FORWARD

Geochemical Probes and Processes is the nineteenth 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: 2011 best paper award winner: DePaolo et al, Integrated Isotopic Studies of Geochemical Systems. Molecular model quantitatively relates Ca precipitation and exchange rates (vertical axis) to solution saturation state (S-1) and Ca$^{2+}$:CO$_3^{2-}$ ratio.

Figure 2: 2011 best paper award winner: PUPA Gilbert & CE Killian. Biomineral crystals found in a sea urchin tooth. Geologic or synthetic mineral crystals usually have flat faces and sharp edges, whereas biomineral crystals can have strikingly uncommon forms that have evolved to enhance function. The image here was captured using environmental scanning electron microscopy and false-colored. Each color highlights a continuous single-crystal of calcite (CaCO$_3$) made by the sea urchin Arbacia punctulata, at the forming end of one of its teeth. Together, these biomineral crystals fill space, harden the tooth, and toughen it enough to grind rock.
Thursday Morning

7:00  Registration/Coffee

8:00  Introductions and Greetings
Nicholas Woodward, Department of Energy

Session 1: Geochemical Probes I –
Chairs: John Bargar and Dimitri Sverjensky

8:15  J. Stubbs, P. Eng, S. Sutton, M. Rivers, M. Newville, and A. Lanzilotti, University of Chicago, GeoSoilEnviroCARS Canted Undulator Upgrade: Enhanced Capabilities and Resources


9:05  Paul Northrup – Stony Brook University and Brookhaven National Laboratory - Progress and opportunities for tender-energy (1-8 keV) X-ray micro-beam spectroscopy at NSLS/X15B and NSLS-II/TES

9:30  A. Lanzilotti, S. Sutton, M. Rivers and S. Wirick, University of Chicago - Hard X-ray Geochemical Probes: Recent Developments and Prospects

9:55  Coffee

10:20  Juergen Thieme, Brookhaven National Laboratory - The SRX Beamline at NSLS-II: X-ray Spectroscopy with Very High Spatial Resolution

10:45  Yutao U. T. Gong¹, Christopher E. Killian¹,², Ian C. Olson¹, Narayana P. Appathurai³, Audra L. Amasino¹, Michael C. Martin⁴, Liam J. Holt², Fred. H. Wilt², and P.U.P.A. Gilbert¹, ¹Wisconsin, ²UC Berkeley, ³LBNL, ⁴ALS-LBNL - Phase transitions and their energetics in calcite biominerals

11:10  Eugene Ilton – Pacific Northwest National Laboratory - Using XPS, aberration corrected TEM, and XAS to understand the influence of coordination environment on uranium oxidation states

11:35  Nancy Birkner and Alexandra Navrotsky - UC Davis - Energetics of Redox Reactions in Bulk and Nanophase Manganese Oxides – Implications for Phase Stability and Catalysis

12:00 – 1:00  Lunch provided
Thursday Afternoon

Session 2 – Geochemical Probes 2 –
    Chairs: Troy Rasbury and Tony Lanzarotti

1:00  Don DePaolo and John Christensen – Lawrence Berkeley National Laboratory - Isotopic probes of mineral surface dynamics, crystal growth, and transport processes

1:25  D. Rumble\textsuperscript{1}, P. Freedman\textsuperscript{2}, E. D. Young\textsuperscript{3}, E. Schauble\textsuperscript{3}, and W. Guo\textsuperscript{4}, \textsuperscript{1}Geophysical Laboratory, \textsuperscript{2}Nu Instruments Ltd, \textsuperscript{3}University of California Los Angeles, \textsuperscript{4}Woods Hole Oceanographic Institution - Panorama: A New Gas Source Mass Spectrometer for the Measurement of Isotopologues in Geochemistry

1:55  Mark D. Kurz and Joshua Curtice – Woods Hole Oceanographic Institution - New Tracers of Gas Migration in the Continental Crust

2:20  Abby Kavner and J. R. Black – University of California Los Angeles – Stable isotope probe of nano-scale mineral-fluid redox interactions


3:10  Coffee


4:00  A. Hope Jahren, Univ of Hawaii and Brian A. Schubert, University of Louisiana, Lafayette – Carbon stable isotope fractionation during $C_3$ photosynthesis and its use in probing the terrestrial rock record

4:25  Ariel A. Chialvo, Oak Ridge National Laboratory - Interplay between neutron diffraction probes, electric conductance measurements, molecular theory and modeling toward the understanding of the structural and thermophysical behavior of water and aqueous electrolytes

4:50  Lawrence M. Anovitz, Oak Ridge National Laboratory - Nanometer to centimeter-scale analysis of the effects of geochemical processes on rock porosity: neutron scattering and imaging

5:15  Adjourn

6:30  Dinner (On your own)
Friday Morning

7:30 Coffee

Session 3 – Geochemical Processes 1 –
Chairs: James Farquhar and Abby Kavner

8:00 Jeffery A. Greathouse, Stephanie L. Teich-McGoldrick, Todd R. Zeitler, Randall T. Cygan, Sandia National Laboratories, Albuquerque - Characterization of Mineral Dynamics and Adsorption through Molecular Simulation and Spectroscopy


8:50 B. Gilbert, J. Erbs, R. L. Penn, V. Petkov and G. Waychunas, Lawrence Berkeley National Laboratory, University of Minnesota, and Central Michigan University – A disordered whole-nanoparticle model for 6-line ferrihydrite

9:15 Ian C. Bourg, Amy E. Hofmann, Laura M. Hamm, Michael Holmboe, Donald J. DePaolo, Lawrence Berkeley National Laboratory - Metal solvation at mineral-water interfaces: Implications for adsorption, diffusion, and kinetic isotope fractionation

9:40 Dimitri Sverjensky – the Johns Hopkins University - Predictive Single-Site Protonation and Cation Adsorption Modeling

10:05 Coffee

10:25 Lynn E. Katz, Heather C. Allen, Kevin Leung, Louise J. Criscenti, University of Texas, Ohio State University, Sandia National Laboratories, Albuquerque, NM - Geochemistry of Environmental Interfaces: Ion-pairing at Fe-oxide/water interfaces


11:15 William H. Casey – University of California, Davis - Pathways for Oxygen-Isotope Exchanges in Nanometer-Size Aqueous Clusters

11:40 Frank Richter – Chicago – Kinetic isotope fractionation in laboratory and natural samples

12:05 – 1:05 Lunch provided
Friday Afternoon

**Session 4 – Processes 2 -**
**Chairs: Udo Becker and Jeff Greathouse**

1:05 Lisa E. Mayhew and Alexis S. Templeton, University of Colorado – New insights into the mechanisms of hydrogen generation during low-temperature water-rock interaction

1:30 Patricia M. Dove1, A.J. Giuffre, and J.J. De Yoreo, Virginia Tech and Pacific Northwest National Laboratory – Systematic control of polysaccharide chemistry on the kinetics of calcite nucleation through competition of interfacial energies

1:55 David C. Elbert and David R. Veblen – the Johns Hopkins University - Development of Energy Dispersive Neutron Imaging

2:20 M.F. Hochella, Jr., H. Veeramani, M. Murayama, T. Echigo, D. Aruguete, Virginia Tech, Nanominerals and mineral nanoparticles: More clues as to how they operate and the chemistry they perform at nanometer to global scales

2:45 Coffee

3:10 Richard J. Reeder and Brian L. Phillips – Stony Brook University - Structural Changes Associated with Dehydration and Transformation of Amorphous Calcium Carbonate (ACC)

3:35 Susan Brantley, Penn State – An Investigation of Roughness and Weathering at the Bedrock-Regolith Interface

4:00 David Cole, Ohio State, Alberto Striolo, Oklahoma and D. Tomsko, Ohio State - Nanopore Confinement of C-H-O Mixed-Volatile Fluids Relevant to Subsurface Energy Systems

4:25 Arndt Schimmelmann, Maria Mastalerz, and Juergen Schieber, Indiana University, Bloomington, Shale gas: Geochemical and physical constraints on genesis, storage, and producibility

4:40 **Nick Woodward**
Concluding remarks

Optional Conference Dinner
ABSTRACTS:
GeoSoilEnviroCARS Canted Undulator Upgrade: Enhanced Capabilities and Resources

J. Stubbs, P. Eng, S. Sutton, M. Rivers, M. Newville, and A. Lanzilotti,
Center for Advanced Radiation Sources, University of Chicago

GeoSoilEnviroCARS (GSECARS) is a national synchrotron X-ray user facility at the Advanced Photon Source (APS) dedicated to research on earth materials and open to the entire scientific community. It supports high-pressure research with the laser-heated diamond anvil cell and multi-anvil press, X-ray absorption fine structure spectroscopy, X-ray fluorescence microprobe, microtomography, microcrystallography, surface and interface diffraction, inelastic scattering and powder diffraction experiments. More than 3700 individual scientists have used this facility since the beginning of full operations in 1997, performing experiments in four X-ray enclosures – two using an APS Undulator “A” (UA) and two using the bending magnet.

A recent upgrade to GSECARS, funded jointly by the Department of Energy’s Basic Energy Sciences program, the National Science Foundation, and the National Aeronautics and Space Administration, doubles the amount of undulator beam time available to users. The upgrade replaces the existing UA with two new undulators in a canted geometry (1 mrad cant), with each undulator better optimized for the end-station requirements, and provides new or upgraded X-ray optics for these instruments.

One undulator is optimized for hard X-ray energies (5.6-80 keV) for the surface scattering, multi-anvil press, and laser-heated diamond-anvil-cell instruments in stations 13-ID-C and 13-ID-D. The other undulator serves a new, dedicated X-ray microprobe at 13-ID-E using small Kirkpatrick-Baez (KB) mirrors that has an energy range from 2.4 keV (sulfur K-edge) to 28 keV.

To accommodate the tight spatial constraints of the canted geometry, many X-ray optical components were updated so that the two branches could work independently and without interference. Components that serve the 13-ID-C/D branch were upgraded to provide enhanced stability and flux, and in combination with the new undulator have already allowed us to collect high quality X-ray diffraction data from H₂O in the diamond anvil cell at 150 GPa, crystal truncation rod (surface diffraction) data at the lanthanum K-edge at 39 keV, and XAFS at the platinum K-edge (78 keV).

The microprobe branch uses new X-ray optics including a state-of-the-art monochromator and micro-focusing Kirkpatrick-Baez (KB) mirrors. In combination with two large mirrors and a high-precision slit upstream, these allow us to now achieve submicron X-ray beams. The new optics configuration allows efficient optimization of the final focus for either high flux or ultimate spatial resolution. K-edge XAFS data have been collected from sulfur (2.4 keV) to silver (26.7) keV, with superb beam stability and reproducibility in edge positions over the full energy range.

The upgrade is complete and all three 13-ID end-stations are now supporting user operations, enhancing the full suite of X-ray techniques GSECARS offers to the earth science community. From the high-pressure experimenters in 13-ID-D, to the mineral surface and interface scientists in 13-ID-C, to the geochemists using the microprobe in 13-ID-E, all will benefit from the brighter, more stable X-ray beams, extended energy ranges, and the doubling of available undulator beam time.
A robust understanding of the processes that control geochemical reactivity and transport in Earth’s near-surface environment requires fundamental knowledge of the relevant molecular-scale interfacial structures and reaction pathways. Our ability to better understand interfacial processes at the surfaces of rock-forming minerals has been challenged by our ability to obtain real-time in-situ observations with molecular-scale sensitivity and resolution. We will review our recent efforts to understand the reactivity of mineral-water interfaces using a powerful suite of state of the art X-ray based probes.

The calcite-water interface is the geochemically ubiquitous carbonate-water system that has been widely studied by both experiment and computation. Recent high resolution X-ray reflectivity (XR) measurements provide a more precise understanding of this system than previously available. These new data enable us to make direct and quantitative comparisons between molecular dynamics simulations and measured XR data, using a new formalism that we developed. This provides a fundamentally new ‘benchmark’ for testing the accuracy of our understanding of this system (for both the experimental and computational results), showing sufficient sensitivity to distinguish interaction potentials.

A second major thrust in our efforts has been in understanding the interaction of ions with charged mineral-water interfaces. This work uses the muscovite-water interface as a well-defined charged surface, using the chemical trends from a series of mono- and di-valent cations to elucidate the controls over the ion adsorption structures, thermodynamics and kinetics. Results show a high complexity to the adsorption distributions of cations that is controlled (at least in part) by the ion hydration energy with multiple coexisting adsorption states. Additional studies demonstrate a novel approach using resonant anomalous X-ray reflectivity (RAXR) to probe the systematic variation of adsorption thermodynamics for the alkali metal ions through competitive adsorption with Rb as a probe ion. This work reveals how the adsorption energy is controlled by a combination of ion size as well as adsorption speciation between distinct states. Our results also demonstrate how the ion adsorption structure is controlled, in part, by the interfacial hydration structure at the interface. Finally, we have demonstrated a new approach for probing site-specific ion adsorption/desorption kinetics through real-time measurements. Initial results show substantial differences in the desorption kinetics with ion charge, and yield new insights into the adsorption/desorption process.

Ongoing studies also include: the role of natural organic matter in controlling ion adsorption at mineral surfaces; the incorporation of metals into carbonates, as well as the growth of carbonate minerals on the calcite surface; and the development of an interfacial X-ray microscope for probing reactions at the mineral-water interface.
Progress and opportunities for tender-energy (1-8 keV) X-ray micro-beam spectroscopy at NSLS/X15B and NSLS-II/TES

Paul Northrup, Stony Brook University and Brookhaven National Laboratory

This instrumentation-development project is making good progress toward creation of a new and unique “tender-energy” synchrotron microprobe user facility for Geosciences. It will complement and extend to lower energies the X-ray fluorescence (XRF) and X-ray absorption spectroscopy (XAS) capabilities typical of “hard” (operating above about 4.5 keV) X-ray microprobes. Hard X-ray microprobes have well-established track records as element-specific non-invasive probes of elemental distribution and local physical and electronic structures and states in crystalline and non-crystalline materials. This facility is designed and optimized for 1-8 keV X-ray micro-spectroscopy and imaging applications, which will offer new opportunities to study the lighter elements Na through Ca. In addition, the new instrument will provide sufficient flux (up to $10^{12}$ photons/sec) and stability during energy scanning to enable high-quality extended X-ray absorption spectroscopy (EXAFS) at microbeam spatial resolution. Its key attributes will be the distinct 1 to 8 keV energy range, user-tunable spot size, stability optimized for high-quality XAFS, options for both XRF and XAS mapping with on-the-fly scanning, and a non-vacuum (helium glove-box) sample environment.

We will first implement these new micro-focusing capabilities at an established and proven macro-focused (~1mm spot size) tender-energy XAFS beamline at X15B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. This will be achieved by focusing the macrobeam to a “secondary source,” and then re-focusing beam with KB mirrors. After testing and commissioning at NSLS, the X15B microprobe and macro-focusing optics will be moved to the new Tender Energy Spectroscopy (TES) beamline on a bend-magnet source at NSLS-II. This strategy will provide immediate benefits for Geosciences research at NSLS/X15B this year, and deliver a tested and optimized instrument for early operation at NSLS-II/TES with a minimum of down-time during transition. This provides the opportunity to cultivate research programs now that will be ready to immediately capitalize on enhanced capabilities at TES, which is important for both the continuity of research programs and the early productivity of NSLS-II. Development of the TES beamline is a collaboration between a strong “Partner User” consortium and the NSLS/NSLS-II facilities. The Partner User group, supported by DOE Geosciences, NSF Earth Sciences, and NASA programs, is facilitating transition of the optical components and the scientific program.

Scientific drivers motivating this effort include several research areas where speciation, local structure and spatial distribution -- of lighter elements -- are all important. Some ongoing examples are:

1) Incorporation of Mg, SO$_4$ and PO$_4$ into carbonates: crystal chemistry, phase stability, biomineralization and paleoclimatology.
2) Mineral surface processes: adsorption, passivation, precipitation, incorporation, and dissolution involving light element species such as SiO$_4$, PO$_4$, SO$_4$ and Ca, as well as interactions of mineral surfaces with CO$_2$.
3) Linked sulfur, iron and uranium (U M$_5$ edge at 3.5 keV) redox cycling and long-term mobility in organic-rich sediment systems.
4) Atmospheric mineral/soil particulates: origin, global cycling and bioavailability of photosynthesis-limiting nutrients, as well as health effects.
Development of hard X-ray microprobe techniques that can be applied to geochemical problems have provided the Earth and environmental science research community with new capabilities in micro-focused X-ray absorption spectroscopy, XRF microprobe analysis, micro-diffraction, and elemental computed microtomography. The research at BNL’s National Synchrotron Light Source (NSLS) has led to important insights into the geochemistry of toxic metals and metalloids in contaminated sediments, tailings, airborne particulates, and well-waters. Studies have also evaluated the efficiencies of various contaminant remediation strategies, how bio-accumulation processes affect the distribution of trace toxic metal species and manufactured nanoparticles in soils and organisms, and improvements in the precision with which oxidation states can be determined by X-ray absorption spectroscopy.

This presentation will describe experiments conducted at the X26A and X27A X-ray microprobe facilities at NSLS including 1) μXANES and μXRD of airborne dust from abandoned mines that demonstrate the persistence of multiple As-bearing mineral species; 2) μXANES determination of Fe oxidation states of MORB glasses that necessitate an upward revision of the ferric iron content of the mantle relative to previous wet chemical determinations; and 3) Fe μXANES from amphiboles collected at the former vermiculite mine near Libby, Montana, U.S.A that indicate variations in Fe oxidation states between differing morphologies that may be related to potential health effects.

The future outlook for availability of these resources nationally throughout the DOE complex will also be discussed as the NSLS ceases operation at the end of FY14. An evaluation was prepared for BES and Brookhaven’s Photon Sciences Directorate on opportunities for X-ray micro-beam resources nationally during the transition from NSLS to NSLS-II. New beamlines that are now in the planning stages, such as the SRX and HXN beamlines that will be available at NSLS-II, promise to routinely provide sub-micrometer spatial resolutions for researchers. The proposed XFM beamline at NSLS-II could provide the geoscience community with a unique facility specifically optimized for micro-focused Extended X-ray Absorption Fine Structure (μEXAFS) spectroscopy allowing detailed information on the local environment of the target atom in-situ. Additionally, the recently commissioned GSECARS 13-ID-E microprobe at the Advanced Photon Source provides exciting new capabilities now, including a tunable energy range from 2.4 keV (sulfur K edge) to 28 keV, the use of KB mirrors to achieve beams with spatial resolution of 500 nm, and an innovative, state-of-the-art, direct-drive rotary stage monochromator that not only provides exceptional stability for sub-micrometer spectroscopy, but also allows for rapid “fly-scan” X-ray absorption spectroscopy opening new scientific opportunities for geochemists.
The SRX Beamline at NSLS-II: X-ray Spectroscopy with Very High Spatial Resolution

Juergen Thieme
Brookhaven National Laboratory, NSLS-II, Building 817, Upton, NY-11973, USA

The National Synchrotron Light Source II will be a source of synchrotron radiation with a very low emittance, horizontally down to 0.5 nm-rad, vertically diffraction limited at 8 pm-rad (for 12 keV), supporting a current of 500 mA. The source characteristics of this facility will be ideally suited for experiments in need of coherent radiation and provides an ideal platform for sub-micrometer focused beam instruments. The Sub-micrometer Resolution X-ray spectroscopy beamline (SRX) under construction at NSLS-II is being developed specifically as an X-ray fluorescence analytical probe utilizing Kirkpatrick-Baez (KB) focusing mirrors. The scientific emphasis is the study of complex systems with chemical heterogeneity at sub-micrometer and sub-100nm length scales. The beamline design provides X-ray spectroscopy capabilities in the energy range from 4.65keV to 23keV. A 1.5m long in-vacuum undulator with 21mm period length in a short low-β straight section will serve as a light source for SRX. The SRX beamline is one branch of a canted sector at NSLS-II, with a second undulator planned as a future upgrade to serve as an independent light source for another beamline, the X-ray fluorescence nanoprobe (XFN). The XFN design envisions a complementary beamline to SRX that will access lower X-ray energies (2-15 keV) and utilize Fresnel zone plate optics. SRX utilizes two sets of KB mirror optics for focusing, a high photon flux set that will deliver more than $10^{13}$ phot/sec in a sub-micron sized spot and a high spatial resolution set that will deliver a focal spot size of less than 100nm but at a lower flux of approximately $10^{11}$ phot/sec. A highly customized horizontally deflecting double crystal monochromator was chosen to provide maximum beam stability while simultaneously providing very high spectral and spatial resolution. The energy range covered by the SRX beamline will allow for X-ray absorption spectroscopy experiments starting at the K-absorption edge of titanium and extending through the K-edge of rhodium. The photon flux SRX delivers in a submicron-spot, ultimately combined with the use of new energy dispersive detectors like the MAIA, will open new possibilities for spectroscopic analysis of major and trace elements in natural and synthetic materials, X-ray fluorescence imaging of their distribution both in two and three dimensions utilizing tomographic methods, and, concurrent micro-diffraction measurements. Diffraction imaging experiments will be developed as well. Commissioning will begin in summer 2014; a detailed description of the SRX beamline will be presented here.
Phase transitions and their energetics in calcite biominerals

Yutao U. T. Gong¹, Christopher E. Killian¹², Ian C. Olson¹, Narayana P. Appathurai³, Audra L. Amasino¹, Michael C. Martin⁴, Liam J. Holt², Fred. H. Wilt², and P.U.P.A. Gilbert¹,*

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Crystalline biominerals do not resemble faceted crystals. Current explanations for this property involve formation via amorphous phases. Here we examine forming spicules in embryos of Strongylocentrotus purpuratus sea urchins, and observe a sequence of three mineral phases: hydrated amorphous calcium carbonate (ACCH₂O)→dehydrated amorphous calcium carbonate (ACC)→calcite. Unexpectedly, we find ACCH₂O-rich nanoparticles that persist after the surrounding mineral has dehydrated and crystallized. Protein matrix components occluded within the mineral must inhibit ACC·H₂O dehydration. We devised a new in vitro assay to identify spicule proteins that may play a role in stabilizing various mineral phases, and found that the most abundant occluded matrix protein in the sea urchin spicules, SM50, stabilizes ACCH₂O in vitro.
It has long been thought that the only two uranium oxidation states of environmental importance are U(IV) and U(VI). The likely, and perhaps reasonable, basis for the belief that the intermediate U(V) is not relevant under environmental conditions is the well documented rapid disproportionation of aqueous U(V) outside of a very narrow Eh-pH window. However, evidence from our laboratory is accumulating in support of the long term existence of sorbed pentavalent uranium, well outside the nominal stability of U(V)aq, suggesting that it could be more than just a transitory intermediate. A common theme was that U(V) associated with solids was never detected as a simple adsorbed complex, although its presence has not been ruled out; rather, it appeared to be incorporated in polymerized uranium forms or secondary precipitates during reduction by Fe(II), where higher U(V) concentrations, determined by XPS, were correlated to increasing uranate coordinated uranium (determined by EXAFS); the term uranate refers to a relatively symmetric coordination environment that lacks the short dioxo uranyl bonds. Unfortunately, the U(V) bearing phase was not identified. These findings spurred theoretical modeling which showed that uranate coordination, combined with a first shell coordination number, CN, less than 8, appears to widen the stability field of U(V) relative to both U(VI) and U(IV).

In order to test the calculations with rigorous experiments, we synthesized U(VI)-doped hematite (~0.6 mole % U). A combination of XAS (Fig. 1) and HAADF-TEM (Fig. 2) indicates that U substituted in the structure of hematite in uranate, likely octahedral coordination. Ab initio modeling also consistently shows that U(VI) can substitute in the octahedral sites of hematite (and goethite) in somewhat distorted uranate coordination. The U(VI) doped hematite with and without excess adsorbed U(VI) was then exposed to two different organic reductants with E° of 0.23 and 0.70 V. XPS of reacted material with and without excess externally sorbed U(VI) indicated that structurally incorporated U(VI) was reduced to U(V), whereas non-structurally incorporated U(VI) was reduced to U(IV) (Fig. 3). EXAFS (Fig. 1) and XANES were consistent with this interpretation.

Subsequent experiments with U incorporated in goethite after reductive transformation of the U(VI)-ferrihydrite system are consistent with the hematite results (in collaboration with the Fendorf group, Stanford University). Consequently, it appears that U(V) stabilization in Fe(III) (hydr)oxides may be a general phenomenon. Cumulatively, the results support the hypothesis, based on early experimental and theoretical work, that U(V) is stabilized relative to U(IV) and U(VI) in uranate coordination environments for CN < 8.
Energetics of Redox Reactions in Bulk and Nanophase Manganese Oxides – Implications for Phase Stability and Catalysis

Nancy Birkner and Alexandra Navrotsky, Peter A. Rock Thermochemistry Laboratory and NEAT ORU and Department of Chemistry, University of California Davis, Davis, CA 95616.

This grant focuses on the thermodynamic properties of solid mineral phases of importance in the crust and critical zone. Using the unique calorimetric, synthetic, analytical, and intellectual capabilities of the Peter A. Rock Thermochemistry Laboratory at University of California, Davis, CA, we measure the enthalpies of formation of both nanophase and bulk materials and relate these properties to structure, bonding, and geochemical reactivity. We are currently working on zeolites, sulfides, and manganese oxides. The major focus of the manganese oxides project, presented at this meeting, is the energetics of formation and surface chemistry of nanophase Mn-bearing oxides and examination of factors that promote mineral phase formation and transformation. Manganese oxides (Mn-oxides) are ubiquitous in the near surface environment and they play important roles in processes critical to geochemistry and life on Earth, including water column oxygen cycling, nutrient transport, surface adsorption and sequestration of heavy metals and radionuclides. Through thermochemical and structural studies, we gain knowledge about these processes to provide a trajectory for understanding geochemical phenomena and developing new technologically useful materials and processes.

Our most exciting findings on manganese oxides this year are:

The surface enthalpy (SE) (essentially equivalent to surface energy) of manganese oxide phases was determined using high temperature oxide melt solution calorimetry and water adsorption calorimetry. The energy for the hydrous surface of pyrolusite (MnO2) is 1.64±0.10 J/m², bixbyite (Mn2O3) is 1.29±0.10 J/m², and hausmannite (Mn3O4) is 0.96±0.08 J/m². Thus the spinel phase (hausmannite) has a lower SE than bixbyite, while the latter has a smaller surface energy than pyrolusite. Surface energy and hydration energy differences promote significant Gibbs free energy shifts in redox phase equilibria at the nanoscale. For particle sizes below 100 nm, these differences affect the free energies of phase transitions and of oxidation-reduction reactions, shifting the latter by as much as several log-(fO2) units at a given temperature. For manganese oxides the stability field of hausmannite, Mn3O4, is greatly extended at the nanoscale (see Fig. 1).

Rapidly reversible surface structural and phase changes occur with water adsorption / desorption for the binary manganese oxide nanophase assemblages. In a current study we find chemisorption of water molecules to degassed binary oxide surfaces promotes rapidly reversible mineral structure phase changes to the lower surface energy phase. Thus surface reduction of bixbyite to hausmannite occurs in nanoparticles under conditions where no redox reactions are seen in bulk materials.

Calcium manganese oxide (CaMnO) materials are proposed water splitting catalysts. These layered birnessite-like phases have lower SE than binary manganese oxides. We studied two series of materials with slightly different Ca/Mn ratios, with members within each series having different particle sizes and average manganese oxidation states. We found that they are thermodynamically stable and have significantly lower SE than bixbyite, hausmannite, and pyrolusite. They also bind water less strongly. The enthalpy of oxidation of CaMnO materials is independent of the average oxidation state (see Fig. 2) and significantly less exothermic that the oxidation of Mn2O3 to MnO2. We suggest that the above factors are important in enhancing the catalytic activity of the layered CaMnO materials. This work has just been submitted for publication. We will be extending studies to birnessites with other cations.
Fig. 1 Calculated phase equilibrium diagrams for MnO2 / Mn2O3 and Mn2O3 / Mn3O4: (a) bulk (b) 10 nm nanophases with anhydrous and hydrous surfaces.

Fig. 2 Enthalpy of formation, $\Delta H^o_{f-ox^*}$ for reaction $m\text{CaO} + [x+y]*\frac{1}{2}\text{Mn}_2\text{O}_3 + [y/4]*\text{O}_2 + n\text{H}_2\text{O} = \text{CaMnO}$ versus moles $\text{O}_2$ (y/4) reacted to form the sample. Squares represent the suite of samples with manganese average oxidation state (Mn AOS) of 3.89 with surface enthalpy of 0.75±0.11 J/m², and circles represent the suite of samples with a Mn AOS of 3.68 with surface enthalpy of 0.57±0.12 J/m². The slope gives an enthalpy of oxidation of -101.2 kJ per mole of $\text{O}_2$, considerably less exothermic than the value of -168.1 kJ per mole of $\text{O}_2$ for the Mn2O3/MnO2 equilibrium.

Publications supported by the project 2012-13:


Isotopic probes of mineral surface dynamics, crystal growth, and transport processes

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Differences in mass between isotopic molecular and atomic species generally lead to differences in rates of chemical reactions. These differences are exploited to obtain information about the conditions of formation of geological materials, and hence represent a powerful means of looking into the geologic and cosmological past. Our focus is on using isotopes to study the microscopic processes that govern ion transport in liquids, and fluid-to-solid phase transformations using a combination of experimental and theoretical approaches. Isotopic measurements constitute a form of microscopy that supplements the information provided by the ever-improving capabilities of electron, neutron, and atomic force methods. Our approach extends to impurity constituents of solids, the incorporation of which is also governed by dynamic processes at fluid-solid interfaces. The focus on mechanisms of transport and phase changes is stimulated by the growing body of measurements of mass-dependent isotopic fractionation of geologically abundant elements such as Li, Mg, Si, K, Ca, and Fe, as well as by improvements in analysis capability that is revealing variations in less abundant elements like Mo, Sr, and U. The link between isotopes and trace impurity constituents is useful because the latter can typically be measured with higher spatial resolution.

We have advanced the theory of isotopic and trace element fractionation as applied to precipitation of calcite from aqueous solution (DePaolo, *GCA*, 2011; Nielsen et al., *GCA*, 2012, 2013; Hofmann et al., *PNAS*, 2012), and in modeling of water isotope fractionation during condensation (Lu et al., *JGR*, 2009; 2013 in review). This work is now being extended with new calcite precipitation experiments (Watkins et al., 2013 in review), which are also allowing us to extend the treatment to O isotopes. Fractionation behavior is dependent on the gross fluxes of ions to and from growing crystal surfaces, and the ratio of these flux values to the growth rate. Understanding and verifying these fluxes using isotopes leads to more general mechanistic formulations of precipitation kinetics, as well as to delineation of the relative roles of equilibrium and kinetics. Establishing equilibrium isotopic fractionation factors has arisen as a particular challenge.

We investigate isotopic and trace element fractionation of natural systems to augment experiments. Transferring experimental and theoretical results to field scale systems is typically challenging, but there is potential to learn much more about the natural systems, and they access a much greater range of time and length scales. This presentation will touch on results from deep sea sediment pore fluids, hydrothermal systems, and vascular plants, which provide interesting extensions of our experimental studies. An example of a more traditional Sr isotopic approach that yields unanticipated results will also be covered.

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.
The Panorama is a gas-source, electron-impact, double-focusing 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 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 instrument is scheduled for delivery in early 2014 to UCLA where it will be located in the Department of Earth and Space Sciences. Our initial goal is to measure high-resolution mass spectra of single- and double-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 instrument is designed to achieve (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 concepts of Prof. Hisashi Matsuda of Osaka University have been used in the design to improve the transmission and decrease the aberrations of the mass spectrometer by deploying electrostatic lenses along the ion flight path. The new instrument will be available for use by all qualified scientists. It will be commissioned and operated under the supervision of an Advisory Council of internationally known scientists.

Figure 1: The Panorama mass spectrometer measures 5 by 4 meters in plan view.
New Tracers of Gas Migration in the Continental Crust

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An understanding of gas migration in the continental crust is central to many scientific and societal issues. Noble gases are exceptional tracers in continental settings due to the remarkable isotopic variability between the mantle, crust, and atmosphere (i.e. with respect to $^{3}$He/$^{4}$He) and because they are inert. Due to systematic variability in physical properties, such as diffusion, solubility, and production rates, the combination of helium, neon, and argon provides unique but under-utilized indices of gas migration. The radiogenic production ratios of $^{4}$He/$^{21}$Ne and $^{4}$He/$^{40}$Ar are relatively well constrained by abundance ratios of Th, U, and K, providing unique crustal production reference values, and making the ratios excellent indicators of fractionation processes when combined with isotopic compositions. However, existing noble gas data sets are dominated by measurements of gas and fluid phases from gas wells, ground waters and hot springs. There are very few noble gas measurements from the solid continental crust itself, which means that this important reservoir is poorly characterized and gas migration rates are poorly constrained. The central goal of this proposal is to enhance understanding of gas distribution and migration in the continental crust using new measurements of noble gases in whole rocks and minerals from existing continental drill cores, with an emphasis on helium, neon, argon and their relationships to carbon and nitrogen. We also will test the idea that the large range of $^{3}$He/$^{4}$He ratios in the continental crust can be used as a diagnostic for gas origin, beyond the simple mantle versus crust dichotomy that is commonly used.

This project has allowed the design and construction of a new ultra-high-vacuum extraction line devoted to continental rocks, which may contain hydrocarbons and thus require special handling to avoid mass spectrometric interferences. The construction phase for the extraction line is now in progress. Several new results from this laboratory bear directly on the overall goals of the project and will be presented. New helium data from a lithologically homogeneous shear zone in the Josephine peridotite (Oregon, USA) suggest a systematic relationship between deformation (grain size) and helium content (Recanati et al., 2012). This supports the hypothesis that deformation can enhance peridotite helium abundances, most likely relating to grain boundary (defect) residence sites as originally suggested by a study of oceanic peridotite mylonites. A new study of an amphibole diorite vein within young (11 Ma) oceanic crust shows that amphibole is an important noble gas bearing phase in the crust. A transect across the amphibole vein shows that the noble gases are remarkably heterogeneous on a millimeter to centimeter scale. The amphibole and plagioclase at the vein center have 5-10 times higher abundance of He, Ne, and Ar, with slight isotopic anomalies. The millimeter scale coherence between the transect noble gas abundances suggest that these heterogeneities were produced by hydrous crustal melting, and that post emplacement diffusion played a minor role. Overall, these new data highlight the importance of crustal gas distribution in the context of global geodynamic models.
Stable-isotope probe of nano-scale mineral-fluid redox interactions

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In a series of experiments on Fe, Zn, Cu, Mo, and Li, we have shown that electro-deposition results in large and tunable isotope fractionations at an electrode. The observed fractionations increase as we increase the mass transport rate of material to the reactive interface using a rotating disc electrode, demonstrating that the mechanism responsible for the fractionation is most likely adjacent to the interface. Thus, stable isotopes of redox-sensitive materials are promising markers for elucidating processes that occur at a reacting interface. In earlier publications (Kavner et al., 2005; Kavner et al. 2008), a theoretical description of isotope fractionation far from equilibrium due to one-electron transfer processes based on Marcus theory was presented. We show that an updated and more general version of the isotope-Marcus theory, which predicts isotope kinetic behavior close to equilibrium, provides an explanation for our observed data showing isotope fractionation during voltage-controlled deposition.
Uranium-series geochemistry and geochronology have a wide range of applications for paleoclimatology, volcanology, environmental risk assessment, and other fields. Our project aims to develop new tools and techniques for U-series measurements. We are applying these new developments to better measure, model, and understand U-series isotopic distributions over a range of spatial and temporal scales (micron to kilometer and years to millennia) in support of basic geoscience research for energy and waste concerns. The technique we are particularly interested in at present is femtosecond-laser ablation. We are currently evaluating a NWRFemto266 laser ablation system and a Nu Plasma II MC-ICP-MS for this work. Femtosecond laser ablation systems can provide some relief from the elemental fractionation observed with nanosecond lasers and can reduce reliance on matrix-matched standards. Even so, a range of well-characterized reference materials are required for high precision U-series work.

We will present U-series data obtained by MC-TIMS and MC-ICP-MS for a number of newly available glass reference materials (Chinese Geological Standard Glasses, CGSG) exhibiting a range of chemical compositions including basalt, syenite, andesite and a soil. Uranium concentrations for these glasses range from 2 to 14 µg g⁻¹ and Th/U ratios range from 4-6. Uranium and thorium concentration and isotopic data will also be presented for a rhyolitic obsidian from Macusani, SE Peru. This obsidian can also be used as a rhyolitic reference material and has a very low Th/U (0.076 atom ratio). Our data on Th and U concentrations are in agreement with prior measurements and provide significantly improved precision. Our data also suggest that these standards show a range of disequilibria for ²³⁴U/²³⁸U (0.93-1.02 activity ratio) and ²³⁰Th/²³⁸U (0.98-1.12 activity ratio) (Figure 1). The disequilibria appear to be primarily due to open system behavior. Characterization of these materials with ²³⁸U-²³⁴U-²³⁰Th disequilibria and extreme Th/U ratios will provide useful reference points for the U-series geoanalytical community.

We are currently developing and evaluating laser ablation methodologies by studying U-series transport and retention in fractures close to natural uranium deposits in Peña Blanca, Mexico. Suitable samples from vertical fractures in the PB-1b core have been identified and preparation is underway for both in situ and bulk measurements (via laser ablation, MC-ICP-MS and MC-TIMS). Our initial data from these samples indicate that uranium concentrations range from 600 to 5000 µg g⁻¹ and U/Th atom ratios vary from 40 to 400. Some of the U concentrations are nearly as high as in the ore deposit (0.55%). Given the large range in U/Th ratios, construction of whole rock ²³⁸U-²³⁰Th isochrons should be feasible. Isochron dates will provide information on the timing of U-series mobility in the vertical fractures during the past 350 ka.

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, nuclear forensics and climate change. Finally, the new methods and understanding from this work can contribute to interests of other agencies such as environmental monitoring and threat reduction.
Figure 1: Plots showing (a) $^{234}\text{U}/^{238}\text{U}$ and (b) $^{230}\text{Th}/^{238}\text{U}$ activity ratios for the CGSG glass and the Macusanite rhyolitic obsidian reference materials. Uncertainties are 2s and in (a) are smaller than the symbols.
Microanalysis, Sandstone Diagenesis, and Evolution of the Illinois Basin

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The goals of this project include:
1) Improve SIMS techniques for in situ microanalysis of O and C isotope ratios by SIMS and explore applications in sedimentary environments.
2) Measure stable isotope zoning in individual silicate and carbonate cements at 1-10 µm scale.
3) Determine the presence, timing, and genesis of porosity reducing silicate and carbonate cements in the Illinois Basin.
4) Test the new basin evolution model for quartz overgrowths of Hyodo et al. (2013) by analysis of feldspar and carbonate cements.

The spot size, precision, accuracy, reliability and ease of in situ stable isotope analysis by SIMS have been improved by modifications to hardware and software, new protocols for tuning and analysis, development of new standards, better sample preparation and imaging (Valley and Kita 2009, Kita et al. 2011, Kozdon et al. 2011, Peres et al. 2012). At WiscSIMS, these advances have led to discovery and study of systematic zonation that was not previously detectable with applications in biomineralization (Olson et al. 2012, Vetter et al. 2013), paleoclimatology (Kozdon et al. 2011, Orland et al. 2012), fisheries management (Matta et al. 2013) and sandstone diagenesis (Pollington et al. 2011, Hyodo et al. 2013, Harwood et al. 2013).

We are studying quartz, feldspar, and carbonate overgrowths in the basal Cambrian Mt. Simon and the Ordovician St. Peter sandstones, and in thin sand lenses of the Cambrian Eau Claire fm. Porous zones in these sandstones form major aquifers, while cemented zones and mudstones in the intervening Eau Claire fm. form seals. The oxygen isotope ratios of these diagenetic cements provide a sensitive record of fluid and temperature history. In situ analysis of δ18O by SIMS (Fig. 1) shows that clastic quartz averages 10‰ (VSMOW) in all three units (Fig. 2A), consistent with a dominantly igneous detrital source. In contrast, quartz and feldspar overgrowths range in δ18O from 17-28‰ (Fig. 2B). Traverses across single overgrowths, 50-100µm thick, show consistent zoning of up to 9‰ with δ18O decreasing in later cements (Figs. 1, 2C). These values of δ18O in quartz overgrowths decrease on average and the gradient of early vs. late cement increases for more deeply buried rocks. The consistent zoning of overgrowths indicates a prolonged period of growth during burial and heating with silica likely provided by pressure solution. This conclusion contrasts with “conventional wisdom” that specific cements formed in discrete events driven by fluid flow. Taken together, these results support a model where precipitation of quartz and feldspar cements began at ~450 Ma in a shallow environment at temperatures of ~45°C and continued until maximum burial at 250 Ma (Hyodo et al. 2013). This model links δ18O, temperature, depth and time for the early Paleozoic sandstones of the Illinois basin. If correct, the age of this quartz can be inferred from δ18O.

Applications of this research include CO2 sequestration, such as the on-going MGSC mega-ton injection experiment; paleoclimatology; and the exploration and development of fossil fuels, MVT Pb-Zn deposits, and groundwater.
Fig. 1. Values of $\delta^{18}O$ measured at WiscSIMS in a traverse of one quartz overgrowth (OG) in Eau Claire Fm.

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Carbon stable isotope fractionation during C₃ photosynthesis and its use in probing the terrestrial rock record

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Because atmospheric carbon dioxide is the ultimate source of all land-plant carbon, workers have long suggested that $p$CO₂ level may exert control over the amount of $^{13}$C incorporated into plant tissues. Prior to our work supported by the current grant period, there was no experimental observation of isotope fractionation during C₃ photosynthesis ($\Delta \delta^{13}C = \delta^{13}C_{CO₂} - \delta^{13}C_{\text{plant tissue}}$) across multiple levels of highly elevated $p$CO₂. While records of $\Delta \delta^{13}C$ in modern wood had been observed to show a positive correlation with increasing $p$CO₂ over the last 160 years, early meta-analyses of published data revealed no correlation with $p$CO₂. However, these laboratory and field experiments were relatively uncontrolled across treatments (especially with respect to water availability), therefore any direct influence of $p$CO₂ on $\Delta \delta^{13}C$ was subject to being masked or cancelled by the multiple direct and indirect effects of environmental heterogeneity on stomatal conductance. During the current grant period we engineered growth chambers that feature enhanced dynamic stabilization of moisture availability and relative humidity, as well as provide constant light, nutrient, $\delta^{13}C_{CO₂}$, and $p$CO₂ levels for up to four weeks of plant growth. This unprecedented level of environmental stabilization allowed us to quantify the fundamental relationship between $p$CO₂ and carbon isotope fractionation in C₃ land plants. Here we report upon a total of 191 C₃ plants (128 Raphanus sativus plants and 63 Arabidopsis thaliana) grown across fifteen different levels of $p$CO₂ ranging from 370 to 4200 ppm (Schubert and Jahren, 2012). From each plant we isolated several substrates for carbon isotope analysis, including leaf-extracted $nC_{31}$-alkanes, a specific compound commonly isolated from terrestrial sediments of various ages. All of our substrates showed an increase in carbon isotope discrimination ($\Delta \delta^{13}C$) with increasing $p$CO₂ that closely fitted (i.e., $R \geq 0.94$) the hyperbolic relationship:

$$\Delta \delta^{13}C = \frac{[A](B)(pCO₂ + C)}{[A + (B)(pCO₂ + C)]}$$ (1)

where $A$ is the asymptote; $B$ is a measure of the responsiveness; $pCO₂$ is offset by the value $C$, such that $\Delta \delta^{13}C = 4.4$‰ at $pCO₂ = 0$ ppm (after Farquhar et al., 1989). Values for $A$ and $B$ were determined by iterative optimization to minimize the sum of the residuals squared (Schubert and Jahren, 2011b). On the basis of our experiments on A. thaliana and R. sativus as well as published data across small changes (<350 ppm) in $p$CO₂ we optimized the variables in Equation 1 to produce a single equation describing the relationship between $\Delta \delta^{13}C$ and $p$CO₂ (Figure 1 inset):

$$\Delta \delta^{13}C = \frac{(28.26)(0.21)(pCO₂ + 25)}{[28.26 + (0.21)(pCO₂ + 25)]}$$ (2)

This quantification of the $p$CO₂-dependency of carbon isotopic fractionation during photosynthesis has far-reaching ramifications for the interpretation of carbon isotope measurements in terrestrial Corg; it suggests that for any large release of isotopically depleted carbon to the ocean or atmosphere, the isotopic composition of resultant terrestrial photosynthetic tissues will be affected both by the change in atmospheric $\delta^{13}C_{CO₂}$ and by changes in $p$CO₂. We have successfully quantitatively reconciled differences in magnitude in terrestrial versus marine carbon isotope excursions (“CIE”) by incorporating the effect of changing $p$CO₂ on terrestrial carbon isotope fractionation. In this presentation we will show our calculations for the well-studied, globally widespread terrestrial CIE that marks the Paleocene-Eocene Thermal Maximum (PETM).
Figure 1. The effect of $p$CO$_2$ concentration on C$_3$ land-plant carbon isotope fractionation across the entire range of Late Paleozoic, Mesozoic, and Cenozoic estimates of $p$CO$_2$ (200 – 4200 ppm). The amount of carbon isotope fractionation per change in $p$CO$_2$ ($S$, ‰/ppm) decreases within increasing $p$CO$_2$ level (black curve; $R = 0.95$; $n=28$). Red closed circles reflect data from our experiments (Schubert and Jahren, 2012); open black circles represent data compiled from published studies. Horizontal bars encompass the range of $p$CO$_2$ levels variation within each experiment; the circle is plotted at the midpoint of the range. The gray curve (inset) represents the integral of the black curve, and follows the relationships described by Equations 1 and 2 within the text.

Most Important Publications Supported by the Funding Period:
Interplay between neutron diffraction probes, electric conductance measurements, molecular theory and modeling toward the understanding of the structural and thermophysical behavior of water and aqueous electrolytes

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The need for tools to probe the microstructure of water and aqueous electrolytes, regardless of its source — experiment, simulation, or theory — highlights the fact that we might be able to evaluate the corresponding equilibrium thermophysical properties provided that we determine how water distributes around all species. The presence of ions alters the microstructure of water, and consequently, the macroscopic thermophysical properties of the resulting solution. This microstructural or local density perturbation, the consequence of the ion–water interactions not present in the pure water environment, measures the molecular asymmetry between the water–water, the ion–water and the ion-ion interactions, whose macroscopic manifestation is the system’s thermodynamic nonideality.

Neutron diffraction with isotopic substitution (NDIS) is a powerful tool to probe the microstructure of aqueous environments, and to potentially provide not only the water structure, but also that for the ion–water and the ion–ion interactions. The outcome, however, might depend on the interpretation of the shape, location, and resolution of scattering peaks as well as on detecting the signature of peak overlapping associated with ion pairing (IP). Therefore, we pursue an interplay between NDIS and molecular simulation to determine the extent of IP formation in, for example, CaCl₂ aqueous solutions, to detect its signature in the neutron-weighted distribution function, and to facilitate the interpretation of raw data from NDIS. For that we invoke the statistical mechanics formalism of Poirier and DeLap to link the IP distribution functions with the corresponding Ca-Cl distribution functions, an analysis that (a) provided the first significant clue about the lack of conclusive evidence for the IP in aqueous CaCl₂ solutions from experimental probes that cannot distinguish contact from solvent-shared IP configurations, and (b) pushed the development of an MD-inspired null-water NDIS approach to identify, isolate, and ultimately determine the IP strength.

A second key source of understanding of the IP phenomena in aqueous electrolytes comes from electric conductance measurements which not only provide ionic mobility and limiting conductance of the salt, but also a direct route to the corresponding ion-pair association constants. For that purpose we integrated the use of theory, molecular simulations, and electric conductance measurements (available at liquid-like density conditions) for the parameterization of accurate ion-pair interaction potentials for the prediction of association constants and the exploration of ion speciation in aqueous environments over wide ranges of state conditions. Our simulation results highlighted some relevant modeling challenges related to the peculiar behavior of these systems around the zero-density limit, in particular, the occurrence of a temperature crossover, a behavior with profound consequences in the macroscopic modeling of these systems. In fact, supported by these results, we have demonstrated the inability of traditional IP approaches to describe, and macroscopic correlations to regress, properly the association behavior of simple salts in aqueous electrolyte solutions.
Selected BES-Supported Publications:


Nanometer to centimeter-scale analysis of the effects of geochemical processes on rock porosity: neutron scattering and imaging

Lawrence M. Anovitz, Oak Ridge National Laboratory

The microstructure and evolution of pore space is a critically important factor controlling fluid flow in geological formations, including the migration and retention of water, gas and hydrocarbons, and the evolution of hydrothermal systems. The size, distribution and connectivity of these confined geometries collectively dictate how fluids migrate into and through these micro- and nanoenvironments, wet and react with the solid surfaces, and link the thermal, hydrological, geochemical and geomechanical properties and processes that redistribute mass and energy. In order to interpret the history of any geological system, the physical and chemical “fingerprints” of this evolution must be fully explored from the nanoscale to the macroscale.

It is, however, difficult to satisfactorily describe changes in the multiscale porosity of rock samples using direct imaging techniques because of the wide variation in length scales involved. We have, therefore, developed an approach based on small angle neutron scattering, augmented at larger scales by SEM/BSE imaging, that is uniquely suited to this task. Scattering contrast in rocks arises primarily from the difference in the scattering length densities of the rock and the pores within it. Thus scattering data reflect the pore structure of the sample, and provide information on surface and mass fractal dimensions, surface area, and pore volume of the sample as a function of scale. The percentage of connected porosity can also be analyzed using the sensitivity of neutron scattering to variations in hydrogen isotope concentration. As we typically analyze samples by (U)SANS that are 150 microns thick and 2 cm in diameter, this allows us to characterize the pore structures of rocks from the namometer to the centimeter scale of a reasonably large sample in a statistically-meaningful manner.

Our results show there are significant primary and evolutionary differences between the multiscale pore structures of carbonate and clastic rocks. In the St. Peter sandstone in SW Wisconsin total porosity correlates with changes in pore structure, including pore size ratios, surface fractal dimensions, and lacunarity (“gappiness”, or textural inhomogeneity). There is no evidence of mass-fractal scattering and while previous scattering data suggest scattering is dominated by surface fractal behavior over many orders of magnitude, our analysis shows they demonstrate both fractal and pseudo-fractal behavior. The results also show that submicron porosity may represent a significant fraction of total porosity and reactive surface area. During overgrowth formation larger pores fill faster than small pores as overgrowths form, leading to a further increase in the small/large pore ratio. Overall, therefore, the relative importance of fluid reactions in confined geometries is likely to increase with increased silcrete formation.

The results for carbonates are significantly different. Unaltered limestones show a pattern of mass fractal scattering at larger scales, and surface fractals at smaller scales not observed in other materials. Hydrothermal alteration increases total porosity and the surface area to volume ratio, but tends to eliminate mass fractal behavior and increase the size range over which surface fractal behavior is observed. Oxidation of organic matter in the limestone may also have a significant effect on the pore structure. Thus, during hydrothermal processes increases in pore mass density and formation of less branching pore networks may be accompanied by roughening
of pore/grain interfaces. In some cases pore evolution is characterized by reduced contributions from small-scale pores to the cumulative porosity in the higher-grade rocks. This may be correlated to the nucleation of phases, closing small pores and producing a rougher surface morphology. The observed roughening may be a consequence of entropic contributions that yield pore (liquid)/grain surface free energies smaller than those at solid-solid phase contacts.

Figure 1: Comparison of Porod-transferred scattering curves for samples from the Hatrurim Fm, Israel (left) and St Peter Sandstone from SW Wisconsin (right)

Selected BES-Supported Publications
Anovitz, LM; Cole, DR; Rother, G; Allard, LF Jr.; Jackson, A; and Littrell, KC; Diagenetic changes in macro-to nano-scale porosity in the St Peter Sandstone: an (Ultra) small angle neutron scattering and backscattered electron imaging analysis. Geochimica et Cosmochimica Acta 2013, 102, 280-305.
Cole, DR; Chialvo, AA; Rother, G; Vlcek, L; Cummings, PT; Supercritical Fluid Behavior at Nanoscale Interfaces: Implications for CO2 Sequestration in Geologic Formations. Phil. Mag.: Special Issue on Layer Silicate Materials and Clays 2010, 90, 2339-2363.
Jin, L; Rother, G; Cole, DR; Mildner, D; Duffy, CJ; Brantley, SL; Characterization of Deep Weathering and Nanoporosity Development in Shale – A Neutron Study. Am. Mineral. 2011, 96, 498-512.
Kim, M; Doh, J; Han, S; Chae, K; Yu, B; Hong, K; Jackson, A; Anovitz, LM; The Pore Wall Structure of Porous Semi-Crystalline Anatase TiO2. J. Appl. Crystallogr. 2011, 44, 1238-1245.
Characterization of Mineral Dynamics and Adsorption through Molecular Simulation and Spectroscopy

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We use a combination of spectroscopic methods and molecular simulation to understand the structure and dynamics of the mineral-aqueous solution interface. In particular, classical molecular dynamics (MD) simulations based on pairwise interaction parameters from our Clayff force field include the effects of pH, ion exchange, and ion concentration while still providing atomistic detail of interfacial structure and dynamics. Through ongoing collaborations, we compare our simulation results with a range of spectroscopic methods, including inelastic neutron scattering, nuclear magnetic resonance, sum frequency generation, second harmonic generation, and infrared.

Clayff was initially developed to model basal surfaces, so additional development is required to simulate mineral edges. Toward that end, we have developed parameters for Mg-O-H interactions at edge sites and in the bulk. Using hydroxylated edges of brucite as model systems, we have validated our new parameters by comparing vibrational power spectra with normal mode analyses using density functional theory (DFT). Our results show that Mg-O-H modes at brucite edges are shifted to lower frequencies compared with the corresponding bulk modes.

The adsorption of inorganic and organic species onto mineral surfaces represents a major focus of our efforts. Simulations of competitive K$^+$ and UO$_2^{2+}$ adsorption at external muscovite surfaces are compared with second harmonic generation spectroscopy to better understand adsorption trends as a function of solute concentration. We have also studied the adsorption of small alcohol and thiol molecules onto gibbsite and lepidocrocite surfaces. These molecules adsorb at specific surface sites via hydrogen bonding, and the resulting monolayer structure is in good agreement with spectroscopic data. Finally, simulations of the dye molecule methylene blue near kaolinite surfaces reveal that these tricyclic molecules preferentially adsorb at the hydrophobic siloxane surface. Although adsorption is energetically favored, strong solute-solute interactions prevent these molecules from forming an adsorbed monolayer on the siloxane surface.

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.
Despite several examples of heteroepitaxy occurring in nature, our understanding of heteroepitaxial nucleation and growth at mineral-water interfaces in conditions relevant to natural systems is limited. The limitations of our current knowledge are due to the difficulties in probing mineral coatings with nanometer-scale dimensions and structures similar to those of their substrates and to the lack of theoretical support to rationalize experimental observations. Importantly, an understanding of heteroepitaxy is critical to radically improve current predictive models since this phenomenon leads to non-equilibrium conditions that cannot be described based on thermodynamic equilibrium assumptions. Recent progress in investigating the nucleation and growth of several metal carbonates on calcite single crystals will be presented. The nature of the divalent cation gives us direct control over the lattice misfit between the calcite substrate and the epitaxial metal carbonate phase thus allowing us to isolate the effect of strain on the rate and extent of growth and nucleation. Growth experiments have been performed in the heterogeneous nucleation regime whereby the solution is undersaturated with respect to calcite but supersaturated with respect to the carbonate phase. Cadmium-, manganese-, and cobalt-bearing solutions were selected to cover nominal lattice misfits between -4% and -15%. High-resolution transmission electron microscopy was used to probe the atomic-scale structure of the calcite-metal carbonate interface (Fig. 1). Atomic force microscopy was employed extensively to determine the morphology and orientation of growth features as well as their growth rates as a function of initial metal concentration (Fig. 2). X-ray photoelectron spectroscopy was used to determine precipitate composition and relative extent of growth. A kinetic Monte Carlo model of strained heteroepitaxy is also being developed to help guide and interpret experimental observations.
A disordered whole-nanoparticle model for 6-line ferrihydrite

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Ferrihydrite is a probably the most widespread and environmentally important natural inorganic nanoparticle, composed of defective nanocrystals of hydrous iron(III) oxide. For many years, the accepted description of the structure of ferrihydrite has been a multi-phase model developed by Drits and co-workers (Drits et al., 1993). Recently, Michel and coworkers published a single-phase model for the structure of ferrihydrite (Michel et al., 2007, 2010). Remarkably, the Drits and Michel models each achieve arbitrarily good agreement with different forms of X-ray scattering data obtained from powder samples: the reciprocal-space diffraction patterns and real-space pair distribution function (PDF), respectively. Understanding this apparent paradox, and developing realistic structural models for ferrihydrite, remain a pressing need.

We implemented a new code to explore different types of occupational and structural disorder in whole-nanoparticle models of 6-line ferrihydrite. The approach used the reverse Monte Carlo method to evolve the nanoparticle structure so as to improve goodness of fit simultaneously to the experimental structure factor and PDF. This approach reproducibly generates nanoparticle models that are a better match to the total scattering data than either the Drits or Michel models. The improved agreement is correlated with the development of types of structural disorder that are difficult to reproduce by a single-unit-cell approach, and include the incorporation of explicit distributions of iron vacancies, subnanoscale internal porosity, and considerable structural disorder.

References:
Metal solvation at mineral-water interfaces: Implications for adsorption, diffusion, and kinetic isotope fractionation

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The solvation shells of metal ions play important roles in aquatic geochemistry as mediators of metal-ligand and metal-mineral interactions. For example, solvation energy has long been known to be a key factor in determining the swelling properties of clays and the adsorption of inert electrolyte ions on charged surfaces. Advanced spectroscopic and computational techniques are now able to provide detailed atomic-scale insights into the role of metal solvation in geochemical phenomena [such as the relative stability of inner- vs. outer-sphere surface complexes on charged surfaces (Lee et al., 2010; Bourg and Sposito, 2011) or the promotion by organic ligands of Mg uptake during calcite growth (Hamm, 2012)]. Here, we present our latest molecular dynamics (MD) simulations of the role of solvation in the geochemistry metals near mineral surfaces. We focus on two topics: firstly, we discuss the influence of metal size on the adsorption and diffusion of alkali metals on phyllosilicate surfaces. We show that larger, more weakly solvated metals (e.g., Cs⁺ vs. Na⁺) have a greater tendency to form inner-sphere surface complexes and (when adsorbed) have a lower diffusion coefficient and higher activation energy of diffusion. Secondly, we show that the lability of the solvation shells of aquated metals has an inverse dependence on metal isotopic mass (Hofmann et al., 2012). This mass dependence suggests that any rate-limited metal ligand-exchange reactions (for example, metal attachment to mineral surfaces during precipitation) may cause a significant kinetic isotope fractionation.

References:


Predictive Single-Site Protonation and Cation Adsorption Modeling

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Tests of predictive surface complexation modeling are crucial to establishing the credibility of the predictive capability. For organic molecules interacting with mineral surfaces, tests can be made using in situ spectroscopic techniques. In the past, we and many others have used Fourier transform infrared spectroscopy (FTIR). However, the effects of surface attachment in FTIR are subtle, because signal can arise not only from the species attached to the mineral surface, but also from water and species in aqueous solution.

In contrast, surface-enhanced Raman spectroscopy (SERS) is extremely sensitive to the adsorbed species only. We have carried out the first SERS study of an organic molecule on a mineral surface under different pH and surface coverage conditions. The Raman signal enhancement arises when a charge transfer (CT) complex forms between our TiO₂ nanoparticles and an adsorbed amino acid DOPA (dihydroxyphenylalanine). This Raman signal is exclusively from the surface-bound complexes with great sensitivity to the binding and orientation of the DOPA attached to the TiO₂ surface.

Our SERS spectra show peaks that progressively change with pH and surface coverage, indicating changing surface speciation. At low pH and surface coverage, DOPA adsorbs on the surface lying down, with probably three points of attachment, whereas at higher pH and surface coverage DOPA stands up on the surface as a species involving two attachment points via the two phenolic oxygens. Our results demonstrate experimentally the varying proportions of the two surface species as a function of environmental conditions. The results are closely consistent with our previously published surface complexation modeling of DOPA on TiO₂.

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Geochemistry of Environmental Interfaces: Ion-pairing at Fe-oxide/water interfaces

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During the last few years, we have focused on understanding and modeling adsorption processes on Fe-(oxy)hydroxide surfaces in aqueous solution both from the bottom-up and the top-down. A surface complexation model (SCM) that can address the adsorption of both cations and anions on goethite has been developed within the context of the charge-distribution multisite complexation (CD-MUSIC) model. New approaches for estimating surface site density and acidity constants for the hydroxyl groups on particular crystal faces have led to a more accurate and robust approach to modeling complex systems. Surface site densities obtained via the titration congruency method, in conjunction with maximum oxyanion adsorption data and pertinent crystallographic information regarding the adsorbent of interest provide the best estimate of surface site density. We successfully predicted Pb²⁺/Cd²⁺, Pb²⁺/SeO₃²⁻ and Cd²⁺/SeO₃²⁻ bi-solute adsorption on goethite with CD-MUSIC. It was determined that the model best describes bi-solute sorption/competition behavior by utilizing reactions sites from three goethite crystal faces ((101), (001), (210)) with ternary complexation reactions.

At the same time, ab initio (AIMD) and classical molecular dynamics (MD), and spectroscopic techniques have been used to probe some of the fundamental assumptions in the SCM models. Acidity constants (pKₐ) of hydroxyl groups on mineral surfaces determine the charges at water-material interfaces. We applied AIMD simulations coupled to the potential-of-mean-force technique to compute the free energy of deprotonation, which is directly related to the pKₐ. We focused on a type 2 FeOOH₂ group on the (101) surface of goethite which has been previously predicted to be the most stable doubly-protonated group on this surface. The calculated pKₐ for an isolated type 2 FeOOH₂ group is 7.0, which is different from values used in previous CD-MUSIC modeling. In addition, the simulations show that the oxygen atom of the deprotonated type 2 Fe₁OH acid group is always involved in two inter-hydroxyl hydrogen bonds while SCMs assume two hydrogen bonds with water molecules.

Classical MD simulations are being used to examine the electric double layer (EDL) on two goethite surfaces (101) and (001) as a function of NaCl, MgCl₂ and BaCl₂ concentrations. The simulations show that NaCl pairing is evident at high NaCl concentrations, Na⁺ usually adsorbs as an inner-sphere complex, and Cl⁻ always adsorbs as an outer-sphere complex. Preliminary results suggest that large alkaline earth metals such as Ba²⁺ may adsorb as inner sphere on the (101) surface and outer-sphere on the (100) surface. In addition, ion adsorption on the (101) surface has greater impact on the surface charge than on the (100) surface. These results suggest that ascribing electrolyte and alkaline earth ion adsorption to one plane in an SCM is an oversimplification.

In order to study the Fe-oxide/solution interface, we have developed total internal reflection (TIR) Raman spectroscopy to study the Fe-oxide/solution interface. We have used this technique to probe sulfate ion behavior at the hematite/solution interface. Our data suggest that inner-sphere sulfate adsorption proceeds in a bidentate fashion at the hematite surface consistent with our surface complexation modeling of selenite sorption on goethite surfaces. These results help clarify questions regarding sulfate surface species based on attenuated total reflection-infrared (ATR-IR) observations.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.
Figure 1. CD-MUSIC Surface Complexation Model Predictions of Bi-Solute Adsorption Data at Varying Surface Coverages

References


Our program focuses in two areas: amorphous alkaline earth carbonates and clay-organic composites. In both cases we use a combination of computational molecular modeling and experimental methods (principally NMR spectroscopy, along with outer supporting methods) to investigate the structure, dynamics and energetics of these geochemically important but poorly understood materials. This presentation will discuss experimental $^{13}$C and $^{25}$Mg NMR results for amorphous Ca,Mg carbonate (ACMC), quantum chemical calculations of $^{25}$Mg NMR parameters in this system that help interpret the spectra, computational molecular dynamics (MD) results for the dehydration of amorphous Ca carbonate (ACC), $^{23}$Na NMR spectra for a clay-natural organic matter (NOM) composite, and computational MD results for a clay-polymer composite that help explain experimental data for such systems.

The $^{25}$Mg NMR spectra of ACMC are very broad and are dominated by quadrupolar effects. In contrast to the $^{43}$Ca NMR results for the same system, however, they show the presence of several quite well-defined Mg sites with a range of quadrupole coupling constants. The spectra of samples with Mg/Ca+Mg ratios of 0.6 and 1.0 are very similar, indicating similarity in the local Mg coordination environments in these samples. Quantum chemical CASTEP calculations of the $^{25}$Mg NMR parameters for the known Ca,Mg hydroxycarbonate phases suggests that the different Mg sites are coordinated to variable numbers of carbonate groups, water molecules and hydroxyl groups. The $^{13}$C NMR spectra of ACMC samples with Mg/Ca+Mg ratios from 0 to 1 all contain only symmetrical, Gaussian resonances similar to the spectra of spin $I = \frac{1}{2}$ nuclei in oxide glasses and do not demonstrate the presence of separate Ca- and Mg-rich volumes. The MD results for progressively dehydrated ACC show that CO$_3^{2-}$ groups coordinated by 6 Ca$^{2+}$ have a structural environment similar to vaterite and that these sites become more abundant as dehydration proceeds.

The $^{23}$Na spectra of a montmorillonite-NOM composite at 43% relative humidity contain two resonances representing tightly held Na` similar to that in systems without NOM and dynamically averaged Na` associated with the NOM. MD modeling will be required to understand the details of the dynamics and local structures. The MD results for a composite of montmorillonite and the polymer (poly)ethylene glycol (PEG) with and without interlayer CO$_2$ molecules illustrate the power of such calculations to investigate clay-organic composites and demonstrate the ability of ether oxygens (-C-O-C-) in organic compounds to coordinate alkali cations. As illustrated in Figure 1, the PEG interacts strongly with the clay surface and attracts Na` ions away from it.
Figure 1. Computed probability density plot perpendicular to the basal surface of the clay for a montmorillonite-PEG composite. The results show formation of disordered layers of the C- and O-atoms of the PEG in the interlayer and migration of much of the Na⁺ away from the near-surface sites it occupies in the absence of PEG.

Recent Papers:

Pathways for Oxygen-Isotope Exchanges in Nanometer-Size Aqueous Clusters

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I discuss two developments: (1) Design of a microcoil-based NMR probe that is suitable for experiments on aqueous solutions to 20 kbars of pressure; (2) Spectroscopy to detail controls on the catalytic evolution of O₂ from a hydrotalcite-like Co(II,III,IV) oxide.

NMR Solution Spectroscopy to 20 kbars. We have developed an inexpensive NMR probe (Figure) that allows spectroscopy on solutions up to 20 kbars. The sample volume is only 20 microliters and the NMR coil has an internal volume of 1 mm. Construction costs only a few thousand dollars and it can be used in a commercial spectrometer to collect molecular spectra at in situ pressures up to the pressure-freezing point of the solution. Examples are shown.

Water oxidation by a hydrotalcite-like CoOOH(s) solid. Greg McAlpin received the Best Dissertation Award for this DOE-supported research to examine clay-like materials from the “artificial leaf” of Nocera and others [1] which is able to harvest up to 4.7% of incident photonic energy for water-splitting and solar fuel production. It is made of earth-abundant elements and mimics the structure and functionality of materials precipitating in the Hanford Site and the Mn oxygen-evolving complex in photosystem II. At its heart is a clay-like material that catalyses the difficult oxygen half of the water-splitting reaction. We used electron-paramagnetic resonance (EPR) to characterize the resting state of the film’s prepared in phosphate buffers and showed that the formation of a Co(IV) species was closely associated with water oxidation activity[2, 3]. This work was expanded to include extensive study of this system prepared in a variety of buffers and polarizing potentials[3], allowing us, with collaborators both at UCD and other institutions, to develop a thermodynamic model for the structure and mechanism of this water oxidation. We believe it to be a layered cobalt-hydroxide material with interlayer buffer ions acting as proton shuttles[4], much like material found in contaminated soils. These findings, collected in collaboration with other researchers from UCD [5], U. Wisconsin and MIT, led us to delve further into the characterization of Co-ooxo and Co-peroxo containing species as models for the structure and reaction pathway for this system. CW and Pulse EPR in conjunction with DFT studies, were used to investigate the electronic structure of a model complexes and found that the unpaired formally Co(IV) electron was delocalized over all atoms in the core structure[6]. We are interested in the reaction dynamics of this material not only because it is among the top catalysts for electrolytic storage of energy as H₂(g), but also because it is, we believe, a good model for green rust reactivities. Similar materials are thought to be a sink for ⁶⁰Co at the Hanford Site, for example, and we can follow the reactions in this material with superb resolution by comparing the results to model clusters.
Figure: We designed an NMR probe that allows geochemists to collect molecular spectra at 20 kbar in solutions. The test solution and $^{29}$Si spectra were collected first in a standard Bruker commercial probe at ambient conditions (A), then, recollected at 8 kbar and 298 K in our microcoil probe (B called the 'Potato Cannon'). The microcoil (C) has $\sim$1-mm internal diameter and excites a sample of about 20 microliters in PEEK tubing. The probe is small, inexpensive (D) and can easily achieve 20 kbar.

Cited References
Mass transport by diffusion in gases, liquids, and solids produces kinetic isotope fractionations that are in many cases easily measured given the analytical precision of modern mass spectrometers. This provides a means by which one can distinguish between different mass transport processes. Because in many natural geological settings one is interested in unraveling the history of mass transports that are no longer operating, one needs to be able to interrogate the record preserved in zoned minerals. I will focus on kinetic isotope fractionations, especially of lithium because of the large mass ratio of $^{6}\text{Li}$ to $^{7}\text{Li}$ and because it diffuses exceptionally fast in minerals and silicate liquids. In marked contrast to its behavior in silicates, in water lithium diffusion is not especially fast or significantly fractionating of isotopes. Long-range transport of lithium in geological settings can take place by fluid flow or by grain boundary diffusion. In the case fluid flow, isotopic fractionations will arise due to exchange with matrix grains during growth, solution-reprecipitation or by diffusion. When mass transport involves grain boundary diffusion, kinetic isotope fractionations will result from both diffusion along the grain boundaries and by volume diffusion into mineral grains. I will report on our recent laboratory experiments and measurements of natural samples that demonstrate and calibrate isotope fractionation by diffusion in olivine and pyroxenes and show how they can be used to constrain the extent and duration of mass exchange.
New insights into the mechanisms of hydrogen generation during low-temperature water-rock interaction.

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Hydrogen gas is commonly produced from the hydrothermal alteration of (ultra)mafic rocks. However, there is insufficient thermodynamic and mechanistic data to accurately predict the amount and rate of H₂ generation from the hydration of ultramafic rocks and minerals during water-rock exchange at near-surface temperatures (i.e. below ~100°C). We have recently demonstrated that peridotite, pyroxene, fayalite and magnetite produce significant H₂ gas at 55 and 100°C over short time-scales. While investigating the mechanisms of H₂ generation through detailed characterization of the solid-phase, we observed a strong positive correlation between the extent of H₂ generation and the presence of trace spinels (e.g. magnetite, chromite and gahnite) in the reacting materials. Synchrotron-based multiple-energy x-ray fluorescence mapping and microspectroscopy analyses of reaction products revealed Fe(III)-oxide layers entirely localized to spinel surfaces. We have developed a model where low-temperature H₂ generation is promoted by electron-transfer reactions between adsorbed Fe(II) and water mediated by spinel surfaces. This work provides a testable hypothesis that can be further investigated mechanistically in experimental and natural samples. Our results also suggest that in subsurface aquifers, peridotite hydration may locally support H₂-utilizing microbial activity, which has important implications for the fate of dissolved carbon and the forward progression of mineral hydration and carbonation reactions.
Systematic control of polysaccharide chemistry on the kinetics of calcite nucleation through competition of interfacial energies

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Calcified skeletons are produced within complex assemblages of proteins and polysaccharides whose roles in regulating the onset of mineral formation are not well understood. One of the oldest dogmas in the biomineralization community is the belief that proteins are the main players in promoting the formation of calcium carbonate mineralization. The polysaccharides, in particular, are relegated to chemically inert roles as framework molecules. In recent years, several in vitro and biological studies of polysaccharides and their influence on calcite formation have attempted to challenge this idea but the studies have been piecemeal and a consistent picture has not emerged.

Here we quantify the kinetics of calcite nucleation onto a series of high purity polysaccharides that were selected for their range of functional group chemistries. We prepared substrates of these polysaccharides using electrodeposition and measured the rate of nucleation under controlled conditions across a series of supersaturations. From these data, we find the energy barrier to nucleation is polysaccharide-specific by a systematic relationship to PS charge density and substrate structure that is rooted in competing interfacial energies of the substrate-crystal and substrate-liquid system. Chitin presents a low energy barrier to nucleation because its near-neutral charge favors formation of a substrate-crystal interface, thus reducing substrate interactions with water. Progressively higher barriers are measured for negatively charged alginates and heparin that favor contact with the solution over the formation of new substrate-crystal interfaces.

The findings challenge the long-standing theory for mechanisms of epitaxy that assume nucleation is driven primarily by substrate-crystal interactions. (Turnbull and Vonnegut, 1952; Chernov, 1984) Rather, cation-substrate interactions are one end-member in a larger continuum of competing thermodynamic drivers that form (or preserve) crystal-substrate and liquid-substrate interfaces. Local charge density and molecular structure act as “coarse” and “fine” knobs, respectively, to tune the energy barrier to nucleation. Absolute rates are further modulated by the chemical driving force of supersaturation.

Insights from this study suggest the biomineralization community needs to revisit the current focus on proteins and reconsider calcification processes in a broader chemical and structural context. That is, functional group chemistry and conformation can be the primary drivers to mineral nucleation rather than macromolecular class.

Significant Studies Supported by Project over Current Funding Period

Giuffre, A.J., L.M. Hamm, J.J. De Yoreo, P.M. Dove (in revision) Controls of polysaccharide chemistry on kinetics and thermodynamics of calcium carbonate nucleation. PNAS.
Lee, J.R. I., Han, T.Y-J, Willey, T.M., Nielsen, M.H., Klivansky, L.M., Liu, Y., Chung, S.,
Terminello, L.J., van Buuren, T., De Yoreo, J.J. (in revision) Cooperative Reorganization of
Giuffre, A.J., A. Gagnon, J.J De Yoreo, P.M. Dove (in prep.) Deciphering the pathway to
crystallization of amorphous calcium carbonate using isotope tracers. *Geochemica Cosmochimica
Acta.*

Hamm, L.M., A.J. Giuffre, N. Han, J.J De Yoreo, P.M. Dove (in advanced prep.) Systematic
controls of substrate chemistry on the kinetics and thermodynamics of calcite nucleation..
Nielsen, L.C., De Yoreo, J.J. and Depaolo, D.J. (In review) Co-dependent calcite growth

Han, N., C.R. Blue, J.J. De Yoreo, P.M. Dove (in press) The effect of carboxytes on the Mg
content of calcites that transform from ACC. *Water-Rock International.*


Wang, D., T. Echigo, A.J. Giuffre, L.M. Hamm, J.D. Rimstidt, J.J. De Yoreo, J. Grotzinger, P.M.
Dove (2012) Revisiting geochemical controls on patterns of carbonate deposition through the
lens of multiple pathways to mineralization. *Faraday Discussion: Biological Crystallization*,
159, 371-386.

Wang, D., L. M. Hamm, R. J. Bodnar, P.M. Dove (2012) Raman spectroscopic characterization
of the magnesium content in amorphous calcium carbonate. *Journal of Raman Spectroscopy.*
DOI 10.1002/jrs.3057.

Hu, Q., Nielsen, M.H., Freeman, C.L., Hamm, L.M., Tao, J., Lee, J.R.I, Han, T.Y.J., Becker, U.,
Classical vs. non-classical pathways. *Faraday Discussion: Biological Crystallization*, 159, 509-
523.

Li, D. M.H. Nielsen, Lee, J.R. I., Frandsen, C., Banfield, J. and De Yoreo, J.J. (2012) Direction-

formation pathways and energetic controls during template-directed nucleation of CaCO3,
*Faraday Discussion: Biological Crystallization*, 159, 105-121.

166-181.

Stephenson, A.E., J. Hunter, J.J. De Yoreo, P.M. Dove (2011) Effect of ionic strength of the Mg
content of calcite: Toward a physical basis for minor element uptake during step growth.
*Geochimica et Cosmochimica Acta.*

Hamm, L.M., A.F. Wallace, P.M. Dove (2010) Molecular dynamics of ion hydration in the
presence of small carboxylated molecules and implications for calcification. *Jour. Physical
Chemistry B*, 114, 10488-10495.

Toxic metals in acidic groundwaters, surface waters, and industrial wastes react rapidly with minerals in soils and near-surface rocks. These interactions exert primary controls on the migration and ultimate fate of contaminants in the environment. In an effort to develop more quantitative understanding of these interactions, our recent work has focused on mineral-fluid interaction at near-surface conditions with particular emphasis on uranium contaminated environments. A common thread in our work is the use of high-resolution imaging techniques that leverage diffraction and spectroscopic information. Integrating electron-beam, ion-beam, X-ray synchrotron and neutron scattering methods utilizes the different strengths of the methods while providing insight across scales. At this symposium we present preliminary work on one of our most exciting new directions, the collaborative development of isotope-specific neutron imaging to track reactive fluid flow of toxic metals in geological materials.

Neutron radiography and associated tomography has proven a valuable tool for imaging grain and pore structures in a variety of materials by using dedicated beam lines of varied capabilities around the world. Neutron imaging generally exploits attenuation and scattering phenomena that depend on total neutron cross sections, but imaging prospects are dominated by beam and detector characteristics. Our work specifically focuses on combined neutron-resonance and Bragg-edge imaging at spatial resolutions of 10’s of microns. Such imaging is unavailable elsewhere in North America, but will prove valuable to a range of investigators in the U.S. For this approach we leverage the FP5 beamline at the LANSCE spallation source. FP5 provides a unique time-structure of white beam, moderated neutrons covering a wide energy range (keV to meV). In addition, we are using newly developed detector technology with time and spatial resolution allowing energy-dispersive characterizations far surpassing conventional white X-ray or neutron radiography capabilities. The inherent energy sorting of neutrons on the pulsed LANSCE source allows time-filtered imaging to select isotopes (chemical imaging) through neutron resonances and crystal structure through Bragg-edges. The large scattering cross section for deuterium (coherent) and hydrogen (incoherent) offer the capability to image fluid infiltration in a wide range of geologically important materials. Our preliminary images show excellent spatial and time resolution for uranium in fuel elements. We are currently designing flow experiments through porous sandstones to image uranium-phosphate reactive flow.
Nanominerals and mineral nanoparticles: More clues as to how they operate and the chemistry they perform at nanometer to global scales

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Nanominerals and mineral nanoparticles are measurably ubiquitous in the universe. Earth is certainly no exception, and we have recently estimated the amount generated annually in the world’s soils, and of that, the amount transported to the oceans via riverine and aeolian transport. These nanomaterials also enter the oceans via glacial, hydrothermal, and continental margin erosional inputs. Thus, across the continents, throughout the atmosphere, and in the oceans, nanominerals and mineral nanoparticles exist, and are thought to significantly contribute to every aspect of the Earth’s function and behavior in its abiotic, biotic, and mixed venues.

Besides estimating Earth-scale nanomineral and mineral nanoparticle inventories, it is just as important to understand their specific nanometer scale attributes and dynamic behavior not seen in bulk materials. In this study, we have been looking carefully at mineral nanoparticles of the iron oxide hematite and the iron sulfide mackinawite, both of which provide outstanding examples of mineral nanoparticle behavior. The objectives of this portion of our project include determining 1) the reactive sites on nanohematite, 2) the effect of particle size, morphology and aggregation state on the kinetics of the reductive dissolution of nanohematite, 3) the catalytic reactivity of nanohematite by studying heterogeneous aqueous Mn²⁺ oxidation, and 4) the structure and reactivity of nano-thin mackinawite.

Hematite nanoparticles (two populations averaging 7 and 31 nm in size) were synthesized and characterized using powder-XRD, TEM, BET surface area measurements and Mössbauer analysis. Advanced TEM imaging of the 31 nm hematite, including high-resolution tomographic analysis, was used to study its structure at the nanometer and sub-nanometer levels. HAADF-STEM analyses of these nanohematites identified nanochannels within the rhombohedra that serve as active sites for dissolution. The presence of these channels suggests that large molar volume shrinkage during the crystallization of the poorly crystalline nanoparticulate precursor (ferrihydrite) generates the nanochannels in the hematite nanocrystals. These findings are of fundamental importance in controlling the particle size, crystal morphology and the generation of defects in nanoparticles formed from an amorphous precursor.

The influence of size, morphology and aggregation state on the reductive dissolution of hematite with ascorbic acid has been investigated. The surface area normalized initial rate of reductive dissolution in the case of the 7 nm hematite was about two times greater vs. the 31 nm hematite. High-resolution TEM (HRTEM) of individual crystals and aggregates revealed contrasting differences in the 7 nm and 31 nm hematite; the former being free of defects and the latter displaying nanoscale steps on the surface and internal defects within the crystal. The 7 nm hematite particles were found to dissolve uniformly from the edge of the crystal with corresponding changes in the aggregation state. In contrast, the dissolution of the 31 nm hematite was found to initiate from the steps, defects, or sharp edges of the crystals.

The reactivity of nanohematite was tested by its proclivity to oxidize aqueous Mn²⁺. The end product of Mn(II) oxidation was a mixed-valent manganese oxide identified as the mineral hausmannite (Mn₃O₄) having a unique nanosized, wire-like morphology. The hausmannite nanowire has been identified and characterized by employing a suite of analytical techniques including HR-TEM, EELS mapping, nanometer-resolved SAED, high-resolution tomographic analysis, and HR-SEM. A cross-section of the hausmannite nanowire revealed its prismatic
morphology. The formation of the hausmannite nanowire was influenced by the composition of its surrounding environment, as well as by the interfacial solute–solid chemistry of the colloidal mixture.

The dissimilatory metal-reducing bacteria (DMRB) *Shewanella putrefaciens* strain CN32 was used to synthesize biogenic nanometer-sized iron sulfide (mackinawite). The biogenic mackinawite was characterized using TEM, HRTEM, BET surface area analysis and Mössbauer spectroscopy. The biogenic mackinawite aggregates were rosette shaped and composed of nano films as confirmed by electron microscopy. The reactivity of the biogenic mineral was tested by its propensity to reduce hexavalent uranium. The uranium was reduced to nanoparticulate uraninite (c.a. 2.5 nanometers) that coated the surface of biogenic mackinawite. XPS analysis identified sulfide to be the source of electrons for uranium reduction. XPS and Mössbauer spectroscopy confirmed the inertness of structural ferrous ions during uranium reduction. This study signifies the relevance of low-temperature interfacial redox geochemistry in the formation of environmentally pertinent biogenic nanominerals.

Very recent DOE/BES-sponsored references relevant to this abstract:
Overall goals of our research program include development of structure-stability relationships for amorphous calcium carbonate (ACC) and identification of structural changes associated with transformation to crystalline calcium carbonate. 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. These studies are intended to provide a structural basis for understanding and predicting reactivity of ACC in different environments and in applications 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.

Recent work has been focused in two areas: (1) kinetics and pathways of the transformation of ACC to crystalline calcium carbonate, and (2) characterization of water loss in hydrous ACC via thermal treatment. Both in situ and ex situ studies of ACC transformation were coupled with total X-ray scattering and NMR characterization to identify rates and pathways for crystallization of ACC synthesized by three different methods. The samples produced by these methods differ mainly in their hydrous components and exhibit different rates and pathways of crystallization under conditions ranging from high relative humidity to fully wet. Simultaneous formation of vaterite and calcite is observed during crystallization of ACC synthesized by one method.

ACC samples from the three different synthesis methods were partially dehydrated by heating to temperatures below the crystallization temperature, resulting in loss of 45-75% of the total water content. EXAFS and total X-ray scattering results showed no evidence of significant structural changes with heating, indicating that the X-ray based techniques are largely insensitive to the effects of partial dehydration. The ¹H NMR spectra of hydrous ACC, obtained both directly and indirectly (the latter via ¹³C-detection), contain signals from three principal hydrous environments: rigid structural water, a restrictedly mobile water environment, and hydroxyl. Dehydration of ACC leads to a reduction in both rigid and mobile water that increases with dehydration temperature but with little change in their relative proportions. Some mobile water remains even after heating to 200 °C, suggesting the presence of water isolated or trapped in pores. The retention of some restrictedly mobile water and the lack of change in the PDFs from total X-ray scattering in dehydrated ACC suggest that thermal dehydration at temperatures below the crystallization temperature does not significantly disrupt the calcium-rich framework of the ACC. Results of in-situ ¹H NMR during heating and thermal analysis of samples dehydrated isothermally for extended periods indicate that water loss is kinetically hindered. The final loss of residual mass (ca. 6 %, 0.1 moles remaining water) coincides with the crystallization reaction suggesting that complete dehydration induces crystallization.

We also used total X-ray scattering, EXAFS, and NMR to study structure in biogenic hydrous ACC, for comparison with synthetic samples. These ACC samples, taken from gastroliths of pre-molt lobsters, show short- and medium-range structure that is nearly identical to that for synthetic, hydrous ACC. ¹H NMR however shows very little mobile water in close proximity to carbonate groups. These results demonstrate that differences in structure and composition of ACC, and the transformation behavior, are linked to the method of formation, suggesting that further study of different ACC samples is needed.
An Investigation of Roughness and Weathering at the Bedrock-Regolith Interface

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At the Earth's surface, bedrock formed at high temperature and pressure re-equilibrates to surficial conditions. During this equilibration, a mantle of disaggregated rock known as regolith forms due to interactions between minerals, water, biota, organic matter, and gas. The interface between weathered and unweathered rock is the weathering front. At this front, the predominant reactants O₂, CO₂, and H₂O enter bedrock, initiating chemical reactions. To make quantitative models of weathering requires a better understanding of the weathering front and how it advances with time at the scale of mineral grains, clasts, pedons, and hillslopes. For example, we are studying the initial stages of regolith formation by making observations showing how pores open and become connected in low porosity rocks during weathering. Pores ranging in size from nanometers to tens of microns are probed using neutron scattering to investigate the mineral-pore interface. For example, we have used neutron scattering to analyze the interface between unweathered and weathered shale, andesite, diabase, and granite. Scattering intensity increases with extent of weathering as the porosity and surface area increases. We have observed that the interfaces inside rocks that scatter neutrons can sometimes be characterized as mass fractals while in other cases the interfaces are surface fractals. Furthermore, in basaltic and granitic material, scattering occurs from both, i.e., from pores (mass fractal) and bumps on pore surfaces (surface fractal). In contrast, in scattering from shale, it is common that only one fractal is observed. The fractal dimensions also vary with the extent of weathering. For example, in several cases we have observed that weathering causes the mass fractal to transform to a surface fractal as pores become interconnected. We also hypothesize that surface fractal dimensions may decrease when weathering reactions are transport-limited. As we use neutrons to explore the interface of pores inside rocks during weathering, we are moving forward in developing models for predicting these processes quantitatively and putting such micro-scale observations into context with macro-scale observations related to regolith formation at the grain, clast, pedon, and hillslope scales.
Nanopore Confinement of C-H-O Mixed-Volatile Fluids Relevant to Subsurface Energy Systems
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Collaborators: K. Mueller, David Hoyt, Nancy Washton, Pacific Northwest National laboratory, G. Rother, M. Gruszkiewicz, E. Mamontov, Oak Ridge National Laboratory, A. Asthagiri, The Ohio State University, Steve Greenbaum, Hunter College

The overarching objective of this effort is to obtain a fundamental atomic- to macro-scale understanding of the sorptivity, structure and dynamics of simple and complex C-H-O fluids at mineral surfaces or within nanoporous matrices over temperatures, pressures and compositions encountered in near-surface and shallow crustal environments. To achieve this goal we (a) assess the adsorption-desorption behavior of methane, related hydrocarbons and CO₂ on a variety of mineral substrates and in nanoporous matrices, (b) characterize the microstructure and dynamical behavior of methane and related HC volatiles at mineral surfaces and within nanopores with and without H₂O present at relevant P-T-x subsurface conditions, and (c) utilize molecular-level modeling to provide critically important insights into the interfacial properties of these mineral-volatile systems, assist in the interpretation of experimental data and predict fluid behavior beyond the limits of current experimental capability. A scientifically diverse, multi-institutional team (Ohio State University, Oklahoma University, Oak Ridge National Lab, Pacific Northwest National Lab, Hunter College) are utilizing novel experimental and analytical techniques in concert with state-of-the-art theory, modeling and simulation approaches to address these issues. There is a special emphasis on building synergistic links between results obtained from various neutron scattering and NMR studies which are integrated into our research portfolio with molecular dynamics modeling, to provide new phenomenological insights.

Thus far, we have conducted a number of different kinds of experiments focusing on the behavior of propane, methane, carbon dioxide or their mixtures interacting with different types of mesoporous matrices (e.g., SiO₂, Al₂O₃, TiO₂, ZrO₂). High temperature-high pressure gravimetric measurements on these fluids have revealed profound fluid densification in nanopores as the density (pressure) approaches that of the bulk critical density followed by a dramatic density decrease (fluid depletion). Densification of propane in model silica pores has been observed in MD simulations, in qualitative agreement with experiments. The CO₂ adsorption on TiO₂ has been modeled with density functional theory (DFT) that employs a new version of the dispersion correction. Quasielastic neutron scattering (QENS) experiments have been conducted at Oak Ridge National Laboratory on the system propane-mesoporous silica with or without CO₂ present. Results from these experiments are interpreted in terms of translational “diffusive” motion of propane, residence times between diffusion jumps and the jump distances. Interestingly, the presence of CO₂ seems to enhance the mobility of propane in the mesopores. Mixed water-methane and water-ethanol systems have also been investigated using MD simulations, suggesting that preferential adsorption might be responsible for the results observed experimentally in mixed systems. Preliminary NMR experiments have been conducted on the diffusion and relaxation behavior of water and methanol in mesoporous silica at ambient temperature but for pressures up to 250 MPa. In the case of water, we observe a pronounced decrease in the T₁ relaxation with increasing pressure.
Shale gas: Geochemical and physical constraints on genesis, storage, and producibility
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Indiana University, Bloomington, IN

Shales are important source and reservoir rocks for hydrocarbons (shale gas, oil). The three research goals of this project encompass: (1) Quantification of the character and development of porosity in organic-rich rocks as a function of organic matter content, type of organic matter, thermal maturity, and the degree of compaction; (2) evaluation of the natural outgassing of methane from shales into the atmosphere and its potential contribution to global warming by delivering potent methane greenhouse gas; and (3) testing of shales’ ability to generate thermogenic gas (or natural gas via catalysis) at relatively low temperatures (60, 100 and 200 °C) and different pressures (ambient, 100 MPa, 300 MPa) over months to years; the first batch of samples has been heated for 6 months and is currently being analyzed.

A variety of porosimetric methods was used to assess macro- meso- and microporosity in shales. Porosity strongly depends on the presence of organic matter and its thermal maturity. Porosity in shale at low maturity initially diminishes due to ongoing compaction, but incipient thermal cracking at the beginning of the oil window generates new porosity. Further into the oil window, the generation of additional liquid hydrocarbons fills pores and effectively reduces the pore space available for gas storage. At even higher maturity, secondary cracking and gas generation expels some liquid hydrocarbons from pores and opens new pore spaces for gases (see Figure next page).

Natural outgassing of shale gas into the atmosphere in the absence of drilling and fracking was evaluated on numerous field trips to New York, Pennsylvania, Kentucky and Indiana. A naturally occurring spectacular “eternal flame” and associated non-burning shale gas seeps in western New York State mark a gas macroseepage system of dominantly thermogenic origin emanating directly from deep shale source rocks. Such an occurrence makes this a rare case in contrast to most Petroleum Seepage Systems where gas derives from conventional reservoirs. The unusual chemical and isotopic compositions of the gas can be traced to deep Upper Devonian shales. The seep gas holds the current world record with regard to the highest ethane and propane concentration ever reported for a natural gas (\([C2+C3] \approx 35 \text{ vol. \%}\)). The occurrence of gas seeps fed by deeper shales through tectonically-induced conduits proves that strong fluxes and point sources of shale gas can indeed contribute to atmospheric greenhouse gas loading. However, we found no evidence that smaller fluxes of shale gas from tectonically undisturbed areas can deliver methane to the atmosphere. Limestone caves in Kentucky and Indiana are overlying deeper shales and were expected to accumulate methane in cave air if fractures permit upward flux of shale gas. Instead, we typically found less methane in cave air than in the atmosphere. We hypothesize that methanotrophic microbes are lining the walls of underground gas passageways and rapidly oxidize the methane from shale gas to carbon dioxide before methane can reach the atmosphere.

Figure below: Overall interpretation of trends in porosity observed in organic-rich New Albany Shale samples with increasing maturity. Black circles in the last column indicate the positions of measured samples along maturation history. Much of the porosity is associated with organic matter (OM) in shales. Cracking of OM tends to enhance porosity, but during catagenesis the filling of pores and connections among pores with oil and solid bitumen not only reduces shales’
ability to store gas, but also limits gas producibility. Secondary cracking of oil and bitumen at higher maturity enhances porosity (Mastalerz et al., in review for *AAPG Bulletin*).

<table>
<thead>
<tr>
<th>Pre-metamorphic zones</th>
<th>Coal rank</th>
<th>$R_o$</th>
<th>Organic diagenesis phases</th>
<th>Hydrocarbon generation from source rocks containing kerogens type I and type II</th>
<th>Maturity</th>
<th>Types</th>
<th>Hydrocarbons generated</th>
<th>Porosity of shales measured in this study (m/g)</th>
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