7:45 **Introductions and Greetings**
Nicholas Woodward, Department of Energy

Session 1

Chairs: William McDonough (Maryland) and Patricia Dove (VPI)

8:00 Donald DePaolo, Lawrence Berkeley National Laboratory
The Magic of Deep Sea Sediments as a Geochemical Laboratory; U, Sr and Ca Isotope Studies

8:30 Mack Kennedy, Lawrence Berkeley National Laboratory
Development of Isotope Techniques for Reservoir and Aquifer Characterization

9:00 John Valley, University of Wisconsin
Microanalysis of Oxygen Isotope Ratios by Ion Microprobe

9:30 David Cole, Oak Ridge National Laboratory
Mineral Reaction Zones and Associated Interfaces

10:00 **Coffee/refreshments**

10:15 Lee Riciputi, Oak Ridge National Laboratory
Multi-scale Studies of Fluid-Rock Interactions

10:45 Edward Stöpler, California Institute of Technology
Diffusion of Water in Silicate Melts

11:15 Marty Grove, University of California at Los Angeles
Measurement of High Spatial Resolution $\delta^{18}O$ Variations in Modern and Pleistocene Spelothems

11:45 Wasserburg, G. J., California Institute of Technology
Transport and Water Rock Interaction in Carbonate Aquifers and Isotopic Fractionation in Calcite: A Physical-Chemical Approach

12:15 **Lunch** (on your own)

Monday, June 5 (PM)

Session 2

Chairs: Louis Derry (Cornell) and Satish Myneni (Princeton)

- 1:30 Juske Horita, Oak Ridge National Laboratory
Biotic and Abiotic Isotope Fractionations of Magnetite and Carbonates
- 2:00 Mike Murrell, Los Alamos National Laboratory
The Uranium Decay Series at a Finer-Scale
- 2:30 Frank Richter, The University of Chicago
Kinetic Isotope Fractionation during Mass Transport
- 3:00 Juske Horita, Oak Ridge National Laboratory
Theoretical and Simulation Study for the Isotopic Properties of Fluids
- 3:30 **Coffee/refreshments**
- 3:45 Jeffrey Seewald, Woods Hole Oceanographic Institution
Carbon Isotope Exchange during Hydrocarbon Maturation: Constraints from Laboratory Experiments and Field Data
- 4:15 Christopher Reddy, Woods Hole Oceanographic Institution
Using Comprehensive Two-Dimensional Gas Chromatography to Explore Transformation Processes Acting on Petroleum Hydrocarbons
- 4:45 Alexandra Navrotsky, University of California at Davis
Oxide Metal Solution Calorimetry of Sulfides
- 5:45 **Adjourn**
- 6:00 **Dinner** (On your own)

Monday, June 6 (AM)

7:30 **Coffee/Continental Breakfast**

Session 3

Chairs: Joel Blum (Michigan) and Jim Kirkpatrick (Illinois)

8:00 Richard Hervig, Arizona State University
Analyzing Li and B Isotopes by SIMS

8:30 David Wesolowski, Oak Ridge National Laboratory
Experimental Studies of Fundamental Hydrothermal Processes Employing In Situ pH Monitoring and other Unique Approaches

9:00 Paul Fenter, Argonne National Laboratory
Mineral-water Interface Structure and Reactivity: New Insights from High Resolution X-ray scattering

9:30 Steve Sutton, The University of Chicago
Geochemical Studies using Surface Scattering and Microprobe Analysis at GSECARS

10:00 **Coffee/refreshments**

10:15 Antonio Lanzirotti, The University of Chicago
Insights into the Geochemistry of Contaminants using Combined Synchrotron X-ray Microbeam Diffraction, Adsorption Spectroscopy, and Fluorescence Analysis at NSLS X26A

10:45 Glenn Waychunas, Lawrence Berkeley National Laboratory
Water at Mineral Surfaces: New Information from Phase-Sensitive Sum Frequency Vibrational Spectroscopy (PS-SFVS)

11:15 Satish Myneni, Princeton University
Probing the Electronic States of Molecules in Aqueous Solutions and at Interfaces

11:45 John Weare, University of California at San Diego
First-principles Simulation of the Solvation Structure and Deprotonation Reactions of Ore Forming Metal Ions in Very Nonideal Solutions

12:15 **Lunch** (on your own)

Monday, June 6 (PM)

Session 4

Chairs: John Hanchar (Memorial University) and Jeffrey Seewald (Woods Hole)

- 1:30 James Kirkpatrick, University of Illinois
Computational and Experimental Investigations of Water and Solute Species on Mineral Surfaces and in Confined Spaces
- 2:00 Steven Higgins, Wright State University
Carbonate Mineralization and Interface Chemistry: Sensing Compositional Heterogeneities with Scanning Probe Microscopy
- 2:30 Patricia Dove, Virginia Tech University
Investigating the Physical Basis of Biomineralization
- 3:00 Scot Martin, Harvard University
Growth of Iron and Manganese Oxide film on Carbonate Minerals
- 3:30 **Coffee/refreshments**
- 3:45 Martin Schoonen, Stony Brook University
Resolving Reaction Mechanisms and Intermediate Reaction Products in the Oxidation of Pyrite
- 4:15 Randall Cygan, Sandia National Laboratories
Structure and Dynamics of Amino Acids in Layered Double Hydroxide Materials
- 4:45 Louise Criscenti, Sandia National Laboratories
The Structure of Interfacial Water and Metal Surface Complexes at Silica and Alumina Surfaces: Evidence from Molecular Modeling Simulations, Macroscopic Sorption Experiments, and X-ray Adsorption and Sum Frequency Generation Spectroscopies
- 5:30 **Adjourn**
- 6:30 **Refreshments**
- 7:00 **Banquet**

The Magic of Deep Sea Sediments as a Geochemical Laboratory; U, Sr and Ca Isotope Studies*

D. J. DePaolo, J. N. Christensen, K. Maher, M. S. Fantle

Lawrence Berkeley National Laboratory, Berkeley, CA

A substantial part of the research pursued by the Center for Isotope Geochemistry is directed at measuring and understanding the rates of mineral-fluid chemical reactions in nature. We use isotopic measurements to monitor reaction rates, and the derived rates can be used to evaluate what controls reaction rates in natural systems. Deep sea sediments are particularly useful because they are highly porous and subjected to temperature, pressure, and pore fluid chemical conditions that are slowly changing and predictable over millions of years. Pore fluid chemistry and isotopic composition are excellent monitors of fluid-mineral interaction, and the transport in the pore fluid is dominated by molecular diffusion. In comparison to soils and fractured rock systems, there are fewer complications for interpreting data relating to reaction rates.

Data will be presented on U, Sr, and Ca isotopic compositions of a 60m sediment core from the North Atlantic (ODP Site 984A) made mostly of siliciclastic material with subordinate carbonate, and an 800m core from the Ontong-Java plateau that is mostly (Site 807A, >90%) carbonate. In the Site 984 core, ^{234}U in pore fluids and sediments has been used to estimate mineral dissolution rates. The rates have been further evaluated using a multicomponent reactive transport code in a collaboration with C. Steefel. The dissolution rates are very low by comparison with laboratory determinations (applied via Transition State Theory), and this discrepancy is not due to lack of exposed surface area or approach to equilibrium. In this core microbial processes strongly affect the pore fluid chemistry maintaining the fluid composition far from equilibrium with silicate phases. The reaction rates are similar to those inferred for soils with the same general age ($1-4 \times 10^5$ yr), supporting the contention that empirical reaction rates are much more accurate than TST-based estimates. Leaching experiments on the sediments have led to a new application of ^{234}U measurements to studies of erosion and sediment deposition.

The Site 807 core provides direct estimates of carbonate recrystallization rates for sediment varying in age from 3×10^5 yr to 3×10^7 yr. In this case the pore fluids are in “equilibrium” with the carbonate solids for virtually the entire 800m depth of the core, but the solution-precipitation rates decrease by a factor of 100 in inverse proportion to sediment age. Sr isotopes give the estimates for recrystallization rate for the older sediment ($>3 \times 10^6$ yr) and Ca isotopes give the rates for the youngest sediments. There is no measurement of pore fluid chemistry that can be made precisely enough to calculate the slow dissolution rates, so standard TST formulations of reaction kinetics are useless. The data from Site 807 also require that the equilibrium isotopic fractionation factor for $^{44}\text{Ca}/^{40}\text{Ca}$ between calcite and $\text{Ca}^{2+}(\text{aq})$ must be zero ($\alpha = 1.0000 \pm 0.0001$, or $\Delta = 0.0 \pm 0.1$), in conflict with inferences made recently by Lemarchand et al. (2004). The data also require that the ratio of the aqueous diffusivities of $^{44}\text{Ca}^{2+}(\text{aq})$ and $^{40}\text{Ca}^{2+}(\text{aq})$ must be 1.0000 ± 0.0001 (in agreement with results on $\text{Mg}^{2+}(\text{aq})$ from Richter et al.). Our results indicate that previous interpretations of $\text{Ca}^{2+}(\text{aq})$ profiles in deep sea pore fluids are incorrect, and suggest that the changes in the Mg concentration of the oceans over the past 20 million years could be retrieved from the pore fluid data.

*The title of the project represented by this talk is “Integrated isotopic studies of geochemical process,” which includes B.M. Kennedy, M.E. Conrad and J.N. Christensen as PI’s. The grant supports work on radiogenic, stable, and noble gas isotopic studies related to basic energy issues. BES provides core support for our labs that now contain 3 TIMS, 2 Noble gas and 2 stable isotope mass spectrometers, and an Isoprobe MCICPMS.

Development of Isotope Techniques for Reservoir and Aquifer Characterization

B. Mack Kennedy

Lawrence Berkeley National Laboratory, Berkeley, CA

This project focuses primarily on developing and improving existing techniques for using the concentrations and isotopic compositions of noble gases for reservoir and aquifer characterization. Specific interests include safe geologic sequestration of CO₂ and placing time constraints on fluid flow and aquifer related processes.

Emissions related to human activities are substantially increasing the atmospheric concentrations of greenhouse gases (CO₂, CH₄, CFC's, and N₂O). One of several proposed strategies to reduce atmospheric emission is to capture CO₂ evolved during the burning of fossil fuels and sequester it deep underground in natural geologic formations or reservoirs. Many oil and gas reservoirs are complexly partitioned by differing structural, petrologic, stratigraphic, and hydrologic controls that will inhibit efficient injection and limit reservoir potential. Of particular interest is the amount of interstitial pore water, the extent of gas-water interaction, the integrated gas/water volume ratio and the degree of reservoir compartmentalization. Modeling suggests that gases of different solubility will exhibit chromatographic separation along a flow path with continued gas-water interaction and predicts that precisely measured details of a chromatographic separation profile for a suite of gases with different solubility would provide important information for modeling transport, the extent of gas-water interaction and an integrated aqueous phase saturation. Noble gases are well suited for chromatographic separation studies because they exhibit a smooth increase in solubility by a factor of ~10-15 from Ne to Xe and are chemically inert with very low concentrations in most rocks and minerals, thus minimizing the effects of water-rock interaction.

The recent CO₂ sequestration experiment in the Frio Formation in the Gulf Coast South Liberty Field, Texas, provided our first shot at evaluating chromatographic separation. Monitoring a noble gas and SF₆ cocktail injected as a slug along with CO₂ clearly demonstrated the utility of this approach. Differential arrival times for SF₆ and Kr translates to aqueous phase saturation along the flow path of ~22-51%. When arrival times are similar, due either to comparable solubility or short travel distances, small uncertainties in the arrival times translate to large uncertainties in aqueous phase saturation.

Microanalysis of Oxygen Isotope Ratios by Ion Microprobe

John W. Valley and Noriko Kita

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Oxygen isotope analysis by ion microprobe attains the smallest sample size and best spatial resolution of any stable isotope technique (Valley 2003). The use of multicollection has improved accuracy, precision, sample size, and speed for in situ analysis of oxygen isotope ratios.

Careful use of appropriate standards, bracketing unknown analyses, yields accuracy that approaches precision. Analytical precision of 0.5‰ is routine and under favorable conditions, reproducible precision of 0.1-0.2‰ (1SD, $\delta^{18}\text{O}$, spot to spot) has been attained for 10-20 μm spots (~ 1 ng) in many silicate minerals (5-20 min./analysis) in at least four labs by CAMECA ims-1270 with dual Faraday cups. Spot to spot precision of 0.4‰ is attained for $\delta^{17}\text{O}$ by use of three Faradays in 20 minute analyses employing careful background measurements (Kita et al. 2004). Linear spatial resolution can be better than 1 μm in depth profile mode. Spot size of 0.3 μm is possible and, even at poorer precision, is useful for isotopically labeled experiments. Design improvements to the new Wisconsin CAMECA ims-1280 are intended to enhance reliability and precision of analysis, including: digital electronics; PC control; continuous monitoring of primary beam intensity; automatic focusing of the secondary beam in the field aperture and entrance slit, and of the objective lens; NMR control of the magnetic field; and better control of stray magnetic fields in the sample chamber and secondary column.

Ion microprobe analysis is required for samples that are zoned, precious, or rare. Published studies include: zoned zircons (Bindeman et al. 2001, Cavosie et al. 2005), quartz overgrowths, coesite inclusions in diamond (Schulze et al. 2003), speleothems (Kolodny et al. 2003), and single microbes (Orphan et al. 2001). Future studies will explore new applications and biological targets. Most traditional and non-traditional stable isotope systems will enjoy the advantages of small spot size and enhanced accuracy by multiple collector ion microprobe.

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- Cavosie AJ, Valley JW, Wilde SA, and EIMF (2005) Oxygen Isotopes in Early Archean Zircons: Correlating In-Situ $\delta^{18}\text{O}$ Ion Probe Analyses with Concordant U/Pb Domains and CL Zoning. *Earth Plan. Sci. Lett.*, in press.
- Kita N, Ikeda Y, Togashi S, Liu YZ, Morishita Y, Weisberg MK, (2004) Origin of ureilites inferred from a SIMS oxygen isotopic and trace element study of clasts in the Dar al Gani 319 polymict ureilite. *Geochimica et Cosmochimica Acta*, 68:4213-4235.
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- Schulze, DJ, Harte, B, Valley, JW, Brenan, JM, Channer, DMR (2003) Extreme crustal oxygen isotope signatures preserved in coesite in diamond. *Nature* 423: 68-70.
- Valley JW (2003) Oxygen isotopes in Zircon. In: J Hanchar & P Hoskin (eds) *Zircon*. Min. Soc. Am. Rev. Mineral. Geochem., 53:343-385.

Mineral Reaction Zones and Associated Interfaces

David R. Cole, Lee R. Riciputi, Mostafa Fayek, and Juske Horita

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Despite the utility of the equilibrium approach in quantifying the elemental and isotopic behavior in numerous mineral systems, there is mounting evidence that isotopic heterogeneity and disequilibrium may be more widespread than previously appreciated. The geometry of the isotopic and chemical redistribution within a single grain or across a grain boundary is commonly the result of heterogeneous reactions that produce a complex reaction layer in the parent phase. Most notably, processes such as hydration/dehydration, cation exchange, decarbonation, and oxidation-reduction can lead to either passivated mineral surfaces or the formation of reaction rims such that further exchange requires diffusion of matter across the zone to the interface between the reacted and unreacted parent phase – a coupled process. Therefore, a quantitative understanding of the rates and mechanisms of isotopic exchange between minerals and fluids influenced by coupled chemical reaction-diffusion is critical to the interpretation of the extent of isotopic equilibrium and factors that influence exchange in natural systems.

The over arching goal of this project is to develop a quantitative nanoscale and molecular-level understanding of mechanisms and rates of elemental and isotopic exchange within mineral reaction zones and at associated interfaces. The near-term objectives include: (a) characterization of the chemical, isotopic and structural features of the reaction zone and its rate of formation, (b) assess the nature of the chemical and isotopic communication across the reaction zone and the nanoscale confinement effects on fluid properties and behavior, and (c) explore the nanoscale and molecular details of the reaction interface. Experimental studies focus on simple model mineral-fluid systems at ambient conditions to extreme temperatures (up to 850°C) and pressures (up to 400 MPa). These experiments take full advantage of novel isotopic labeling (e.g. ^{18}O , ^{13}C , D) as monitors of the interaction among fluids and solids. Advanced electron microscopy and secondary ion mass spectrometry (SIMS; Cameca 4f; NanoSIMS) techniques are used to characterize structures and chemical/isotopic patterns, respectively, within the reaction zone and at the reaction interface. We also use both neutron and X-ray scattering to interrogate the porous structures within the reaction zone and fluid properties within nanoporous regimes.

Our current effort is focused on three types of coupled reaction-diffusion mineral-fluid systems:

Cation exchange: $\text{NaAlSi}_3\text{O}_8 + \text{KCl}_{\text{aq}} \rightarrow \text{KAlSi}_3\text{O}_8 + \text{NaCl}_{\text{aq}}$ (400-600°C, 200 MPa)

Decarbonation: $(\text{Ca, Mg})[\text{CO}_3]_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{MgO} + \text{H}_2\text{O} + \text{CO}_2$ (650-750°C, 100 MPa)

Hydrolysis: $\text{MgO} + \text{H}_2\text{O} \text{ (or } \text{D}_2\text{O)} \rightarrow \text{Mg}(\text{OH})_2 \text{ or } \text{Mg}(\text{OD})_2$ (20-500°C, 1/v-200 MPa)

The chemically-imaged boundary between the core feldspar phase (as isolated grains) and the replacement rim is sharp and decorated with micro-pores. At the resolution of the NanoSIMS, ~250 – 500 nm, ion images and line scans indicate the interface is sharp in the distribution of ^{18}O and ^{16}O . However, based on TEM analysis, the nature of the reaction interface in the feldspar

system depends strongly on crystallographic control with an overall jagged appearance, exhibits microporosity along the reaction front, and has an unusual corrugated or stitch-like nano-texture right at interface indicative perhaps of stress build-up. The combined electron probe and NanoSIMS analyses indicate that both cation and isotope exchange occurred during fine-scale dissolution and reprecipitation of the feldspar.

SIMS ion imaging of rock cores shows extensive enrichment of ^{18}O within dolomite breakdown reaction products and along dolomite grain boundaries and fractures. Ion imaging of ^{18}O rich zones provide direct evidence for fluid infiltration along grain boundaries. Isotope-ratio analyses along traverses within dolomite grains show an enrichment in ^{18}O from core to rim. The lack of Fe, Mn, and Sr mobility within dolomite near reaction grain boundaries indicates that diffusion rather than recrystallization is the primary mechanism for ^{18}O exchange.

TEM, neutron diffraction (ND), and inelastic neutron studies (INS) have been initiated to assess the structure, dynamics and interaction of water films on MgO and brucite. Preliminary results on INS and ND have been obtained for H_2O on MgO that provide insight into the rotational and vibrational dynamics, water structure, and the configuration of the potential energy surface (PES).

Multi-scale Studies of Fluid-Rock Interactions

Lee Riciputi, David Cole, Mostafa Fayek

Oak Ridge National Laboratory, Oak Ridge, TN

Although the signatures of fluid-rock interactions can be monitored at geologic scales up to those affecting 1000s of km³ of rock (e.g., sedimentary basins, metamorphic haloes around batholiths), fluid-rock interaction and the resultant isotopic variations are controlled by various nano- and microscale processes, including (1) recrystallization, (2) replacement, (3) solution/precipitation, (4) surface and grain boundary diffusion, and (5) volume diffusion. Isotope exchange rate, and hence temporal dependency, varies with dominant transport mechanism – exchange controlled by chemical reaction typically occurs much faster than diffusive-dominated exchange. In most natural systems (and many experiments), isotope exchange may result from a combination of exchange mechanisms, and the relative interplay between these mechanisms can change with time as the system evolves. Isotopic (and chemical) heterogeneities are a potentially powerful source of information on the conditions and temporal history of fluid-rock interaction, providing crucial evidence of processes and rates that impact mass transfer up to the global scale. However, to properly interpret this information, we must understand the complex interactions among the different mechanisms and rates by which these isotopic, chemical, and textural features form.

This effort seeks to quantify fluid-rock interactions through the use of chemical and isotopic imaging, focusing on the nano-and micro-scale mechanisms controlling isotopic exchange through studies of both natural and experimental systems. High precision, microscale SIMS isotope analyses performed with our Cameca 4f are complimented with higher spatial resolution imaging techniques (e.g., HRTEM, SEM, micro Raman/FTIR, NMR, NanoSIMS), allowing us to link specific isotopic signals with mechanistic signatures and textures at the nanoscale. We are plan exploratory neutron scattering studies to take advantage of new capabilities coming on-line at ORNL (High Flux Isotope Reactor (HFIR), Spallation Neutron Source (SNS)).

Our work is currently focused on three major systems,

- (1) feldspars, examining coupled reaction/diffusion in natural systems as well as collaborating on experimental studies;
- (2) oxides, particularly uraninite, where we are studying links between nanoscale textural features and both cation and anion isotope chemistry in response to major fluid-rock events (e.g., tectonics);
- (3) glasses, where we are investigating the complex process of low-temperature (<150°C) glass hydration.

Additionally, we are undertaking exploratory studies studying mineralization mechanisms in fluid-rock-microbe systems utilizing chemical and isotope imaging methods.

Diffusion of Water in Silicate Melts

Edward Stolper¹, Sally Newman¹, Eduard Persikov², and Youxue Zhang³

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The diffusion of water in silicate melts and glasses has significant impact on the explosivity of volcanic eruptions, the development and persistence of water-enriched melts at the boundary layers of growing crystals and at the edges of magma chambers, and the alteration of silicate glasses in nature and in industrial settings. Study of the diffusion of water in melts and glasses is complicated by the strong dependence of the diffusivity of water on melt composition, including water concentration. The dependence of the diffusion coefficient of water on water content has been used to infer molecular-level mechanisms of water diffusion and to develop models of water diffusion that quantitatively relate melt structure and this critical transport property. However, a quantitative description of the dependence of water diffusion on melt composition over the full range from acidic to basic compositions of geological interest has not previously been available.

Although diffusion of water in acidic silicate melts has been studied extensively, little has been done on basic silicate melts, reflecting the high diffusivity of water in these systems and the difficulty of quenching such melts to glasses. For example, there has been only one study of the diffusion of water in basaltic melts, and this was done only at water contents up to 0.4 wt. %. Such studies are important both for their petrological significance and because the molecular structures of basic melts differ considerably (e.g., they are less polymerized) than the more extensively studied acidic melts.

We have studied the diffusion of water in melts with the following compositions: high-Al basalt, Ab₅₀Di₅₀, Ab₇₅Di₂₅ (the last two are simple-system analogs of basalt and andesite), and rhyolite. Experiments were done either in an internally heated pressure vessel (1250-1300°C, 0.5-1 kbar, up to 25 minutes) or a rapid-quench TZM pressure vessel (600-950°C, 0.5-1 kbar, up to 44 hours). Two types of experiments were done: hydration experiments, in which a water-poor melt was placed in contact with water vapor; or diffusion couple experiments, in which two melts with different water contents were placed in contact. After quenching, concentration profiles were measured using FTIR spectroscopy. Concentration profiles were fit using water diffusion coefficients with a variety of functional forms for the dependence of this diffusion coefficient on water concentration; additionally, the dependence of water diffusivity on water content was calculated directly using a Boltzmann-Matano method for calculating diffusion coefficients along the profiles.

Key results include: (1) Hydration and diffusion couple experiments give similar results. (2) The diffusivity of water in basaltic melts at high water contents is consistent with the previous measurements at lower water content. (3) The observed concentration dependence of the diffusion of water in these melts is generally consistent with previous studies and with simple models that assume water diffuses as water molecules in equilibrium with immobile hydroxyl groups. (4) The diffusivity of water over a wide range of melt compositions appears to be correlated with calculated melt viscosity. This correlation has the potential to provide a basis for estimating the diffusion coefficient of water in silicate melts for which experiments are unavailable.

Measurement of High Spatial Resolution $\delta^{18}\text{O}$ Variations in Modern and Pleistocene Speleothems

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T, John Chappell², Michael K. Gagan²

¹*University of California, Los Angeles, CA*

²*The Australian National University, Canberra, Australia*

We present high resolution $\delta^{18}\text{O}$ results from both modern and Pleistocene speleothems. A record of seasonal and inter-annual oxygen ($\delta^{18}\text{O}$) isotope ratios from an 81-year-old stalagmite from Moondyne Cave, southwest Australia. The growth history of stalagmite MND-S1 is known since it grew on a cave boardwalk that was installed in 1911 and removed in 1992. This stalagmite provides an excellent test of speleothem climate proxies because the regional climate is strongly seasonal (wet winter/dry summer) and has experienced a 200 mm (20%) reduction of mean rainfall since the mid-1960's, and a 0.8°C temperature rise since ~1953. Seasonal variations in calcite $\delta^{18}\text{O}$ were measured *in situ* by high spatial resolution ion microprobe, whilst inter-annual variations of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ were measured by conventional gas-source mass spectrometry. Comparison of the speleothem stable isotopes and instrumental temperature records reveals that $\delta^{18}\text{O}$ variations are too large to be driven by temperature alone, and are in the opposite sense. However, daily rainfall $\delta^{18}\text{O}$ measurements show that the mean seasonal range in $\delta^{18}\text{O}$ of rainfall in southwest Australia is large (2x) and inversely correlated with rainfall amount. A rainfall driver for the speleothem $\delta^{18}\text{O}$ is confirmed by the detection of seasonal shifts of 0.7–1.5x in speleothem $\delta^{18}\text{O}$ that track rainfall $\delta^{18}\text{O}$, smoothed by storage in the overlying limestone. The seasonal range in speleothem $\delta^{18}\text{O}$ is larger than any interannual and decadal variation observed in the record. The prominent annual cycles in speleothem $\delta^{18}\text{O}$ revealed by ion microprobe analysis indicate that subtle changes in the frequency of intense winter rainfall events, or possibly also moisture sources, could produce significant changes in mean speleothem $\delta^{18}\text{O}$. The ion microprobe results also raise the possibility that the masses of speleothem calcite deposited in winter and summer could vary as a function of the seasonal drip rate and carbonate saturation state of these waters. If this is the case, then small changes in the relative masses of calcite deposited in winter and summer could produce significant shifts in mean $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ that have a complex relation to climate. This finding should be generally applicable to the interpretation of long-term trends in speleothem geochemical records for shallow cave. Determining the timing, duration and structure of rapid climate events requires annual to sub-decadal resolution that is not achievable in the poorly resolved chronologies of the deep sea cores which preserve Heinrich events. We are critically examining the suitability of the SIMS technique for speleothem O isotope analyses by applying it to a portion of the well-known Hulu Cave record over the most recent Heinrich event: H1 or Termination I at 16.1 ka. We compare the SIMS $\delta^{18}\text{O}$ analyses to previously published $\delta^{18}\text{O}$ analyses obtained by micro-shaving and conventional methods and also consider *in situ* LA-ICPMS trace element data in the interpretation of the Hulu Cave results.

Transport and Water Rock Interaction in Carbonate Aquifers and Isotopic Fractionation in Calcite: A Physical-Chemical Approach

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Two major studies have been completed and published. The first of these is the study of isotopic fractionation of Ca during calcite growth from solution. It was found that the isotopic shifts widely reported in the literature and attributed to biological processes are in fact due to a small equilibrium fractionation factor that is suppressed by supersaturation of the solution. These effects were demonstrated in the laboratory and with consideration of the solution conditions in natural systems where $[Ca^{2+}] \gg [CO_3^{2-}] + [HCO_3^-]$. The controlling rate is not the diffusion of Ca as was earlier proposed, or unknown biochemical effects, but rather the rate of supply of $[CO_3^{2-}]$ ions to the interface. This now opens the issues of isotopic fractionation of many elements to a more physical-chemical approach. The isotopic composition of Ca ($^{44}Ca/^{40}Ca$) in calcite crystals has been determined relative to that in the parent solutions by TIMS using double spike. Solutions were exposed to an atmosphere of NH_3 and CO_2 , provided by the decomposition of $(NH_4)_2CO_3$. Alkalinity, pH and concentrations of CO_3^{2-} , HCO_3^- , and CO_2 in solution were determined. This procedure permitted us to determine $\Delta(^{44}Ca/^{40}Ca)$ over a range of pH conditions, with the associated ranges of alkalinity. The results show that $\Delta(^{44}Ca/^{40}Ca)$ is a linear function of the saturation state of the solution with respect to calcite (Ω) and are very well correlated over a wide range in Ω . Diffusive flow of CO_3^{2-} into the immediate neighborhood of the crystal-solution interface is the rate-controlling mechanism and the diffusive transport of Ca^{2+} is not a significant factor. The data are simply explained by the assumptions that: a) the immediate interface of the crystal and the solution is at equilibrium with $\Delta(^{44}Ca/^{40}Ca) \sim -1.5 \pm 0.25$ ‰; and b) diffusive inflow of CO_3^{2-} causes supersaturation, thus precipitating Ca from the regions, exterior to the narrow zone of equilibrium. We consider this model to be a plausible explanation of the available data reported in the literature. It is shown that there is a clear temperature dependence of the net isotopic shifts that is simply due to changes in Ω due to the equilibrium “constants” dependence on temperature, which changes the degree of saturation and hence the amount of isotopically unequilibrated Ca precipitated.

The second report treats the problem of Sr isotopic changes in aquifer waters in carbonate terrains. It was found that while dolomite dissolution, calcite precipitation and clay exchange may govern the bulk chemistry of such waters, the major source of Sr is from the dissolution of the minor phase Anhydrite. A theoretical analytical flow model following Tricca et al (2001) is presented which shows that the coupling of intrinsic reaction rates of the participating phases, the concentration of Sr in these phases and the modal abundances of the mineral phases are the key parameters. Large amounts of anhydrite or clays calculated by the standard “bulk solution” model do not represent the mineral abundances in the aquifer. The approach laid out in this study has broad implications in problems relating to understanding and modeling of element abundances in groundwater.

A theoretical treatment of the astrophysical sources of U Th and the Trans-actinides is now under preparation and will be submitted for publication shortly.

Biotic and Abiotic Isotope Fractionation of Magnetite and Carbonates

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An increasing number of studies suggest that bacteria play an important role in the nucleation and growth of various minerals (carbonates, iron oxides, phosphates, *etc.*) under low-temperature (<100°C), surface and subsurface environments. It is well known that some minerals (*e.g.*, dolomite) are difficult to synthesize inorganically in the laboratory at low temperatures and the microbial precipitation of minerals may provide an answer to the enigma of their widespread occurrence in nature. Microbial mineral precipitation also provides us with opportunities to investigate various important issues on biogeochemistry, including isotopic fractionation associated with mineral precipitation at low temperatures and possible differences between biological and abiological processes.

We have been conducting laboratory experiments for microbial and inorganic precipitation of magnetite and carbonates (dolomite, siderite) at low temperatures. Fine-grained (10's to 100's of nm) magnetite were produced by: (a) thermophilic (45-75°C) iron-reducing bacteria, which reduced amorphous Fe(III) oxyhydroxide to form magnetite-rich (>60% in most samples) iron oxides in acetate- or H₂/CO₂-enriched cultures and (b) inorganic precipitation from a stoichiometric Fe²⁺-Fe³⁺ solution or a mixture of KNO₃/KOH and FeCl₂ solution at 25-90°C. Our results on oxygen isotope fractionation between magnetite (microbial and inorganic) and water, along with recent literature data on magnetotactic bacteria at 5-35°C, produced generally consistent fractionation behaviors, which differ significantly from the data available in the literature. A similar experiment was also conducted for the inorganic precipitation of dolomite from a Na-Mg-Ca-SO₄-CO₃ solution at 80°C, which produced fine-grained (15 nm), nearly stoichiometric CaMg(CO₃)₂ with ordering peaks. Oxygen isotope fractionation of this inorganic dolomite is consistent with recent data of dolomite produced by sulfate-reducing bacteria at 25 - 45°C (Vasconcelos *et al.*, 2005). Although still inconclusive, these data pose important questions regarding the origin and occurrence of fine-grained magnetite and dolomite under low-temperature environments, including how to distinguish minerals formed by biological and inorganic processes in nature.

Reference:

Vasconcelos, C., MaKenzie, J.A., Warthmann, R., and Bernasconi, S.M. (2005) Calibration of the δ¹⁸O paleothermometer for dolomite precipitated in microbial cultures and natural environments. *Geology* 33, 317.

The Uranium Decay Series at a Finer-Scale

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Uranium-series disequilibria techniques are well-established and valuable tools for geochronology and geochemistry. Such measurements have historically been made by decay counting; however, there are considerable advantages in using mass spectrometric techniques for most applications. Our current emphasis is on developing methods that provide in-situ spatial resolution for U-series studies for geologic materials. We are working towards this goal by combining the multiple collector ion counting of the Isoprobe ICPMS with laser ablation. Our plan is to move from what is currently known about laser ablation MC-ICPS from studies of minerals, metal particles, coral, etc. into new areas such as U-series studies of young volcanics, fracture filling material, hominid fossils, and deep sea corals. This work will provide information on the recent evolution of magmatic systems, human evolution, radionuclide transport, and the carbon cycle.

We have made a number of upgrades to the interface region of the Isoprobe that have reduced backgrounds and increased sensitivity. We are currently in the process of installing the Cetac LSX-213 laser ablation system on this instrument. Our initial work will focus on U-series measurements in high U materials, including zircons from young volcanic rocks. In collaboration with P. Gauthier at U. Clermont, we are studying U-Th-Pa mineral isochrons for the Puy de Dôme trachyte. Our ^{238}U - ^{230}Th isochron for bulk mineral separates from this sample indicates an crystallization age of 12.3 ka. Mary Reid (NAU/UCLA) has preformed ^{238}U - ^{230}Th analyses of the Puy du Dôme zircons using the ion microprobe at UCLA. Preliminary data shows good agreement between the mean age from the ion microprobe analyses and the mineral isochron. This indicates a relatively simple crystallization history for the sample. In addition to the work with zircon, we plan to use the laser to examine fracture materials obtained from the NOPAL I uranium ore deposit in Chihuahua, Mexico. We will compare mineral and spatial rock analyses with whole rock results obtained by TIMS as well as ion microprobe data from Mustafa Fayek at ORNL in order to better understand the extent and timing of radionuclide migration at this analog for Yucca Mtn.

Kinetic Isotope Fractionation during Mass Transport

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The experimental results that I will present have as their common theme kinetic isotopic fractionations associated with mass transport between or within phases. The classic example of isotope fractionation by transport between phases is that associated with evaporation, which to date we have studied in the high-temperature limit where equilibrium fractionations are generally negligible compared to the kinetic isotopic fractionations. New high-precision isotopic measurements of Mg and Fe (and preliminary data on Si) in evaporation residues show that the usual assumption that the kinetic isotope fractionation factor (i.e, the isotope ratio of the flux relative to that of the substrate) is equal to the inverse square root of the mass of the evaporating species is rarely correct. Both this and the fact that we resolve a temperature dependence to the kinetic isotope fractionation even at very high temperatures presents an interesting challenge for understanding the chemical physics of the evaporation process.

Laboratory experiments have also been used to study kinetic isotope fractionation by diffusive transport in both silicate and aqueous fluids. As one example of this work I will show the isotopic fractionation of Li, Ca, and Mg that takes place during the interdiffusion of a natural rhyolite and a MORB basalt. The isotopic fractionation of Li ($\delta^7\text{Li}\sim 40\text{‰}$) was measured by SIMS (secondary ion mass spectrometry), that of Ca ($\delta^{44}\text{Ca}\sim 6\text{‰}$) by double spike TIMS (thermal ionization mass spectrometry), and Mg ($\delta^{26}\text{Mg}\sim 5\text{‰}$) by Laser ablation MC-ICPMS (multi-collector coupled plasma mass spectrometry). Even those that were the most scathing in their skepticism regarding the likelihood of measurable isotopic fractionations by diffusion in molten silicates are now quite vociferous in letting us know that they could have predicted the outcome of our experiments, which goes to show that knowing the answer is the surest way of predicting the answer.

The move to expand our study of isotope fractionation by diffusion to include water led to almost the exact reverse of our experience with silicate liquids. The skeptics now predicted large effects (as had also been claimed in some earlier studies) and yet we found little or no isotopic fractionation associated with ions diffusing in water. The experimental design we use is a Rayleigh fractionator that amplifies even very small fractionations, which we validated by measuring the fractionation of K from Li quantitatively consistent with their known relative diffusion rates in water. An interesting point regarding the distinctiveness of water (or of silicate liquids if you prefer) is that in water K diffuses faster than Li, while in a silicate melt, the diffusion coefficient of Li is 100 to 1000 times larger than that of K. We found the isotopic fractionation of ions diffusing in water to very small in the case of Li and Cl, and negligible in the case of Mg.. The explanation for this is very likely due to the fact that water is a strongly polar liquid and that the diffusing units are significantly heavier than the ions themselves due to hydration. We believe the earlier reports of significant Li isotope fractionation during the diffusion of LiCl in water misinterpreted their results and that the isotopic fractionations actually occur by transport across membranes, not in water itself.

Theoretical and Simulation Study for the Isotopic Properties of Fluids

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A quantitative understanding of the isotopic properties of water and other fluids are of great importance to the interpretation of isotopic behavior in crustal and mantle systems at elevated pressures and temperatures. Statistical-mechanical calculations of isotope effects are based on the behavior of isolated molecules, i.e. ideal-gas at infinitely low pressures. We have been conducting theoretical and simulation studies to investigate the isotopic properties of fluids under realistic geologic conditions.

First, we have developed a simple, yet accurate theoretical method for calculating the reduced isotope partition function ratio (RIPFR) of water at elevated pressures. This approach requires only accurate equations of state (EOS) for pure isotopic end-members (H_2O and D_2O), which are available in the literature. For gaseous and low-pressure (ca. ≤ 15 MPa) supercritical phases of water, the RIPFR increases slightly (1 – 1.3 ‰) with pressure or density in a fashion similar to those of many other geologic materials. However, in liquid and high-pressure (>20 MPa) supercritical phases, the RIPFR of water decreases (2 – 5 ‰) with increasing pressure (or density) to 100 MPa. This rather unique phenomenon is ascribed to the inverse molar volume isotope effects (MVIE) of water, $V(\text{D}_2\text{O}) > V(\text{H}_2\text{O})$, while other substances show the normal MVIE, including minerals. These theoretical predictions agree with an experimental study by Horita *et al.* (2002) for the system brucite – water.

A second approach is based on classical, molecular-based simulations (NVT-Molecular Dynamics and Gibbs Ensemble Monte Carlo). First, vapor – liquid and vapor – solid isotope fractionation factors of simple atomic molecules ($^{36}\text{Ar}/^{40}\text{Ar}$, $^{20}\text{Ne}/^{22}\text{Ne}$, $^{80}\text{Kr}/^{84}\text{Kr}$) was predicted using the \hbar^2 -order Kirkwood-Wigner free energy expansion for specific Lennard – Jones parameterizations (Chialvo and Horita, 2003). Our simulation results compare very well with the existing experimental data, including the composition dependence of the corresponding fractionation factors for binary *Ar–Kr* mixtures. This approach is currently being extended to polyatomic molecular systems of geochemical interest (O_2 , N_2 , CO , and H_2O), and the advantages and limitations of these theoretical and simulation approaches are discussed.

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Reference

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Carbon Isotope Exchange during Hydrocarbon Maturation: Constraints from Laboratory Experiments and Field Data

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Despite the widespread application of carbon isotopic analysis as a tool to determine the thermal maturity and source of oil and natural gas, geochemical processes that regulate the carbon isotope composition of individual hydrocarbons at elevated temperatures and pressures are poorly understood. We have conducted a series of laboratory experiments to identify specific reactions that may influence the isotopic composition of low molecular weight hydrocarbons in natural gas. In particular, the role of carbon isotope exchange between aqueous carbonate and hydrocarbons has been investigated.

Aqueous organic acids were heated at 250 to 350°C with and without a vapor phase present. All experiments initially contained 20 to 70 mmolal of C₂-C₅ straight chain organic acids and 100 mmolal H₂ and 99.9 % ¹³C labeled CO₂. No minerals were added to the experiments. Variations in the isotopic composition of C₂-C₅ organic acids revealed extensive exchange of carboxyl carbon at 250 to 350°C according to the reaction:



The rates of reaction (1) increased with increasing temperature and decreased with increasing organic acid chain length. The rate of carboxyl exchange decreased slightly upon creation of a headspace, a likely result of reduced reaction rates for volatile acids that had partitioned into the vapor phase. Extensive reduction of aqueous organic acids to their corresponding *n*-alkanes resulted in the production of ¹³C labeled hydrocarbons during the experiments. In natural systems, aqueous organic acids may be generated as reaction intermediaries during the oxidative degradation of long chain *n*-alkanes and exchange carbon with aqueous carbonate species. The subsequent reduction of these acids provides a reaction pathway for the incorporation of carbonate carbon into petroleum hydrocarbons.

Examination of carbon isotopic trends for short-chain *n*-alkanes, carboxylic acids, and CO₂ associated with petroleums from a variety of environments suggests similar exchange reactions may be occurring in nature. Accordingly, models that describe the isotopic evolution of short-chain hydrocarbons during the thermal maturation of petroleum may need revision to include the effects of carboxyl exchange reactions.

Using Comprehensive Two-Dimensional Gas Chromatography to Explore Transformation Processes Acting on Petroleum Hydrocarbons

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Comprehensive two-dimensional gas chromatography (GC×GC) can provide nearly complete composition data for petroleum hydrocarbons. However, the potential wealth of physical property information contained in the corresponding two-dimensional retention time maps has remained largely untapped. We developed a simple but robust method to estimate GC×GC retention indices. By exploiting alkanes as reference solutes in both dimensions, calculated retention indices were insensitive to uncertainty in the enthalpy of gas stationary-phase transfer for the analyzed compounds. Thus, we circumvented a difficult barrier to generating GC×GC retention indices. The resulting two-dimensional retention indices successfully explained more than 99 percent of the variability in both the molecular sizes and polarizabilities of a representative subset of diesel fuel compounds. These two molecular properties (size and polarizability) were found to control the partitioning behaviors of diesel fuel hydrocarbon solutes in several liquid phases. As a result, GC×GC retention indices can be used to estimate the liquid vapor pressures, aqueous solubilities, octanol-water partition coefficients, and vaporization enthalpies of a complete set of diesel-range hydrocarbons. These powerful relationships will allow rapid and incisive analysis of phase transfer processes affecting fuels and oils. Examples of using GC×GC retention data to deconvolve the effects of subsurface and surface processes such as gas washing, water-washing and volatilization on petroleum hydrocarbons will be discussed.

Oxide Melt Solution Calorimetry of Sulfides

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Sulfides, selenides, arsenides, etc. form an important class of Earth materials- beneficial as metal ores but problematic as pollutants. Similar materials are also important in technology as semiconductors, phosphors, quantum dots, and sensors. Many sulfide systems are characterized by complex structures and large homogeneity ranges. Fundamental thermochemical data for such materials are rather incomplete, reflecting the difficulty of calorimetric measurements of heats of formation. Yet such data are essential to both understanding of structure-property-provenance relations and to materials processing and contaminant control. Based on earlier experience with nitrides and sulfates, we have developed a general approach to measuring heats of formation of sulfides using high temperature oxide melt calorimetry.

Oxidative drop solution calorimetry is being developed as a general method for sulfide thermochemistry. The samples are dropped from room temperature into molten $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ solvent at 975 K, with oxygen bubbling through the melt to ensure rapid and complete conversion of sulfide to dissolved sulfate. Complete dissolution of sulfides and retention of sulfur in the solvent is documented by furnace tests and visual observation, consistent determination of enthalpy of drop solution, and comparison with previous data for the heat of formation of ZnS, PbS and CdS. Enthalpies of formation (kJ/mol) from the elements (ΔH_f°) are determined for sphalerite (ZnS) (-206.53 ± 4.03 kJ/mol), galena (PbS) (-98.12 ± 4.37 kJ/mol), greenockite (hexagonal CdS) (-148.79 ± 4.13 kJ/mol) and hawleyite (cubic CdS) (-147.65 ± 4.28 kJ/mol). Thus, hawleyite appears to be energetically very similar to greenockite but possibly slightly metastable by about 1 kJ/mol. The results confirm that oxidative drop solution calorimetry in molten sodium molybdate is a viable method for sulfide thermochemistry. It will be most useful for sulfides with moderate heats of oxidation (e.g. the Fe-S, Co-S, and Ni-S systems), and should be applicable to ternary compounds, e.g. the Fe-Ni-S and Ni-Co-S systems; and systems showing large homogeneity ranges, as well as to other chalcogenides and pnictides.

Analyzing Li and B isotopes by SIMS

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Over the last several years, we have been studying the fractionation of light stable isotopes between diagenetic minerals and water. Our ultimate goal is to obtain chemical information on diagenetic clay minerals in thin sections to trace the migration of hydrocarbons. Because of our need for microanalyses of light stable isotopes, we have worked with secondary ion mass spectrometry (SIMS). These efforts have revealed many analytical issues in general, giving our work an impact broader than hydrocarbon research.

Matrix effects on Li and B isotope measurements. Comparison of SIMS and bulk analyses of boron isotopes in clay minerals and many other matrices (rhyolitic, andesitic, and basaltic glasses) has shown that the role of chemistry on influencing the measured $^{11}\text{B}/^{10}\text{B}$ ratios is small, allowing quantitative analyses even if the clay chemistry varies. We do not yet know if the same is true for Li isotope measurements of different clay minerals because the availability of appropriate bulk-analyzed materials to test is extremely small. Preliminary work suggests that olivines, clinopyroxenes, and anhydrous basaltic glasses show similar SIMS calibrations, but we find that many bulk analyzed materials show isotopic zoning within a crystal or glass fragment (e.g., 10 ‰ or more).

Sample preparation for clay minerals. Lithium and boron are adsorbed to clay mineral surfaces and are common substituents in the interlayer of expandable clays. Because elements at these locations are easily exchanged, we have made a major effort to remove adsorbed and interlayer species prior to analysis so that our boron and lithium isotopic analyses represent elements in the tetrahedral and octahedral layers of the clay mineral, respectively.

Li and B isotopes in clay minerals and size fraction. An exciting development has been the observation that the boron and lithium isotopic composition of naturally occurring clay minerals sometimes varies with size fraction. Hydrothermal experiments (300 °C, 100 MPa) reacting montmorillonite to illite have been conducted, and the isotopic compositions were measured as a function of reaction progress and size fraction. These data show Li and B isotopic differences on the order of 10‰ between $>2\mu\text{m}$ and $<0.2\mu\text{m}$ size fractions. Preliminary interpretation suggests that the larger size fraction represents crystals growing in equilibrium with the fluid while smaller crystallites did not grow after nucleation and did not exchange over the duration of the experiment. One implication is that diffusion does not isotopically re-equilibrate clay minerals (at 300°C); rather that precipitation of new growth is required for isotopic re-equilibration in low temperature environments.

SIMS analyses of fluids. We have carefully controlled the chemistry of our starting water and minerals, but have only been able to analyze the solid run products. We recently conducted a test using our experiment water (1000 ppm B, 0 ‰ $\delta^{11}\text{B}$) adsorbed onto B-free synthetic clay (Syn-1). When the sample was dried at room temperature, SIMS analysis of the adsorbed-B returned $0 \pm 1.4\text{‰}$ and ~ 1002 ppm boron ($\pm 3\%$). This suggests that analysis of coexisting solids *and* fluids is possible by SIMS.

Experimental Studies of Fundamental Hydrothermal Processes Employing *In Situ* pH Monitoring and other Unique Approaches

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Dense, complex aqueous solutions are the ubiquitous fluxes of Earth-surface and shallow-crustal geochemical processes. The pH might be considered the master variable in such processes, controlling the nature and reactivity of dissolved organic and inorganic species; the rates of dissolution, precipitation and organic decomposition reactions; the charge and ion-sorption capacities of mineral surfaces; and the nucleation, reactivity and transport of naturally-occurring nanoparticles. The ability to accurately and precisely monitor the solution pH by potentiometric measurement of the activity of H^+ , H_3O^+ , or OH^- (through the known self-dissociation constant of water) over wide ranges of temperature, pressure and solution composition was first made possible by the invention of the hydrogen electrode concentration cell at Oak Ridge National Laboratory (Mesmer et al., *J. Phys. Chem.*, v74, p.1937-42, 1970). This and similar experimental systems, such as our sulfate-electrode concentration cell (Xiao et al., *Environ. Sci. Technol.*, v36, p.166, 2002) have been employed by ORNL's Aqueous Chemistry and Geochemistry Group to investigate many of the homogeneous and heterogeneous reactions and species of interest to geochemists studying global elemental cycling, weathering, geothermal and hydrocarbon reservoir dynamics, waste remediation, biogeochemical processes, and so on.

Our hydrogen-electrode cells operate from 0 to 295°C at pressures from liquid/vapor saturation to several hundred atmospheres, and aqueous reactions can be investigated across the entire pH range of natural and industrial systems with resolution up to 0.0001 pH units and accuracy on the order of 0.01 pH units in experiments lasting as much as a month or more. By using these cells to determine the acid/base properties of non-complexing aqueous pH buffers at elevated temperatures and pressures, we have been able to conduct parallel mineral-solution interaction studies in packed-column, flow-through cells to 350°C and 500 atmospheres, with highly accurate pH control.

In earlier stages of the ongoing project named above, we focused primarily on homogeneous aqueous speciation and reactions, such as the hydrolysis of metal ions and the acid/base properties of organic and inorganic ligands of importance in natural systems. More recently, we began investigating heterogeneous reaction equilibria, such as mineral solubilities, surface charge and ion adsorption, and have published the world's only direct measurements of the latter at temperatures above 100°C. Currently, we are focusing on the kinetics of mineral dissolution and precipitation, the thermal decomposition of organic acids and redox-metastable reactions. Highlights of our current studies include the remarkable persistence of hematite resulting from magnetite dissolution under highly reducing conditions at 100-250°C, and the determination of limiting reaction rate slopes of mineral dissolution and precipitation reactions at very-near-equilibrium conditions. Future studies will include determination of the rates of nanoparticle nucleation, growth and dissolution with pH used as the reaction progress variable, obviating the need for extensive sampling. We are also developing new high temperature electrodes for use under oxidizing conditions.

Mineral-water Interface Structure and Reactivity: New Insights from High Resolution X-Ray Scattering

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A central challenge for understanding geochemical processes is the need to fully resolve the complexities of mineral-water interfaces, which may include structural, chemical and elemental components, and either kinetical or thermodynamical control. Synchrotron-based X-ray techniques (Fenter et al., 2002) are ideally suited to meet this challenge as X-rays readily penetrate matter (especially water), and have: molecular-scale ($< 1 \text{ \AA}$) structural resolution, direct chemical and elemental sensitivities, and the ability to probe dynamically evolving systems in real-time. We have been applying and developing such synchrotron based techniques to provide new insights into fundamental aspects of mineral-water interactions. Substantial progress has been made in understanding the structure of interfacial water adjacent to mineral-water interfaces, the adsorption of ions to the mineral-water interface, and the dissolution of feldspars. Recent technical advances have also allowed us to acquire and analyze data substantially faster (Fenter and Park, 2004, Fenter and Zhang, 2005).

The structure and properties of water at interfaces are fundamental to all solid-liquid interfacial phenomena. High-resolution specular X-ray reflectivity has provided new insights into the vertical and lateral distribution of water molecules immediately adjacent to mineral surfaces, with recent results for calcite (104) (Geissbuhler et al., 2004), and fluorapatite (100) (Park et al., 2004). These results, and others, were reviewed revealing that interfacial hydration layers are a general feature of mineral-water interfaces and showing that their properties are strongly controlled by interaction with the mineral substrate (Fenter and Sturchio, 2004).

Measurements of ion adsorption and incorporation using traditional methods were used to explore the interaction of uranyl with calcite (Kelly et al., 2003; Rihs et al. 2004). We also demonstrated and applied a new “X-ray Standing Wave imaging” approach for the first time (Cheng et al., 2003; Zhang et al., 2004; Bedzyk et al., 2004) to probe ion adsorption at the oxide-water interface. A lack of interface specificity of these techniques, however, limits the range of systems that can be studied. To address this limitation, we have recently established a new approach for simultaneously probing geometric and spectroscopic structures at the mineral-water interface that combines the interface specificity of X-ray reflectivity with the chemical sensitivity of X-ray absorption spectroscopy (Park et al., 2005). This “resonant anomalous X-ray reflectivity” (RAXR) is ideally suited to probe complex interfacial processes, especially for understanding the correlated changes in geometric structure and oxidation states that often can only be studied separately. In this case, the interface specificity of RAXR allowed us to probe the structure and spectroscopy of an outer-sphere species under conditions that were inaccessible to X-ray fluorescence based techniques (X-ray absorption spectroscopy or X-ray standing waves).

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Geochemical Studies using Surface Scattering and Microprobe Analysis at GSECARS

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The GSECARS science program encompasses research on geochemical processes at length scales from the atomic and molecular level to the planetary scale. Surface spectroscopies and scattering techniques are used to obtain fundamental knowledge on the structures of surfaces, how these surfaces are modified during hydroxylation and dehydroxylation processes, sorption reactions that occur on these surfaces and the role of biota in controlling the stabilization of toxins and contaminants on these surfaces. Crystallography techniques are used to determine the structures of complex minerals and, in particular, how contaminants and strategic elements are incorporated in these minerals with the goal of providing fundamental information on transport mechanisms and encapsulation strategies. X-ray microprobe techniques are used for fundamental geochemical studies of the complex heterogeneous systems such as soils including redox reactions that occur during diffusion, the complex interplay between roots and soils in controlling the sequestration of metals, the chemical nature of hydrothermal fluids and melts as recorded by fluid and melt inclusions in minerals, and development of oxygen barometers for igneous materials. Element-specific tomographic imaging techniques are used to study the chemical properties of systems during reactions, diffusion and fluid transport.

Example studies include the following:

A Novel Microreactor for In Situ Observations of CO₂ Sequestration via Mineral Carbonation (M. McKelvy et al.). Initial studies have focused on the optimal process to date, in which the 0.64 M NaHCO₃ + 1.0 M NaCl aqueous solution reacts with the heat-activated meta-serpentine feedstock under supercritical CO₂ at moderate temperatures and pressures (e.g., 150 atm CO₂ and 180°C).

Oxybarometer for Igneous Materials Based on Vanadium Valence (S. Sutton et al.). A promising proxy for oxygen fugacity is the valence of vanadium because it has a large number of possible valence states in nature (2+, 3+, 4+ and 5+) and is ubiquitous in earth materials. The XANES-based method has been applied to terrestrial basaltic glasses (as well as those from the Moon and Mars) showing good agreement with inferences by other approaches.

Microbial versus Abiotic Dissolution of Volcanic Glasses (A. Templeton et al.). Bacterial activity may alter the rates and mechanisms of glass dissolution, which can significantly affect the flux of important cations over geological timescales. Surface-sensitive scattering and spectroscopic techniques are being employed to measure changes in Fe and Mn distribution and speciation at the angstrom to nanometer scale. Much greater rates of glass alteration are induced by Fe-oxidizer biofilms.

Microtomographic Imaging of Intra-granular Solute Diffusion (T. Tokunaga et al.). Element-specific microtomographic methods are providing the opportunity for time-resolved study of chemical diffusion within individual natural soil grains. One such study is attempting to directly test the importance of intragranular diffusion in interactions between uranium (VI) and sediments from Oak Ridge National Laboratory, a DOE facility where U waste solutions have contaminated some sediments.

Insights into the Geochemistry of Contaminants using Combined Synchrotron X-ray Microbeam Diffraction, Absorption Spectroscopy, and Fluorescence Analysis at NSLS X26A

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Analytical techniques with high detection sensitivity and high spatial resolution are crucial for understanding the chemical properties of complex earth materials and environmental samples. These so-called “microprobes” have become workhorses of the geochemical community as well as important tools for environmental scientists. Synchrotron based x-ray microprobes such as X26A at the National Synchrotron Light Source typically operate with spatial resolutions in the μm range and yield elemental sensitivities using synchrotron x-ray fluorescence (SXRF) in the sub-mg kg^{-1} range. They offer distinct advantages for geochemical studies because they allow for wide versatility in sample state, including in-situ analyses of liquids and hydrated solids. Another unique capability is spatially resolved applications of X-ray absorption fine structure spectroscopy (XAFS) for the determination of chemical speciation. Thus, not only can one obtain the concentration of a trace element but also its oxidation state, coordination number, and the identity of nearest neighbors. This capability has proven particularly useful in studying the biogeochemistry of toxic metals in the environment, particularly because of the often reside in materials that are heterogeneous at micron length scale and since their toxicity is chemical-species dependent.

Within the last several years, these x-ray microprobes have incorporated microbeam x-ray diffraction (μXRD) capabilities into their beamlines through the addition of CCD area detectors. The high beam intensity of these synchrotron based microprobes favors the use of CCD detector technology for its fast readout speed over the much slower imaging plate technology. This μXRD capability allows for direct mineralogical characterization with high spatial resolution and rapid read rates. Additionally, this allows for μSXRF , μXAS , and μXRD data to be collected in-situ near simultaneously and potentially imaged in two dimensions.

Several examples of such coupled studies from X26A will be presented. One example involves arsenic-rich sub-aqueous gold mine tailings and lacustrine sediments from Yellowknife Bay, NWT, Canada (Walker, et al.) Sixty years of mining and roasting gold ores in the Yellowknife area (Canada) has left a complex legacy of arsenic-bearing tailings, soils and sediments. Identifying the mineralogical form of the arsenic in solid phases is critical for understanding arsenic behavior and assessing stability in various geochemical environments. Results of μXAS indicate that fresh flotation tailings contain only sulfide-bound arsenic (As^{-1}). Coupled μXRD and μXAS analyses show that roaster-generated hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) in all ages of tailings contain arsenic in mixed oxidation state (As(V) and As(III)). In contrast, iron oxyhydroxides formed by weathering of pyrite (FeS_2) and arsenopyrite (FeAsS) contain only As(V) . The presence of iron oxide phases possessing high levels of As(III) (most toxic arsenic species), even after 50 years of residence in unsaturated, oxidizing tailings, suggests the arsenic represents a long term environmental hazard. Similar coupled studies of Yellowknife Bay sediments show that arsenic is almost exclusively trivalent in aggregates from 10.5 cm depth. μXRD and μXRF analyses in these sediments show that As is hosted by several mineral phases, including iron oxides, layer silicates, and a non-sulfidic Fe component. Although

μ -XRD reveals for the presence of maghemite and hematite, μ XAS shows that As(V):As(III) ratios are significantly lower compared to the arsenic ratios of roaster oxides at the submerged beach tailings. It is hypothesized that iron oxide phases are persisting in reduced sediments and microbial activity has mediated the transformation of significant amounts of pentavalent arsenic into the trivalent form.

Water at Mineral Surfaces: New Information from Phase-Sensitive Sum Frequency Vibrational Spectroscopy (PS-SFVS)

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Despite the critical importance of understanding molecular structure and processes at the solid-water interface, research in this field has been held back by the inability to quantitatively compare models and experiments. From the experimental side few techniques can be used to investigate water structure just at the interface, and all such techniques have limitations. X-ray reflectivity can yield the positions of surface waters as long as there is sufficient order present at the interface, but cannot sense less ordered structure or the position of protons. Neutron reflectivity offers a way around that problem but may never be sensitive enough to probe single crystal/water interfaces in other than bulk (multi-crystal) aggregate samples. X-ray emission spectroscopy offers another new route to structural information, but is limited by burial of the interface under at least multiple layers of water (unless one is studying just “sorbed” isolated water molecules). Hence the prevailing techniques used are non-linear spectroscopies optical second harmonic generation (SHG) and sum-frequency generation (SFG). The basic processes of these techniques are forbidden in media with inversion symmetry, but allowed at interfaces, creating high surface-specificity and sensitivity to the net polar ordering at the interface even under thick (cm) solution coverage. In addition, the techniques are sensitive to sub-monolayer concentrations of molecules at an interface, and can be applied to systems in vacuum, at high temperatures, at solution/gas interfaces, and under a wide range of conditions.

Despite much success, especially on the gas/water interface, SFVS results have been difficult to interpret or compare with theory or simulations. Part of the difficulty is due to the usual application of the experiment, which discards the phase information and uses only the net spectral magnitude. Because of this, largely similar spectra have been subject to fairly wide-ranging detailed interpretations, leading to a great deal of confusion. We have developed a SFVS application that recovers the real and imaginary parts of the spectrum, and hence the phase information [1] resulting in a complete spectrum of the interface. This allows determination of net molecular dipole orientations, and hence greatly improves our ability to interpret SFVS spectra. In this talk the technique is described, as well as the way in which we have analyzed spectra for the quartz (0001)/water and quartz (10-10)/water interfaces. Results are in general good agreement with MD simulations performed by our collaborators, and with common-sense pictures of water binding at the protonated (0001) surface. In particular, our findings are consistent with a molecular model in which interfacial water molecules arrange so as to minimize the number of broken hydrogen bonds. Water molecules can create hydrogen bonds by pointing their hydrogen side to the surface oxygens and by pointing their oxygen side to the hydrogen of a SiOH. In the protonated surface case (low pH), the two types of hydrogen bonds coexist, while as the pH increases and the surface becomes deprotonated, the hydrogen orientation toward the surface prevails. There is also a considerable difference in the response of interface water having ice-like local hydrogen bonding from that of more liquid-like water to increasing pH and surface charge [2]. The changeover in dipole orientation of the liquid-like

waters occurs at relatively low pH values (low surface charge), while the ice-like water component undergoes reorientation at a relatively high pH range (highly charged surface).

[1] Ostroverkhov, Waychunas and Shen PRL 94, 046102 (2005).

[2] Ostroverkhov, Waychunas and Shen Chem Phys Lett 386 (2004) 144-148.

Probing the Electronic States of Molecules in Aqueous Solutions and at Interfaces

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The reactivity and behavior of molecules in the environment are determined by their electronic states. While probing the electronic states of different atoms and molecules in clean aqueous solutions is complicated by the experimental difficulties associated with the collection of their electronic spectra, studies of molecules in heterogeneous natural systems were almost impossible until recently. The recent developments in different X-ray techniques permitted the direct probing of the chemical states of molecules containing high atomic number elements at concentrations representative of natural systems. However, X-ray absorption by air limits the probing of the electronic states of several molecules of geochemical interest, such as water, organic molecules and other chemical species composed of elements of low atomic number in aqueous solutions. We developed a soft X-ray synchrotron endstation to probe the chemical states of such species in aqueous systems and at particle-water interfaces. Using this analytical system, we are probing the structure of water and its variations with pH, the chemical state of water in the solvation shells of ions, and the functional group chemistry of biological macromolecules in aqueous solutions and at interfaces. A detailed discussion of applications of soft X-ray spectroscopy to the studies of above systems will be presented.

First-principles Simulation of the Solvation Structure and Deprotonation Reactions of Ore Forming Metal Ions in Very Nonideal Solutions

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Recent advances in algorithms and computational performance have allowed the atomic level simulation of properties of complex nanoscale materials using interparticle forces calculated directly from an accurate solution to the electronic Schrödinger equation. These 1st principles simulation methods have provided chemical interpretations of very complex systems with an unprecedented level of accuracy and detail. The structure of the solvation region neighboring an M^{3+} ion in an aqueous solution is very different from that of bulk water. The many-body behaviors of the ion-water and water-water interactions in this region are difficult to capture with conventional two-body or even three-body potentials. 1st principles force calculations provide the needed flexibility. However, large numbers of waters (up to 128 waters) are needed to fully describe chemical events in the extended hydrations shells. Long simulation times are required to reliably sample the system. Taken together this makes simulation at the 1st principles level a very large computational problem. Our simulation results using these methods agree remarkably well with the measured octahedral structure of the 1st solvation shell of Al^{3+} . Our calculated average 2nd shell radius is also in excellent agreement with the measured value. Less can be determined experimentally about the structure of the 2nd shell. Our simulations suggest that this shell contains roughly 12 water molecules, which are trigonally coordinated to the 1st shell waters. This structure cannot be measured directly. However, the number of water molecules in the 2nd shell predicted by the simulation is consistent with experimental estimates. Tetrahedral bulk water coordination reappears in the third shell. We see qualitative changes in the structure of the third shell in changing from 64 to 128 water molecules in the simulation. Simulations with 128 waters are close to the maximum size that can effectively be performed with present day methods. While the time scale of our simulation are not long enough to observe transfers of waters from the first to the 2nd shell, we do see transfers occurring on a picosecond time scale between the 2nd shell and 3rd shell via an associative mechanism. This is faster than, but consistent with, the results of measurements on the more tightly bound Cr^{3+} system. For high temperature simulations, proton transfers occur in the solvation shells leading to transient hydrolysis species. The reaction coordinate for proton transfer involves the coordinates of neighboring solvent waters as in the mechanism for proton transfer in bulk water. Directly removing a proton from the hexaqua Al^{3+} ion leads to a much more labile solvation shell and to a five coordinated Al^{3+} ion. This is consistent with very recent rate measurements of ligand exchange. For the Al^{3+} - H_2O system results for high but subcritical temperatures are qualitatively similar to room temperature simulations. However, preliminary simulations for supercritical temperatures suggest that there may be a dramatic change in behavior in the solvation structure of ions above the critical temperature. For transition metal ions the presence of d valence electrons plays a significant role in the behavior of the system. Our preliminary results for the Fe^{3+} ion suggest that this ion which is larger radius than the Al^{3+} ion has somewhat less rigid 1st and 2nd solvation shells. Results for the solvation structure of Fe^{3+} will be presented as time allows. In addition we will discuss various improvements of our methods that will lead to more accurate predictions, for example, the implementation of exact-exchange and the inclusion of many more molecules through the coupling of the region described by fully quantum methods with a much larger region described by molecular mechanics interactions.

Computational and Experimental Investigations of Water and Solute Species on Mineral Surfaces and in Confined Spaces

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Computational molecular modeling can provide otherwise unobtainable molecular scale insight into the structure, dynamics, and energetics of the interaction of water and solute species with mineral surfaces and in confined nano-spaces such as mineral interlayers. We describe here three sets of studies that take advantage of these capabilities. One is a series of combined experimental and molecular dynamics (MD) modeling studies of the interaction of carboxylic species and amino acids with layered double hydroxides (LDHs), another is an MD study of water sorption on the (001) surface of quartz that helps clarify previously published sum frequency generation spectroscopic data for this surface, and the third is a novel 2-dimensional ice structure predicted to form at elevated pressures between two talc surfaces. The MD simulations of the LDH-organic systems were carried out using a new combination of the CLAYFF force field for the inorganic mineral substrates and the CVFF force field for organic species. This combination provides significantly improved capability to model the interaction of organic and biomolecular species with minerals. For the Mg,Al LDH hydrotalcite, NMR data show that the ^{13}C chemical shifts of citrate and glutamate are little effected by incorporation in the interlayer or interaction with the surface, and for glutamate the pH dependence is essentially the same as in bulk solution. ^{27}Al NMR confirms the absence of crosslinking. XRD shows large and unexpected interlayer expansion for both. MD modeling of the structure, dynamical behavior and hydration energetics of these systems and hydrotalcite with a series of smaller carboxylic species in the interlayer demonstrate that the origin of the observed behavior is due to a preference of the surface for water molecules over carboxylic groups and the need to both solvate the organic anions and develop a coherent H-bond network among the surface, anions and water molecules within the interlayer and across the surface. Natural organic matter develops much of its negative charge in solution due to deprotonation of carboxylic groups, and similar phenomena are likely to control its interactions with mineral surfaces. For hydrated quartz (001), the MD results again show a structure controlled principally by the development of a coherent H-bond network among the surface and water molecules. The near-surface water forms well ordered 2-dimensional arrangement of $\text{O}_{\text{H}_2\text{O}}$ with disordered H positions due to dynamical H-bond reformation. The results show that the “ice-like” and “water-like” bands observed in the sum frequency spectra are not due to the presence of near-surface ice-like and water like regions, but to the effects of relatively weak and strong H-bonds that are distributed across the surface. Power spectra of O-H stretching computed by Fourier transformation of the velocity auto-correlation functions show strong vibrational anisotropy at the surface and suggest stronger H-bonding between the surface Si-OH and $\text{O}_{\text{H}_2\text{O}}$ than among water molecules. The predicted high pressure ice in talc follows the ice-rules for H-bonding, is similar in some ways to ice Ih, but includes H-bond interaction with the talc surface.

Carbonate Mineralization and Interface Chemistry: Sensing Compositional Heterogeneities with Scanning Probe Microscopy

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Structure, composition, and reactivity of mineral surfaces in fluid environments are important characteristics used in chemical reactive transport modeling in groundwater. Characterization of mineral surface microtopography by scanning probe microscopy provides, for example, valuable surface site distribution and dynamic information from in-situ measurements. However, these types of studies often implicitly assume that the surface and interface structure and composition are fairly well defined based on knowledge of the bulk solid and liquid composition and application of various macroscopic interface models. Part of this presumptive tendency lies in the relative lack of chemical sensitivity in the scanning probe microscope. But perhaps more important (and directly relevant to the problem of low-temperature geochemical modeling) is that real mineral surfaces are difficult to characterize due to their complexity. Therefore, advancing our characterization methods to meet the needs of real system studies is crucial.

Studies on various chemically-modified surfaces over the past decade utilizing chemically-modified SPM tips has revealed that the lack of chemical sensitivity may be overcome by focusing on the forces of interaction at the tip-surface interface. In our in-situ studies of crystal growth at carbonate mineral surfaces, we have employed friction force microscopy in conjunction with topographic imaging as a means toward describing the chemical properties of monolayer growth/sorption. The self-limiting nature of the growth on dolomite under room temperature provided an ideal template for frictional force studies, where both monolayer regions and the original dolomite surface co-exist leading to image contrast in the friction micrograph, while topographic and deflection signal images showed no difference between the two regions. By varying the cantilever load applied to the surface, friction vs load data were obtained and unexpected non-linear trends in the data were observed. Differences between the native dolomite and monolayer surface terminations, while obvious in the friction images, were subtle in the complete friction characterization. The repeating structure of the friction data suggests deformation and penetration of discrete layers by the AFM tip. Examination and modeling of total stiffness of the cantilever and contact through friction loop measurements revealed that the contact could not simply be modeled (mechanically) as though it were comprised of the two bulk materials of the tip and sample (silicon and dolomite), but that the interface reduced the effective shear modulus of the substrate as would be expected if the tip was capable of wearing through the interfacial region with increasing load. While a quantitative model is not yet possible for predicting the relationship between the friction/stiffness measurements and interface composition, preliminary in-situ x-ray reflectivity studies of dolomite-water interfaces have offered new insights into the contrast mechanism important in friction imaging.

In related work, calcite and barite crystal growth were investigated to characterize the dynamics of individual molecular attachment at surface step edges. In principle, the length dependent behavior of elementary steps is directly linked to the dynamics of ion attachment and detachment from surface sites. In these studies, step speeds at very short step lengths (< 300 nm) are generally found to increase with step length, but the observations are dependent on the

experimental parameters chosen and thus, potentially biased. When these parameters were optimized, data scatter precluded quantitative comparison of different theoretical growth models in light of the experimental data. Analysis of experimental errors revealed that significant experimental bias in the determination of step edge properties such as the edge free energy and kinetics of kink propagation and nucleation are introduced if the instrument bandwidth is not appropriate for the specific dynamics of the step edge. In light of step growth models based on either equilibrium assumptions or non-equilibrium assumptions, these biases tend to favor one model over the other.

Investigating the Physical Basis of Biomineralization

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An urgent research need in biomineralization science is a fundamental understanding of kinetic and thermodynamic controls on the morphology and compositional signatures of minerals formed in complex systems. Through our work on interrelated research problems, we are uncovering a broad-based and mechanistic understanding of these controls on growth, nucleation, as well as dissolution processes. Four projects are highlighted:

1) The paradigm of "stereochemical recognition" has been popularized to explain the ability of organisms to produce crystals with shapes that differ dramatically from those obtained during laboratory growth from pure solutions. Because biominerals typically contain significant levels of inorganic and macromolecular species, stereochemical matching of macromolecules to the crystal lattice of otherwise unexpressed faces leads to their stabilization, presumably by lowering surface energies, thereby generating a new crystal shape. Our *in situ* AFM investigations of a number of crystal-impurity systems argue for a change in this concept. We find that the growth kinetics and crystal habit are defined by modifications to atomic steps on existing crystal faces and that the degree of modification on a given face is step-specific. Changes in macroscopic crystal shape mimic the modifications seen at the atomic level. While the exact mechanism of growth modification differs in each system, these systems share the common feature that the molecular-scale interaction that drives crystal modification can now be fully understood and modeled on the basis of step-impurities interactions. Molecular models that calculate the modifier-crystal interaction energy support these conclusions.

2) Conventional analysis of mineral growth from aqueous solutions is based on the Gibbs-Thomson (GT) effect, a thermodynamic principle that relates the size of atomic features on a crystal face to the driving force for crystallization. Experimental results obtained on calcite in recent years using AFM call into question the basic GT requirement that thermal fluctuations along step edges on a crystal face are fast enough to assure that step growth is controlled by molecular incorporation at kink sites along the steps. Rather, the generation of the kinks themselves by so-called "1D nucleation" appears to become the rate limiting step. We have found that calcite (and brushite) growth is best explained by assuming step motion is limited by kink availability. In particular, we have found that the biologically-relevant inorganic and organic constituents such as Sr^{2+} and a wide variety of aspartic acid-rich peptides, cause a dependence of step kinetics on impurity content and saturation state that differs dramatically from the GT prediction. We explain these results by replacing the GT-based analysis with a kinetic description in which the essential step to stopping growth is the blocking of newly formed kinks. Kinetic Monte Carlo simulations of this effect give good predictions of the measured behavior in the *in situ* AFM experiments. These findings explicitly reveal the importance of 1D nucleation and kink-site blocking during growth and inhibition.

3) The nucleation stage of biomineral formation is believed to allow organisms to deterministically produce mineral components with specific location, crystallographic

orientation, and phase. In new research, we are turning our attention to understanding nucleation processes. In particular, we are working to explore the validity of Ostwald's Law of Phases, which states that crystal nuclei will sequentially transition through all less stable phases before transforming to the most stable phase. In the first part of this work, we are investigating CaCO₃ nucleation onto nanoscale patterned templates formed by depositing self-assembled monolayers of alkane thiols on block copolymer films and by creating polypeptide arrays formed by dip-pen nanolithography. Our goal is to create patterns with different chemical functionalities to determine the relation between substrate chemistry and energy barriers to nucleation. The results will be analyzed within the framework of classical nucleation and growth theories. This work will lead to a comprehensive picture of the physical controls on calcite growth imposed by Asp-rich polypeptides and a major constituent of biomineralizing proteins, as well as an understanding of the stereochemical relationships and consequent energetic factors that drive those controls. By obtaining quantitative results on CaCO₃ nucleation at chemical templates, we hope to determine the relative importance of thermodynamic drivers and kinetic factors in inducing templated nucleation, and the first test of Ostwald's Law of Phases.

4) The paradigm for *dissolution* has become based upon so-called kinetic 'laws' that are largely empirical, sometimes with serious inconsistencies. Our research into mineral growth and nucleation has led to the discovery that the nucleation rate theory that was originally developed for crystal growth also predicts dissolution. This theory should, in principle, also apply to dissolution but has never been tested. By generalizing nucleation theory across the potential energy continuum of growth to dissolution, we have found a quantitative and mechanistic model that predicts how quartz dissolution processes change with increasing undersaturation from simple step edge retreat, to dislocation and defect-driven pit nucleation. We show that the so-called salt effect, that was recognized almost 100 years ago, arises from reductions in energy barriers to cause a transition in the dominant mechanism from dissolution at dislocations to the nucleation of 2D vacancy islands, to greatly increase site density. Nucleation rate theory also predicts the dissolution kinetics of K-feldspar and resolves controversial discrepancies in 80° and 150°C data reported for kaolinite—The differences arise from a temperature-activated crossover in the dominant mechanism to dissolution by nucleation of vacancy islands. 2D nucleation has not been previously recognized as possible for oxide or silicate minerals. Our findings argue that dissolution and growth are controlled by similar processes that are symmetric about driving force. Nucleation rate theory may be the missing link to understanding the dissolution-growth continuum.

Recent Publications:

Dove, P.M., N. Han and J.J. De Yoreo (in review) Classical nucleation theory predicts the dissolution and growth kinetics of quartz and silicate minerals. *Nature*.

Elhadj, S., A. Salter, A. Wierzbicki, N. Han, J.J. De Yoreo, P. M. Dove (in review) Peptide controls on calcite mineralization: Polyaspartate chain length affects growth kinetics and acts as a stereochemical switch on morphology.

Wasylenki, L.E., P.M. Dove, D.S. Wilson, and J.J. DeYoreo (in press) Nanoscale effects of Sr on calcite growth: An insitu AFM study in the absence of vital effects. *Geochim. Cosmochim. Acta*.

Wasylenki, L.E., P.M. Dove and J.J. DeYoreo (in press) Effects of temperature and transport conditions on calcite growth in the presence of Mg²⁺: Implications for paleothermometry. *Geochim. Cosmochim. Acta*.

De Yoreo, J.J. and P.M. Dove (2004) Shaping crystals with biomolecules. *Science*, **306**, 1301-1302.

Davis, K.J., P.M. Dove, L.E. Wasylenki, J.J. De Yoreo (2004) Morphological consequences of differential Mg^{2+} incorporation at structurally distinct steps on calcite. *American Min.*, **89**, 714-720.

Growth of Iron and Manganese Oxide Film on Carbonate Minerals

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In surface and ground waters, iron and manganese oxides form thin coatings on mineral surfaces and affect the fate and transport of toxic heavy metals. We use atomic force microscopy to investigate the growth and the dissolution of iron and manganese oxides films. Example results are that $\text{Fe}^{\text{III}}(\text{OH})_3$ hillocks form at steps on $\text{Fe}^{\text{II}}\text{CO}_3$ for $7 < \text{pH} < 10.3$ in the presence of $\text{O}_2(\text{aq})$ whereas rapid dissolution occurs for $\text{pH} > 10.3$ because of oxidative attack. Surface-bound Mn^{2+} reacts with $\text{O}_2(\text{aq})$ at circumneutral pH to form Mn oxide islands on MnCO_3 . In comparison to the $\text{Fe}(\text{OH})_3$ hillocks, these Mn oxide islands grow only in two dimensions (i.e., self-limited z -height) and grow with orientation in the lateral plane.

The growth of the Mn oxide film was investigated in detail, including the effects of the substrate surface morphology, the substrate atomic structure, the aqueous concentration of Mn^{2+} , and the addition of $\text{Co}^{2+}(\text{aq})$. On terraces, rhombohedral oxide islands form with 90° rotation relative to the crystallographic axis of the underlying carbonate substrate. Although the island heights self limit between 2 and 3 nm depending on reaction conditions, the islands grow laterally to several square microns before separate islands collide and coalesce. The islands do not grow over substrate steps. The growth rules change markedly in the presence of $\text{Co}^{2+}(\text{aq})$. Addition of $\text{Co}^{2+}(\text{aq})$ leads to the partial or complete dissolution of the manganese oxide film. Simultaneously, there is growth of new islands having multilayer structures that are unrestrained in the z -direction. The chemical composition of these new islands appears to include both Co and Mn. The islands readily grow over steps.

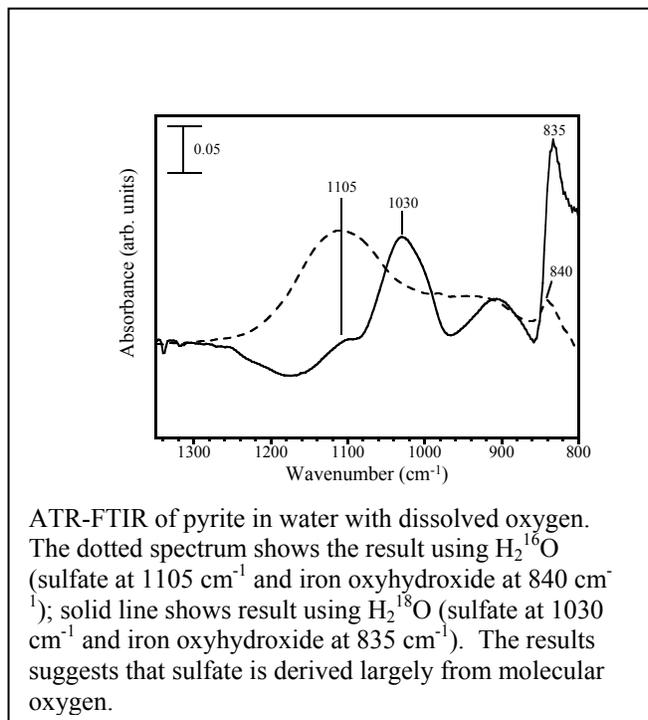
The atomic force imaging observes the final result of the aggregate motion of surface ions during dissolution and growth. To better understand these non-resolved processes, we have begun a series of experiments responsive to surface ion mobility. Mobility is probed using the polarization forces between a modified, electrically biased AFM tip and the mineral surface (a technique developed by Miquel Salmeron at LBNL). We conducted measurements on carbonate minerals of the density and the mobility of surface ions and the structure of the adsorbed water layer at several relative humidities (RH). The density and the mobility of surface ions increase with rising humidity, a finding which is consistent with increasing surface hydration. Hour-scale changes in the mobile ion response on CaCO_3 at constant RH provide evidence of surface dehydration, surface ion immobilization, and surface reconstruction. We also establish a correlation between ion relaxation time and mineral dissolution rate for the carbonate mineral family. The vision guiding the continued development of these experiments is that experimental data will become available to constrain the several rate constants of the kink-kink-annihilation (KKA) model. Improvement in quantitative mechanistic descriptions of dissolution/growth, hydration, and ion exchange should result.

Resolving Reaction Mechanisms and Intermediate Reaction Products in the Oxidation of Pyrite

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Pyrite oxidation is the root cause of the development of Acid Mine Drainage, which affects many streams in mining districts. In this study, we have developed several new techniques to resolve



some of the key steps in the pyrite oxidation reaction at the molecular level and determine intermediates formed during the reaction. Attenuated Total Reflection FTIR was used to resolve the roles of water and oxygen in the oxidation of pyrite. Labeled water (H₂¹⁸O) and ¹⁶O₂ were reacted with pyrite and the isotopic composition of sulfur oxyanion and Fe-O-H product surface species were determined in real time. Using this approach we have determined directly for the first time that sulfate-oxygen is mostly derived from water-oxygen if oxidation takes place in solution. When the oxidation takes place in air, the humidity determines how much of the oxygen in sulfate product is derived from water-oxygen. The oxygen in Fe-O-H appears is largely derived from molecular oxygen.

By employing Electron Resonance Spectroscopy, we have demonstrated the formation of OH radicals and hydrogen peroxide as intermediates during the oxidation of pyrite. OH radicals are extremely reactive and can decompose organic molecules. For example, as shown by our research group, nuclei acids (RNA and DNA) are readily decomposed in the presence of pyrite. On the basis of these results, we speculate that the presence of pyrite in coal may be an important factor in the development of lung disease in coal miners. The formation of OH radicals may be beneficial if they can be used to decompose organic solvents or other pollutants that can be decomposed via a radical-mediated reaction.

The spectroscopic techniques and methods to study pyrite oxidation and detect the presence of OH radical and H₂O₂ may also be of use in the study of other mineral-water systems.

Structure and Dynamics of Amino Acids in Layered Double Hydroxide Materials

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Natural layered double hydroxides (LDH) are comprised of edge-sharing magnesium and aluminum octahedra that form layered structures with positive layer charge, and therefore can accommodate negatively-charged exchangeable species and water in the interlayer. These so-called inverse clays have structural, physical, and chemical properties that are quite similar to normal clays, except for structural differences in the charge distribution. LDH materials have widespread practical applications including use as catalysts, ceramics precursors, plastic fillers, drug carriers, and phases for treatment of chemical and radioactive wastes (perchlorate, arsenate, iodide, pertechnetate, *etc.*). It has been suggested that LDH compounds may have provided an environment suitable for the origin of life where amino acids can adsorb and condense into more complex macromolecules such as proteins. To better understand the atomistic behavior of these complex materials, we combined experimental and molecular simulation methods. Molecular dynamics simulations were completed for LDH intercalated with acetate, glycinate, leucinate, isoleucinate, and other related anions. X-ray diffraction and vibrational spectroscopy were used to characterize synthetic LDH amino acid compounds.

We have developed molecular models of derivative LDH compounds with high (Mg:Al; 2:1) and low (Mg:Al; 3:1) charge density, in the presence and absence of water, and studied the orientation and hydrogen bonding behavior of the glycinate anion. We have also simulated LDH acetate in the presence and absence of water. We find the strongest interactions to be those involving the carboxylate group as hydrogen acceptor, and layer hydroxide or, to a smaller extent, water as hydrogen donors. The amino group is a very poor hydrogen donor, and a moderate hydrogen acceptor. In this capacity, it bonds less strongly than water to layer hydroxide, but in the absence of water the glycinate anions bridge the hydroxide layers, with carboxylate and amino groups acting as hydrogen acceptors to different layers. We infer, and confirmed through simulations, that in LDH derivatives of larger amino acids, hydrogen bonding to the amino group will not play a significant role. We also completed molecular dynamics simulations of the naturally-occurring amino acids leucine and isoleucine, and, for comparison, of hexanoic acid and 2-aminohexanoic acid, as their anions incorporated into high charge density LDH. In all cases, the carboxylate group is hydrogen bonded to layer hydroxide. When water is present, it segregates into the region next to the hydroxide layer, and hydrogen bonds to carboxylate and hydroxide, as well as itself.

We compared the conformational dynamics of these anions in isolation, and when incorporated into the LDH. For the straight chain species, in all cases, we found a rapid (on the 100 ps timescale) distribution over conformers, with a reasonably strong preference for *trans* conformation around each bond. With leucine and isoleucine, the situation is more complicated: the amino group has a steric blocking effect comparable to that of carboxylate. With isoleucine, in particular, the rearrangement dynamics are not fast and are strongly dependent on initial conformation. We expect these facts will prove relevant to the condensation of amino acids and the uptake of peptides on LDH, as well as to protein folding in a more general context.

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 Structure of Interfacial Water and Metal Surface Complexes at Silica and Alumina Surfaces: Evidence from Molecular Modeling Simulations, Macroscopic Sorption Experiments, and X-ray Absorption and Sum Frequency Generation Spectroscopies

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The major goal of this research is to examine the adsorption of divalent metals to different oxide surfaces in the presence of electrolyte and hydroxide anions in order to probe the possibility suggested by Criscenti and Sverjensky (1999, 2002) that, depending on the dielectric constant of the oxide, ternary metal-anion surface complexes will dominate at some oxide-water interfaces. We are using a suite of different techniques including molecular modeling, macroscopic sorption experiments, X-ray absorption spectroscopy (XAS) and vibrational sum frequency (VSFG) generation spectroscopy to investigate the potential for ion-pairing at the mineral-water interface from different directions. Our initial investigations focus on ion adsorption to alumina and silica surfaces.

Macroscopic adsorption data has been gathered for the sorption of Sr²⁺, Pb²⁺, and Co²⁺ on quartz from different background electrolytes. These data suggest that divalent metals adsorb to silica without the electrolyte anion. This result is consistent with the low dielectric constant of quartz. Strontium adsorbs as outer-sphere complexes on quartz surfaces and the extent of sorption is affected by the ionic strength in the solution phase. Cobalt forms kerolite-like clay on quartz surfaces under the experimental conditions (0.01 or 0.1 M NaCl, NaClO₄, or NaNO₃; 10⁻⁵ M Co) at pH>7. The extent of Co removal is affected by different solid solubility limits at the two ionic strengths. Lead adsorbed as inner-sphere complexes on quartz, the formation of Pb-Cl complexes in solution decreases Pb²⁺ adsorption on quartz surfaces. XAS data should provide more specific information on the coordination between each metal and the quartz surface, as well as the precipitation of a solid phase.

Vibrational sum frequency generation spectroscopy studies have focused on investigating the structure of water at alumina and silica surfaces as a function of relative humidity and adsorbing anion. The SFG spectra of the H₂O and D₂O adsorption studies show that the surface aluminol (Al-OH) groups are not fully occupied until ~60% relative humidity (~15 torr) through hydrogen bonding with surface water molecules. Previously reported adsorption isotherms indicate that there are 4 to 5 monolayers of water adsorbed on the α -Al₂O₃ (0001) surface at 60% RH. This suggests that water molecules form three-dimensional cluster islands on the α -Al₂O₃ (0001) surface, and leave a significant amount of Al-OH sites exposed to the air at relative humidities below 60%. It also suggests that the water-water interaction is stronger than that of the water-surface interaction; i.e., that the free energy favors water-clustering. Additionally, studies on organic anion (i.e., ethylene glycol, piperidine, 4-picoline, and ethylene diamine) adsorption show that we can identify changes in the interfacial water structure as a function of adsorbing anion, and can bracket surface acidity constants for different surface hydroxyl groups.

Classical molecular dynamics (MD) simulations using the CLAYFF force field [Cygan et al. (2004)] have focused on investigating the adsorption of Na⁺, Sr²⁺, and Pb²⁺ from chloride solutions to the basal surface of gibbsite [Al(OH)₃], and on distinguishing whether each of these cations prefers to adsorb alone or as an ion-pair. Initial results suggest that Na⁺ forms an outer-

sphere complex at a distance of $4.4 \pm 0.28 \text{ \AA}$ from the gibbsite surface, consistent with the predictions of Sverjensky (2001) for Na^+ adsorption to alumina. In addition, calculated distances of Pb-O and Pb-Al for inner-sphere adsorption of Pb^{2+} agree with XAS distances derived for alumina phases (Bargar et al., 1997). Simulations comparing Sr-Cl and Pb-Cl pairing in solution and at the surface suggest that more ion-pairing occurs at the surface. This result is consistent with the lower dielectric constant of interfacial water compared to bulk aqueous solution.

In summary, we are investigating the structure of water and adsorbing metal surface complexes using a suite of different techniques. Macroscopic adsorption data collected at several ionic strengths provide evidence of the influence of the electrolyte on metal adsorption. XAS data should provide specific information regarding the distance of the metal from the oxide surface and may provide indirect evidence for anion co-adsorption. VSFG spectroscopy techniques have been developed to detect anion adsorption at oxide surfaces in solution. Molecular dynamics simulations can be used to investigate differences in metal speciation in solution and at different oxide surfaces.

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