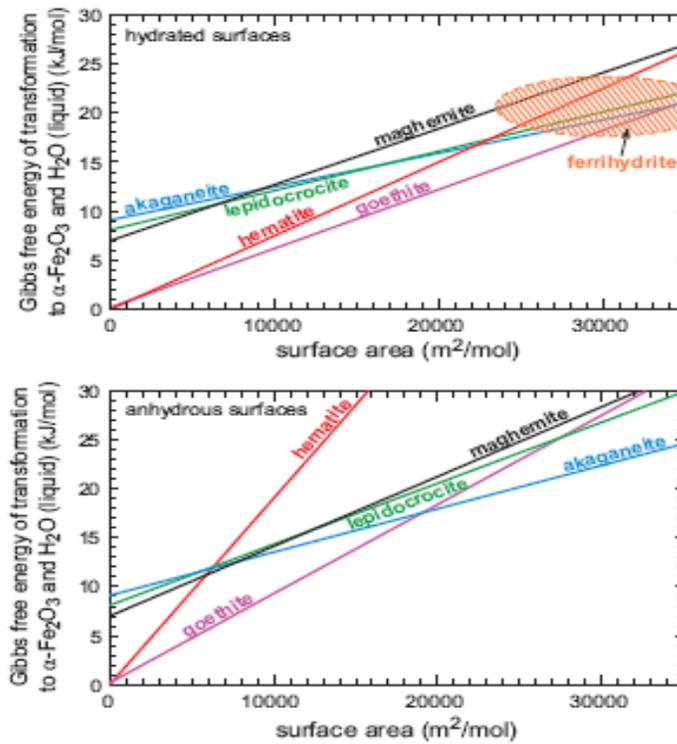
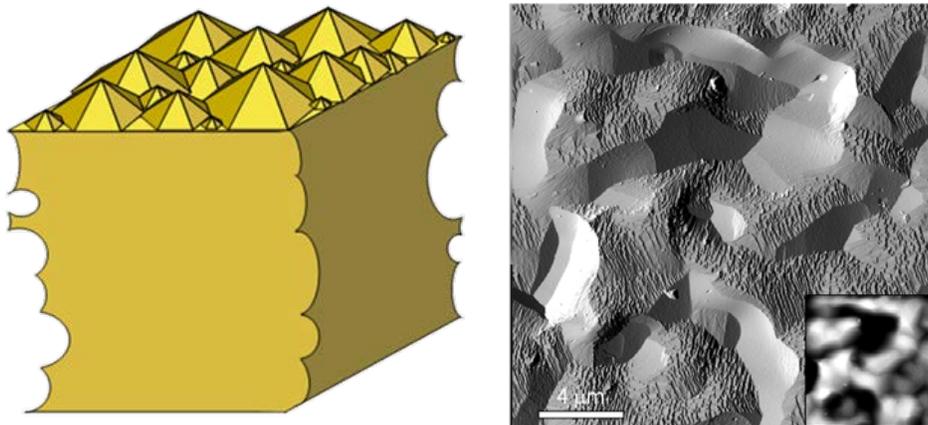


Geochemical Dynamics



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Geosciences Research Program, Office of Basic Energy Sciences
Gaithersburg, Maryland, September 8-9, 2011

FORWARD

“Geochemical Dynamics” is the seventeenth 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. 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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Captions for cover illustrations:

Figure 1: Enthalpy of Iron Oxides Relative to Bulk Hematite plus Water, Nanophases- Generalizations for Thermodynamics in the Critical Zone, Navrotsky, 2009 Best Paper Award Winner.

Figure 2: Contact AFM image ($20 \times 20 \text{ nm}^2$) of a vicinal hematite surface after treatment in an anoxic mixture of $10^{-3} \text{ M FeCl}_2 + 10^{-2} \text{ M oxalic acid}$, 0.01 NaCl at 75°C for 63 hours. Height scale = 25 nm. Coupled Dynamics at Mineral-Water Interfaces: Redox Transformation of The Iron Oxides, Kevin M. Rosso, Svetlana Yanina, and Sebastien Kerisit, Pacific Northwest National Laboratory, Paul Meakin, Idaho National Laboratory, 2009 Best Paper Award Winner

Agenda - Geochemical Dynamics, Gaithersburg, MD, September 8-9, 2011

Thursday Morning, September 8, 2011

7:30 **Registration/Continental Breakfast**

8:00 **Introductions and Greetings** - Nicholas B. Woodward, Department of Energy

Session 1: Isotopic Studies / System Dynamics

Chairs: Andy Felmy and Bill Casey

8:15 Michael Murrell, Steven Goldstein, and Joanna Denton, Los Alamos National Laboratory
Uranium-Series Environmental Transport and Geochronology Studies

8:40 Donald J. DePaolo, John N. Christensen, B. Mack Kennedy, M.E. Conrad, Ian C. Bourg
Lawrence Berkeley National Laboratory
Isotopic Molecular Geochemistry

9:05 Frank Richter, University of Chicago
Kinetic Isotope Fractionation in Condensed Systems: Experimental and Natural Examples

9:30 Abby Kavner and J. R. Black, University of California at Los Angeles
Stable Isotope Probe of Nano-Scale Mineral-Fluid Redox Interactions

9:55 **Coffee/refreshments**

10:20 John W Valley, Anthony D Pollington, Ayumi Hyodo, Reinhard Kozdon, University of Wisconsin
Quartz Cements and Basin Evolution: Illinois Basin and Wisconsin Arc

10:45 A. Hope Jahren and Brian A. Schubert, University of Hawaii
Dependence of Carbon Isotope Fractionation on Atmospheric $p\text{CO}_2$: Fundamental Photosynthetic Mechanism

11:10 Douglas Rumble Carnegie Institution of Washington and, Edward Young, UCLA
Development of Double-focusing, Electron Impact, Gas Source Mass Spectrometer for Measurement of Rare Doubly-Substituted Isotopologues in Geochemistry

11:35 Antonio Lanzirrotti, Steve Sutton, and Mark Rivers, University of Chicago
Revealing Geochemical Dynamics in Surface and Sub-surface Environments using X-ray Microprobe and Microtomography Techniques

11:50 Joanne E. Stubbs, Peter J. Eng, Steve Sutton, Mark Rivers, University of Chicago
Modification of Mineral Surface Structure and Reactivity by Hydration, Sorption, and Chemical Reaction

12:15 – 1:30 **Working Lunch – BES Geosciences Program Core Research Area Briefing**

Thursday Afternoon, September 8, 2011

Session 2 – Surface Properties

Chairs: Jeremy Fein and John Valley

1:35 Jeffery A. Greathouse, Louise J. Criscenti, Randall T. Cygan, Kevin Leung, Lynn E. Katz, and Heather C. Allen, Sandia National Laboratories, University of Texas and Ohio State University

Model Development and Applications for Minerals and Environmental Interfaces

2:00 May Nyman and Yu Hou, Sandia National Laboratories, Albuquerque

Geochemically-Relevant Molecular Clusters

2:25 Glenn A. Waychunas, Jaeho Sung, and Y. Ron Shen, Lawrence Berkeley National Laboratory and University of California at Berkeley

Sum-frequency vibrational spectroscopy (SFVS) studies of R-plane corundum: functional group protonation, hydroxyl orientations, hydrogen bonding, and acid-base properties

2:50 William Casey, University of California at Davis

Reaction dynamics in nanometer-size aqueous oxide clusters and in layered structures for photoenergy production

3:15 **Coffee/refreshments**

3:35 Dimitri Sverjenski, the Johns Hopkins University

Predictive Surface Complexation Modeling

4:00 Geoffrey M. Bowers^{*}, R. James Kirkpatrick[†], Andrey G. Kalinichev^{‡†}, Ozgur Yazaydin[†], Christin Morrow[†], Jared W. Singer^{*}; ^{*}Alfred University, [†]Michigan State University, [‡]Ecole des Mines de Nantes, [†]Surrey University

Dynamics at Geochemical Solid-Fluid Interfaces: Combined NMR and Molecular Dynamics Insight into Amorphous Calcium Carbonates and Behavior of Clay-Water Systems

4:25 Richard J. Reeder and Brian L. Phillips, Stony Brook University

Structure and transformation behavior of amorphous calcium carbonate (ACC)

4:50 Patricia .M. Dove¹, Dongbo Wang¹, James J. DeYoreo^{2, 1}Virginia Tech, ²Lawrence Berkeley National Laboratory

Investigating the Physical Basis of Biomineralization

5:15 Pupa Gilbert, University of Wisconsin

Mapping the Amorphous-to-crystalline transitions in CaCO₃ biominerals, with 20-nm resolution

5:40 **Adjourn**

6:30 **Dinner** (On your own)

Friday Morning, September 9, 2011

7:30 **Coffee/Continental Breakfast**

Session 3 – Surface Properties

Chairs: Rich Reeder and Sorena Sorensen

8:00 Harris E. Mason, Robert S. Maxwell, and Susan A. Carroll, Lawrence Livermore National Laboratory

The formation of metastable alumino-silicates in the Al-Si-H₂O system: Results from solution chemistry and solid-state NMR spectroscopy

8:25 Henry Teng, George Washington University and Huifang Xu, University of Wisconsin
Interface and Solvent Effect on Carbonate Mineralization

8:50 Brian Gorman, Colorado School of Mines
Early stage carbonate precipitation mechanisms in saline waters

9:15 Andrew G. Stack, P. Raiteri, J.D. Gale, D.J. Wesolowski, J.N. Bracco, D.M. Warren, Oak Ridge National Laboratory
Mechanisms and rates of reaction of ionically-bonded minerals

9:40 Gernot Rother¹, Lawrence M. Anovitz¹, David J. Wesolowski¹, David R. Cole², and Susan L. Brantley³ ¹Oak Ridge National Laboratory, ²Ohio State University, ³Pennsylvania State University

Fluid interactions with minerals and rocks – dynamics and evolution from picoseconds to thousands of year

10:05 Coffee/refreshments

10:25 Ian C. Bourg, Kideok D. Kwon, and Garrison Sposito, Lawrence Berkeley National Laboratory
Computational Geochemistry: Applications to metal adsorption at mineral-water interfaces

10:50 Kevin M. Rosso¹, Piotr Zarzycki¹, Shawn Chatman¹, Jordan Katz², Benjamin Gilbert³, Robert M. Handler⁴, Michelle M. Scherer⁵, Paul Meakin⁶, ¹Pacific Northwest National Laboratory, ²Denison University, ³Lawrence Berkeley National Laboratory, ⁴Michigan Tech and ⁶University of Oslo

Reactive Fe(II) and Electron Exchange Dynamics in Iron Oxides

11:15 Daniel R. Strongin, Temple University and Martin A. A. Schoonen, Stony Brook University
Reactivity of ferric iron bearing minerals in the presence of supercritical CO₂, SO₂ and H₂S

11:40 David C. Elbert and David R. Veblen, the Johns Hopkins University
Dehydration Phase Transitions in Uranyl Phosphates

12:05 – 1:20 **Working Lunch – ASCEM Presentation**

Friday Afternoon, September 9, 2011

Session 4 – Reactive Flows and Particles

Chairs: Frank Richter and Rich Lane

1:20 Carl Steefel, Lawrence Berkeley National Laboratory
Continuum Models for Reactivity in Confined and Nano-Confined Porous Media

1:45 Rob Sanford, Craig Bethke, Ted Flynn, Brian Farrell, Matt Kirk, Matt Kyrias and Derik Stratton, University of Illinois, Urbana-Champaign
Chemical Energy and the Distribution of Subsurface Microbial Activity

2:10 Russell Detwiler, University of California at Irvine
Quantifying coupled chemical-mechanical alteration of fractured rocks: An integrated experimental and computational approach

2:35 Anthony Ladd, University of Florida
Multiscale Modeling of Dissolution in Rough Fractures

3:00 Coffee/refreshments

3:20 James R. Boles, UC Santa Barbara, Grant Garven, Tufts University and Sidney Omelon, University of Ottawa
Isotopic Studies of Rapid Carbonate Precipitates

3:45 Benjamin Gilbert¹, J.E.Katz², X.Zhang³, K.Attenkofer³, C.Frandsen⁴, P.Zarzycki⁵, K. Rosso⁵, R.W.Falcone¹, and G.A.Waychnuas¹,¹Lawrence Berkeley National Laboratory, ²Denison University,³Argonne National Laboratory, ⁴Technical University of Denmark, ⁵Pacific Northwest National Laboratory
Mineralogical constraints on redox reactions of iron (oxyhydr)oxide phases

4:10 Harish Veeramani, Takuya Echigo, and Michael F. Hochella, Jr., Virginia Tech
Dissolution rates and sorption/catalytic reactivity of mineral nanoparticles: Examples involving nanohematite

4:35 Andrew R Felmy, Odeta Qafoku, Jianzhi Hu, H. Todd Schaefer, Carolyn I. Pearce, Nancy J. Hess, Mary Hu, Eugene S. Ilton and Kevin M. Rosso, Pacific Northwest National Laboratory
The Reactivity of Forsterite in Low Water Content Supercritical CO₂: Water Recycling and the Low Temperature Formation of Magnesite

5:00 Nick Woodward
Concluding remarks

Working Dinner 6-8 PM

ABSTRACTS:

Uranium-Series Environmental Transport and Geochronology Studies

Michael Murrell, Steven Goldstein, and Joanna Denton

Nuclear and Radiochemistry Group (C-NR), Los Alamos National Laboratory, Los Alamos, NM

Uranium-series geochemistry and geochronology have a wide range of applications for paleoclimatology, volcanology, environmental monitoring, and other disciplines. Our project aims to develop new tools and techniques for U-series mass spectrometry. Our goal is to apply these new developments to better measure, model, and understand U-series distributions over a range of spatial and temporal scales in support of basic geoscience research for energy and waste concerns.

The primary analytical tools we employ are uranium-series geochemistry, bulk and micro sampling techniques, and mass spectrometry. Our presentation will highlight our research in these areas. For example, we will present our efforts to use autoradiography, micro XRF, and femtosecond laser ablation to measure U-series transport in U-rich fractures. Femtosecond laser ablation systems can provide some relief from the elemental fractionation observed with nanosecond lasers and can reduce reliance on matrix matched standards. These in-situ data can be compared to our studies of forest fire ash, air filters, and soil cores that investigate near surface transport of anthropogenic and natural components in environmental collections. These studies provide data on actinide migration rates or geochemical retardation factors in the upper part of the UZ at LANL and other natural analog sites. In addition, new results for a different type of core, the GISP2 Greenland ice core, will be presented which suggest recent (3.5-6.9 kyr) melting/freezing event(s) have occurred at the base of the GISP2 core.

This work contributes to our understanding of the geochemistry of mineral-water interactions and assessment of radioactive waste repositories, along with other hydrologic and geochemical processes. These techniques will also have applications to human evolution, plate tectonics, forensics and climate change. Finally, the new methods, new understanding, and newly trained researchers that result from this work can contribute to interests of other agencies such as environmental monitoring and threat reduction.

Isotopic Molecular Geochemistry

D. J. DePaolo, J. N. Christensen, B.M. Kennedy, M.E. Conrad, Ian C. Bourg

E.O. Lawrence Berkeley National Laboratory

We have been using experimental and theoretical approaches to understand how mass dependent isotopic fractionation is controlled during phase changes (condensation, evaporation), mineral precipitation from aqueous solutions, and diffusive transport in aqueous and silicate liquids. Our particular focus is on mid-mass stable isotopes such as Ca, Mg, K, although some of our studies also involve Li, O, C, and H.

We have developed a theory for kinetic control of stable isotope fractionation during precipitation of calcite from aqueous solution. The initial form of this theory is a macroscopic transition-state version, where Ca and O isotopic effects are related to the ratio of gross and net ionic fluxes to a calcite surface growing from aqueous solution (DePaolo, GCA, 2011). This theory explains observed experimental data and most data on natural biogenic calcite. A limitation of the theory is that it relies on estimates of the surface exchange flux of Ca ions that derive from calcite dissolution rates and empirical relationships based on precipitation rate experiments. The second version of the theory is a quantitative microscopic ion-by-ion growth model that relates the surface exchange fluxes explicitly to solution saturation state, $\text{Ca}^{2+}/\text{CO}_3^{2-}$, and the energetics of ion attachment and detachment (Nielsen et al., 2012; submitted). This second version confirms that the inferences made in the original theory are approximately correct, but is more rigorous and provides the possibility for explaining other effects due to trace element and solution composition variations. MD studies of the effects of *cation mass* on solvation shell water molecule lifetimes (Hofmann, in prep.) suggest that mass dependence of desolvation rate may account for kinetic effects associated with calcite precipitation.

Preliminary studies of calcite and epidote precipitated from high temperature aqueous solutions suggest that surface kinetic effects are present also under these conditions (150° to 400°C). Studies of deep-sea sediment and pore fluid Ca isotopes provide further constraints on isotopic fractionation during calcite precipitation, and controls on surface ion fluxes. In sediment composed of nearly pure biogenic calcite, secondary calcite precipitates – at extremely low rates - with no Ca isotopic fractionation relative to pore fluid. In mixed carbonate – clay sections, pore fluid data suggest that calcite surface ion exchange fluxes are effectively zero (Turchyn et al., 2012; in press).

Diffusion of Ca in silicate liquids of differing composition provides evidence that the binding of Ca to the aluminosilicate network strongly affects the *mass dependence* of diffusivity (Watkins et al., GCA, 2011). In some liquids, Ca mass dependent diffusion is almost as extreme as Li. The observed behavior can be explained in terms of a two-species model of cation binding in silicate liquids, and overall, there is coherence to the mass dependence of diffusivities in both silicate liquids and aqueous solutions – mass dependence being determined by the strength of bonding between cation and “solvent.”

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

Kinetic Isotope Fractionation in Condensed Systems: Experimental and Natural Examples

Frank Richter, *University of Chicago*

Kinetic processes that can produce large stable isotope fractionations (i.e., large compared to analytical precision and the natural variability of these isotopes) include evaporation, chemical diffusion in water, silicate liquids and minerals, grain-boundary diffusion, and thermal (Soret) diffusion. The table below provides an overview of kinetic isotope fractionations in condensed systems that have been documented in laboratory experiments and in natural settings along with selected references that will serve as an introduction to the subject.

<i>Process</i>	<i>Isotopic systems</i>	<i>Laboratory Examples</i>	<i>Natural Examples</i>	<i>Theoretical Models and MD</i>
Evaporation	Mg,Fe,Si,O, H	[1], [2], [3], [4],[7]	CAIs [5] cosmic spherules [6] water [8]	
Chemical diffusion water,melts,mi nerals	Li,Ca,Mg,Fe K	[9],[10],[11] , [12]	VinalCove, Maine[10] Augite [13]	[11]
Grain- boundary diffusion	Li		Tin Mtn. Pegmatite[14]	
Thermal diffusion (silicate liquids)	Mg,Ca,Fe,Si, O Li,K	[15],[16]		[16],[17],[18]

Time permitting; I will discuss recently reported examples of isotopic fractionations arising from each of the four kinetic processes listed above. In those cases where there are both laboratory and natural examples, I will focus on the commonality of what has been found. Another important connection is between experimental data and recent efforts to provide a theoretical understanding of kinetic isotope fractionations. In the case of ionic species in water there is excellent agreement between the lab data on the element-specific isotope fractionations and molecular dynamics simulations. However, several recent papers that proposed theoretically-based parameterizations of thermal diffusion in silicate liquids based on a limited set of isotopes are now seen to require revision given new data on the thermal fractionation of a larger set of isotopic systems.

[1] Richter *et al.* (2002) *GCA* **66**, 521-540. [2] Dauphas *et al.* (2004) *Anal. Chem.* **76**, 5855-5863. [3] Richter *et al.* (2007) *GCA* **71**, 5544-5564. [4] Knight *et al.* (2009) *GCA* **73**, 6390-6401. [5] Clayton *et al.* (1988) *Phil. Trans. Roy. Soc. London A* **325**, 483-501. [6] Taylor *et al.* (2005) *GCA* **69**, 2647-2662. [7] Craig *et al.* (1963) *JGR* **68**,5079. [8] Craig & Gordon (1965) *Geologia Nucleare*, Pisa. [9] Richter *et al.* (2009) *Chem. Geol.* **258**, 92-103. [10] Chopra (2010) *PhD dissertation*, Univ. Chicago [11] Bourg *et al.* (2010) *GCA* **74**, 2249-2256. [12] Watkins *et al.* (2011) *GCA in press*. [13] Beck *et al.* (2006) *GCA* **70**, 4813-4825. [14] Teng *et al.* (2006) *EPSL* **243**, 701-710. [15] Richter *et al.* (2009) *GCA* **73**, 4250-4263. [16] Huang *et al.* (2010) *Nature* **464**, 396-400. [17] Dominguez *et al.* (2011) *Nature in press*. [18] Reitz *et al.* (2000) *J. Chem. Phys.* **112**, 2436-2443.

Stable-isotope probe of nano-scale mineral-fluid redox interactions

A. Kavner and J. R. Black, *University of California Los Angeles*

In a series of experimental studies we have shown that large and rate-dependent isotope fractionations occur during metal deposition at an electrode. This work demonstrates that metal isotopes are promising markers for elucidating processes that occur adjacent to a non-equilibrium fluid/solid interface. Our hypothesis is that three distinct processes control the isotope fractionation at a redox interface: mass transport to the interface, speciation changes associated with the interface chemistry, and a redox-sensitive isotope marker. We compare our predictions of isotope fractionations during these processes with results from experimental studies of metal deposition as a function of solution chemistry, deposition rate, and temperature. We show results from three systems: Fe—a multi-valent transition metal with many applications in natural and biological systems; Zn—another transition metal with simpler redox chemistry; and Li—a simple alkali metal whose chemistry is more amenable to *ab initio* approaches. We show how our work enables prediction and generation of laboratory-tunable isotope fractionations, providing a better understanding of how to use isotopic markers for tracing redox-related chemistry, with applications in natural systems, environmental remediation, and the nuclear power industry.

Quartz Cements and Basin Evolution: Illinois Basin and Wisconsin Arch

John W Valley, Anthony D Pollington, Ayumi Hyodo, Reinhard Kozdon
University of Wisconsin, Madison

The thermal, mechanical, and chemical evolution of a sedimentary basin exerts important controls on porosity and permeability of reservoir rocks. Oxygen isotope ratios of individual diagenetic cements record evidence of this history, but cannot be accurately analyzed by conventional techniques. Recent improvements for in situ analysis by ion microprobe provide high precision and accuracy at 3–10 μm scale. In combination with cathodoluminescence imaging, in situ analysis of $\delta^{18}\text{O}$ (quartz) from the Cambrian Mt. Simon Sandstone and overlying Eau Claire Shale in the Illinois Basin reveals gradients within single overgrowths of as much as 7.7‰/50 μm (1). While the inner portions of overgrowths remain approximately constant in $\delta^{18}\text{O}$ across the basin, the $\delta^{18}\text{O}$ of the rim becomes lower with depth. These data suggest that overgrowths formed during burial and heating, possibly with minimal changes in $\delta^{18}\text{O}$ of pore fluids. A majority of analyzed healed microfractures cutting detrital grains have low $\delta^{18}\text{O}$ and formed in the pre-sedimentary parent rocks. Thus the percentage of these fractures does not provide an estimate of burial depth. In contrast to the Illinois Basin, samples of sandstone and shale from the Wisconsin Arch have not been buried deeply (< 1km), overgrowths are not zoned in $\delta^{18}\text{O}$, and quartz cementation was at low T (< 40°C). In the Illinois Basin, both $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ of quartz are consistent with local derivation of silica, largely from pressure solution of originally igneous detrital quartz. If $\delta^{18}\text{O}(\text{H}_2\text{O}) = -3\text{‰}$, the highest temperature calculated for the rim of an overgrowth is 107°C at a paleo-depth of 3.5 km. The variability both in average $\delta^{18}\text{O}$ of overgrowths and zoning patterns from individual overgrowths correspond with a geotherm of 30°C/km. Thus there is no evidence of quartz precipitation from higher temperature hydrothermal fluid events, and quartz overgrowths likely formed over a period of 100-200 million years synchronous with deposition in the basin.

(1) Anthony D. Pollington, Reinhard Kozdon, and John W. Valley (2011) Evolution of quartz cementation during burial of the Cambrian Mt. Simon Sandstone, Illinois Basin: In situ microanalysis of $\delta^{18}\text{O}$. *Geology*. accepted

Dependence of Carbon Isotope Fractionation on Atmospheric pCO₂: Fundamental Photosynthetic Mechanisms

A. Hope Jahren and Brian A. Schubert, *University of Hawaii*

Numerous studies on multicellular plants have reported increasing carbon isotope fractionation with increasing concentrations of atmospheric carbon dioxide (pCO₂), but the magnitude of the effect is highly variable (i.e., 0.62 to 2.7‰ per 100 ppm CO₂). The majority of these experiments tested only small differences in CO₂ levels (<100 ppm), with maximum concentrations of elevated pCO₂ = 700 ppm. These studies conclude that carbon isotope discrimination [$\Delta\delta^{13}\text{C} = (\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{plant}}) / (1000 + \delta^{13}\text{C}_{\text{plant}})$] increases linearly as pCO₂ increases. A linear response suggests that the activity of RuBisCO, an enzyme fundamental to photosynthesis, is not limiting under any pCO₂ level. Such a conclusion further suggests that $\Delta\delta^{13}\text{C}$ will eventually exceed the enzymatic fractionation due to RuBisCO and that pCO₂ will be concentrated within leaves at levels greater than that outside the leaf. Because these conclusions violate fundamental understanding of photosynthesis, we conducted experiments within controlled growth chambers in which light, water, temperature, and relative humidity were maintained constant, and only varying the pCO₂ level under which plants grew. Two species of model plants, *Arabidopsis thaliana* and *Raphanus sativus*, were grown under 17 different pCO₂ levels ranging between 370 and 4200 ppm, in order to encompass the entire range of pCO₂ levels under which plants have evolved on Earth. From this large dataset of nearly 200 plants, we show that $\Delta\delta^{13}\text{C}$ is indeed a function of pCO₂, however, the relationship is hyperbolic, rather than linear, as is typically assumed. Across the small changes in pCO₂ previously studied, the response appears linear, however, our experiments across a very wide range of pCO₂ levels clearly shows that increases in $\Delta\delta^{13}\text{C}$ level off at high pCO₂, which is consistent with the ultimate control over fractionation being the activity of RuBisCO as the concentration of pCO₂ inside the leaf approaches the pCO₂ level outside the leaf. The response we measure indicates that changes in pCO₂ can affect $\Delta\delta^{13}\text{C}$ by as much as 7‰ across Geologic time, which is as great an effect as is measured among plants growing in desert to rain forest sites due to extreme variations in mean annual precipitation. Investigation of published data suggests that the $\Delta\delta^{13}\text{C}$ response to changes in pCO₂ is consistent across diverse plant types and our data show that the response is recorded in bulk below- and above-ground tissues, as well as *n*-alkanes, suggesting the potential for application to fossil plant materials in order to reconstruct pCO₂ across critical intervals.

Development of Double-focusing, Electron Impact, Gas Source Mass Spectrometer for Measurement of Rare Doubly-Substituted Isotopologues in Geochemistry

Douglas Rumble, *Carnegie Institution of Washington* and Edward Young, *University of California at Los Angeles*

We are designing and building a gas-source, electron-impact, mass spectrometer with sufficient mass resolving power and sensitivity to make it possible to analyze the clumped isotopologues of gas molecules present in volcanic eruptive plumes, planetary atmospheres, geothermal hot springs, hydrocarbon deposits, deep crustal reservoirs, and low-temperature gas hydrates. The proposed instrument will be used to calibrate experimentally the temperature dependence and kinetic rate constants of reactions involving clumped isotopologue molecules as reactants and products and to apply these calibrations to the interpretation of the measured abundances of clumped isotopologues occurring naturally in the lithosphere, hydrosphere, and atmosphere. The immediate goal is to build a fully functional high-resolution mass spectrometer in two years. The following, third year, will be used to measure high-resolution mass spectra of single- and doubly-substituted isotopologues of molecules of geochemical interest, develop analytical protocols, and calibrate the instrument. The long-term goal of our research is to apply the calibrated instrument to such problems, for example, as quantitatively distinguishing between methane derived by thermal degradation of relict organic matter, or produced by inorganic synthesis, or generated by methanotrophs. The guiding design principles for the new mass spectrometer are (1) high mass resolution; (2) high sensitivity; (3) low abundance sensitivity (minimal peak tailing); and (4) adaptability to the measurement of the abundances of the widest possible variety of molecular isotopologues. The new instrument will be available for use by all qualified scientists. It will be designed, built, commissioned, and operated with input from an Advisory Council of internationally known scientists. Dr. Phil Freedman, chair of Nu Instruments, Wrexham, Wales, United Kingdom, is working with the PI's and the Advisory Council to develop a high-resolution mass spectrometer capable of measuring the abundances of such difficult to resolve species as $^{12}\text{CD}_2\text{H}_2$ and $^{13}\text{CDH}_3$. The instrument will be located in the Geology Building at the University of California, Los Angeles.

Revealing Geochemical Dynamics in Surface and Sub-surface Environments using X-ray Microprobe Techniques

Antonio Lanzirotti, Steve Sutton, and Mark Rivers
Center for Advanced Radiation Sources, University of Chicago

Synchrotron-based X-ray absorption fine structure spectroscopy (XAFS) and hard X-ray microprobe techniques such as X-ray fluorescence (XRF) and X-ray diffraction (XRD) are being used by geoscientists for evaluating dynamic geochemical changes in earth materials with high sensitivity to trace elements and with high spatial resolution. This presentation will describe experiments conducted primarily at the X26A beamline at the National Synchrotron Light Source (Upton, NY).

μ XRD and μ XAFS are being used to understand how mineralogical factors control arsenic mobility in mine waste over its weathering history. Historic gold mine sites in Nova Scotia, Canada, contain As-rich tailings which have been exposed to the atmosphere for many years. In these tailings, arsenopyrite has oxidized to ferric arsenate minerals and microprobe measurements show that in areas where the sulfide concentration is high, the oxidation product is scorodite and the associated pore waters are acidic (DeSisto et al. 2011). In areas where carbonate is still present to neutralize acidity associated with the oxidizing sulfide, the As is converted to Ca-Fe arsenates such as yukonite (Walker et al. 2009).

Researchers are using flow-through experiments to investigate the evolution of fractured carbonate caprock during flow of CO₂-acidified brine (Ellis et al. 2011). In these experiments, CO₂ acidified brines flow through cores of Amherst limestone at 14 MPa confining pressure. Fracture evolution is monitored in real-time using computed tomography with fracture mineralogy and chemistry evaluated before and after flow via μ XRF and μ XRD. CT imaging shows that the CO₂ acidified brines can erode fractures in a carbonate caprock via mineral dissolution. X-ray microprobe analysis shows that dissolution rates are dependent on the composition and mineralogy of phases along pre-existing fractures, as well as mineral grain orientation, surface coatings and adsorbates.

Geoscientists are also measuring the properties of residual brine films confined between supercritical CO₂ and mineral surface with μ XRF techniques (Tokunaga 2009). Such films are significant in controlling flow, surface chemical reactions and chemical transport in these systems. These experiments use in-situ changes in the measured XRF of ions such as Se, Cs or I in the brine to monitor the properties of water films that form on quartz glass surfaces of known surface roughness. Applying the Langmuir film equation, the experiments give researchers the ability to resolve film thicknesses between 10 to 400 nm for solution concentration of 300 mM.

References: Ellis, B., et al. (2011) *Greenhouse Gas Sci. Tech.* 1, in press; Tokunaga, T. K. (2009) *Geosciences Research Program, Office of Basic Energy Sciences conference proceeding on Experimental and Theoretical Geochemistry*, 48-89; DeSisto, S. et al. (2011) *Applied Geochemistry*, in press; Walker, S. et al. (2009) *Canadian Mineralogist*, 47, 533-556.

Modification of Mineral Surface Structure and Reactivity by Hydration, Sorption, and Chemical Reaction

Joanne E. Stubbs, Peter J. Eng, Steve Sutton, Mark Rivers
Center for Advanced Radiation Sources, University of Chicago

Mineral surfaces are highly reactive due to unfulfilled bonding requirements, and are therefore inherently dynamic geochemical microenvironments. Vacuum-terminated surfaces are significantly altered at ambient pressure, and are further modified by hydration, sorption, and oxidation/reduction reactions. The processes of crystal growth, dissolution, and solute adsorption are fundamentally surface-driven, and understanding these phenomena requires detailed knowledge of atomic-scale interface structures. We present the mineral surface science capabilities and recent results obtained at the GSECARS facility at the Advanced Photon Source (Argonne, IL).

Synchrotron-based analytical methods are invaluable for the in-situ study of chemical reactions at mineral surfaces. Crystal truncation rod (CTR) x-ray diffraction allows the determination of atomic structure at surfaces, including the positions of water molecules and adsorbates. Elemental specificity is gained when CTR measurements are made above and below the absorption edges of the elements of interest in resonant interface diffraction spectroscopy (RIDS). X-ray reflectivity provides information about surface roughness and the development of films (e.g., biofilms), and long period x-ray standing waves (XSW) allow for depth profiling of chemical elements and their redox states. Grazing incidence x-ray absorption spectroscopy (GI-XAS) and powder x-ray diffraction (GI-XRD) add further insights into the products of surface reactions. All of these measurements can be made in the presence of liquid water, and their value is significantly enhanced by the exploration of reaction chemistry in real time on the diffractometer with custom-built, flow-through reaction cells.

Recent mineral surface studies at GSECARS have determined the structures and chemical reactivities of several geologically and environmentally relevant minerals under hydrated conditions, including calcite (Heberling et al., 2011), goethite (Ghose et al., 2010), magnetite (Petitto et al., 2010), and hematite (Tanwar et al., 2007a,b; 2008; 2009). Research on these surfaces and others continues, and includes in-situ study of environmentally important adsorbates such as arsenic, lead, and antimony.

New work includes investigation into the oxidative corrosion of uraninite (UO₂), which is a principal uranium ore, the primary component in nuclear fuels, and a central product of bioremediation efforts for uranium-contaminated soils and aquifers. This work is made possible by the development of new reaction cells designed to meet the challenges of working with radioactive and redox-sensitive materials. These cells have been applied to this and several other systems.

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Model Development and Applications for Minerals and Environmental Interfaces

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A main focus of this project has been the development of the Clayff energy force field for molecular simulations of layered minerals and aqueous interfaces. While Clayff was originally developed with nonbonded energy terms for bulk minerals, a proper description of hydroxyl edge sites requires bonded terms (bond stretch and angle bend). Our recent work has involved parameterizing the hydroxylated edge site species, Al-O-H and Si-O-H of gibbsite and cristobalite. For simulations involving a bulk fluid such as water in contact with a mineral phase, we have discovered that the choice of thermodynamic ensemble has a direct effect on the water density throughout the aqueous region. A simple estimation of water-accessible volume using the Connolly surface method gives reasonable results compared with the preferred constant-pressure ensemble. In support of spectroscopic-simulation studies of ion adsorption on muscovite surfaces, we have further validated Clayff by computing temperature-dependent mechanical properties of bulk muscovite. The resulting moduli and compressibilities are in good agreement with experiment. Additionally, we have successfully simulated the structure and interlayer dynamics of several environmentally important birnessite phases.

Another focus area has been the adsorption of oxyanions and ion-pairs at the oxide-water interface. During the last two years, we have moved toward understanding the co-adsorption of contaminant cation-oxyanion pairs on goethite surfaces at the atomistic level to improve surface complexation models. We are calculating pKa's for goethite surface sites that are independent of any surface complexation model framework using *ab initio* molecular dynamics simulations. Classical molecular dynamics methods are being used to examine the electric double layer on two goethite surfaces (101) and (001) as a function of NaCl and Na₂SO₄ concentrations and to evaluate the formation of ternary complexes (e.g., CoSO₄) at these surfaces. Sulfate is presently being used as a proxy for oxyanions such as AsO₄³⁻, SeO₄²⁻, and SeO₃²⁻ in these simulations. Sum frequency generation spectroscopy has been used successfully to investigate the structure of SO₄²⁻ surface species as a function of concentration on CaF₂. A method for creating thin films of iron oxide was developed; however, the thin films did not maintain their integrity during SFG analysis. Finally, bulk adsorption data for combined heavy metal-oxyanion systems have been fitted using both the Triple Layer Model and a variant of the Multisite Complexation Model, in order to evaluate the weaknesses in both models to predict multi-ion adsorption to oxide surfaces. Ongoing research involves iterating between modeling results at different scales and evaluating the impact of electronic and atomistic scale model results on surface complexation models.

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Geochemically-Relevant Molecular Clusters

May Nyman and Yu Hou
Sandia National Laboratories

Anionic, cationic and neutral discrete polymetalates composed of earth-abundant metals (i.e. Si, Al, Fe, Ca, K, Na) are relevant to investigating geochemical or environmental processes such as ion association with colloid and mineral surfaces, acid-base behavior of interfaces and ions, and transport of contaminants. Formation of these discrete species is a great synthetic challenge, in that the hydrolysis and condensation reactions of the oxo- anions and cations are rapid and difficult to control. The polycationic alumina clusters are an exemplary system; yet further development of even these is stymied.

We have made modest progress on the development of new ferric, alumina and aluminosilicate based clusters with the use of protecting ligands, pH control and counterions or addenda metals. Synthesis, structure and solution characterization of a series of iron and aluminum based clusters will be described. Furthermore, in our effort to capture the elusive Fe₁₃-Keggin ion, we have characterized aqueous solutions of partially-neutralized iron solutions via ESI-MS (electrospray-ionization mass spectrometry), and these results will also be discussed.

Sum-Frequency Vibrational Spectroscopy (SFVS) studies of R-plane corundum: functional group protonation, hydroxyl orientations, hydrogen bonding, and acid-base properties.

Glenn Waychunas¹, Jaeho Sung^{1,2}, and Y. Ron Shen²

¹*Lawrence Berkeley National Laboratory*, ²*University of California, Berkeley*

SFVS allows quantitative measurement of the density of protonated functional groups on mineral surfaces [1]. This is demonstrated for the corundum (1-102) interface where the orientation and nature of surface hydroxyls on the dry protonated surface can be obtained and compared with models for the surface termination obtained from crystal truncation rod (CTR) and X-ray reflectivity (XRR) measurements, and with the most likely functional group assignments [2]. Hydroxyl orientations are determined by measurement of the non-linear optical susceptibility for each absorption band over a range of azimuthal angles and appropriate set of beam polarizations, and the polar orientation (up-down with respect to the z-direction) is determined from measurements of the imaginary part of the susceptibility. A scheme for describing the hydrogen bonding among these protonated groups is found to be consistent with surface symmetry and the particular vibrational frequencies observed. The addition of aqueous solution to the interface alters the hydrogen bonding of the hydroxyls, and introduces water-functional group hydrogen bonding [3]. Plotted as a function of solution pH, both hydroxyl and water band amplitudes can be used to determine acid-base properties and pKa values at the interface. We can thus directly link interfacial acid-base properties to precise molecular surface entities and their protonation states.

This research has been in part supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy.

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Adding reactivity to structure - isotope-exchange pathways in nanometer-size oxide molecules

William H. Casey, University of California at Davis

Reactions involving minerals and glasses in water are difficult to follow at the molecular scale because the reactant structures aren't known with confidence. As an alternative, we've been examining isotope-exchange pathways in nanometer-size oxide ions where the structures are known and where the isotope-exchange reactions can be followed spectroscopically at individual oxygen sites. These oxide ions typically have 40-1400 atoms and are synthesized to test specific ideas about reactions involving larger structures. Use of these large ions allows answers to geochemical questions that could have been otherwise approached. For example:

- 1) Rates of ligand substitution of bulk and bound waters in clusters made of trivalent metal oxides is a robust reaction that is well suited for simulation, even for minerals. Rates can be measured in large clusters and separately simulated using rare-event molecular-dynamic methods. They are surprisingly insensitive to small changes in structure, but profoundly sensitive to the presence of adjacent bound waters.
- 2) In contrast, isotope exchanges into oxide bridges in nanometer-size ions are extraordinarily sensitive to structural details. The pH dependencies can be reversed with simple metal substitutions but, when a series of molecules are followed as a function of a single metal substitution, it is clear that these 40-atom structures exhibit the same broad amphoteric kinetics found for oxide minerals.
- 3) Isotope-exchange pathways, and dissociations, are mitigated by metastable equilibrium with low-energy intermediate forms of the structure. These intermediates form by partial detachment of bonds to the highly coordinated oxygens deeper in the structure, whether the Al_{13} Keggin ions or niobate ions. For the polyniobate ions, sets of low-energy structures form by facile hydroxide addition into the coordination shells of the metal sites. Hydroxide additions are also driven by highly coordinated oxygen atoms which impart a high degree of flexibility to the coordination geometries. The hydroxide affinities of the metals and the proton affinities of oxygen atoms are close for sites throughout these molecules. Thus, a 40-atom oxide molecule already exhibits much of the averaged reactivity trends found for extended surfaces. Metastable equilibrium with these intermediate structures explains why the pH dependences of rates for a given oxide structure are so similar, and can be shifted throughout a structure by a single-metal substitution. These metastable structures, instead of activated transition states, provide a new view of the oxide-solution interface that explains many of the heretofore puzzling trends in reactivity, including the amphoteric distribution of rates, the influence of counter ions and the surprisingly muted effect of single-atom substitutions on a dissolution rate.

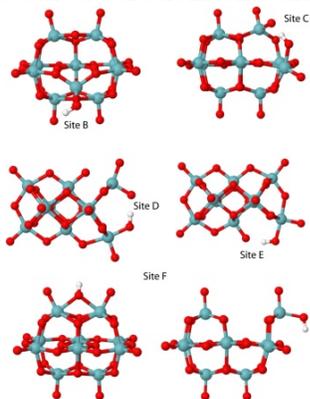


Figure: Low-energy intermediates formed by OH^- addition to the Nb_{10} molecule uncovered by DFT calculations. These intermediate forms are in constant equilibrium with the stable form of the molecule and mitigate oxygen-isotope-exchanges and dissociation, leading to a broad, averaged amphoteric chemistry.

Predictive Surface Complexation Modeling

Dimitri A. Sverjensky, *the Johns Hopkins University*

Surface complexation plays an important role in the equilibria and kinetics of processes controlling the compositions of soilwaters and groundwaters, the fate of contaminants in groundwaters, and the subsurface storage of CO_2 and nuclear waste. However, there is no currently-available model of surface complexation that can be used to analyze these processes by predicting surface protonation and adsorption of metallic cations, anions and organic species for the wide range of fluid compositions, minerals, and temperatures and pressures that exist in nature.

My previous studies have shown that all the parameters in the extended triple-layer model (ETLM) can be predicted for alkalis and alkaline earths, enabling prediction of proton surface charge for oxides in 1:1 and 2:1 electrolyte solutions and mixtures of these. Over the last three years the predictive ETLM for oxides has been extended to 1:2 electrolytes involving environmentally important oxyanions such as carbonate as well as the adsorption of the oxyanions of silica, which enables surface chemistry calculations more relevant to natural waters than previously possible. Second, by applying the ETLM to oxyanionic organic acids such as glutamate it has been demonstrated that prediction of surface species with the ETLM was consistent with measured ATR-FTIR spectra and quantum chemical modeling. Finally, it has become clear that electrolyte, transition, heavy metal and rare earth element cations prefer larger site densities and different sites than inorganic and organic oxyanions, which implies the need for a two-site model in order to treat natural waters that contain mixtures of cations and anions with a variety of valences. Organic oxyanions in particular can be used as a probe of the surface structures on minerals, including defects such as steps.

Current work is focused on continuing to develop the predictive capabilities and generality of the ETLM by expanding the scope of previous applications: first to finish the development of a predictive model for silica adsorption on all oxides; second to investigate the applicability of a general two-site approach; and third, to improve theoretical relations for predicting metal and oxyanion adsorption, including an investigation of extending the ETLM to higher temperatures and pressures. By so doing, the proposed research aims to integrate the results of the work of many experimentalists and to extrapolate their work to provide estimates of surface chemistry for systems not yet studied experimentally and for natural and anthropogenically perturbed systems.

Dynamics at Geochemical Solid-Fluid Interfaces: Combined NMR and MD Insights into ACCs and Behavior of Clay-Water Systems

Geoffrey M. Bowers^{*}, R. James Kirkpatrick[†], Andrey G. Kalinichev^{‡†}, Ozgur Yazaydin[†], Christin Morrow[†], Jared W. Singer^{*}; ^{*}Alfred University, [†]Michigan State University, [‡]Ecole des Mines de Nantes, [§]Surrey University

The overall objective of our project is to advance fundamental molecular-level understanding of the structure, dynamics, energetics and reactivity of confined and near-surface aqueous fluids in geochemically relevant mineral systems and to develop general principles for understanding and predicting these behaviors on time scales from picoseconds to seconds. We achieve this by combining computational modeling (MD and quantum methods) with complimentary experimental approaches (NMR and neutron methods). Our project currently has three primary thrusts.

Thrust 1: Structure and Dynamics at the Mineral-Water Interface. Current work in this project focuses on understanding the molecular-scale behavior of cations and H₂O at smectite-H₂O interfaces as a function of system H₂O content and temperature, with particular emphasis on understanding how the cations and H₂O molecules influence one another dynamically and structurally. Our current variable temperature (VT) ²³Na and ²H NMR studies of Na-hectorite paste, combined with our previous work on K-hectorite and Cs-hectorite pastes, has allowed us to identify several important general trends in the interfacial dynamics. For example, we find that the reorientation dynamics of surface proximity-restricted ²H₂O in alkali metal-hectorite pastes is independent of the alkali cation between -50°C and -20°C and involves a combination of 2-fold and 3-fold motions at rates > 100 kHz. Based upon the trends for alkali metal-hectorites, we predict that the higher charge and more strongly hydrated alkaline earth metals will exhibit diffusion-dominated cation dynamics at low temperatures. This was confirmed at temperatures as low as -120°C by the first ever ⁴³Ca VT NMR results for confined Ca²⁺ in a ⁴³Ca-enriched two-water layer Ca-hectorite. Complimentary ²H VT NMR and MD studies of Ca-hectorite as a function of ²H₂O content are currently in progress.

Thrust 2: Structure, Dynamics, and Transformations of Amorphous Calcium Carbonates (ACCs). Our efforts here are focused primarily on understanding the formation and stability of pre-nucleation clusters and ACC, particularly the molecular-scale mechanism responsible for the stabilization of ACC by Mg²⁺. We report the first ever ⁴³Ca and ²⁵Mg NMR spectra of ⁴³Ca-enriched ACCs prepared with and without Mg²⁺ and show that the presence and concentration of Mg²⁺ in the parent solution has little effect on the ⁴³Ca environment, that we can capture the transformation of ACC to crystalline calcium carbonate in situ, and that the Ca²⁺ resonance spans the range from calcite to vaterite to aragonite. Based on our ⁴³Ca NMR results and known relationships between the chemical shift and mean Ca-O bond distance, we calculate upper and lower limits on the mean Ca-O bond distance in ACCs of 2.46 Å and 2.65 Å. This range includes the mean Ca-O bond distance predicted by the Goodwin model¹ and excludes the mean Ca-O distance observed in our MD simulations of pre-nucleation clusters using the force field of Raiteri and Gale² and those observed in most crystalline calcium carbonates. Preliminary ²⁵Mg NMR results suggest that two different Mg environments exist in Mg-inclusive ACCs, with the relative abundance of these sites exhibiting a dependence on the [Mg²⁺] in the parent solution.

Thrust 3: Influence of Cation-Organo-Mineral Interactions on Nucleation, Aggregation, and Transport. Three related projects focus on understanding how ion-organic matter-surface interactions influence the nucleation and aggregation of minerals and the transport of contaminants in the environment. One project examines the fundamental chemical role of Ca²⁺-organic interactions on mineral precipitation and aggregation by exploring biomineralization in the renal system, a second concentrates on the interfacial properties of clay-organo complexes and how they affect metal transport in the environment, and the third uses combined quantum chemical and MD techniques to study the interaction of pharmaceuticals with clay surfaces. (1) Goodwin, A. L.; Michel, F. M.; Phillips, B. L.; Keen, D. A.; Dove, M. T.; Reeder, R. J. *Chem Mater* 2010, 22, 3197. (2) Raiteri, P.; Gale, J. D.; Quigley, D.; Rodger, P. M. *J Phys Chem C* 2010, 114, 5997.

Study of Structure and Transformation Behavior of Amorphous Calcium Carbonate (ACC)

Richard J. Reeder and Brian L. Phillips, *Stony Brook University*

The overall theme of our research program is development of structure-stability relationships for amorphous calcium carbonate (ACC), with the goal of providing a structural basis for understanding and predicting transformation of ACC into more stable crystalline forms. Our focus has been on model systems that have application to initial stages of calcium carbonate precipitation in terrestrial and marine systems, both inorganic and biogenic, as well as subsurface mineralization related to CO₂ sequestration. We have also studied natural ACC for comparison with model systems. In our work, traditional methods used for determining structure in crystalline materials have been supplanted by techniques suited for non-crystalline materials. We have used synchrotron-based X-ray total scattering and X-ray absorption spectroscopy in combination with ¹H and ¹³C NMR spectroscopic methods to assess short- and medium-range structure in ACC. These methods have allowed characterization of structural changes throughout the transformation of ACC into crystalline products, including the effects of dopants.

Synchrotron X-ray total scattering data and atomic pair distribution functions (PDFs) for synthetic ACC were used in combination with reverse Monte Carlo (RMC) refinement methods to produce the first structure model for dopant-free ACC. The model shows a distribution of local coordination environments for Ca encompassing the linkages of all the known crystalline forms of CaCO₃. This suggests that potential nucleation sites exist for crystallization of any polymorph. The structure model also shows that the medium-range structure observed in pair distribution functions is dominantly attributable to Ca...Ca pairs linked through bridging oxygen corners of CO₃ groups and through adjacent oxygens in CO₃ groups, with smaller contributions from associated Ca...O pairs. An unexpected feature of the structure model is the nano-scale segregation of Ca-rich and carbonate/H₂O-rich domains. ¹H NMR confirms the presence of two populations of H₂O molecules that differ in their dynamic character. If shown to be correct, this nano-porous like feature of ACC suggests possible sites for dopants as well as pathways for H₂O loss during crystallization. This RMC model provides a starting point for further refinement of short- and medium-range structure in different types of ACC.

X-ray total scattering and NMR spectroscopy were used to monitor structural changes accompanying transformation of ACC to crystalline forms. Minimal changes to the ACC were observed in PDFs and by NMR, both of which showed appearance of sharp peaks attributable to vaterite, calcite, and less commonly aragonite, along with features from a small amount of ACC that persists for weeks after the appearance of crystalline phases. Transformation kinetics exhibit Avrami-type behavior.

We explored the use of heating to promote ACC transformation. Heating to 110-120 °C results in partial dehydration, with an average mass reduction of 14%, while still retaining an amorphous state, and this may offer a synthetic analog to anhydrous ACC identified as the immediate precursor to crystalline CaCO₃ in biogenic systems. Dehydrated ACC shows only subtle differences from hydrated ACC in PDFs and by NMR, which shows that both rigid and mobile water remain in the dehydrated form. These results point to the need for further structural and kinetic studies of dehydration and the subsequent formation of crystalline products.

We also used X-ray scattering, absorption spectroscopy, and NMR to study structure in biogenic ACC, for comparison with synthetic samples. Hydrated ACC from gastroliths of pre-molt lobsters show short- and medium-range structure that is nearly identical to that for synthetic, hydrated ACC, with similar crystallization behavior. This result provides support for parallel studies of natural and synthetic samples for establishing the structural basis for the role of ACC in formation of stable calcium carbonate minerals.

Investigating the Physical Basis of Biomineralization: Influence of mineralization pathway on Mg fractionation in calcite and insights for polymorph selection

P.M. Dove¹, D. Wang¹, J.J. DeYoreo,² ¹*Virginia Tech*, ²*Lawrence Berkeley National Laboratory*

Much of our understanding of carbonate mineralization is based upon experimental studies of calcite precipitation that were interpreted through the lens of classical crystal growth. This type of growth occurs by the ion-by-ion attachment of solutes to the step edges of surfaces. While step propagation models provide the foundation for interpreting many aspects of mineralization in aqueous systems, the process is unable to explain some carbonate compositions and textures. For example, extensive experimental efforts to grow high Mg carbonates at low temperatures by this process have failed to produce calcites with more than 10-15 mol% MgCO₃. *In situ* observations confirm that calcite growth by step propagation becomes fully inhibited at Mg levels far below those measured in seawater, thus precluding the idea that very high Mg carbonates, such as protodolomite, are formed by classical growth processes.

The biomineralization community has faced similar questions regarding the processes by which organisms have species-specific controls on the Mg content of carbonate skeleton that sometimes contain as much as 30-50 mol% MgCO₃. It is now recognized that these very high Mg calcite structures form by a two-stage mineralization process that begins with the accumulation of amorphous calcium carbonate (ACC) in a localized environment followed by its transformation to 5-100 nm nanoparticles. The resulting crystals can have significant crystallographic co-alignment at the nanoscale to produce the complex superstructures we know as skeletal biominerals. Studies of synthetic inorganic materials show a similar process can produce crystalline coherent aggregates of nanoparticles— sometimes referred to as mesocrystals. One aspect of our work is to determine factors that bias pathways to mineralization and the consequences for carbonate formation in biological and sedimentary environments.

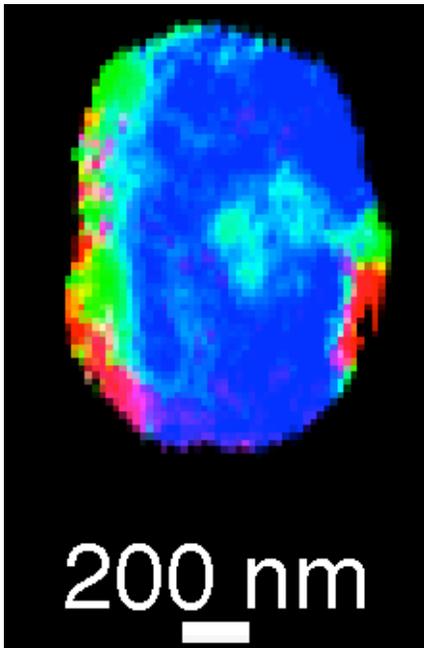
In this study, we determine the influence of mineralization pathway on the texture and composition of calcites that transform from the ACC precursor. When Mg concentration is insufficient to inhibit step growth, ACC transforms into crystallites of Mg calcite (0-15 mol% MgCO₃) whose compositions exhibit the expected linear fractionation with Mg/Ca of the initial solution. In contrast, when initial Mg levels are above the threshold that prohibits step growth, ACC transforms to nanoparticle aggregates of very high Mg calcite (30-50 mol% MgCO₃). Compositions are independent of initial solution chemistry with no evidence of fractionation. Analysis of the data shows mineralization is biased to this alternative pathway when the local environment: 1) contains sufficient MG to inhibit crystallite growth through increased solubility – a thermodynamic factor; and 2) achieves saturation with respect to ACC on a timescale that is shorter than the rate of aragonite nucleation – a kinetic factor. The findings provide a physical basis for long-standing claims that complex patterns of carbonate precipitation arise from a combination of kinetic and thermodynamics effects. The resulting process-based framework may reconcile discrepancies in reported fractionation patterns while demonstrating the geochemical basis for high Mg carbonate biominerals and a plausible pathway to protodolomite formation. (Wang, Echigo, Giuffre, Hamm, De Yoreo, Grotzinger, Dove, submitted)

Mapping the Amorphous-to-crystalline transitions in CaCO₃ biominerals, with 20-nm resolution

Pupa Gilbert, *University of Wisconsin-Madison*

One of the most fascinating aspects of calcite biominerals is their intricate and curved morphology, quite different from the normal rhombohedral crystal habit of geologic calcite. These morphologies are achieved via amorphous precursor mineral phases (1). In this talk we will show that in sea urchin larval spicules two distinct phase transitions occur, 1→2 and 2→3 (2). The 1→2 transition is regulated by inhibiting proteins, while the 2→3 is thermodynamically driven, and occurs spontaneously (3).

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3. YUT Gong, CE Killian, IC Olson, NP Appathurai, RA Metzler, AL Amasino, FH Wilt, PUPA Gilbert. Phase Transitions in Sea Urchin Larval Spicules. In preparation.



Cross-section of a spicule, freshly extracted from a 48-h sea urchin embryo, caught in the act of transforming from ACC (type 1 = red, type 2 = green) to crystalline calcite (type 3 = blue), and imaged with XANES-PEEM spectromicroscopy. Notice the crystalline phase at the center, and the amorphous phases at the left and right edges of the spicule.

The formation of metastable aluminosilicates in the Al-Si-H₂O system: Results from solution chemistry and solid-state NMR spectroscopy

Harris E. Mason, Robert S. Maxwell, Susan A. Carroll,
Lawrence Livermore National Laboratory

We present the results of a series of experiments designed to probe the interactions between Al and the amorphous silica surface as a function of thermodynamic driving forces. The results from ²⁷Al single pulse magic angle spinning (SP/MAS) and ²⁷Al{¹H} rotational echo double resonance (REDOR) allow us to identify the reaction products and constrain their structure. In all cases, despite low Al and Si concentrations we observe the formation of metastable aluminosilicates. Results from low temperature experiments indicate that despite thermodynamic driving forces for the formation of gibbsite we observe the precipitation of separate octahedrally coordinated Al (Al^[6]) and tetrahedrally coordinated Al (Al^[4]) silicate phases. At higher temperatures the Al^[4] silicate phase dominates the speciation. Structural models derived from the NMR data are also proposed, and the results are discussed as they relate to previous work on Al/Si cycling.

Interface and Solvent Effect on Carbonate Mineralization

H. Henry Teng, *George Washington University* and Huifang Xu, *University of Wisconsin*

Carbonate mineralization has been at the forefront of surficial geochemistry for the past two decades and is attracting more attention recently due to the concerns of possible feedbacks of high atmospheric CO₂ to global climate as well as the need for carbon sequestration. Our investigations in the current funding period focused on the following two aspects of carbonate formation: (1) template effect on the crystallization of Ca-CO₃; (2) solvent effect on the precipitation of Mg-Ca-CO₃. The motivation to study template effect stems from the need to understand how silicates affect the nucleation and growth of Ca-Mg-carbonates in geological C storage media. In this area, we investigated calcite crystallization on biotite and pyroxene to determine the orientation relations between calcite and the substrates. In the other front, the inability for anhydrous Mg-CO₃ to precipitate at ambient conditions continues to pose a great challenge to geochemistry. We tested Mg-CO₃ crystallization in dry solvent methanol (MeOH) and formamide (FM), as well as MeOH-H₂O and dimethylformamide (DMF)-H₂O binary solvents. We hypothesized that (1) in dry conditions, the organic solvation shell is weaker than that of H₂O due to the steric effect of large or hydrophobic groups such as CH₃; (2) in binary system, organic molecules may substitute one or more solvation H₂O to distort and weaken the water cage.

Our results show that biotite has a strong controlling effect on the orientation of calcite nucleation. The primary orientation relationship between the growing calcite crystals and biotite substrate are: calcite (001) ~// biotite (001) and calcite (010) ~// biotite (010). Our analysis indicates that calcite crystals initially nucleate from the Ca²⁺ layers and occupy the original K⁺ sites on the biotite surfaces, followed by the attachment of CO₃²⁻ groups on the calcium monolayer to form the first unit cell of calcite. The geometry of this Ca²⁺ layer, which matches the calcite structure, could be the control factor on calcite *a*-axis direction. The slight difference (with overall area mismatch of +1%) can be accommodated through distortion of the first calcite layer. We suggest the pseudo-hexagonal symmetry on biotite (001) surface leads to the observed (001) twinning in calcite. We found biotite substrate can enhance Mg incorporation into calcite. As much as 19% MgCO₃ can incorporate into the calcite lattice using a solution with Mg/Ca ratio of 5. Results from both natural and synthesized samples show that pyroxene (e.g. diopside) can also enhance epitaxial growth of calcite with preferred orientations between calcite *a*-axis and diopside *c*-axis. The observed large interface area between diopside and synthesized calcite indicate that the exposed Ca²⁺ and Mg²⁺ ions on surfaces with pseudo-hexagonal arrangements may serve as heterogeneous nucleation sites and therefore lower the nucleation energy barrier.

Numerous observations were made from a series of Mg-CO₃ crystallization experiments. (1) Precipitates are poorly crystallized or even amorphous in binary MeOH system. No anhydrous Mg-CO₃ was observed in pure MeOH at minimal water content. XPS results showed a likely formation of basic Mg-CO₃ phases. (2) Only amorphous MgCO₃ was observed in dry FA. FT-IR revealed that there was no H₂O or -OH in the precipitates. Further, for Ca-CO₃-FA system, well crystallized calcite and vaterite were observed. What's interesting is that when equal amount of Mg and Ca ions were present in the system, the only phase identified by XRD was dolomite. (3) Tri-hydrate Mg-CO₃ phase nesquehonite was the only phase crystallized in the DMF-water binary solvent. It was found that, after solubility correction, DMF accelerated the nesquehonite formation. Analysis of induction time showed the acceleration was not due to reduction of system energetics. Further analysis based upon the Smoluchowski's coagulation theory, suggested that the faster rate was likely due to aggregation of sub-critical nuclei resultant from the higher surface energy in the DMF-H₂O system. These results show the strong affinity of Mg²⁺ to H₂O, but also suggest that hydration may not be the only factor hindering the formation of anhydrous MgCO₃.

We have synthesized disordered dolomite at room temperature in aqueous solutions (similar to seawater and groundwater) with very low concentrations of dissolved hydrogen sulfide and polysaccharides that act as catalysts through hydrogen bonding with surface [CO₃]²⁻. The adsorbed catalysts with low dielectric constants can lower dehydration energy barrier of surface Mg²⁺-water complexes dramatically, and therefore enhance Mg²⁺ incorporation into the dolomite structure.

Early Stage Carbonate Precipitation Mechanisms in Saline Waters

Brian P. Gorman, *Colorado School of Mines*

Rising atmospheric $p\text{CO}_2$ is causing a concurrent rise in the $p\text{CO}_2$ of upper ocean waters and a resultant decrease in carbonate ion concentration. It has been observed for close to half a century that this decrease in the saturation state of seawater with respect to carbonate minerals alters carbonate precipitation rates. Specifically, aragonite precipitation frequently does not behave as would be predicted by simple thermodynamic solubility consideration. There is considerable indirect evidence that a surface phase with different properties may be responsible for this anomalous precipitation behavior.

The primary focus of this program is to gain a more fundamental understanding of the processes controlling precipitation and dissolution reactions kinetics and ultimately to provide a consistent thermodynamic solubility model. To that end, nanoscale characterization is being completed on carbonate surfaces following exposure to saline waters with widely varying degrees of saturation. Surface structure and chemistry is analyzed using a combination of μ -Raman spectroscopic imaging, grazing incidence XRD, SEM, FIB, TEM, EELS, AFM, and atom probe tomography.

Studies have initially been focused on short (10 hr) and near equilibrium (40 d) exposures of calcite and aragonite single crystal substrates to $\Omega = 0.8$ to 3.48 saturation saline (NaCl) water. At short exposure times, carbonate precipitation is independent of the saturation state and forms via a layer-by-layer epitaxial growth. At longer exposure times, the growth mechanism changes to an island growth mechanism, and is capped with a <100 nm thick, sub-stoichiometric amorphous calcium carbonate. This Stranski-Krastanov type of crystal growth is most likely due to chemical changes from the substrate to the film, resulting in a film strain in the precipitated material. In order to determine if the precipitated film is sub-stoichiometric (as in the precipitated ACC) or contains secondary cations such as Mg, atom probe tomography has been applied successfully to the precipitated carbonates. Although this is the first time APT has been utilized in the study of carbonates, the potential for understanding precipitation and growth at the atomic scale is very high, especially with respect to the role of hydrogen.

Mechanisms and rates of reaction of ionically-bonded minerals.

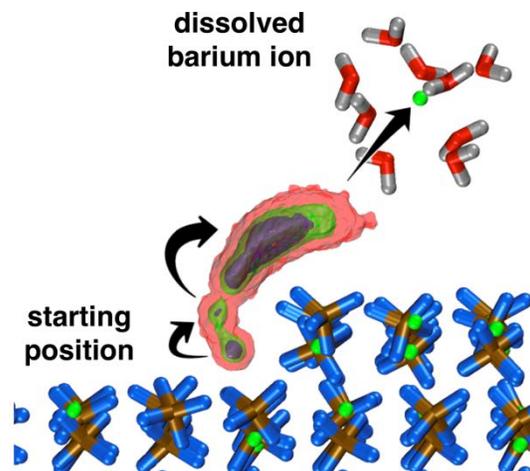
Andrew G. Stack, P. Raiteri, J.D. Gale, D.J. Wesolowski, J.N. Bracco, D.M. Warren,
Oak Ridge National Laboratory

Growth and dissolution of minerals can occur whenever native subsurface fluids are displaced by others, for example, during scale formation in oil, gas and geothermal energy production. In other cases, it is desirable to engineer the growth or dissolution of an incorporating mineral directly in the subsurface *in situ* in order to remediate toxic contaminants, or to predict the long term fate of contaminants in the subsurface. The focus of this talk will be our ongoing efforts to examine geochemically relevant reactions in terms of their molecular-level mechanisms and to use this knowledge to explain reactivity observed at larger scales.

A method to simulate the rates and equilibrium constants of geochemical reactions whose mechanism is not known ahead of time will be discussed. Specifically, the attachment and detachment of an aqueous barium ion onto a barite (BaSO_4) [120] step edge is examined. Metadynamics is used to determine the reaction mechanism (Figure 1), while the more conventional umbrella sampling and reactive flux calculations are used to simulate rate and equilibrium constants. In contrast to common practice, the attachment and detachment reactions are found to pass through multiple structurally and energetically distinct intermediate states. The Arrhenius activation energies for the limiting reactions quantitatively match the experimental estimates made from atomic force microscopy. The result will have significant implications for the prediction of the rates of geochemical reactions and for the design of growth modification or inhibition agents.

We also describe our recent efforts using atomic force microscopy to examine the growth of calcite (CaCO_3) under solutions with varying ratios of aqueous calcium-to-carbonate in the presence of strontium, which is of significant concern to DOE as a radioactive contaminant. Of particular interest is amount of strontium necessary to inhibit growth, which correlates with the aqueous calcium concentration, but not carbonate. This has significant implications for the mechanism of step pinning. Finally, future plans will be outlined to incorporate these measurements and simulations into larger time- and length-scale phenomena.

Figure 1. Free energy isosurfaces for detachment of a barium ion from the barite step edge. Multiple intermediate steps are observed (denoted by black arrows).



Fluid interactions with minerals and rocks – dynamics and evolution from picoseconds to thousands of years

Gernot Rother¹, Lawrence M. Anovitz¹, David J. Wesolowski¹, David R. Cole², and Susan L. Brantley³ ¹Oak Ridge National Laboratory, ²Ohio State University, ³Pennsylvania State University

We aim to develop a fundamental, atomic- to macro-scale understanding of natural fluids in geologic environments. This presentation will focus on water-solid interactions, which impact water mobility near mineral surfaces on the pico- to nanosecond time scales, but also critically contribute to large-scale rock transformation processes over much longer periods of time. Water is essential to life on earth; rock diagenesis and weathering are important processes shaping the face of earth. I will discuss, by example of our recent work, the use of dynamic and static neutron scattering as a powerful tool for the measurement of structure and dynamics of geologic systems [1].

In a multi-investigator, multi-technique effort we study the atomic-scale structure and pico- to nanosecond dynamics of water at the rutile, cassiterite, and quartz nanoparticle interfaces [2]. Using Quasi-elastic neutron scattering (QENS) and X-ray reflectivity combined with molecular dynamics simulation reveal strong interfacial layering with layer-specific structural and dynamics properties. Recently, neutron spin-echo spectroscopy was utilized to assess the collective motions of water contained in the first molecular layers formed at the rutile surface.

Dissolution/precipitation processes play an important role in rock weathering and diagenesis/metamorphism. (Ultra) Small-Angle Neutron Scattering ((U)SANS) is a powerful tool for the characterization of multi-scale porous systems often found in rocks. Unlike electron microscopy, scattering data give statistically meaningful information averaged over cross sections of about 2 cm² and volumes of ca. 0.1 ml, including the pore volume, specific surface area, fractal dimension and pore size distribution in the nm to tens of μm size ranges. In collaboration with Prof. Brantley's group at Penn State, we studied the nano-scale structural changes associated with rock weathering in shale at the Susquehanna Shale Hill Observatory [3]. Samples were taken along the weathering front and their SANS patterns recorded. Total nano-scale porosity, comprised by the sum of connected and unconnected porosity, increases from 5% in the bedrock to 10% in intensely weathered samples. Soaking the samples with neutron contrast-matching H/D water removes scattering from open and connected pores, i. e. the SANS signal now arises from unconnected pores only. We find that at depth nearly all porosity is unconnected, while in the more weathered samples the connected porosity is above 50% of total porosity. Characteristic changes in specific surface area and fractal dimension are found throughout the weathering zone, and can be linked to the weathering mechanism.

The structural evolution of Hueco limestone during contact metamorphism was studied by SANS techniques [4]. The scattering curves show mass fractal scattering at large length scales, resulting from pore and grain scattering, and surface fractal scattering regions at shorter length scales. The fractal properties as well as the pore volume and specific surface area change as a function of distance to the contact aureole. A strong spike in the surface area for samples near the metamorphic limit indicates reaction of organics to graphite and strong increase in pore volume.

[1] D. R. Cole, E. Mamontov, G. Rother, In: Neutron Applications in Earth, Energy, and Environmental Sciences, L. Liang et al. (eds.), Springer Science+Business Media, 2009. [2] E. Mamontov, L. Vlcek, D. J. Wesolowski, P. T. Cummings, J. Rosenqvist, W. Wang, D. R. Cole, L. M. Anovitz, G. Gasparovic, *Phys. Rev. E* **79** (2009), 051504. [3] L. Jin, G. Rother, D. R. Cole, D. F.R. Mildner, C. J. Duffy, S. L. Brantley, *Am. Miner.* **96** (2011), 498. [4] L. M. Anovitz, G. W. Lynn, D. R. Cole, G. Rother, L. W. Allard, W. A. Hamilton, L. Porcar, M.-H. Kim, *Geochim. Cosmochim. Acta* **73** (2009), 7303.

Computational Geochemistry: Applications to metal adsorption at mineral-water interfaces

Ian C. Bourg, Kideok D. Kwon, Garrison Sposito, *Lawrence Berkeley National Laboratory*

During the last twenty years, extensive efforts have been made to constrain macroscopic adsorption models using molecular-scale information provided by spectroscopy and molecular modeling techniques. In this talk, we present our latest contributions to elucidating chemical speciation at mineral-water interfaces using molecular dynamics (MD) simulations and quantum-mechanical density functional theory (DFT) calculations. We focus on two systems of particular relevance to the energy sciences. Our first system, the basal surface of smectite (phyllosilicate) nanoparticles, contributes the largest portion of mineral surface charge and surface area in many soils and sediments and constitutes an ideal model system for probing the structure of the electrical double layer at charged solid-water interfaces using MD simulations. Our second system, the basal and edge surfaces of birnessite (manganese oxide) nanoparticles, contributes significantly to transition metal adsorption and redox reactivity in metal-impacted ecosystems and constitutes a singular illustration of the ability of DFT calculations to assist in the interpretation of both spectroscopic results and adsorption data.

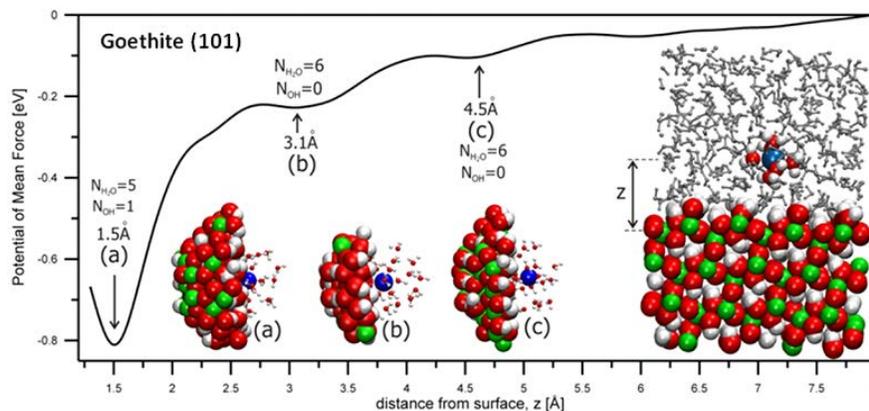
Reactive Fe(II) and Electron Exchange Dynamics in Iron Oxides

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¹Pacific Northwest National Laboratory, ²Denison University, ³Lawrence Berkeley National Laboratory, ⁴Michigan Tech, ⁵University of Iowa, ⁶University of Oslo

Ferrous-ferric electron exchange is central to the biogeochemical cycle of iron and determines iron forms and availability in the subsurface. For most environmentally relevant conditions this exchange involves interaction between soluble ferrous iron and solid-phase iron oxides and oxyhydroxides, with complex involvement of solid-state charge migration. Examples include Fe(II)-catalyzed transformation of Fe(III)-oxides and oxyhydroxides, and spinel ferrite nanoparticles acting as a mineralogic source and sink for reactive Fe(II) due to their topotactic solid-solution property and stable multi-valent nature. This presentation focuses on the interdependence of Fe(II) fluxes at these mineral-water interfaces with structural and electronic properties of mineralogic iron oxide forms. Single-crystal electrode potentiometry on individual crystal faces of hematite is used to comprehensively measure the range of surface potential differences as a function of pH that create electrical biases across the crystal. The measurements reveal a strong surface structure dependence on the potential distribution and solution conditions under which the bias is capable of directing diffusive charge migration through the bulk. For nanoscale systems, where these biases are likely present but difficult to measure, we examine Fe(II)-catalyzed iron isotope exchange kinetics in goethite as a function of pH and particle dimensions. Molecular dynamics simulations of the potential of mean force of Fe(II) adsorption, the free energy of electron transfer into the goethite surface, and diffusive electron hopping in goethite crystals show face-specific energetically favorable paths for electron injection and bulk current flow. Thermodynamic estimates of the free energy required to overcome associated Joule heating in the crystal are consistent with the magnitude of iron isotope mixing free energy using Gibbs' theorem. Finally, we also examine the mobility and accessibility of solid-state Fe(II) in mixed-valent spinel ferrite nanoparticles. A lattice Monte Carlo model was developed and used to simulate the dynamics and fate of Fe(II) electrons photoinjected into maghemite ($\text{Fe}_{8/3}\text{O}_4$) nanoparticles, for comparison with highly time-resolved pump-probe measurements over six decades of time-scale. The simulations demonstrate that that the pH-dependent surface potential biases the flow of mobile electrons and for electropositive net surface charge can trap them in the near-surface after injection. The distribution and decay of electrons from within the solid is therefore governed by surface charging properties, conceptually consistent with our single-face potentiometry measurements. Details covered will include free energy requirements for bulk crystal conduction and possible free energy sources sustaining bulk currents, ferrous iron adsorption energies at iron oxide surfaces and the kinetics of interfacial electron exchange, the structural dependence of ferrous-ferric electron exchange in the solid, and internal charge compensation mechanisms.

Calculated free energy of Fe(II) adsorption on the goethite (101) crystal face showing stable inner- and outer- sphere distances from the surface.



Reactivity of iron-bearing minerals and CO₂ sequestration

Daniel R. Strongin¹ and Martin A.A. Schoonen²
¹Temple University and ²Stony Brook University

Research will be presented that has investigated chemistry that may occur during the sequestration of supercritical CO₂ in underground geologic formations (e.g., deep saline formations) beneath the Earth's surface. In particular, in situ vibrational spectroscopy and reaction study results will be presented, that were obtained under conditions that closely mirror those that will be present in the environment. An area of focus of the research has been to learn how the presence of contaminants such as H₂S and SO₂ in the CO₂ injectate affects the reaction of CO₂ with iron bearing minerals to form, for example, immobile mineral phases such as FeCO₃. In the case of the exposure of hematite to supercritical CO₂ with 1% H₂S, the primary products are siderite and pyrite. The type and amount of product, however, is a strong function of the concentration of H₂S (or SO₂), reaction temperature, and solution pH. Overall, the research gives insight into chemistry during sequestration that can potentially increase the long-term storage of CO₂. The techniques being used to characterize the chemistry and products are in situ infrared spectroscopy and ex situ techniques that include electron microscopy, Mössbauer spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy.

Dehydration Phase Transitions in Uranyl Phosphates

David C. Elbert and David R. Veblen, *the Johns Hopkins University*

Sheet structured, uranyl phosphates are the predominant solid uranium host in a wide range of U-contaminated soils. The low solubilities and high U concentrations of many uranyl phosphates exert critical controls over U mobility in the environment. Despite this importance, understanding of the structures and stabilities of these phases is severely limited. Such crystal chemical knowledge is central to identification of uranyl phosphates in contaminated environments, design and interpretation of laboratory experiments, and modeling reactive hydrologic transport. In addition, increased focus on remediation strategies utilizing uranyl phosphates in reactive barriers or with subsurface chemical amendments depends on understanding their crystal chemistry.

Recent work on U-contaminated soils has highlighted the importance of autunite group minerals in groundwater zones of several DOE sites and weathered ore deposits. Autunite group minerals are characterized by sheets of actinyl square bipyramids linked by phosphate tetrahedra with interlayer sites occupied by H₂O-coordinated cations. An important characteristic of autunite-group minerals is a series of complex transitions in hydration state sensitive to temperature and aH₂O. We are using electron diffraction, x-ray powder diffraction and neutron diffraction to investigate the structures and phase relations of autunite group lower hydrates to better understand how their phase transitions control U mobility in contaminated environments. In our first in situ, synchrotron x-ray investigations of metatorbernite (Cu[UO₂]₂[PO₄]₂•8H₂O, basal spacing ~8.7 Å) we used continuous heating to produce lower hydrate phases with ~8.3, 6.9 and 5.4 Å basal spacings. A highlight of that work was identification in the second lower hydrate (6.9 Å phase) of a complete reconstruction of the sheets to uranophane-type layers with edge-sharing uranyl pentagonal bipyramids linked by sharing vertices and edges with the phosphate tetrahedral. This transformation allows the reduction of the basal spacing associated with dehydration to two H₂O per formula while still accommodating Cu in the interlayer. Further synchrotron investigations were carried out on the GSECARS Sector 13BMC beamline using relative-humidity sensors, microheaters and manual gas mixing to characterize temperature- aH₂O relations of the dehydration reactions. Under dry conditions, transition to the 8.3 Å phase occurs at ~64 °C, with the first appearance of the 6.9 Å phase at ~76 °C. Transformations are reversible in both temperature and aH₂O space, although they can take hours or even days at low humidity.

While our x-ray work has resulted in refinements to reasonable structures, the strong x-ray scattering character of U limits our ability to investigate details of lighter element positions. We are using neutron scattering to overcome this problem. With neutrons, each of the elements in metatorbernite (deuterated to avoid the strong incoherent neutron scatter of hydrogen) has similar scattering power (coherent neutron scattering lengths for D, O, Cu, P, and U are 6.67, 5.80, 7.72, 5.13 and 8.42 fm respectively). Preliminary neutron results refine position and occupancy of the two symmetrically independent H₂O molecules in metatorbernite and cast light on the degree of distortion of the equatorial oxygen in the uranyl polyhedral of the 6.9 Å phase.

Continuum Models for Reactivity in Confined and Nano-Confined Porous Media

Carl I. Steefel, *Lawrence Berkeley National Laboratory*

Developing reliable models for the rates of geochemical processes at the field scale remains a challenge. Although progress has been made in paring the laundry list of possible explanations for the laboratory-field discrepancy in rates, most work is still reductionist in character and of limited applicability to the “real world” of natural porous media. On the other hand, studies of geochemical dynamics carried out at the larger scale often lack meaningful mechanistic insights, so the challenge remains to somehow bridge the gaps between molecular, pore, and field scale geochemical dynamics.

Geochemical explanations for the “discrepancy” between laboratory and field rates have matured. The suggestion of Zhu et al, 2004 that slow rates of clay precipitation could regulate the departure from equilibrium with respect to primary dissolving mineral phases (principally feldspar) has been pursued in field settings (Maher et al, 2006; Maher et al, 2009). This effect, when combined with the nonlinear rates of dissolution for feldspars demonstrated by Hellmann and Tisserand (2006) and Oelkers and co-workers (e.g., Oelkers et al, 1994), resolves the “discrepancy” altogether for some reactive systems, as demonstrated by Maher et al (2009).

Maher et al (2006), Peters (2009), and Navarre-Sitchler et al (in press) have highlighted a second effect that can contribute to the “discrepancy”. In crystalline rocks in particular, not all of the pores are connected, which implies that not all of the reactive surface area is accessible other than through very slow grain boundary diffusion. In uncemented materials, rates measured in the laboratory can be applied to the field by normalizing them with the specific surface area of the subsurface material measured with BET. While this approach may give a reasonable estimate in uncemented materials, it works poorly for cemented sediments, or for crystalline rock where pore connectivity is poor (Navarre-Sitchler et al, in press). The challenge, therefore, is to map correlations between reactive phases and connected porosity, folding these eventually into fully dynamic models that take into account the actual pore structure of the subsurface material (Peters, 2009). To our knowledge, only 2D maps obtained by SEM-BSE and SEM-EDX have identified and characterized the spatial distributions of the mineral phases in direct contact with the pores (Peters, 2009). The medium must be assumed to be isotropic to equate the surface area from the 2D map obtained with the SEM techniques to a 3D volume. In this study, a multiple-technique approach is employed to correlate in 3D the reactive surface area of a rock where carbonate precipitation reactions occur, with the connected pore structure. The pore structure in the sample is measured in small volumes and at resolution lower than 1 μm by FIB-SEM, as well as in larger volumes and lower resolution, by synchrotron-based x-ray μ -tomography. The spatial distributions of the silicate and carbonate mineral phases in contact with the pores are determined with SEM-BSE and μ -XRF coupled with an image thresholding technique, as well as SEM-EDX and μ -XRD. These data will be combined with larger scale reactive transport experiments, augmented by pore and continuum scale modeling, to interpret the effects of pore connectivity on geochemical reactivity.

A second effort that will contribute to our understanding of rates in natural porous media involves continuum models for nanoporous materials. We have developed a model for multicomponent transport through clay-rich material that explicitly accounts for electrical double layers developed along charged mineral surfaces. An approach based on the assumption of Donnan equilibrium, with calculation of an average electrostatic potential within the double layer, is able to capture some of the behavior observed (e.g., anion exclusion). However, closer inspection indicates that it is likely necessary to consider the full Poisson-Boltzman equation coupled to the Nernst-Planck equation in order to capture the range of electrochemical effects operating in confined and nano-confined media.

Chemical Energy and the Distribution of Microbial Activity in the Subsurface

Rob Sanford, Craig Bethke, Ted Flynn, Brian Farrell, Matt Kirk, Matt Kyrias and Derik Stratton,
University of Illinois, Urbana-Champaign

A central tenet of the geomicrobiology of anoxic waters is that microbial life arranges itself into zones according to a thermodynamic ladder. By this concept, the functional group of microbes that can derive the most chemical energy from its environment dominates less-advantaged groups. Microbes that use ferric iron as their electron acceptor are expected, where ferric iron is present, to predominate over those that reduce sulfate. And those groups are taken to hold an advantage over methanogens. We use theory, modeling, field study, and laboratory experiment to take a fresh look at this idea. Using arrays of passive samplers, we monitored wells in the Mahomet aquifer of east central Illinois. The samplers allowed us to detect the active microbial populations in the aquifer, as well as analyze for major ions and dissolved gas in the groundwater. From the relative levels of ferrous iron and dissolved sulfide, the aquifer falls by convention into the strongly iron reducing category. Nonetheless, about the same amount of usable chemical energy is available to sulfate reducers and methanogens as to iron reducers. More strikingly, at all wells studied, regardless of groundwater composition, we found actively growing within the aquifer significant populations of not only iron reducers but sulfate reducers. Many of the wells, furthermore, host active methanogenesis. We believe the coexistence observed in the aquifer reflects a mutualistic relationship: the sulfide ions produced by the sulfate reducers react with the ferrous iron ions generated by the iron reducers. The reaction forms an insoluble precipitate, promoting the metabolisms of the two groups. Indeed, just such a relationship is observed in long-term bioreactor experiments. We propose the distribution of microbial activity in the subsurface can be understood in terms of a conceptual framework that honors the requirements of thermodynamics and is consistent with biologic observations.

Quantifying coupled chemical-mechanical alteration of fractured rocks: An integrated experimental and computational approach

Russell Detwiler, *University of California at Irvine*

Chemical alteration of fracture surfaces caused by reactive fluid flow can alter regions of contact between opposing fracture surfaces, which, in turn, affects the mechanical properties of the fracture. Predicting the potentially complex feedback between chemical and mechanical alteration in fractured rock requires scalable models that accurately represent these potentially competing mechanisms. Furthermore, development of such models requires evaluation through comparison to controlled experiments. Our previous experiments in analog fractures demonstrated that mineral dissolution from a homogeneous crystalline surface depends upon the relative magnitudes of advection and local reaction kinetics. When advection is rapid relative to reaction kinetics, dissolution from mineral surfaces occurs preferentially in locations of small fracture aperture, or in the vicinity of contacting asperities. An applied confining stress may then result in closure of the fracture, resulting in the potential for decreased permeability caused by mineral dissolution. Mechanistic models that explicitly represent coupled chemical alteration and mechanical deformation can provide improved understanding of the dynamics of these coupled processes in fractured rock.

We present an approach for modeling deformation between rough contacting surfaces in which contacting asperities deform elastically until their compressive strength is exceeded, upon which they experience brittle failure. The model reproduces the characteristics of published experimental observations of deformation due to normal stress cycling: nonlinear elastic deformation with a loss of total volume after each subsequent cycle caused by damage of contacting asperities. This modeling approach lends itself to coupling with our previously developed model of reactive transport in variable aperture fractures. To test the model, we have developed a new method for accurately measuring fracture apertures in fractured cores at high spatial resolution. The approach combines a high-resolution noncontact surface profilometer a precision-milled core-holder and careful image processing techniques to allow reproducible measurements of fracture aperture fields. This new approach allows us to extend results from previous experiments in analog fractures to pressures and temperatures representative of the deep subsurface and directly quantify alteration due to mechanical deformation and coupled chemical-mechanical alteration. Furthermore, experiments in rock cores provide the ability to directly measure the influence of mineral heterogeneity on these coupled processes.

Multiscale Modeling of Dissolution in Rough Fractures

Anthony Ladd, *University of Florida*

The dissolution of individual fractures is being studied by analytical and numerical methods. A linear stability analysis shows that fracture dissolution is inherently unstable, with channels of high permeability developing in an initially uniform fracture. At later times these channels compete with one another for the available flow up until the point where breakthrough occurs. We are investigating the growth of individual channels to try to identify the parameters that determine the growth rate of a single channel. This is a key component in a macroscopic model of fracture dissolution that nicely describes the competition between the growing channels in terms of the pressure field in the fracture.

Once the leading channel has reached the end of the fracture there is a large jump in flow rate, which reactivates existing channels. The flow in the large channels becomes turbulent, increasing both the frictional resistance to the flow and the degree of mixing of the reactant across the aperture. We have been investigating breakthrough with two-dimensional simulations, including empirical models for the turbulent mixing and drag. Preliminary results do not suggest qualitative changes in the dissolution patterns when compared to assumptions of laminar flow. Although solutional caves develop from initially narrow fractures, the passages are usually close to circular in cross section – how does this change in shape take place and at what stage of the dissolution process? We are developing a robust 3D simulation to study the evolution of shape under laminar and turbulent flow conditions.

Isotopic Studies of Rapid Carbonate Precipitates

James R. Boles, *University California at Santa Barbara*, Grant Garven, *Tufts University* and Sidney Omelon, *University of Ottawa*

We are investigating the fractionation of stable isotopes ($^{13/12}\text{C}$, $^{18/16}\text{O}$) between CO_2 gas, aqueous CO_2 species and carbonate (mainly calcite and the polymorph vaterite). In geologic systems, stable isotopes of carbon are traditionally used for determining the origin or source of the carbon whereas oxygen isotopes are used to determine the temperature of crystallization and/or isotopic composition of the water from which the carbonate formed. In situations where crystallization is *rapid*, the isotopic systems may be out of equilibrium for the isotopic composition of the fluid and temperature of crystallization. The relevance of the disequilibrium case is interpreting isotopic signatures from carbonate precipitates associated with CO_2 sequestration as well as leakage and degassing associated with hydrocarbon systems. In our studies we have investigated proxies of natural systems including well scales in hydrocarbon production tubing and recently formed calcite speleothems in a man-made tunnel. Crystallization rates are difficult to quantify but resultant precipitates typically have grown at mm/year rates. Results from calcite scales indicate that disequilibrium in the isotopic system results in 1) covariance in $^{13/12}\text{C}$ and $^{18/16}\text{O}$ of the precipitate for CO_2 degassing systems in which the CO_2 content of the system is limited (degassing of thin fluid film). Carbon isotopes in the precipitate of these systems are typically positive due to loss of the light carbon in the escaping CO_2 . Surprisingly, oxygen isotopes are more positive than expected for equilibrium with the water due to light isotopes being stripped by the rapid loss of CO_2 .

Our newest results are from experiments by Calera Corporation to artificially sequester CO_2 from coal combustion. In contrast to the proxies described above, precipitation is *extremely rapid*, (e.g. mixing of calcium into a high pH, CO_3^- charged fluid) and the precipitate has extremely light carbon and oxygen values, up to 20 per mil lighter than expected for equilibrium. We have observed these extreme cases in both the Calera experiments (calcite precipitate) and in a few well bores (vaterite precipitate). The latter involves changing fluid composition whereas the latter appears to involve degassing. In both cases the carbon and oxygen isotopic values of the precipitates are more than 10 to 20 per mil lighter than equilibrium with the fluid. These observations suggest that during extremely rapid crystallization rates the low mass light isotopes are preferentially incorporated into the carbonate. Apparently, the light isotopes can reach the reaction site more readily than the heavier isotopes once crystallization rates exceed some threshold rate. We are currently conducting experiments to determine the relation between crystallization rate, carbonate poly morph type, and stable isotopic composition, by precipitating via one of three precipitation methods: CO_2 off-gassing, supersaturation of CO_3^- in strongly basic solutions, or addition of $\text{CO}_{2(g)}$ at neutral pH.

Mineralogical constraints on redox reactions of iron (oxyhydr)oxide phases

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Reductive transformations of ferric (Fe^{3+}) iron oxide and oxyhydroxide minerals can drive large changes in subsurface biogeochemistry and mineralogy with major impacts upon groundwater quality and human health. In many anoxic zones, reduction of iron (oxyhydr)oxides is dominated by the action of dissimilatory iron reducing bacteria (DFRB) that use these solid phases as terminal electron acceptors (TEA) for carbon respiration. There has been considerable debate about how mineral properties affect the rates and outcomes of environmental iron reduction, particularly the ability of DFRB to utilize different phases. Here we apply an optical-pump/X-ray-probe method to study intermediate electron transfer steps for different phases of iron (oxyhydr)oxides, providing new insights into mineralogical constraints on iron reduction. We provide the first experimental proof that ferrous (Fe^{2+}) iron release into solution is the rate-limiting step, and is determined by mineral structure. We performed the first measurements of electron hopping rates within three phases and propose a new non-thermodynamic constraint on the rate of iron reduction associated with near-surface electron accumulation.

Dissolution rates and sorption/catalytic reactivity of mineral nanoparticles: Examples involving nanohematite

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Nanoscale iron (oxyhydr)oxide minerals are omnipresent in natural environments and past studies have found that their size, morphology and aggregation state influence chemical reactivity. In this study, we have investigated the influence of these factors on the reductive dissolution of hematite with ascorbic acid using two types of nanoparticles with average diameters of 6.8 nm and 30.5 nm, referred to as Hem-7 and Hem-30, respectively. Hematite nanoparticles were synthesized by forced hydrolysis of ferric nitrate and characterized with powder XRD, TEM, and BET surface area measurements. Reductive dissolution experiments were conducted at 23.0 ± 0.5 °C in the absence of light under nitrogen. Aqueous [Fe(II)] was measured by the ferrozine assay. High-resolution TEM (HRTEM) revealed that the Hem-7 crystals are pseudo-hexagonal plates and the Hem-30 crystals are rhombohedral. Initial and steady state dissolution rates were determined from batch experiments and compared after surface area (SA) normalization. The initial rates of reductive dissolution are about two times greater for Hem-7 vs. Hem-30, but the steady state rates are the same within experimental error. HRTEM observation of individual crystals and aggregates of Hem-7 reveal that this hematite is defect-free and dissolves from the edges of the crystals uniformly. Additional TEM measurements indicate that previous to dissolution, Hem-7 is present as both dispersed particles and as aggregates. Dispersed particles dissolve initially before aggregates, which influences the dissolution rate. HRTEM and high angle annular dark field - scanning transmission electron microscopy (HAADF-STEM) tomography also revealed that Hem-30 hematite has nanoscale surface steps and internal defects in the form of nanoscale pipes (nanopipes) within crystals, and its dissolution initiates from the steps, defects, or sharp edges of the crystals. In addition, HAADF-STEM was employed to observe the three-dimensional structures of individual aggregates. This reveals that aggregates of nanoparticles dissolve heterogeneously and holes form on the surface of crystals. This study directly shows the importance of size, surface roughness, defects, crystal morphology and aggregation states on dissolution rates of nanoparticles.

In a related study, we investigated abiotic Mn(II) oxidation catalyzed by nanoparticulate hematite in the presence of molecular oxygen in aqueous batch reactors. Manganese oxides typically form by the oxidation of aqueous Mn(II) catalyzed by mineral surfaces and are potent redox-active mineral components commonly found in the environment. They therefore participate in a wide array of reactions with organic and inorganic compounds. They often exhibit high sorptive reactivities and capacities exceeding those exhibited by iron oxides. When present, they can play a key role in the mobility and bioavailability of important aqueous ions. The kinetics of nanohematite/Mn(II) interactions in this study were studied as a function of the hematite particle size and the presence of organic ligands. The effect of organic ligands on the morphology of Mn-oxides was also studied. Surface-area normalized rate constants suggest differences in reactivity of hematite depending on its particle size. The end product of Mn(II) oxidation, a higher valent manganese oxyhydroxide identified as the mineral hausmannite, has been characterized by employing a suite of analytical techniques including high-resolution TEM, EELS mapping, SAED and SEM. The resultant Mn-oxyhydroxides has a unique nanosized, fiber-like morphology. SEM analyses were used to describe the formation and growth of Mn-oxyhydroxides fibers over time. Mössbauer analysis on nanoparticulate hematite after complete Mn(II) oxidation indicate small detectable amounts of Fe(II) suggesting hematite reduction and resorption of ferrous iron. These findings suggest that the formation of Mn-oxides can be influenced by the bulk mineralogical and geochemical composition of the surrounding environment, as well as by the interfacial solute–solid nanochemistry of the solid-phase oxidant. This study further signifies the relevance of low-temperature interfacial geochemistry in the formation and the transformation of environmentally pertinent mineral nanoparticles.

The Reactivity of Forsterite in Low Water Content Supercritical CO₂: Water Recycling and the Low Temperature Formation of Magnesite

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The nature of the reaction products that form on the surface of synthetic forsterite particles were examined during reaction with supercritical CO₂ (scCO₂) over a range of water contents and from 35°C to 80°C at 90 atm CO₂. The reaction products were examined under *in situ* conditions and *ex situ* following reaction. The *in situ* analysis was conducted by X-ray diffraction (XRD). *Ex situ* analysis consisted of scanning electron microscopy (SEM) examination of the surface phases and chemical characterization of precipitates using a combination of confocal Raman spectroscopy, ¹³C and ²⁹Si NMR spectroscopy, and energy-dispersive X-ray Spectroscopy (EDS).

The results show that at higher temperature (80°C) and water contents below the saturation level in scCO₂, reaction products were a complex mixture of partially hydrated/hydroxylated magnesium carbonate solids and hydroxylated silica species that were mainly in an amorphous state, forming a spatially non-resolved layer on the forsterite surface. At water contents above saturation reaction products transformed to anhydrous magnesite and amorphous silica. Transformation of hydrated intermediates to anhydrous phases implies H₂O initially bound in precursor hydrated/hydroxylated reaction products was liberated and thereby available to induce further reaction. Direct evidence was obtained that for a given fluid/mineral ratio there is a water threshold above which a significant portion of the water serves in a catalytic role, unlocking extensive carbonation reaction.

At lower temperatures, (35°C and 50°C) the primary reaction products in water saturated scCO₂ were a mixture of nesquehonite (MgCO₃·3H₂O) and magnesite (MgCO₃) at short reaction times and then magnesite (MgCO₃) and a highly porous amorphous silica phase at longer reaction times (14 days). After 14 days of reaction most of the original forsterite transformed to reaction products. Importantly, the formation of magnesite was observed at temperatures much lower (35°C) than previously thought were needed to overcome its well known sluggish precipitation kinetics. The observation that magnesite can form at lower temperatures implies that water recycling may also be important in determining the rate and extent of mineral carbonation in a wide range of potential CO₂ storage reservoirs. Therefore, in low water content

environments, such as contact between a subsurface wet scCO₂ plume and caprock minerals, the role of local water content is potentially pivotal for predicting mineral carbonation reaction rates and extent.

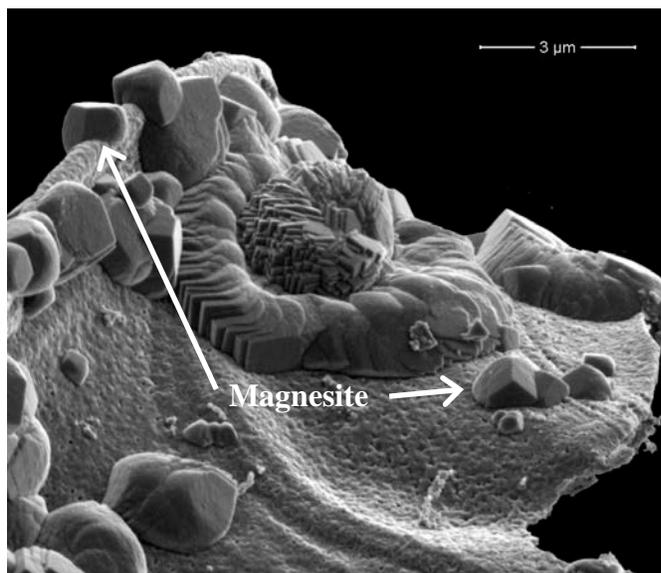


Figure. SEM images of the reacted nanoforsterite at water saturation illustrating the different morphologies of the precipitates. Temperature 35°C, 90 atm CO₂ pressure, 14 days of reaction.

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