Summary of FY 2010 Geosciences Research

May 2011

U.S. Department of Energy

Office of Science
Office of Basic Energy Sciences
Chemical Sciences, Geosciences, and Biosciences Division
Washington, D.C. 20585

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FORWARD

The Department of Energy's Office of Science research provides a foundation of fundamental knowledge in areas relevant to the Department's missions, and this is particularly true in the area of Geosciences, which has applied programs in multiple offices. The Office of Science's research support also maintains our stewardship for geosciences research capabilities at the DOE National Laboratories. Excellent fundamental science that can improve and support DOE's mission needs also provides basic understanding applicable to broader areas of geosciences beyond DOE. Particular focus areas of interest include rock physics, flow and transport of geologic fluids through porous and fractured media, analytical geochemistry and experimental and theoretical geochemistry. The Geosciences Research Program resides within the Division of Chemical Sciences, Geosciences and Biosciences, part of the Office of Basic Energy Sciences of the Office of Science.

The participants in this program include researchers at National Laboratories and academic institutions. These activities are formalized by a contract or grant between the Department of Energy and the organization performing the work, providing funds for salaries, equipment, research materials, and overhead. Collaborative work among these institutions is encouraged. Because of the variety of the research needs in the different applied DOE programs, fundamental approaches with multiple potential applications are favored. The summaries in this document, prepared by the investigators, describe the scope of the individual projects.

The Office of Basic Energy Sciences has recently completed a series of Basic Research Needs workshops including one entitled Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems. http://www.science.doe.gov/bes/reports/files/GEO_rpt.pdf All of the workshop reports can be downloaded from the BES website. Further information on the Geosciences Research Program, including recent program activities and highlights, may be found on the Geosciences Programs home page at:
http://www.sc.doe.gov/production/bes/geo/geohome.html.

The Office of Basic Energy Sciences also launched 46 new Energy Frontier Research Centers during FY 2009 (http://www.science.doe.gov/bes/EFRC/index.html), two of which focus primarily on Geosciences related issues.
(http://www.science.doe.gov/bes/EFRC/CENTERS/NCGC/efrc_NCGC.html;
http://www.science.doe.gov/bes/EFRC/CENTERS/CFSES/efrc_CFSES.html)

THE GEOSCIENCES RESEARCH PROGRAM IN THE OFFICE OF BASIC ENERGY SCIENCES

The Geosciences Research Program emphasizes research leading to fundamental understanding of Earth’s natural processes and properties that will advance the forefront of scientific knowledge, as well as help solve geosciences-related problems in multiple DOE mission areas. A major objective is building the long-term fundamental knowledge base necessary to provide for a range of energy technologies in the future. Future energy technologies and their individual roles in satisfying the nation’s energy needs cannot be easily predicted. It is clear, however, that these future energy technologies will involve consumption of energy and mineral resources and generation of technological wastes. Viable energy technologies for the future must contribute to a national energy enterprise that is efficient, economical, and environmentally sound. Scientific understanding today supports current energy and environmental solutions, but it is our responsibility to continue to investigate the foundations of current and future technology options to lower societal costs and increase public confidence in new energy and environmental applications.

The Geosciences Research Program is divided into two broad categories, ***Geophysics*** and ***Geochemistry***.

Geophysics: This sub-area focuses on innovative and improved approaches to interrogating the physical properties of Earth’s crust though better collection and analysis of rock physics, seismic, electromagnetic and other geophysical data, and improving understanding of geophysical signatures of fluids and fluid-bearing reservoirs.

Geochemistry: This sub-area focuses on innovative and improved ways to interrogate the chemical properties of the Earth’s crust through investigations of mineral-fluid interactions and studies of rates and mechanisms of reactions at the atomistic/molecular scale; studying coupled flow and reactivity in porous and fractured rocks; tracking of mineral-mineral and mineral-fluid processes using isotopes, and understanding the dynamics of geochemical reaction systems that include both bulk and nanophase components.

The Geosciences Research Program evolves with time and progress in these and related fields. Individual research projects supported by this program at DOE national laboratories, academic institutions, research centers, and other federal agencies typically have components in more than one of the categories or subcategories listed. In addition, it is common for research activities to involve a high level of collaboration between investigators and different institutions. Cross-cutting issues include: improving understanding of basic properties of rocks, minerals, and fluids; determining physical, chemical, and mechanical properties of multi-phase, heterogeneous, anisotropic systems; improving analysis of rock deformation, flow, fracture, and failure, and characterization of fluid transport properties of large-scale geologic structures. Research progress, in addition, will be based on developing advanced analytical instrumentation and computational methods, including: higher-resolution geophysical imaging and inversion tools, angstrom-scale resolution analysis of heterogeneous minerals with x-ray and neutron methods, and advancing computational modeling and algorithm development.

PART I: ON-SITE

ARGONNE NATIONAL LABORATORY

Chemical Sciences and Engineering Division, Building 200, Argonne, IL 60439

Grant : DE-AC02-06CH11357

Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source

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Co-I: Neil C. Sturchio (University of Illinois at Chicago)

Website:
http://www.cse.anl.gov/nuclear_enviro_processes/interfacial_processes/index.html

Objectives: The objective of this program is to advance the basic understanding of rock-fluid and soil-fluid interactions through experimental studies on atomic-scale processes at the mineral-fluid interfaces. This is crucial to establishing the relation between atomic-scale processes and macroscopic geochemical transport in natural systems.

Project Description: The principal approach is to observe single-crystal mineral surfaces in situ during chemically controlled reactions with fluids using high brilliance synchrotron radiation. Experimental techniques include high resolution X-ray scattering (X-ray reflectivity, x-ray standing waves, resonant anomalous X-ray reflectivity) as well as X-ray absorption spectroscopy. Phenomena of interest include mineral-water interface structure, adsorption/desorption of ions and organic molecules, dissolution, precipitation and growth. Experiments are performed on common rock- and soil-forming minerals under conditions representative of geochemical environments near Earth's surface. A fundamental understanding of the molecular-scale processes is obtained through direct observations of interfaces before, during and after reaction.

Results: Recent research focused on resolving mineral-water interface structure and reactivity with ~Å-resolution and sensitivities. The primary emphasis of these studies has been on understanding the reaction of mineral surfaces with solution species, including interfacial structure, ion adsorption, and the role of natural organic matter and ionic strength in mediating ion-mineral interactions and growth/dissolution processes. Additional efforts were made in the development of interfacial X-ray based analytical techniques needed to answer fundamental questions in geochemical research.

Feldspar dissolution studies:

Ongoing studies of silicate dissolution processes used *in-situ* X-ray reflectivity (XR) to probe the dissolution of orthoclase(001) surfaces at 85°C and pOH=2. We observed that the addition of 2 *m* NaCl increases the overall dissolution rate by a factor of ~5, and leads to a rougher surface

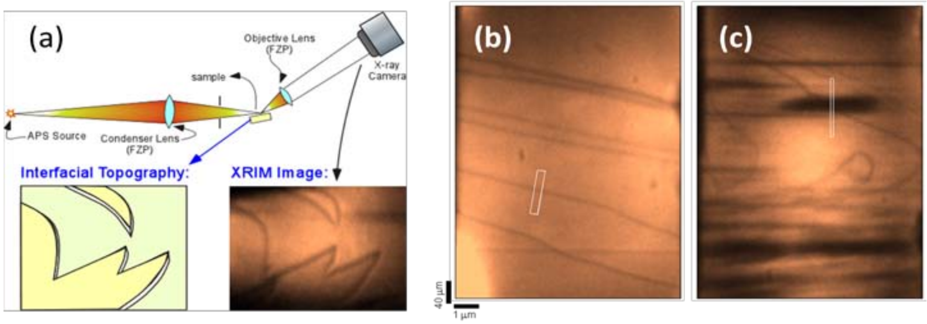

Figure: (**A**) Schematic of the XRIM system. An XRIM image (lower right) corresponds to the topography indicated (lower left). (**B**) Image of an unreacted orthoclase (001) surface, and (**C**) a comparable surface after reaction for 15 minutes at pOH=2, 85°C and with 1 m NaCl. The dark lines in **(B)** and **(C)** indicate elementary steps on an otherwise ideally terminated surface, and the dark patches in **(C)** indicate regions where the dissolution reaction has locally increased the local surface roughness.

than found in the absence of NaCl. Parallel *ex-situ* measurements were made using X-ray reflection interface microscopy (XRIM), a new surface imaging tool developed by this program. Reacted surfaces were imaged revealing that orthoclase initially dissolves inhomogeneously at these high saline conditions, leading to micron-scale regions with locally increased roughness (see figure). These XRIM results complement the *in-situ* XR observations by providing information on the *lateral* variation of interfacial reactivity. At the same time, and these results demonstrate for the first time the ability of XRIM to image interfacial reactivity using this non-invasive X-ray microscopy. This establishes XRIM as a new approach for imaging interfacial processes, complementing existing imaging approaches (e.g., atomic force microscopy).

Fe(II) Interactions with hematite surfaces at acidic to neutral pH:

XR measurements of Fe(II) reactions at the hematite (001), (110) and (012) surfaces reveal significant changes in the surface topography that was independent of pH. On (001) surfaces, this was observed as a growth of <1 nm thick discontinuous films on the (001) surface that were structurally distinct from the hematite substrate structure. Parallel resonant anomalous X-ray reflectivity (RAXR) measurements showed an Fe(II) concentration of < 0.5 to 1 $\mu M/m^2$, indicating that all adsorbed Fe(II) had converted to Fe(III). These observations provide new insights into the redox reactions at oxide surfaces, and suggest that Fe plays a catalytic role in a *delocalized* oxidative adsorption-desorption reaction, in which an electron from the adsorbing Fe(II) reduces and desorbs a lattice Fe(III) cation elsewhere, leading to zero net reduction and zero net adsorption.

Direct comparison of XR data with Computational Results:

A new capability was developed to compare X-ray reflectivity data directly to molecular-dynamics simulations. XR data are normally analyzed through model-dependent fitting so that only semi-quantitative comparisons are made between the structural parameters (e.g., atom positions) obtained from XR data and the simulated structures. A new analysis defined the conditions under which pixelated structures obtained from numerical simulations can be used to calculate XR data accurately. This establishes a new approach to quantitatively compare experimental and computational results, and to assess our conceptual understanding of mineral-fluid interfacial chemistry.

IDAHO NATIONAL LABORATORY

Carbon Resource Management Department
Center for Advanced Modeling and Simulation, Idaho Falls ID 83415

Contract: ID13727

Pathways for Redox Transformation of Semiconducting Minerals: The Iron Oxides

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Objectives. This project aims to: 1) Determine chemical mechanisms for dissolution of specific surfaces of common electrically semiconducting minerals such as the iron oxides, 2) Establish linkages to overall macroscopic dissolution behavior, in particular for chemically and morphologically complex surfaces commensurate with those found in nature, and 3) Develop and apply analytical methods for quantifying complex surface morphologies in microscopic image data, and computational molecular methods for simulating dissolution dynamics of complex mineral surfaces.

Project Description. This project is a closely-coupled experimental and computer modeling study that focuses on characterizing the chemical pathways involved in the dissolution of iron oxide minerals. In particular, this project emphasizes understanding the dynamics from initial well-defined surfaces to advanced stages of dissolution, and in linking this understanding to macroscopic behavior. This project fills gaps in knowledge of the dissolution rates and mechanisms for specific crystallographic surfaces where such information is typically only assumed. Mechanisms of iron oxide dissolution in particular entail a possible role for solid-state charge migration affecting the rate of growth and the resulting morphology of dissolution and growth features. This project relies primarily on surface-specific scanning probe microscopic observations and surface spectroscopic characterization in conjunction with molecular dynamics simulations, electronic structure calculations, and kinetic Monte Carlo simulations to help identify key mechanistic processes.

Results. In FY2011 our efforts to develop a basic understanding of the growth of facetted pyramids on the (001) surface of hematite while dissolution occurred on the other surfaces continued. A 3-dimensional solid-on-solid model that generates mounds and rounded pyramids was developed. The solid-on-solid model had nine independent parameters, and the parameter space was not fully investigated before the focus of the work turned to the isotope exchange in goethite nanorods.

Handler *et al*. have demonstrated that nanorods with dimension of approximately 81nm (perpendicular to the (001) face) × 11nm × 11nm equilibrate with isotopically labeled Fe(II) , which was buffered to a pH of ≈ 7.5. The experiments indicate that the characteristic time scale for equilibration of nanorods of this size is on the order of a few days (10^5-10^6 s). Apparently this process occurs without broadening of the length distribution or width distribution, which indicates that a mechanism based on dissolution and precipitation (regrowth) alone is inconsistent with experimental observations. Handler *et al*. offered an explanation for the isotopic exchange based in dissolution on one end of the nanorod and growth on the other, coupled with the flow of electrons through the nanorod from the surface where Fe^{2+} is being oxidized to Fe^{3+} to the surface where Fe^{3+} is being reduced to Fe^{2+}. However, they did not explain the remarkable symmetry breaking that this would imply or how the energy needed to drive the electrons through the nanorod is provided in a system where there is no net chemical reaction.

Alternative explanations of this remarkable behavior have been investigated. The most plausible of these alternative explanation is based on surface diffusion coupled with relatively slow dissolution and precipitation. This could lead to isotope exchange with only small changes in the size and shape of the nanorods. Figure 1 shows the result of a two-dimensional simulation in which the ratio between the rate of precipitation/dissolution (it was assumed that the system was in equilibrium so that the preciptation and dissolution rates were equal) was 0.00005 times the rate of surface diffusion. The simulation was carried out with two (1+1)-dimensional surfaces, to crudely represent two facets of the same nanorod, and the rate of exchange between the two surfaces, which represents diffusion across the edge between the two surfaces of a three-dimensional nanorod was 0.1 times the rate of surface diffusion. The number of surface diffusion steps was 1,000,000,000, the number of dissolution/precipitation steps was 50,000 and the number of attempted exchange steps was 100,000,000. The system size (the lengths of each surface) was 256. On the left, the red region at the top is solid that has never been dissolved, the green region is the reprecipitated solid (the small red islands are original solid that has never been replaced). The blue region has at some time in the past been filled with solid, but it is now filled with liquid. On the right, the red region at the bottom is solid that has never been dissolved the blue region is the reprecipitated solid (the small red islands are original solid that has never been replaced). The green region has at some time in the past been filled with solid, but it is now filled with liquid.

The simulation supports the idea that fast surface diffusion combined with relatively slow dissolution and growth can lead to extensive isotopic exchange without significant ripening (the net mass change is on the order of $\sqrt{50{,}000 \approx 250}$ sites). Three-dimensional simulations with a model that limits surface rougness will be required to further evaluate the concept of (relatively) fast surface diffusion combined with equilibrium precipitation and dissolution.

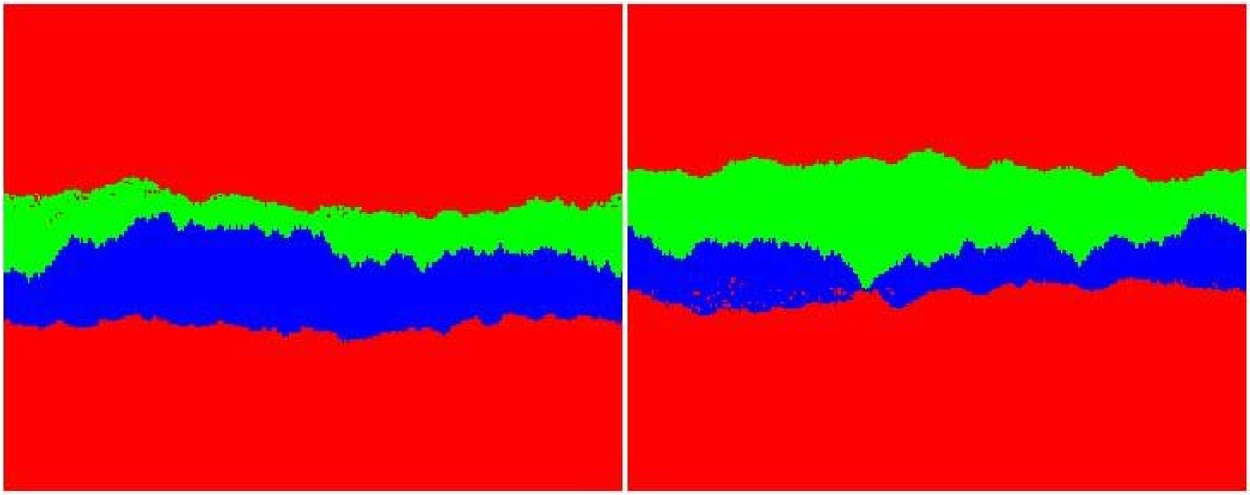

Figure 1. Simulation of isotopic exchange between a 2-dimensional solid with two 1+1-dimensional surfaces and a reactive solution. The solid-on-solid model includes growth, dissolution, surface diffusion and exchange between the two surfaces. The two surfaces were initially flat.

LAWRENCE BERKELEY NATIONAL LABORATORY

Earth Sciences Division, Berkeley CA 94720

Contract: CH11231

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Seismic Wave Propagation in Earth Systems with Fluids and Fractures

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Objectives: Understanding the physics of seismic wave propagation in earth systems, especially those containing fluids (oil, gas, water, CO2) in rock pores, granular and fractured reservoirs, has been the main objective of this continuing project. Measured seismic wave speeds provide a common tool used to image the earth, and thereby locate potential deposits of resources or contaminants, depending on the focus of particular studies. In special cases, the waves can be used to characterize the nature and state of any pore fluids. One example is Amplitude Versus Offset (AVO) analysis (or bright spots), which can be used to distinguish liquids from gases. But other methods with similar objectives have been developed in this project, with special emphasis on fractured and/or granular reservoirs in more recent work.

Project Description: Work of the PI has concentrated on systems that might be intrinsically anisotropic, or that become anisotropic due to the presence of oriented fractures (either dry or containing fluids), or due to applied stress (such as overburden) in granular systems. Anisotropy has been analyzed using both approximate and rigorous analytical methods, as well as computational methods whenever appropriate. Inclusions that are very flat and fluid-filled, or only partially saturated, cracks, and/or dry cracks all might produce strong effects on the seismic wave propagation speed, and also on losses via wave attenuation. Results are particularly important therefore in reservoirs containing, for example, arrays of vertical fractures containing fluids, and have implications for estimating fluid permeability, as well as pore-fluid type and spatial distribution. Another recent focus has been on granular systems, both dry and fluid-saturated. In all cases considered, we take special care to incorporate as much rigorous information (such as mathematical bounds and results from modern effective medium theories) and known-to-be-correct physical theories, such as Biot-Gassmann, for the mechanics of systems having fluids saturating the pores.

Results: Considering fractured systems or granular systems under pressure, in both cases when filled with either gas or liquid or mixed fluids, has been the main focus this work. Some of the research has been published recently in Journal of the Acoustical Society of Am. (with Nakagawa), Int. J. Eng. Sci., and Phys. of Fluids (with Cortis). Other work that has been accepted but not yet published will appear in Geophysics, a geomechanic journal, and others already mentioned. One main result is the observation that with very little outside information (such as knowledge of the fluids present, and general knowledge of grain parameters), it is possible to invert seismic data for otherwise hard-to-measure-directly drained constants of the porous frame underground. This result is important for many systems of current interest. We are also trying to popularize a method of Sayers and Kachanov (1991) for parametrizing the mechanical behavior of fractured systems. The method has been used very little for poroelastic applications, but has a natural generalization to permit rigorous analysis of fluid effects on these fractured systems. The resulting formulas and numerical methods differ significantly from the usual *ad hoc* approach taken by most workers in the field.

Investigation of the Physical Basis of Biomineralization

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Objectives: To determine principles governing interactions of simple protein analogs, polysaccharides and key inorganic impurities with carbonate minerals and the resulting structures, polymorphs and signatures that form. Extend this expertise to organic-Si interactions in biosilicification. A long-term goal is to establish the physical basis for biomineralization in Earth systems.

Project Description: The research is focused on developing a mechanism-based picture of controls imposed by Asp-rich polypeptides and biomineralizing proteins on the formation of carbonate minerals by processes involved in clustering and nucleation. Using quantitative molecular-scale techniques, we are also probing the transient events and phase evolution during $CaCO_3$ nucleation at organic templates and polysaccharides matrices. Growth studies include: AFM and ToF SIMS studies of Mg and ICP MS studies of Ca-isotopes in calcite grown in the presence of polypeptides and proteins. Nucleation studies include: *in situ* AFM, X-ray absorption spectroscopy, eSEM, *in situ* TEM and molecular modeling of directed $CaCO_3$ nucleation and transformation on functionalized SAMs. Investigations into the fundamentals of mineral growth and dissolution utilize *in situ* AFM measurements of kink dynamics, kMC simulations, and development of analytical theories.

Selected results for FY 2010:

Over the last year, we have published a number of articles and completed new studies that reveal previously unknown thermodynamic and kinetic controls on mineral nucleation and growth. We developed a new mechanistic picture of calcite growth based on slow-kink generation that overthrows the long held view and leads to unexpected growth behavior in the presence of impurities. We applied new *in situ* AFM methods to investigate nucleation in the amorphous silica system and found that nucleation onto bio-templates is favored/disfavored by kinetic factors, rather than the thermodynamic barriers long believed to dominate. *In situ* AFM investigations of calcium oxalate growth at true molecular resolution revealed dynamic aspects of peptide-crystal interactions and peptide clustering that lead to rapid switching between growth and inhibition, as well as growth acceleration. Through X-ray spectroscopy research not yet unpublished, we found that film flexibility is a key feature of SAMs that successfully template nucleation. In essence, templates work in part because they enable the crystal to direct the organization of the template.

Rethinking classical crystal growth models through molecular scale insights: Consequences of kink-limited kinetics. *(De Yoreo et al., 2009, Crys. Growth Des.)*

The classical terrace-ledge-kink' model of crystal growth is widely used to interpret mineral formation in biological and geological systems. A key assumption underlying application of the model is that thermal fluctuations of steps are sufficiently rapid to produce an abundance of kink sites for attachment of growth units. High-resolution *in situ* AFM studies and kinetic Monte Carlo simulations of step-edge structure and dynamics show this physical picture to be invalid for the common mineral calcite whose steps exhibit low kink density and weak step edge fluctuations. As a consequence, interactions of impurities with calcite step edges cannot be interpreted with traditional *thermodynamic* models based on minimization of the Gibbs free energy. Instead impurity-step interactions follow a different mechanism determined by the *kinetics* of attachment and detachment. Step advance is unimpeded when the creation of new kinks by attachment of growth units to the step outpaces binding of impurities to the newly created kinks. This kink-*limited* model offers a plausible explanation for reports of 'kinetic disequilibrium' of trace element signatures. Moreover, because kink density is tied to crystal solubility, these findings argue for a theory based on weak fluctuations to interpret growth of many common crystalline phases of importance in geochemical, biological and technological settings.

Kinetics of Silica Nucleation on Carboxyl and Amine-Terminated Surfaces: Insights for Biomineralization. *(Wallace et al., 2009 J. Amer. Chem. Soc.)*

Biochemical investigations have begun to yield information about structural and chemical properties of organic macromolecules involved in biosilicification processes. However, the mechanisms by which their molecules mediate biosilica formation remain unclear. The formation of mineralized structures in organisms is rooted in processes taking place at the nanoscale, and therefore, molecular level investigative probes are required. Insights into how mineral formation occurs within living organisms can be gained by conducting experimental studies with simple model systems that emulate key features of biological systems. Our approach utilizes a novel AFM-based approach to measure the dependence of amorphous silica nucleation kinetics on the chemical and structural nature of the underlying substrate.

Model biological surfaces terminated with carboxyl, hydroxyl, and amine moieties were generated through the spontaneous adsorption of alkane-thiol self-assembled monolayers onto ultra-flat (111) surfaces of gold. Silica nucleation experiments used supersaturated solutions of silicic acid that were produced by the acid-catalyzed hydrolysis of tetramethyl orthosilicate. Measurements of surface nucleation rate were conducted under conditions that simulate current views of conditions within silica deposition vesicles of major diatom species (e.g. ambient temperature, pH = 5.0, NaCl = 0.1 mol/kg). Aqueous silicate levels were varied to examine dependencies on saturation state.

Analysis of the kinetic data within the framework of nucleation theory quantified the height of the kinetic barrier to silica formation, and the net energy of silica-substrate/solution interfaces. By conducting experiments for COOH, NH_3^+, and OH-functionalized substrates, we determined the kinetic and thermodynamic controls of functional chemistry on heterogeneous nucleation of amorphous silica. These are the first *in situ* measurements of their kind. They show templating in this system is due to faster rates of nucleation brought about by a reduction in the activation barrier rather than minimization of interfacial energy, a result that is counter to conventional wisdom.

Sub-nanometer AFM imaging of peptide–mineral interactions links clustering and competition to acceleration and catastrophe. ***(Friddle et al., 2010, Proc. Nat'l. Acad. Sci.)***

In vitro observations have revealed major effects on the structure, growth and composition of biomineral phases; including stabilization of amorphous precursors, acceleration and inhibition of kinetics, and alteration of impurity signatures. However, deciphering the mechanistic sources of these effects has been problematic due to a lack of tools to resolve molecular structures on mineral surfaces during growth. Here we report AFM investigations using a system designed to maximize resolution while minimizing contact force. The result is true molecular resolution of steps and direct imaging of peptide films and clusters during growth.

By imaging the growth of calcium oxalate monohydrate (COM) — a common biomineral found in plants and soils — under the influence of aspartic acid-rich peptides at single-molecule resolution, we reveal how the unique interactions of poly-peptides with mineral surfaces lead to acceleration, inhibition and switching of growth between two distinct states. Interaction with the positively charged face of COM leads to formation of a peptide film, but the slow adsorption kinetics and gradual relaxation to a well-bound state results in time dependent effects. These include a positive feedback between peptide adsorption and step inhibition described by a mathematical catastrophe that results in growth hysteresis, characterized by rapid switching from fast to near-zero growth rates for very small reductions in supersaturation. Interactions with the negatively charged face results in formation of peptide clusters that impede step advancement. The result is a competition between accelerated solute attachment and inhibition due to blocking of the steps by the clusters. The findings have implications for control of pathological mineralization and suggest artificial strategies for directing crystallization.

Center for Nanoscale Control of Geologic CO_2, an Energy Frontier Research Center (EFRC)

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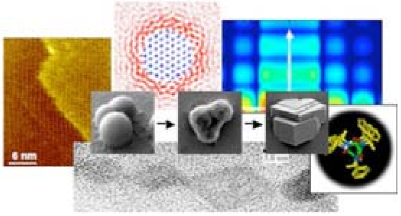
Website: http://esd.lbl.gov/research/facilities/cncgc/

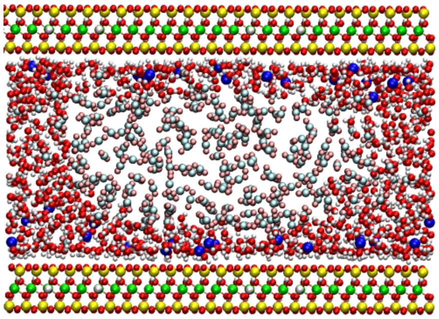
Objectives: Use new investigative tools, combined with experiments and computer simulations, to build a next-generation understanding of molecular-to-pore-scale processes in fluid-rock systems, with the objective of controlling critical aspects of flow and transport in porous rock media, in particular as applied to geologic sequestration of CO_2.

Project Description: A combination of carefully integrated experiments and modeling approaches are used to evaluate essential molecular and nanoscale processes, and to treat the transition from the nanoscale to pore scale, and the effects that arise at the larger scales. Multiscale computational models and lab-scale experiments provide understanding of the the emergence of macroscale properties and processes. Unique BES experimental facilities at the primary work site, LBNL, together with facilities located at ORNL and LLNL, are employed, as well as expertise in materials science, geochemistry, hydrology, biology and geophysics at these and associated academic institutions. The unique character of the center derives from its integrated multidisciplinary approach, and a focus on directing CO_2-rich fluids. The products of the Center are providing fundamental knowledge that will help facilitate safe long-term storage of CO_2 in subsurface reservoirs, to decrease carbon emissions associated with electricity generation, and enhance fluid manipulation for energy resource development and management**.**

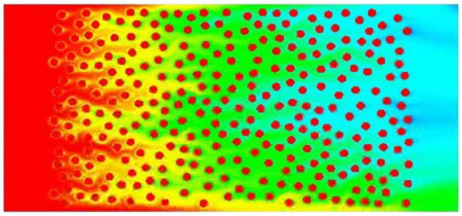
The efforts of the Center investigators are grouped into three Thrust. The Thrusts represent groupings of investigators who use similar experimental approaches and whose work in the Center is directed at closely allied scientific challenges. The three thrust areas have three to six lead scientists, representing all of the institutions involved and constituting the management and scientific leadership of the Center. The lead scientists have extensive experience in designing, organizing, and executing both large and small research projects, and experience in managing laboratory science and coordinating research utilizing large DOE facilities.



Thrust Area 1 - Controlling Nucleation and Growth: The ability to seal deep reservoirs and prevent escape of gases and fluids is one requirement for geological CO_2 sequestration. Reservoirs may be sealed by the precipitation of new minerals in the pore space, or the seal may be maintained by suppressing mineral dissolution. It may also be desirable to control the rate at which mineral precipitation and dissolution occur relative to flow and transport so as to engineer the spatial distribution of reaction products. To manipulate the dissolution, nucleation and growth of minerals in the subsurface environment a detailed understanding of these processes and how they are affected by the special characteristics of porous rock media is required. The objective of Thrust Area 1 is to develop that understanding at the molecular-level, define the role of microbial communities in mediating those processes in reservoir environments and to explore inorganic, biological and biomimetic methods of directing carbonate mineralization in the sub-surface.



Thrust Area 2 - Nanopore Processes: One of our major scientific challenges is to understand the behavior of carbon dioxide-rich aqueous solutions confined at high temperature and pressure in nanoporous matrices under geologic sequestration conditions. The goal of research under Thrust Area 2 is to provide a fundamental understanding of these confined carbon dioxide-aqueous solution mixtures using advanced experimental and computational methodologies to probe fluid behavior from molecular to pore scales.



Thrust Area 3 - Emergent Processes: The injection of CO_2 into the subsurface environment drives the fluid-rock system into "far-from-equilibrium" conditions where new behavior may emerge that is not predictable by considering processes in isolation. Under these conditions, the strong coupling between flow, transport, and reaction may result in emergent structures and pattern formation that develop within the porous structure of the subsurface at scales ranging from the nano-pore and macro-pore all the way up to that of a sedimentary basin. These emergent dynamics must be understood in order to predict how CO_2 will behave when injected into the subsurface.

Integrated Isotopic Studies of Geochemical Processes

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Co-Is: B. Mack Kennedy, John N. Christensen, and Mark E. Conrad
(all - Lawrence Berkeley National Laboratory)

Objective: The primary objectives are to better understand (1) molecular- to microscale processes that control isotopic fractionation during mineral precipitation and transport in fluid phases, and (2) field scale behavior of isotopic ratios in fluid-rock systems and its relation to large scale hydro-geochemical processes. Objective 1 is aimed at developing molecular scale models for mineral formation at both high and low temperatures, using isotopic and trace element fractionation effects as a monitor of molecular fluxes at the mineral surface. An additional objective is to develop models for isotopic fractionation during diffusion in liquids. Objective 2 involves development of new geochronological techniques as well as methods for characterizing transport in larger scale geologic systems using isotopes of solid radiogenic elements (Sr, Nd, Pb, Ca, U, etc.), light stable isotopes (O, C, H, Li, N, S, Ca, Fe, etc.), and noble gases (He, Ne, Ar, Kr, Xe).

Project Description: Molecular to micro-scale processes are addressed with experiments and measurements on natural systems focused on Ca and Mg isotopic fractionation during mineral precipitation, isotopic fractionation associated with aqueous diffusion of cations, anions and dissolved gases, and noble gas incorporation into biogenic and diagenetic minerals. Field scale research includes advancement of geochronological techniques focusing on U-Th-He and groundwater noble gases, studies of noble gases as gas phase partitioning tracers, investigation of sulfur and iron isotopic fractionation during abiotic sulfide reduction, kinetic isotopic effects on soil carbonate isotopes, and modeling studies of isotopic effects due to fracture flow and inhomogeneous permeability in fluid-rock systems.

Results: (1) *U-Th-He*: We continued study of U–Th/^{4}He ages on olivine phenocrysts from late Quaternary basalts. The approach employs abrasion to remove implanted ^{4}He from U-rich groundmass, and an extraction system that allows U, Th and He concentrations and isotopic compositions to be measured on the same sample. The method is being applied to submarine basalts where it may have its greatest value, but where issues with incomplete degassing upon eruption cause complications. Initial results on submarine Hawaiian tholeiitic basalts have so far been difficult to interpret, but complications may be due to mass spectrometer issues, related to the very low He contents of the examined olivines.

(2) *Ca isotope probe of mineral precipitation*: The mechanisms and rates at which dissolved ions are transferred to- and from mineral surfaces as crystals grow from aqueous solution are poorly known but important for interpreting mineral chemistry and isotopic composition. Ca and Mg isotopes can provide unique information about the mineral-fluid interface. Results from studies of diagenetic systems, which evolve over millions of years indicate that at equilibrium there is no Ca isotopic fractionation during precipitation of calcite. Laboratory experiments show fractionation, although at much higher precipitation rates. We find that precipitation in natural systems with high CO_3^{2-}/Ca^{2+} show fractionation that is similar to seawater, which has low CO_3^{2-}/Ca^{2+}. Mg isotopic and Sr/Ca data are now being collected to relate these fractionations to Ca isotopes and precipitation rate.

(3) *Theory of isotopic fractionation during mineral precipitation*. A macroscopic kinetic-thermodynamic model has been developed that relates isotopic and trace element fractionation to precipitation rate. This model so far explains well the observations of Ca isotope fractionation when calcite is precipitated under surface reaction controlled conditions, and also explains the partitioning of Sr/Ca and Mn/Ca. Model results suggest that as equilibrium is approached, molecular exchange rates between mineral and solution decreases.

(4) *Retardation of calcite dissolution by clay and organic material.* We measured the Sr and Ca isotopic composition of pore fluids in deep-sea sediments that consist of mixtures of biogenic calcite, clay and 0.5 to 5% organic carbon. The δ^{44}Ca of pore fluids is different from that observed in sections where the sediments are nearly pure calcite. In these sections either calcite dissolution is suppressed or isotopic fractionation is changed by the presence of organic matter. The effects have implications for geologic carbon sequestration and for reconstruction of past climate changes from sedimentary records.

(5) *U-series alpha-recoil as a nanoscale probe of natural systems*: (^{234}U/^{238}U) of fine-grained sediments shows systematic effects suggesting that alpha-recoil associated with the decay of ^{238}U is primarily responsible for ^{234}U depletions in minerals. Because the rate of ^{234}U loss reflects the scale of recoil, which is 30-50 nm, and the shape and surface properties of mineral grains, the U-series characteristics of minerals constitutes a nanoscale probe of mineral surface structure. Models for quantifying the alpha-recoil loss fraction based on theoretical estimates of recoil range, mineral grain geometry, surface area constraints, and chemical methods have been developed.

(6) *Field scale Ca isotope effects in hydrothermal systems*: A survey of the Long Valley hydrothermal system is continuing for the isotopes of water, Sr, Ca, and noble gases, and the concentrations of major cations, anions, and total CO_2. Correlated variations among total CO_2, noble gases and the concentration of Ca suggest progressive fluid degassing, driving calcite precipitation as the fluid flows across the caldera and generating a 0.5 per mil increase in fluid δ^{44}Ca. Studies have also been done on epidote from selected fossil hydrothermal systems from mid-ocean ridges. Hydrothermal calcite and epidote show evidence of Ca isotope fractionation, which is most likely due to kinetic effects during precipitation are analogous and similar in magnitude to those that affect calcite precipitating at 25°C.

(7) *High pressure biochemical isotopic fractionation effects*: Isotopic signatures are widely used to identify the existence and activity of microorganisms within the earth's crust. Whereas for inorganic reactions pressure has a negligible effect on isotopic fractionation, for biochemical reactions it does. Experiments with researchers from Idaho National Laboratory and Oregon

State University show significant differences in $\delta^{13}C$ of biogenic methane produced at atmospheric pressure and seafloor pressures of ca. 500 atmospheres.

(8) *Phase partitioning tracers:* Modeling has shown that precisely measured details of a chromatographic separation profile for a suite of phase-partitioning tracers with different gas-water solubility can provide important information regarding gas/liquid transport, the extent of gas-water interaction, an integrated gas/H_2O volume ratio and place constraints on the geometry of gas-liquid interaction. Quantitative assessment of tracer return data is limited by a lack of data regarding the solubility partitioning of the tracers in water-CO_2 systems at the relevant P, T and x_i conditions. Preliminary water-CO_2 solubility experiments for noble gases and SF_6 have been conducted under the appropriate P, T and x_i conditions encountered in deep aquifer CO_2 sequestration that indicate a significant increase in noble gas solubility in water in the water-CO_2 system, ranging from a factor of ~3 for Ne to a factor of ~10 for Xe.

(9) *Collaborative studies*: We collaborate with other BES investigators on isotopic fractionation due to diffusion in aqueous fluids and silicate liquids, and in modeling isotopic effects using numerical reactive transport codes. The diffusion studies have the dual objective of characterizing the isotopic effects for application to natural geochemical processes, and using them to understand the chemical structure of fluids and melts. The modeling studies relate isotopic effects to models of mineral reaction kinetics, in order to allow isotopic measurements to be used as monitors of chemical reactions in nature.

KEYWORDS: geochemistry, isotopes, uranium, calcium, strontium, helium, geochronology, chemical kinetics, fractionation

A Documentary Film Project Based on the National Research Council Report, *Origin and Evolution of Earth*

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Objective: The goal of this project is to impart to a broad audience a concise summary of the latest scientific thinking about the Earth in an entertaining and non-technical way. It will produce a two-part film documentary film for national and international broadcast and educational distribution on DVD. The basis of the film will be the National Research Council's 2008 report, *Origin and Evolution of Earth: Research Questions for a Changing Planet*.

Project Description: Two one-half hour films will cover selected parts of the range of topics explored in the NRC report. One film will investigate the Earth's interior and the origin of the planets; the other will explore Earth's exterior, including the origin of life, the earliest history of the Earth's surface environment, climate change, and interactions between geologic evolution, climate evolution, and the evolution of life. A committee of advisors will be assembled to review the film's treatments and scripts for scientific accuracy. Filming will be done in visually impressive and geologically important locales worldwide, and the themes will encompass important issues such as the origin of life, climate change and evolution over Earth's history, environmental stewardship, the origin of earthquakes and volcanoes, and the special properties of the Earth in comparison to other planets. Prominent Earth scientists, representing a wide range of disciplines, will be filmed performing fieldwork and explaining geologic concepts. To provide role models and help address the need for increased diversity in the Earth sciences, the scientists will be a diverse group in terms of gender, ethnicity, and age. Most of the footage generated for this project will be newly shot in super-16 mm film and HD. New footage will be augmented with an extensive library of Earth science footage filmed worldwide by the producers. New 3D animations will be created and original music will be scored to picture. A prominent personality will be recruited to narrate the film.

The films will be mastered in the HD format and delivered to the Public Broadcasting System and other broadcasters internationally.-The DVD version (standard definition and Blue-Ray HD) will be made available through a major media distributor who will market it nationally to schools, libraries, museums, science centers, parks, and individuals. In addition to offering the product on DVD, the distributor will stream the films on the internet for downloading. They will be advertised in national geoscience educational and scientific journals and presented at meetings of the Geological Association of America, the American Geophysical Union, and the NSTA by the PI and the producers.

Results: Research and development of the documentary is completed, and an advisory committee, headed by Donald DePaolo, has been selected. Shooting locations and scientists to be filmed for possible appearances in the documentary have been selected. Filming has proceeded smoothly in Asia, Europe, Hawaii, Alaska, and the western US. Additional shooting has been planned and scheduled. Archival footage of major geologic events has been obtained and will be updated as future events occur. Work has advanced on a draft script for the documentary, and design of 3D animations has begun. Negotiations are underway with PBS and PBS International regarding presentation of the finished documentary to the PBS network and to foreign stations, and a comprehensive promotion, education, and outreach plan is being developed.

KEYWORDS: Earth science, geology, planetary science, science outreach, science education

Coupled Diffusion and Sorption Processes within Nanoporous Aggregates

PI: Ben Gilbert; Tel. (510) 495-2748, BGilbert@lbl.gov

Objectives: The project goal is to achieve a quantitative understanding of the way that aggregation and aggregate morphology affects the accessibility and effective reactivity of the surfaces of natural nanomaterials in the environment. We are combining experimental and simulation studies to identify and characterize the physical and chemical constraints on interfacial chemistry in nanoporous aggregates.

Project Description: Ferrihydrite (an iron oxyhydroxide nanophase mineral) is widespread in the environment and is typically observed to form aggregates. We have performed studies of the nanoscale morphology of ferrihydrite aggregates using small-angle X-ray scattering (SAXS), and shown that aggregate structure has a strong impact on the uptake and sequestration of heavy metal contaminants.

In order to better understand the physical and chemical factors that affect how aqueous ions are sequestered in ferrihydrite aggregates we seek to construct accurate, atomistic, three-dimensional models of aggregate structure, enabling molecular dynamics (MD) studies of interfacial processes. This effort requires two approaches (1) construct 3D models of aggregate structure derived from SAXS data (see 2009 report); (2) construct atomistic models of ferrihydrite nanoparticles.

Michel et al., 2009, published a new structural model for ferrihydrite, but discrepancies between the experimental diffraction and the prediction of based on their proposed unit cell indicate that a full structural solution is not yet known. To obtain a more realistic description of the ferrihydrite structure, we constructed a novel reverse Monte Carlo method that incorporated crystal topologies from a range of proposed structures. Structure configurations were tested against X-ray scattering and pair distribution function data in order to seek a structure that best agreed with all available data.

Results: We successfully used the RMC approach to generate full-nanoparticle structural models of ferrihydrite. The results suggest that ferrihydrite is a defective structure that partly contains the structural topology of the Michel et al. model, but which has similarities to the maghemite structure.

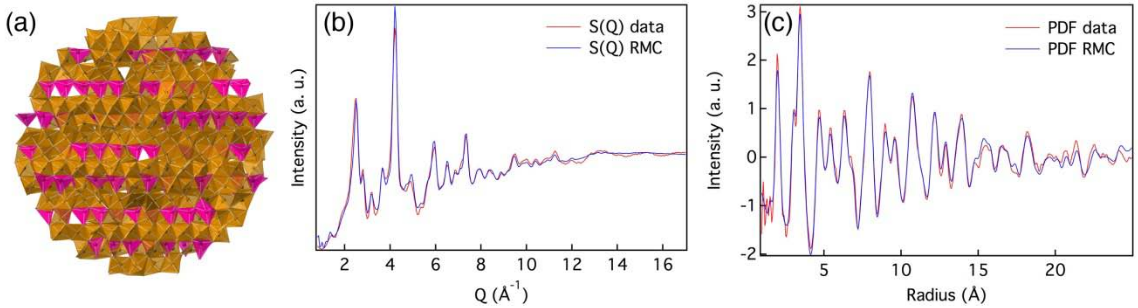

Figure 1 Reverse Monte Carlo (RMC) modeling study successfully created atomistic model of a defective ferrihydrite nanoparticle **(a)** that matches both X-ray scattering **(b)** and pair distribution function **(c)** data.

Propagation of Elastic Waves in Complex Media

PI: Lane R. Johnson; Tel. (510) 486-4173, LRJohnson@lbl.gov

Objectives: The general objective is to perform fundamental research on elastic wave propagation in media with various types of heterogeneity and various scales of heterogeneity. The challenge is to develop computational methods that consistently account for the various types and scales of heterogeneity while retaining fidelity to the basic physics of the problem.

Project Description: At the smallest scale where the media is typically described in a statistical sense a dynamic composite medium approach will be used to model both the velocity and attenuation in a self-consistent manner for all frequencies. In order to treat the effects of large-aspect inclusions such as elongated pores or flattened cracks it will be necessary to derive the solution to the boundary value problem for scattering of elastic waves by a spheroid. The Maslov integral approach will be used to treat wave propagation at the scales where the media can be described in a deterministic manner with a general three-dimensional model that includes both smoothly varying properties and discontinuities. Having developed and integrated these basic approaches, a number of extensions will be considered, guided by testing through application to realistic data sets. The scope of the project was expanded in FY08 to include the study of small earthquakes observed in geothermal areas.

Results: Much of the effort in FY2010 was devoted to the preparation of papers that describe the research results obtained in the previous three years. A paper entitled "An earthquake model with interacting asperities" was submitted, accepted, and published in Geophysical Journal International. For the purposes of interpreting seismic data, this model provides an alternative to the conventional model of an earthquake that was developed in the 1960's. Taking advantage of this result, a new task was initiated with the objective of using waveform data from seismic events in geothermal areas as part of an effort to discriminate between the conventional model, the asperity model, and a damage model. As a first step in this project, complete second-order moment rate tensors are being extracted from the seismic data. Interpreting these moment tensors in terms of the three different models will hopefully help determine which of the three is the most appropriate and in this way lead to a better understanding of the physical processes involved in these seismic events, most of which are induced.

A paper on the scattering of elastic waves by a spheroidal inclusion was almost completed during the year. A description of this boundary value problem and its solution is complete and the only remaining task is the generation of the necessary figures. The numerical parts of this task have been significant, as this required the generation of a complete library of computer programs for the calculation of spheroidal wave functions.

Kinetic Complexity of Mineral-Water Interface Reactions Relevant to CO_2 Sequestration: Atomic-Scale Reactions to Macroscale Processes

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(Wright State University)

Objectives: We seek to address several problems of critical importance to understanding geochemical processes that occur during the geologic sequestration of CO_2. Specifically, we want to understand the geochemical behavior of the CO_2-aqueous fluid-rock system under the near-equilibrium conditions that will be obtained over the bulk of the lifetime of the sequestration process.

Project Description: In order to achieve these objectives, we need to better understand several fundamental processes. First, we need to understand the morphological relaxation that occurs on a mineral's surface in response to a change in fluid composition. On what time scale does this topographic relaxation occur and how is it reflected in the rate and mechanism of fluid-mineral interaction (dissolution or growth)? Understanding and quantifying this relaxation process should allow us to resolve the apparent discrepancies between experimentally determined rates and those estimated from field evidence. Second, we need to understand how the surface reactivity of a mineral varies as a function of orientation. Most geochemical models effectively treat dissolution/growth as an isotropic process, yet we know that this is not the case. Finally, acknowledging that the dissolution and growth processes (and their rates) are crystal face specific, after a long period of near-equilibrium reaction under the perturbed conditions created by CO_2 injection, how does grain morphology evolve with time during dissolution and what are the dominant crystal faces controlling dissolution? Answering this question should further resolve the lab/field discrepancy.

Our approach to addressing these questions is to apply a combination of microscopic and macroscopic experimental techniques that permit us to study process details at the specific mineral-fluid interfaces and then to "scale-up" to integrate those processes over all surfaces. Specifically, *in-situ* fluid cell AFM experiments using our unique Hydrothermal AFM (HAFM) will be conducted on carbonate mineral specimens to characterize the processes of topographic relaxation, crystal face specific dissolution rates and crystal morphology evolution on a nanometer to micrometer distance scale. The corresponding macro-scale experiments will be conducted in custom-built Mixed Flow Reactors with surface analyses made using Vertical Scanning Interferometry (VSI). This scaling-up is a requirement for utilizing the reactive transport simulators that will be employed to assess performance and predict behavior of CO_2 sequestration systems by forward modeling for the thousands to perhaps tens of thousands of years over which CO_2 containment must be evaluated.

Results: Complementing the work at WSU (see Wright State University summary), the project emphasis at LBL is high temperature macro-scale experiment development, HAFM capability development and VSI measurements. During this second year of the project, we continued our development of the HAFM at LBL, began some magnesite dissolution experiments using the modified HAFM flow cell and we designed a Mixed Flow Reactor to be fabricated by Coretest Systems, Inc. and placed the order.

The modifications to the HAFM flow cell consisted of fabricating a Ti pedestal to fit with precise registry on the standard sample disk, thereby raising the location of the sample surface to a height appropriate for the taller Subcritical Crack Growth flow cell. This repositions the sample surface to a point closer to the TopView optical head's laser focal length, resulting in a significant improvement in Sum signal strength: increasing it from +1 to nearly +5V. This should improve the signal to noise ratio considerably. We also added a larger sample injection loop to the HAFM flow path to increase by a factor of ~5x the length of time that an experiment could run with any one solution composition, before needing to switch to the other sample loop. These sample loop switches require briefly disengaging and then re-engaging the tip, hence interrupting the continuous scanning of the sample surface. Using this new HAFM flow cell, we began some magnesite dissolution experiments. As this figure shows, we are able to image clearly at 90°C under flowing conditions.

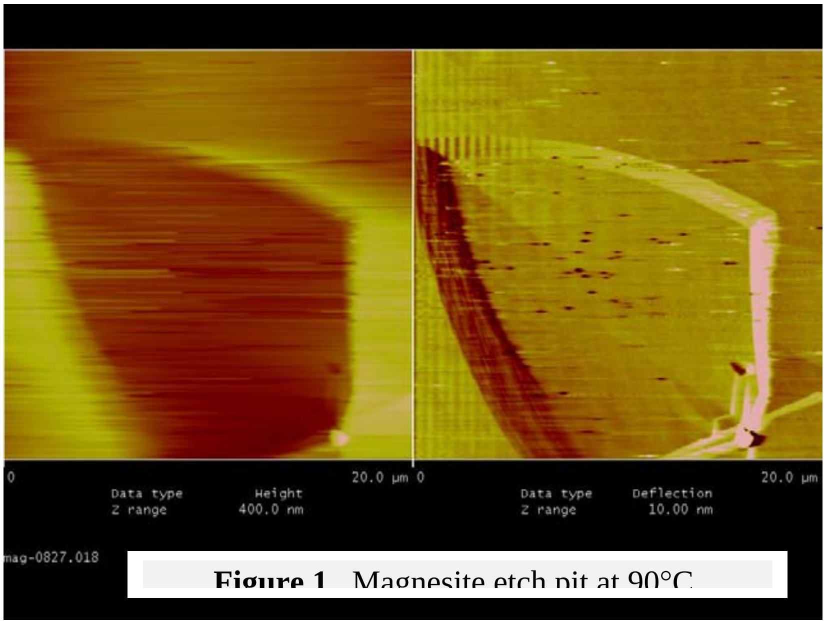

Figure 1 Magnesite etch pit at 90°C

Finally, to explore T&P space beyond that achievable using the HAFM, we designed a new all Ti MFR. This reactor will allow us to react cleaved mineral fragments, held in a sample jig that provides a masked region of the sample surface for comparison, up to 325°C and 130b. Using a Quizix pump for flow control we can achieve flow rates from 0.0001 to 10 mLs/min. The range in residence times will let us cover parts of chemical affinity space ranging from very near to very far from equilibrium. The recovered cleavage fragment can then be examined *ex situ* using the DI MultiMode AFM.

Evolution of Stress-Sensitive Seismic Properties in Sediments and Granular Rock during Compaction

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Co-I: Liviu Tomutsa (Lawrence Berkeley National Laboratory)

Objectives: The primary objectives of this research are to understand from laboratory experiments: (1) how mechanical and chemical compaction of sediments affects their seismic properties; (2) how stress-induced seismic anisotropy evolves in both granular media and fractures during compaction; and (3) how the microscale geometry of intergranular contacts and microcracks in sediments and rock changes during compaction.

Project Description: This project involves conducting a series of laboratory experiments to understand how some of the diagenetic processes occurring in the earth affect the seismic properties of sediments and rock. These experiments involve four steps: (1) First, the process of sediment compaction is simulated using a specially designed sediment compaction cell. The resulting changes in the elastic transverse isotropy are determined via seismic waves. (2) Next, the process of pressure dissolution and cementation is simulated, using halite (rock salt) crystals as analogue sand with concurrent seismic measurements. Using halite allows the experiment to be conducted within a reasonable time period (several days to weeks), compared to using quartz, feldspar, or calcite. (3) Third, the process of intergranular cementation of rock is simulated, using synthetic sandstone samples (fabricated from quartz sand and glass cement) with a controlled porosity. These sandstone samples, together with natural rock samples, are also used to examine how induced microcracks and fractures affect stress-sensitive seismic properties. (4) Finally, shearing of fluid-saturated, single fractures is conducted with concurrent seismic wave measurements.

Results: Using pore cast samples of halite packs at different levels of pressure dissolution and compaction, we examined the development of grain contact anisotropy. This was done by saturating cube-shaped pore cast samples with 1M NaCl solution and measuring their electrical conductivity between the three sets of opposing surfaces (Figure 1). The results showed clear increases in both overall electrical conductivity and decreases in the transverse anisotropy as a function of compaction. The measured electrical conductivity values were related to changes in the grain contact geometry and its anisotropy using a model based upon simple cubic packing of identical conductive spheres. These results were compared to previously measured seismic anisotropy of halite packs undergoing pressure dissolution and compaction.

We used halite also as an analogue intergranular cement to simulate lithification of unconsolidated sand in the laboratory. In this experiment, halite cement was produced from a concentrated aqueous solution by mixing with alcohol (ethanol or isopropanol). Upon mixing, alcohols dry the solution, resulting in precipitation of salt crystals (this is commonly known as “salting out” behavior). The resulting changes in the seismic properties of a sand pack were examined using a modified resonant bar technique (the Split Hopkinson Resonant Bar Method) at frequencies near 1 kHz. The seismic measurements showed that the precipitation and cementation of sand grains did result in increases in the overall elastic moduli of the sample. This effect, however, was larger for samples consisting of smaller sand grains. The difference was attributed to the relative size of the precipitated halite crystals compared to the sand grains.

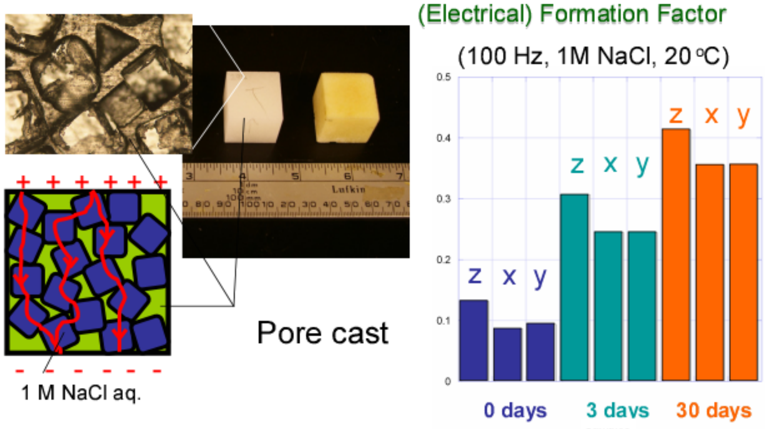

Figure 1. Electrical anisotropy measurement of pore casts of halite packs. Halite was used as an analogue sand undergoing pressure dissolution and compaction. The compaction results in anisotropy in the grain contact, which can be measured from the electrical conductivity (Formation Factor) of the pore casts.

Joint Three-Dimensional Electromagnetic-Seismic Imaging: A Structurally Based Approach

PI: Gregory A. Newman; Tel. (510) 486-6887, ganewman@lbl.gov

Objectives: Provide an enabling technology in subsurface imaging using seismic and electromagnetic (EM) fields, extended to gravitational fields. The project addresses critical needs within the DOE mission, including waste legacy issues and energy and environmental security, which are difficult to treat with existing three-dimensional (3D) geophysical imaging technologies.

Project Description: Quantitative imaging of the subsurface objects employs the different geophysical measurements that sense the subsurface. One of the main problems in the obtaining joint image is the consistent treatment of the different geophysical data and their corresponding attributes due to their differing physical nature. This is essential when analyzing seismic and EM data because seismic energy propagates as a wave, while EM energy is highly dissipative and diffusive. The proposed solution is to low-pass filter the seismic trace via Laplace-Fourier transformation. The effect of Laplace-Fourier transformation changes the behavior of the seismic wave field from wave propagation to diffusion and allows one to treat seismic data with the electromagnetic data in a consistent manner with similar resolution characteristics. Though the resulting image will be of lower resolution than with non-transformed seismic data, it can provide a background macro velocity model essential for effective seismic imaging in complex geological settings. Finally, it is important to emphasize the incorporation of the Fourier component in the transformed wavefield. It provides improved spatial resolution for velocity images over corresponding images based on seismic data that have only been treated with the Laplace transform. In the limit, where the Laplace component vanishes, leaving only the Fourier component, the seismic wavefield information content and resolving capabilities is at its greatest, but successfully imaging such data is now much more difficult.

Results: Our main accomplishment for the past year has been the development of a model that allows the calculation of 3D Elastic Wave Propagation in Laplace-Fourier Domain. The solution approach is based on the solution of the first- order differential equations for velocity-stress components on the staggered grid and is solved using iterative Krylov methods. Implementation of the model to typical seismic problems demonstrates the viability of the approach. The codes can be used for the simulation of direct problems of the elastic wave propagation in 2&3D geometry and allows the analysis of the entire seismic waveform to recover the high spatial frequency components of the seismic image. They can also be used as preconditioners for full waveform simulation. We have also developed and successfully tested the framework in setting up the joint geophysical inverse problem using non-linear conjugate gradient methods, where we link the different geophysical attributes using a structural constraint. A selection process for the inversion design parameters has been quantified, including weights for the different data types, smoothing and the amount of structural correlation in the geophysical attributes.

Permeability Dependence of Seismic Amplitudes

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Objectives: The goal of this research is to develop a quantitative understanding of what seismic attenuation is due to. Many attenuation mechanisms have been proposed over the years, but only a few recent models have both begun to predict attenuation levels that are consistent with field measurements in the seismic band (10 Hz to a few kHz) and been based on a realistic physical description of rocks. These models assume that rock contains "mesoscopic-scale" heterogeneity, which is defined as heterogeneity over scales larger than the grains, but smaller than the seismic wavelengths. When rocks containing mesoscopic structure are stressed, the more compliant parts of the rock respond with a larger fluid pressure change than the stiffer parts, which results in fluid flow and wave attenuation.

Project Description: The approach taken in this study to better understand the mechanism of seismic attenuation in the presence of mesoscopic heterogeneity is largely one of numerical simulation. Computer-generated synthetic rock samples are created that have spatially variable poroelastic moduli and porous-continuum properties (e.g., porosity and permeability) distributed over the pixels. The numerical experiments consist of applying a time-varying stress to the sample surface, and measuring the resultant sample strain (defined as the average local strain throughout a sample). The Fourier transform of the stress and strain determine the sample's complex frequency-dependent moduli, while the ratios of the imaginary and real parts of these moduli define the inverse quality factor $1/Q$ for the compressional and shear modes. The local response within such synthetic samples is obtained using finite-difference approximations of Biot's poroelasticity equations. A range of experiments on diverse synthetic materials are performed in order to learn how seismic attenuation is quantitatively related to the presence of mesoscopic-scale heterogeneity.

Results: For FY 2010, we first focused on the affect of partial water saturation on seismic attenuation. We numerically created fluid distributions in rocks the way they are in the earth; by the invasion of one fluid into a rock sample initially occupied by a second fluid. We used the invasion percolation algorithm to perform this modeling. Invasion percolation is appropriate when the invasion occurs slowly as it does in most geological scenarios and produces tree-like branching structures for the invading fluid. We then numerically obtained the attenuation and dispersion as a function of frequency for rock samples having invasion-percolation clusters within them and observed that depending on which fluid (water, oil or air) was taken to be the invader and which was taken to be the defender, radically different attenuation/dispersion curves were obtained. We then proceeded to make analytical models that could explain the numerical results. The work was submitted for publication in September, 2010.

We also focused on how attenuation and dispersion is affected by anisotropy in the mesoscale structure of the porous materials. We began by measuring numerically the attenuation as a function of frequency for both materials consisting of porous ellipsoidal inclusions and of random porous media having correlations lengths different in the three directions. We then observed that the ratio of peak attenuations measured in different stress/strain modes was a power law of the aspect ratio of the inclusions. We also developed an analytical theory of attenuation and dispersion based on Eshelby theory for porous ellipsoidal inclusions. This theory was shown to explain the numerical results very well. This work has not yet been submitted for publication

In the laboratory, we continued to measure the mesoscale fluctuation in the elastic properties of actual rocks. The method is to use a servo-controlled indentor to measure the fluctuations of the "surface" or "indention" modulus over the surface of planar rock slabs. An apparatus was specially built for this application and experiments on rock floor tiles were performed. It was observed that the elastic moduli in these samples fluctuated by over 50% over the samples surfaces. However, due to the elevated stiffness of the particular rock types studied, only small amounts of attenuation were observed; this is likely the appropriate result for these rocks.

Density-Driven Brine Convection: A Process for Accelerating CO_2 Dissolution and Enhancing Security of Geologic Storage

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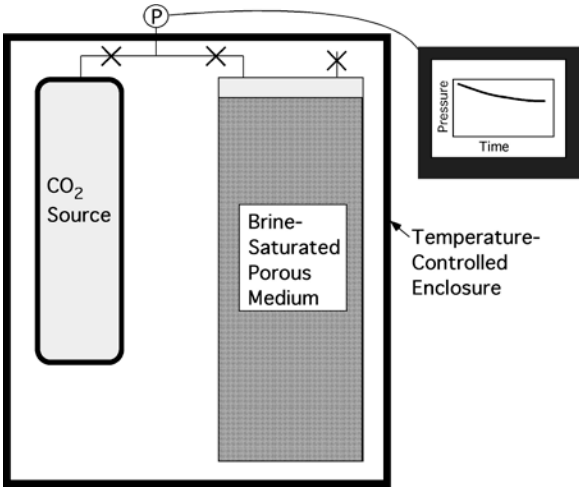
Co-I: Timothy J. Kneafsey (Lawrence Berkeley National Laboratory)

Objectives: The purpose of this project is to investigate through laboratory experimentation and mathematical modeling the process of dissolution-diffusion-convection (DDC) as a mechanism for transferring CO_2 stored in a saline aquifer to the aqueous phase.

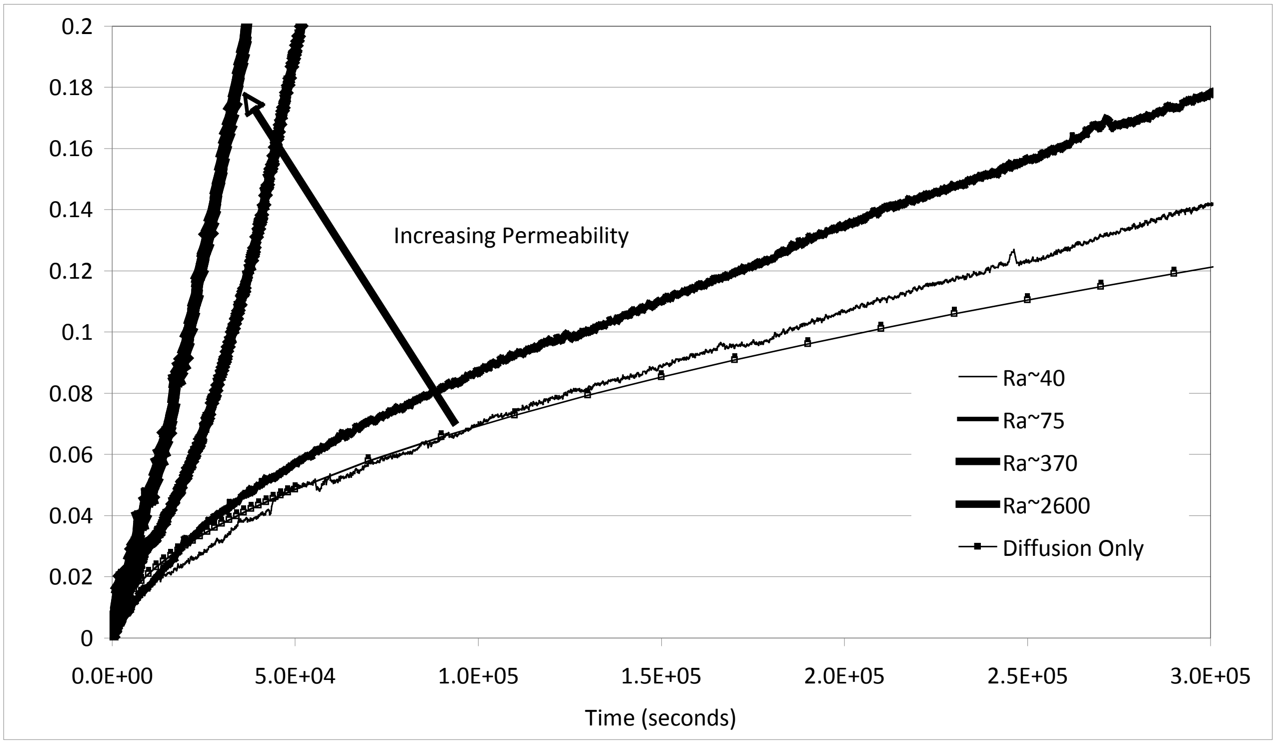
Project Description: CO_2 injected into saline formations at typical subsurface temperature and pressure conditions has lower density than the aqueous phase, will experience an upward buoyancy force, and will rise through the aqueous phase to spread out laterally beneath a low-permeability caprock. Storage security may be enhanced by dissolution into the aqueous phase. Dissolution is limited by the rate at which aqueous CO_2 is removed from the phase boundary by molecular diffusion, but can be greatly enhanced by density-driven convection, induced by a small increase in aqueous phase density as CO_2 dissolves. This project aims to perform laboratory experiments to visualize and quantify the DDC process, and to develop and demonstrate high-resolution numerical models to gain quantitative insight into DDC and its controlling parameters.

Results: Continued flow visualization experiments were performed in Hele-Shaw cells assembled from flat glass plates, and in Hele-Shaw cells containing glass beads or sand. In these experiments, CO_2 was introduced as a gas at ambient conditions atop the water or brine. Dissolution was monitored and visually recorded using pH-sensitive dyes that were added to the aqueous phase. Quantitative CO_2 uptake tests were performed in a temperature controlled two-vessel system using a number of sands with different permeabilities, and different brine salt concentrations (Fig. 1). In these tests, one of the vessels was filled nearly to the top with brine-saturated porous media leaving a very small headspace. The other vessel was sized so that it was large enough to provide approximately constant CO_2 pressure while being small enough to accurately monitor the slight pressure decrease from the CO_2 dissolution, diffusion, and convection through the brine in the porous medium. At the start of the test, the two vessels were connected. Higher permeability sand and lower brine salt concentration result in increases in the nominal Rayleigh number, and cause significant increases in the rate of CO_2 uptake compared to the nonconvective diffusion only case

A parallelized version TOUGH2-MP/ECO2N of our general-purpose CO_2 storage simulation tool was used to investigate effects of convectively enhanced CO_2 dissolution on the long-term fate of CO_2 stored in an aquifer with a sloping caprock. Upscaling from high-resolution simulations of DDC, a first sub-grid scale model was developed and implemented into TOUGH2-MP/ECO$_2$N to represent DDC in a field-scale model. Numerical simulation experiments demonstrated accelerated dissolution of free gas, indicating that for a hypothetical CO_2 storage scheme in the Carrizo-Wilcox aquifer in Texas, about 1/3 of total CO_2 inventory is dissolved over a 300 year period. While convectively enhanced dissolution greatly reduces the thickness of the CO_2 plume, for the parameters and conditions used the rate of plume advancement is not affected. A problem variation that includes a leaky fault attached to the aquifer removes CO_2 from the advancing plume at rates sufficient to temporarily stall the plume advance. However, as the thicker portions of the plume arrive at the leaky fault, plume advancement resumes with the same speed as for the case without a leaky fault. This behavior can be understood by noting that the leading edge of the plume is rather thin, so that fault zone leakage initially amounts to a large fraction of total updip CO_2 flow. Over time the CO_2 plume at the bottom of the fault thickens, so that leakage becomes a small fraction of total CO_2 flow, and impacts on the speed of plume advancement become small. We have also employed adaptive gridding techniques for 2-D and 3-D flows to systematically explore the dependence of transport rates of dissolved CO_2 on hydrogeologic conditions and fluid parameters. Numerical simulations have confirmed the dependence of onset time for convection that was predicted by linear stability analysis.



(a)



(b)

Figure 1. (a) Quantitative CO_2 uptake test schematic, and (b) effect of permeability on incubation time and CO_2 uptake rate.

Clay Mineral Surface Geochemistry

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Objectives: The objective of this project is to investigate the structure and reactivity of layer type minerals at molecular scales using X-ray absorption spectroscopy and computer simulation. Current research focused on determining the sorption mechanisms of trace metal cations by bacterially-produced birnessite (layer-type MnO_2).

Project Description: Birnessite minerals produced by bacteria and fungi are ubiquitous environmental nanoparticles participating in important geochemical processes, particularly trace metal scavenging. The birnessite produced by the soil bacterium *Pseudomonas putida* is nanocrystalline with significant structural disorder created by Mn(IV) cation vacancies [up to 20% of the Mn(IV) octahedral sites], which contribute significantly to the metal-scavenging capacity of this mineral. Our experimental and computational research was designed to determine the molecular-scale structure of surface complexes formed by Ni^{2+} and Zn^{2+} on bacteriogenic birnessite. The surface speciation of metals under conditions of varying surface loading and pH was investigated through batch adsorption experiments and extended X-ray absorption fine structure (EXAFS) spectroscopy at the Stanford Synchrotron Radiation Lightsource (SSRL). The stability of and transitions between different surface species were investigated through geometry optimizations based on quantum mechanical density functional theory (DFT) using the massively-parallel supercomputing resources of the National Energy Research Scientific Computing Center (NERSC).

Results: We found that bacteriogenic birnessite accumulates very large quantities of Ni (0.13 mol Ni mol^{-1} Mn at pH 6) and Zn (0.27 mol Zn mol^{-1} Mn at pH 7) through sorption at well-defined binding sites. For Ni, EXAFS spectra showed two dominant coordination environments (Figure 1A): Ni bound in a triple-corner-sharing (Ni-TCS) complex at vacancy sites and Ni incorporated (Ni-Inc) into vacancies in the MnO_2 sheet, with the latter form of Ni favored at high sorptive concentrations and pH. Our DFT calculations revealed a pH-dependent energy barrier associated with the transition from Ni-TCS to Ni-Inc (Figure 1B). These results are consistent with a rate-limited incorporation of Ni into vacancy sites in our freshly-precipitated samples and significant Ni-Inc in birnessite found in manganese nodule samples. For Zn, our EXAFS spectra showed the co-occurrence of tetrahedral (Zn^{IV}-TCS) and octahedral (Zn^{VI}-TCS) surface complexes at vacancies. Specifically, Zn^{IV}-TCS dominated at very low surface loading, but, as the loading was increased to 0.3 mol Zn mol^{-1} Mn, the mineral adsorbent became saturated with the Zn^{IV}-TCS species at 0.1 mol Zn mol^{-1} Mn, while the Zn^{IV}-TCS species accounted for up to 0.2 mol Zn mol^{-1} Mn. These results were rationalized by our DFT simulations showing that, although an isolated Zn^{IV}-TCS species is favored energetically, H-bonds between adjacent Zn^{VI}-TCS species enhance the stability of this surface species. Our research thus provides insights into the chemical conditions governing the occurrence of differing sorbed metal species in bacterially-produced birnessite and elucidates the details of the metal sorption mechanisms.

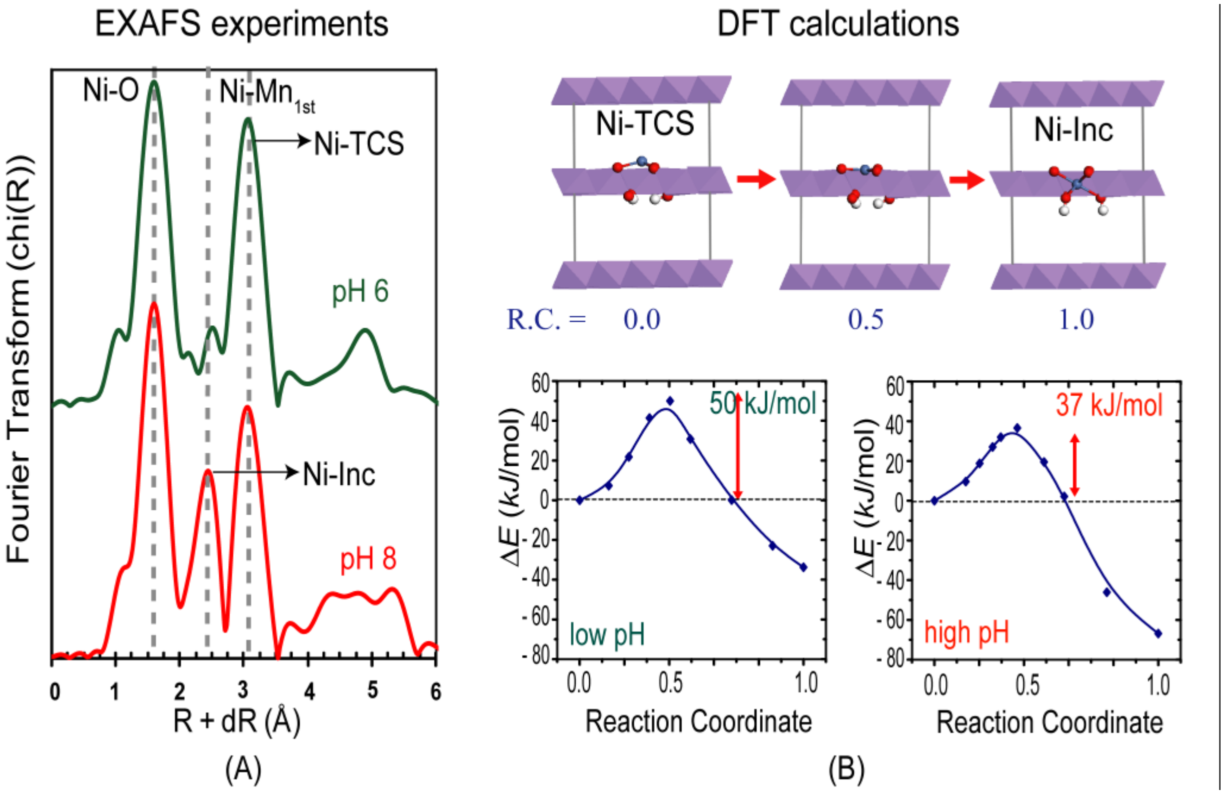

Figure 1. (A) Fourier-transformed EXAFS spectra of Ni sorbed on birnessite produced by *Pseudomonas putida*, showing peaks for Ni-TCS and Ni-Inc species at low and high pH. (B) Total energy of Ni-MnO_2 calculated by DFT geometry optimization during the transition from TCS to Inc species along a reaction coordinate (R.C.) at low and high pH.

Rate Controls in Chemical Weathering: A Reactive Transport Approach

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Objectives: The objective of this project is to improve our understanding of the controls on chemical weathering rates (and by analogy, rates of all water-rock interaction processes in the subsurface) by taking a holistic reactive transport approach.

Project Description: The project consists of complementary experimental and modeling studies directed towards understanding the rates of mineral dissolution and precipitation at the field scale. Work involved determination of the dissolution and precipitation rate of kaolinite at 22ºC and 60ºC, and measurement of the rates of incongruent dissolution of illite going to kaolinite. The results are applied to the Santa Cruz chronosequences (Maher et al., 2009, GCA **73**, 2804–2831; Steefel and Maher, 2009, *Rev.Minera. Geochey* **70**: 485-532), to modeling of weathering at the Biosphere (Dontsova et al, 2009, *Hydrol. Earth Syst. Sci.* **13**:2273-2286), and to a number of deep sea sediments in which silicate weathering is occurring. In addition, a model for weathering rind growth making use of a Diffusion Threshold model (Navarre-Sitchler et al, 2009, *JGR* **114**, doi:10.1029/2008JF001060) allowed for prediction of the linear advance rate of the rind, the coincidence of mineral fronts, and the sharpness of the interface (Navarre-Sitchler and Steefel, in prep.).

Results: The precipitation of clay minerals during water-rock interaction exerts an important control on solution composition, and thus the rate of dissolution of primary phases (Maher et al., 2009, **73**:2804–2831). In this regard, it is essential to quantify the precipitation kinetics of the clays. To do this, we have developed flowthrough reactor experiments in which the dissolving phase (illite) is separated physically from the precipitating phase (kaolinite), which makes it possible to quantify the individual reaction steps within the overall incongruent weathering reaction. This approach makes it possible to avoid the common assumption of equilibrium with respect to the secondary clay phase, a crucial step in modeling the weathering rates of natural sequences at circumneutral pH.

We have also begun developing a new approaching to modeling mineral nucleation and aging based on a modification of that outlined in Steefel and VanCappellen (1990, *GCA* **54:**2657-2677). In the new approach, a size dependent solubility is calculated for discrete crystal sizes within a distribution and these solubilities are then used to compute the saturation-dependent rate for a given bulk solution composition. This represents an alternative formulation for calculating Ostwald ripening to that presented in Steefel and VanCappellen (1990), which relied on a model better suited to describing agglomeration than true ripening. Nucleation is modeled using classical theory according to

$$\frac{\partial n}{\partial t} = J_0 \exp\left(\frac{-\Delta G^*}{k_B T}\right)$$

where n is the number of crystals of a given size, J_0 is the pre-exponential factor, and ΔG^* is the free energy of the neoformed phase at its critical radius. The size dependent solubility, $K_{eq}{}^*$, is taken from the Gibbs-Kelvin equation

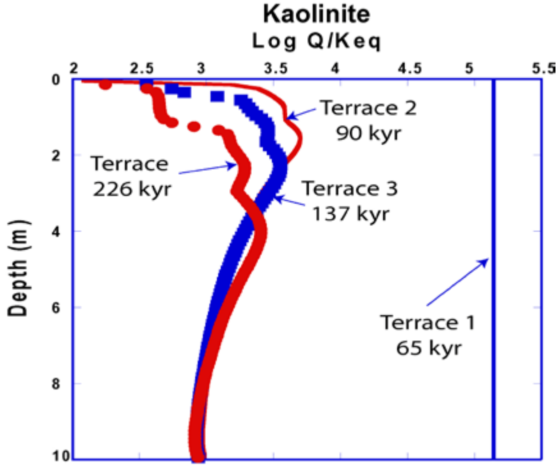
$$K_{eq}^* = K_{eq}^{bulk} + \left(\frac{2\sigma V_m}{RT}\right)\frac{1}{r}$$

where K_{eq}^{bulk} is the equilibrium constant for a large crystal (i.e., the bulk solubility), σ is the interfacial free energy, V_m is the molar volume, and r is the crystal size. The reaction rate, I_r, of a specific crystal size within the distribution is then given by

$$I_r = n 2\pi r^2 k_+ \left(1 - \frac{Q}{K_{eq}^*}\right)$$

where k_+ is the forward rate constant, and Q is the ion activity product in the solution. The total reaction rate is calculated by integrating over all of the crystal sizes included in the distribution.

Figure 1: Aging of kaolinite from reactive transport simulations.



The new formulation is used to model the gradual aging of kaolinite at the Santa Cruz chronosequence. At that site, younger marine terraces within the chronosequence show a greater supersaturation with respect to the reference kaolinite (solubility as determined in Yang and Steefel, 2008, *GCA* **72**: 99-116), while older terraces show a lower supersaturation (Figure 1).

Physicochemical Controls on Unsaturated Flow and Transport in Geological Media

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Objectives: Although water films are known to control rates of mass transfer in many environments, their basic properties remain poorly understood and constitute a challenging frontier in multiphase transport research. The overall objective of this study is to develop quantitative understanding of physicochemical controls on film hydraulics in variably water-saturated geologic media. Using new approaches for equilibration of aqueous solutions on silica, we have been able to measure the matric potential dependence of film thicknesses on surfaces with characteristic roughness ranging from nm to µm.

Project Description: Calculations of thin film equilibrium that combine the effects of adsorption and capillarity are providing a general framework for understanding film hydraulics on mineral surfaces of arbitrary curvature. We have formulated physicochemical predictions of film hydraulic properties, and are experimentally testing models using microscopic (film-scale) and bulk (porous medium) approaches. We are now applying a new, multi-sample chamber to equilibrate solid surfaces with aqueous solutions undergoing radial film flow under sub-atmospheric pressures. The fast hydraulic response time of the ceramic frame (seconds to minutes) relative to that of adsorbed film flow (hours) permits simultaneous equilibration of multiple samples. In addition, a new single sample chamber design was tested for potential improvements in resolution of thin (< 100 nm) films. The chambers are placed in front of an X-ray beam (National Synchrotron Light Source beamline X26A, and Advanced Photon Source, GSECARS beamline 13ID-C) used to determine film thicknesses through X-ray fluorescence of monovalent (Rb^+ and Br^-) and divalent (SeO_4^{2-}) ion tracers in the water films. A hard X-ray synchrotron source is required for efficient X-ray fluorescence detection of ionic tracers in water films within sealed environmental control chambers.

Results: Both chamber designs are suitable for measurements of thicker (>100 nm) films more characteristic of water at near-zero matric potentials on natural, rough mineral surfaces. Experiments on rough silica (root mean-square roughness $\approx$ 9 µm) yielded film thicknesses in the range of 700 to 3,000 nm over the near-zero potential range of -2.2 to -0.2 kPa. Interestingly, we find that the inverse dependence of film thicknesses on ion valence predicted for thin adsorbed films was also detected on the rough surface samples. Average film thicknesses of the divalent $MgSeO_4$ solutions were about 1/3 the thicknesses of monovalent RbBr solutions at any given matric potential, close to the model-predicted value of 1/2. Measurements with the multi-sample chamber indicative of substantially thicker than predicted films on smooth silica surfaces, and insignificant differences between films thicknesses for monovalent and divalent salt solutions motivated testing of an alternative chamber design. Using the alternative chamber design (being developed for experiments under high pressure), results indicative of thinner (30 to 50 nm) films were obtained. Planned improvements in the method and use of higher X-ray fluxes will lead to reduction of measurement uncertainty in the thin film limit. The experimental approach developed here provides a unique capability for measuring water film thicknesses on variably rough mineral surfaces, where reflectivity and ellipsometry methods are problematic. Furthermore, when the primary property of interest is area-averaged film thickness, this fluorescence approach provides the needed information with much finer resolution than is achievable by tomography.

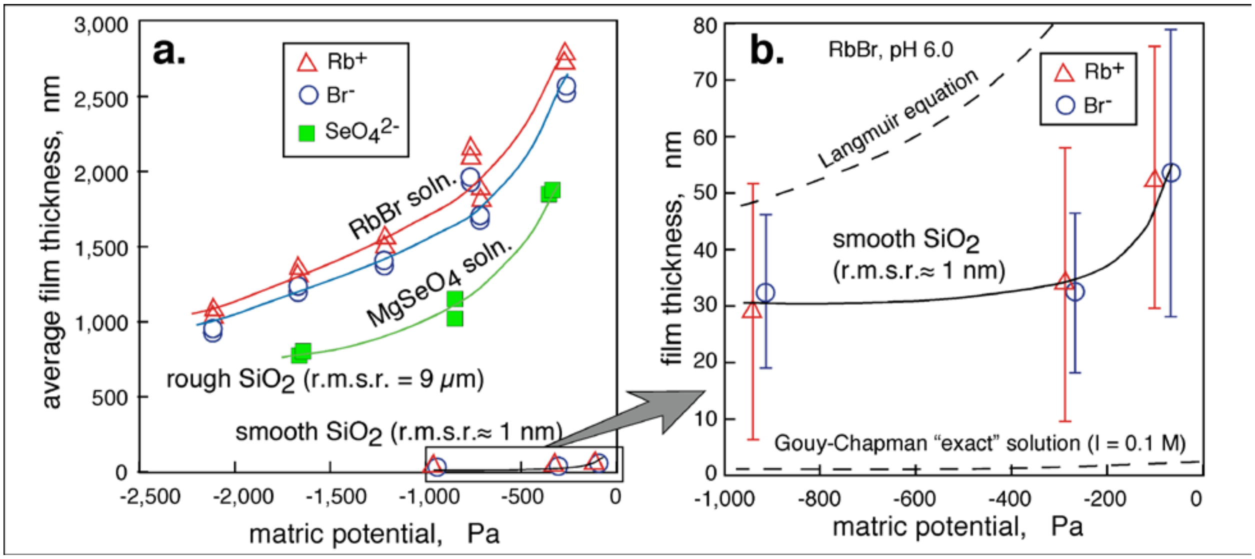

Figure 1. (**a.**) Area-averaged film thicknesses on rough (9 mm root mean-square roughness) and smooth (< 1 nm rmsr) silica surfaces. (**b.**) Thicknesses of water films adsorbed on smooth SiO_2, determined from X-ray fluorescence of Rb^+ and Br^- tracers, compared with predictions of the Langmuir model.

Imaging Permeability and Fluid Mobility in a Deformable Medium Using Time-Lapse Measurements

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Objectives: I am investigating the fundamental relations between changes in time-lapse geophysical attributes and sub-surface flow properties in a deformable medium. A key feature of this work is the development of new ways to relate changes in geophysical observations directly to flow properties. The ultimate goal is to further our understanding of multi-phase flow in the sub-surface and to develop methods for estimating flow properties. Time-lapse geophysical observations are a relatively new source of information, used to infer saturation and pressure change induced by the movement of fluids. It is possible to infer flow properties within the

Earth, such as porosity and permeability, using time-lapse measurements. Doing so requires new approaches for relating saturation and pressure change to flow properties. Time-lapse data includes both geodetic estimates as well as more conventional time-lapse seismic and electromagnetic data.

Project Description: In this project I explore new ways to relate time-lapse measurements and flow properties in the subsurface. One set of methods utilizes trajectory-based modeling of fluid flow and transport in order to map time-lapse observables, primarily time-lapse seismic amplitude changes, into images of subsurface permeability. Another set of methods follows directly from the equation governing pressure evolution in a multiphase environment. In this approach time-lapse geophysical data are used to infer pressure changes in the subsurface. These estimates of pressure change are mapped into subsurface permeability via the multiphase pressure equation. The mapping is linear and allows for an examination of model parameter resolution. The methods have been applied to time-lapse seismic data and to measurements of deformation.

Results:

Trajectory-Based Solution for a Propagating Disturbance in a Deformable Medium Saturated by Two Fluids

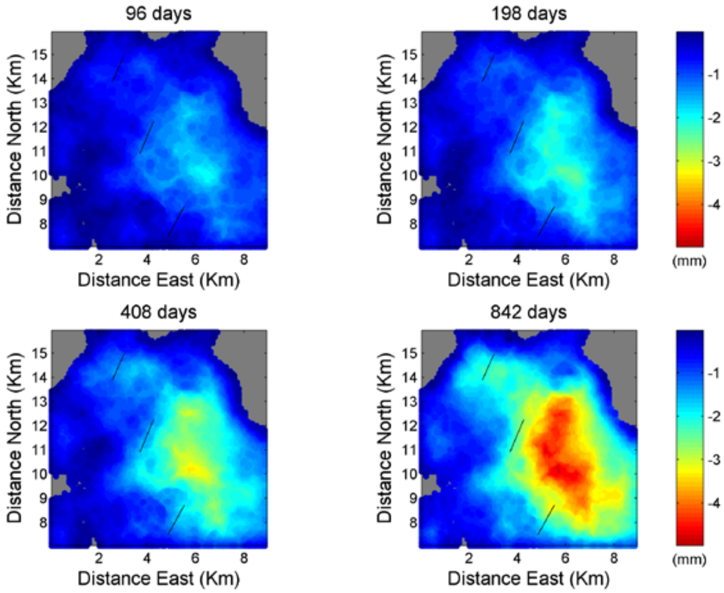
The coupled modeling of the flow of two immiscible fluid phases in an elastic deformable porous material is formulated in a manner analogous to that for a single fluid phase. Under the assumption that changes in the fluid pressure and deformation in the solid matrix propagate faster than the saturation change, I derive three coupled differential equations governing the displacement of the solid matrix and the two fluid phases. An asymptotic technique, valid when the heterogeneity is smoothly-varying, is used to derive equations for the slownesses of the various modes of propagation. A cubic equation is associated with the phase velocities of the longitudinal modes.

The coefficients of the cubic equation are expressed in terms of sums of the determinants of 3 by 3 matrices whose elements are the coefficients found in the governing equations. The algebraic solutions of the cubic equation provide explicit expressions for the slownesses of the three longitudinal modes in terms of the properties of the poroelastic medium and the fluids. In addition to the three longitudinal modes, there is a transverse mode of propagation, a generalization of an elastic shear wave. For a sufficiently smooth medium the expressions for the slownesses are valid across a broad range of frequencies.

Using Time-Lapse Deformation Data to Infer Reservoir Permeability with an Application to Interferometric Synthetic Aperture Data Gathered Over a Producing Gas Field

Deformation in the overburden proves useful in deducing spatial and temporal changes in the volume of a producing reservoir. Based upon these changes we estimate diffusive travel times associated with the transient flow due to production, and then, as the solution of a linear inverse problem, the effective permeability of the reservoir. An advantage an approach based upon travel times, as opposed to one based upon the amplitude of surface deformation, is that it is much less sensitive to the exact geomechanical properties of the reservoir and overburden. Inequalities constrain the inversion, under the assumption that the fluid production only results in pore volume decreases within the reservoir. We apply the formulation to satellite-based estimates of deformation in the material overlying a thin gas production zone at the Krechba field in Algeria. The peak displacement after three years of gas production is approximately 0.5

cm, overlying the eastern margin of the anticlinal structure defining the gas field. Using data from 15 irregularly-spaced images of range change, we calculate the volume change in the reservoir (see Figure below) and the corresponding diffusive travel times associated with the start-up of a gas production well. The inequality constraints are incorporated into the estimates of model parameter resolution and covariance, improving the resolution by roughly 30-40%.



Growth Mechanisms of Fe^{3+} based Molecular Clusters and Nanoparticles in Acid Mine Drainage (AMD) Conditions

PI: Glenn Waychunas, 510-495-2224, gawaychunas@lbl.gov

Co-I: Jillian F. Banfield (UC Berkeley)

Objectives: Our past work has shown that nanoparticles (NPs) can have significant structural changes associated with surface ligand types, size, and aggregation state. In the present study we wish to understand these effects during the development of ferric-based oxyhydroxide clusters and aggregates associated with high sulfate and high base metal (Ni and Zn) content in typical AMD environments. In particular, we expect sulfate to adopt both inner and outer sphere complexation with growing oxyhydroxide polymers, changing as a function of local pH, and influencing NP structure and aggregation state. These changes are expected to dictate both the NP reactivity and ability to sorb and transport other pollutants.

Project Description: Our studies are done using a combination of molecular probes, bulk measurements, and thermodynamic measurements. Some of the analysis is done in concert with molecular dynamic simulations. For nanoparticle size and shape we employ small angle x-ray scattering (SAXS) and dynamic light scattering (DLS), while the specific molecular nature of surface species is determined with extended x-ray absorption fine structure (EXAFS) spectroscopy. Other aspects of nanoparticle structure are determined via determination of pair correlation functions with high energy x-ray scattering (PDF). The x-ray measurements are done at the APS (SAXS, PDF), ALS (SAXS), SSRL (XAFS), and NSLS (quick XAFS) facilities. In all cases we utilize both stopped-flow and continuous flow reactors to develop the AMD materials *in situ* at the beamlines.

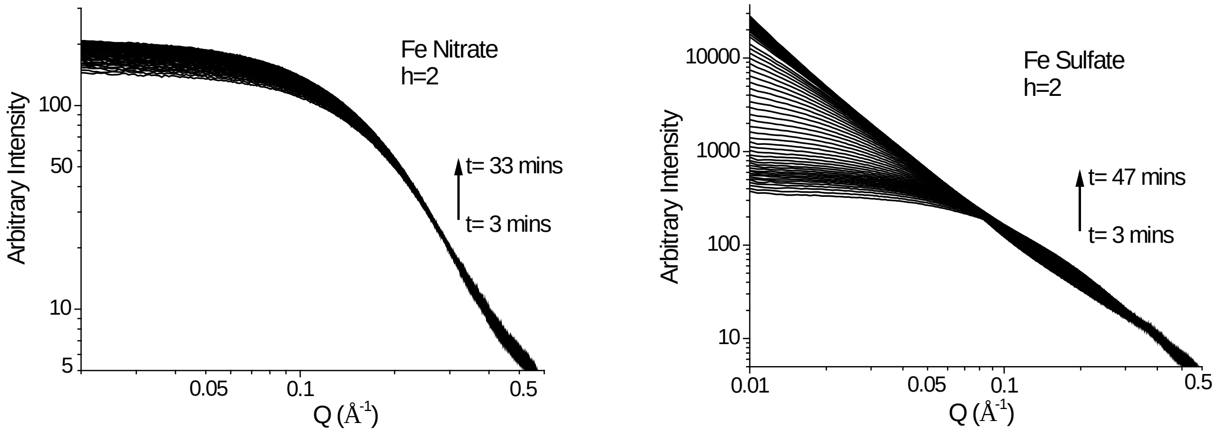


Figure 1. SAXS profiles taken at 40 S intervals of NP precipitation from Fe nitrate (left) and Fe sulfate (right) solutions of equal concentration. Less evolution is seen after the initial 40 S in the nitrate solution and the density of NPs is low. In the sulfate solution there is considerable growth over several tens of minutes accompanying loss of smaller units. Q is the scattering wavevector, inversely proportional to NP size.

Results: Recent work has focused on characterization of the initial steps in the nucleation and growth process of AMD-based Fe oxyhydroxyl polymers. This process can be followed by UV-VIS spectroscopy in the laboratory, and by time-resolved SAXS (Figure 1). Sulfate has been shown to affect the initial NP formation process dramatically, reducing the size of initially seen NPs, and accelerating the aggregation and precipitation processes into tens of minutes. NPs formed from nitrate solutions are lower in number, but grow to a larger size more quickly, possibly due to lower surface interaction of the nitrate compared to sulfate. Studies are in progress to identify the structures associated with each type of NP during its size evolution, as well as the type of sulfate sorption (or coprecipitation) complex.

Imaging Electronic and Atomic Redistribution during Redox Reactions at Surfaces: Application of Surface X-Ray Scattering and Spectroscopy to Capture Redox Reaction Intermediates

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Objectives: Our goal is to develop a suite of ultra-fast x-ray methods to visualize the coupled electronic and molecular steps that occur during redox transformations at the water-mineral interface of sulfide and oxide minerals and to quantify the rates of intrinsic steps.

Project Descriptions:

Controls on the Reductive Transformations of Iron (Oxyhydr)oxide Nanoparticles

Ferric iron oxide and oxyhydroxide nanoparticles are often the most important redox active minerals in soils and sediments. The products of the reductive transformations of these these natural nanomaterials are determined by competition between rates of transport (electron propagation within solid phase minerals) and the rates of chemical steps such as bond breaking. To date, no experimental approaches have been able to determine the timescales of these fundamental processes in iron oxides. We used light-initiated electron transfer (ET) approach to study interfacial reduction of ferrihydrite and maghemite nanoparticles at nanosecond-to-microsecond timescales to study the ferrous iron dynamics in these materials.

The Structure of the Unreacted and Oxidized Pyrite (100) – Water Interface

The structure and reactivity of the hydrated pyrite (100) surface is of great commercial and environmental importance. We seek to solve the structure of the unreacted pyrite surface using crystal truncation rod (CTR) analysis as a foundation for subsequent studies of adsorption and oxidation reactions at this common mineral surface.

Results:

Controls on the Reductive Transformations of Iron (Oxyhydr)oxide Nanoparticles

We performed time-resolved pump-probe and steady state investigations of the formation of ferrous iron by light initiated ET. **Figure 1** shows ferrous iron dynamics in dye-sensitized ferrihydrite and maghemite nanoparticles observed on nanosecond (A), microsecond (B) and minute (C) timescales. The data show that although the fast electron transfer processes in ferrihydrite and maghemite occur at the same rates, the rate at which ferrous iron atoms are released into solution from ferrihydrite is substantially greater than from maghemite. The comparison shows that the internal and interfacial electron transfer processes of these iron oxides are identical, and that the reductive dissolution rate must be determined by structural differences.

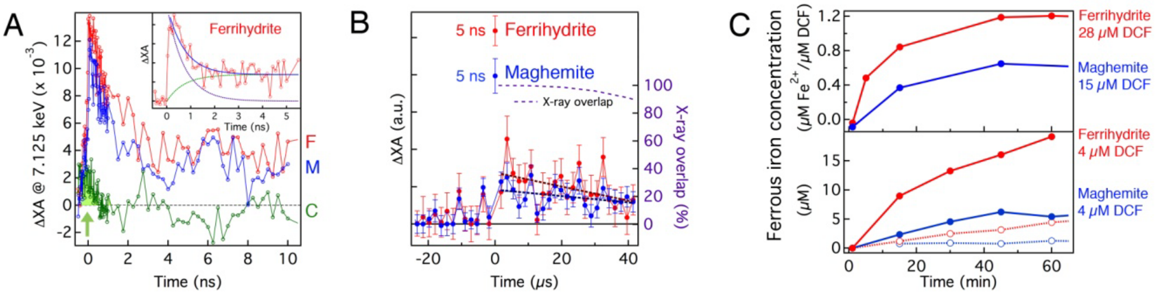

Figure 1 The fate of ferrous iron sites formed in dye-sensitized ferrihydrite and maghemite nanoparticles monitored by pump probe spectroscopy at the nanosecond (**A**) and microsecond (**B**) timescales. (**C**) The rate of generation of $Fe^{2+}(aq)$ in the same samples under continuous illumination.

The Structure of the Unreacted and Oxidized Pyrite (100) – Water Interface

We optimized a method for preparing pyrite (001) surfaces that are completely reduced (from X-ray photoelectron spectroscopy), flat (from atomic force microscopy, **Fig 2a**) and highly crystalline, permitting strong crystal truncation rod (CTR) signal to be acquired from surface in He(*g*) and H_2O(*l*). *In situ* studies of oxidation showed the surface to be chemically accessible. We acquired CTR data on the specular (00L) and eight off-specular diffraction rods, and refinement of the surface structure is underway.

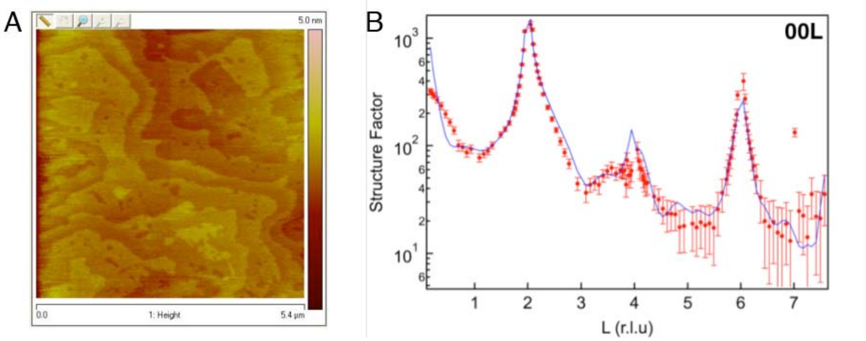

Figure 2 A Atomic force microscopy analysis of pyrite (001) surface prepared by an anaerobic polishing method. **B** Specular (00L) crystal truncation rod pattern acquired from pyrite (001) surface, compared with a surface model composed of two chemically distinct terminations.

Molecular-Level Studies of Mineral-Water Interface Structure and Chemistry

PI: *Glenn Waychunas, 510-495-2224, gawaychunas@lbl.gov*

Co-I: *Y. Ron Shen (UC Berkeley)*

Objectives: We wish to define the specific molecular geometries of mineral surfaces equilibrated with aqueous solutions, including the nature of surface relaxations or reorganizations, the attachment sites and type of binding of sorbates, and the structure of interfacial water. This type of information is important for the testing of molecular reaction models and simulation techniques that model the sorption/desorption and incorporation of migrant species in natural fluids, and hence determine the fate and transport of both toxic and nutrient species in the environment.

Project Description: Our studies are done using a combination of molecular probes, largely synchrotron-based, with relatively simplified model systems. The chief synchrotron methods are: surface diffraction by which we can refine the position and occupation of surface atoms at an interface; surface x-ray spectroscopy by which we can obtain specific structural information about the local molecular environment of a sorbed molecule at an interface; and nonlinear optical spectroscopy whereby we can probe the infrared vibrational spectrum of water molecules only at the solid-aqueous solution interface. Variations on these techniques also yield specific information such as the redox state of surface atoms, or the lifetimes of particular surface species.

Results: Our most recent work focuses on the local water structure and hydrogen-bonding at the (1-102) corundum surface. Past x-ray scattering and reflectivity studies have shown that there are several possible terminations, each one having a different ratio of surface functional groups (e.g. Al_2OH; $AlOH_2$), and hence possible types of hydroxyls. By using nonlinear optical spectroscopy we have been able to show that only one type of termination, originally suggested from CTR surface diffraction, is consistent with the observed ratios of functional groups and the types of hydroxyls observed. We further have obtained the three-dimensional arrangement of the hydroxyls, and we were able to propose a model for the hydrogen bonding on the dry surface (Figure 1). When water is added to this system the surface hydroxyls are modified by hydrogen-bonded to the nearest waters. However we are able to correlate the acid-base behavior of the surface with the kinds of hydroxyls in our model, obtaining good agreement with literature pka values. Work on other corundum surfaces is ongoing.

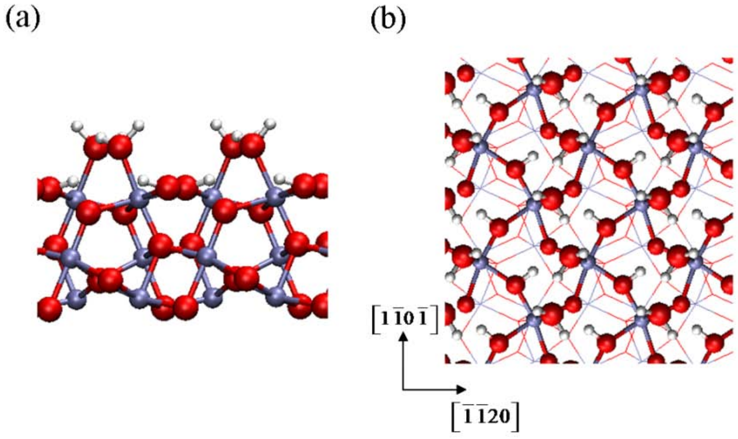

Figure 1. Model of the dry hydroxylated (1-102) surface of corundum. The protons are shown as white spheres. The surface is terminated by $AlOH_2$ and Al_2OH functional groups under most conditions, with the protons nearer to the surface on the $AlOH_2$ groups forming donor bonds to other adjacent $AlOH_2$ oxygens along [1-10-1]. The proton on the Al_2OH group is bonded weakly to the oxygen on an adjacent Al_3O group.

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Aqueous Geochemistry at High Pressures and Temperatures

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Objectives: The goal of this study is to further our understanding of deep subduction zone processes that involve aqueous fluids, including halide and CO_2-bearing fluids. This will be achieved through equation-of-state measurements of H_2O- and CO_2-rich fluids at high pressures and temperatures, and by X-ray and neutron scattering experiments.

Project Description: Convergent margins are critical for understanding the global geochemical cycles of volatiles such as hydrogen (as H_2O) and carbon (as CO_2). Despite the essential role of deep fluids in subduction zone processes, the absence of experimental thermodynamic data precludes quantitative modeling of reactions and mass transfer in this setting. The vast majority of aqueous geochemistry studies have been conducted at pressures below ~0.3 GPa, and the widely-used Helgeson-Kirkham-Flowers equations of state for aqueous species are applicable to $\leq$ 0.5GPa (~ 15km depth). The aim of this project is to determine the sound velocities, equations of state (EOS), and atomic-scale structures of model fluid systems to the high pressures and temperatures appropriate to subduction zones. Brillouin scattering measurements of velocities and EOS on aqueous fluids will be performed to at least 10 GPa and 700° C, and X-ray and neutron scattering experiments will be performed to constrain the atomic-scale structures of the same solutions.

Results: We have measured the sound velocity of Ice VII by Brillouin spectroscopy using membrane-style diamond anvil cell with an external Mo-wire resistance heater at elevated temperatures to 873 K at pressures of 2 GPa to 19 GPa. The unit cells of Ice VII and Au were determined by synchrotron X-ray diffraction, using Au as an in situ pressure gauge. All our samples contained were contained within and chemically insulated from the Re-gasket hole by a gold liner. We determined the melting of Ice VII by monitoring the sound velocity drop and the disappearance of diffraction pattern of Ice VII upon melting. Below ~8 GPa, our results are consistent with the previously determined melting curves (Datchi et al. 2000; Frank et al. 2004; Lin et al. 2004; Goncharov et al. 2005), . However, our determination of the melting temperature at 12.5 GPa results in a discrepancy of at least 130 K. Given thecare taken in the present experiments to avoid potential contamination of the water sample due to reactions at high temperatures between the sample and the gaskets and/or pressure gauges,our new measurement likely provide the first measurements on pure water which displaies an extended stability field of the liquid phase. Thus, our new measurements suggest that the melting curve of H_2O at high pressure needs to be reevaluated.

Why Does Aluminum Inhibit Silicate Dissolution Rates? An Experimental Study Combining Kinetics with HAFM and NMR to Determine the Reaction Mechanism

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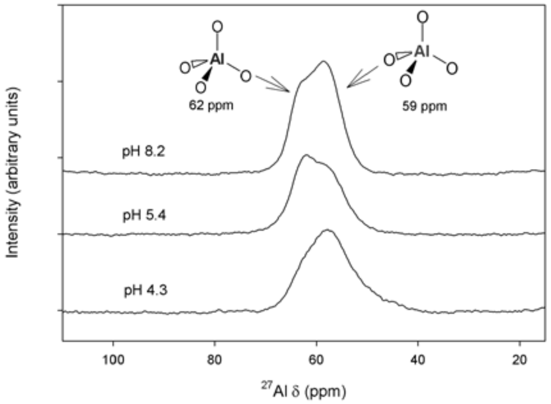
Objectives: This project investigates aluminum geochemistry in the presence of silicate phases combining water chemistry with NMR to determine the reaction mechanism responsible for the observed effect of dissolved aluminum on silicate reaction rates.

Project Description: Characterizing the structural form of Al(III) associated with silicate solids has been the subject of interest for a number of years because dissolved Al(III) is known to inhibit dissolution rates and correspondingly enhance precipitation rates for silicate minerals. In order to determine the reaction mechanisms responsible for this behavior, we use both bulk and surface-selective solid-state NMR techniques to identify the coordination geometry and chemical environment of Al(III). Work focused on the coordination of Al at silica surface with increasing temperature.

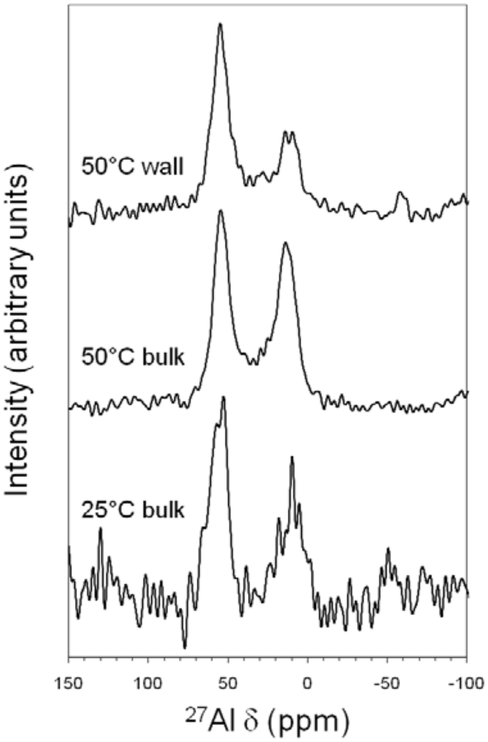
Results: Al complexation to amphorous silica and quartz has been investigated at elevated temperatures. In the presence of an amorphous silica substrate, our data show that Al precipitates as an amorphous aluminosilicate solid over pH 4.5+/- 0.5 pH units (T = 50, 75 and 100°C). We find no evidence of kaolinite under these conditions because ^{27}Al MAS NMR data indicates that Al is tetrahedrally coordinated ($^{[4]}$Al). Furthermore, water chemistry measurements indicate that large amounts of aqueous silica are consumed during the Al uptake event. Preliminary experiments involving quartz show that little silica is consumed during the Al uptake time (T = 25^{o}C; pH = 3.5 and 4.6), which rules out the possibility of $^{[4]}$Al-aluminosilicate precipitation in the presence of crystalline quartz over this narrow pH range.

^{27}Al MAS NMR data taken at the Pacific Northwest National Laboratory (EMSL) show that uptake of Al at room temperature in the presence of amorphous silica produces two chemically distinct $^{[4]}$Al coordination environments from pH 5.4-8.2 (Figure 1). This data is consistent with our previous



study that indicates two reaction pathways dominate at high pH; [4]Al complexation at the surface of the substrate and precipitation of an [4]Al-aluminosilicate phase.

Flow through experiments were also conducted where solutions containing a low concentration of Al (initial pH = 4.5 – 4.6, [Al] = 10^{-7} M) were constantly passed over amorphous silica for a period of 2 weeks at both room temperature and 50 °C. The ^{27}Al NMR results for the bulk amorphous silica indicate that the increase in the reaction temperature coincides with an increase in the relative abundance of [6]Al with respect to [4]Al (Figure 2; bottom and middle respectively). Upon completion of the 50 °C experiment a portion of amorphous silica was found adhered to the wall of the reaction vessel. The adhered sample was removed separately from the bulk and analyzed by ^{27}Al NMR. This sample produced a spectrum reduced in [6]Al compared to that of the bulk amorphous silica (Figure 2; top). Given the reaction pH and Al concentration it is expected that these systems are dominated by the sorption of Al on the surface of amorphous silica. However, the samples collected from the 50 °C experiment may suggest that despite conditions favoring sorption other processes such as precipitation may also be active which lead to the difference in speciation observed.



Evaluating the Ability and Limitations of Geophysical Electric Resistance Tomography to Track Moving Multiphase Fluids in Porous Media

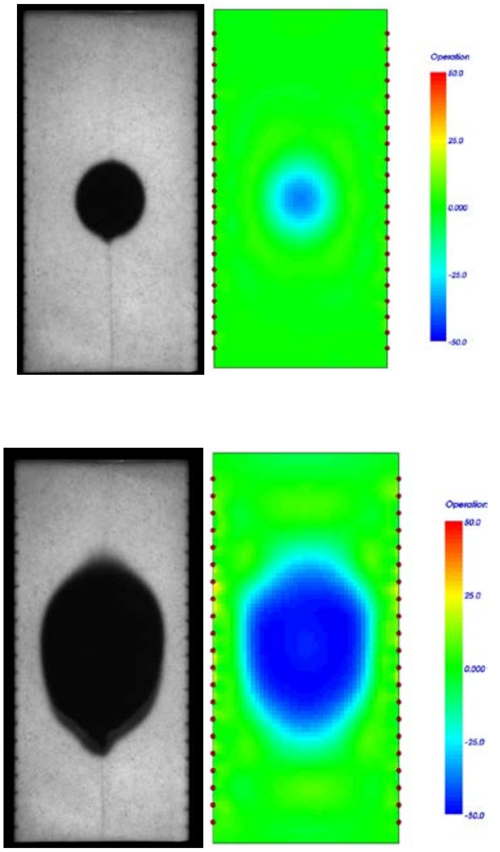
PI: *Charles R. Carrigan, (925) 422-3941, fax: (925) 423-4077, carrigan1@llnl.gov*

Objectives: The primary objective of the proposed research is to explore how the nature of multi-phase flows in porous media influences the electrical resistivity distribution of the fluid-filled porosity in the context of electrical resistance tomography (ERT) imaging.

Project Description: We have proposed a series of novel bench-scale porous flow experiments to be carried out at UC Irvine. The experiments are unique in combining electric resistance tomography (ERT) imaging with optical visualization of fluid flows in a porous medium. This comparison approach allows us to relate the development of a flow in a porous medium to high resolution ERT images of the changing electrical resistivity distribution in the porous medium created by that flow. This work has bearing on any attempt to image flows in a porous or subsurface regime.

Results: In the first year of this project, the LLNL activities for FY10 were principally focused on designing and constructing laboratory test sections that allowed simultaneous optical and ERT imaging. A 2D thin-cell system was ultimately selected over other possible visual/ERT imaging arrangements owing to cost and flexibility considerations. In this type of test section, a sand layer is confined between two vertical optically transparent glass plates separated by a one centimeter spacer forming a cell. Stainless steel ERT pin electrodes (22 with centimeter separations) penetrate each of the vertical sides of the plastic spacer separating the glass plates. This particular cell has a vertical-to-horizontal aspect ratio of about 2:1. The cell is sufficiently thin that the quartz sand readily transmits light from a lamp situated behind the cell to a ccd camera mounted in front. Each of the ERT electrodes are connected to a channel of a data acquisition system that allows a schedule of 4-wire current measurements to be made that are required to compile the ERT imaging data set.

Following construction of two identical cells at LLNL, they were set up in the imaging lab at UC Irvine where several experiments have been performed to date. The initial experiment involved injecting a plume of dyed, more conductive liquid into the center of the cell (see below).



Expanding plume sequence with optical imaging (b&w, left) and ERT imaging (right). Plume (blue) is more conductive than green background. These results are only preliminary.

The figure illustrates both optical and ERT imaging of an expanding conductive plume. A subsequent experiment involved growth of a more resistive plume. Because of preferential channeling of current within a cell through more conductive parts and away from more resistive parts, some differences in the ERT images of the plumes is anticipated. The data for the conductive and resistive plumes is currently undergoing analysis to evaluate this effect. In addition to comparing the general size and shape of the optical and ERT plumes for different types of conductivity contrasts, we are also comparing the contours of light intensity within an optical plume with the contours of resistivity in the ERT plume. The ability to accurately track the evolution of resistivity contours and relate them to the level of actual plume mixing or concentration is considered important for such things as monitoring the saturation of CO_2 plumes produced during sequestration. In addition to learning about the advantages and limitations of ERT imaging, these high-resolution data sets are a resource for improving the ERT imaging process both in terms of optimizing algorithms and developing adequate skill levels to maintain fidelity in the imaging process.

Permeability and Electrical Resistivity in Partial Melts: An Integrated Study Combining Laboratory Measurements, X-ray Computed Tomography, and Computational Methods

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Objectives: The objectives of this project are to address the questions of percolation threshold, melt interconnectivity, and permeability in partial-melts by synthesizing materials and performing electrical conductivity measurements at high pressure and temperature followed by characterization using x-ray microtomography (XRCT) and lattice-Boltzmann simulations of permeability and to test the hypothesis that non-wetting melt compositions can be extracted on timescales constrained by geochemistry to form metallic cores in planetesimals.

Project Description: We propose to synthesize FeS/FeNiS olivine partial-melts with a variety of compositions and melt fractions and determine melt percolation threshold and interconnectedness through the use of *in situ* electrical measurements and XRCT on run products. Lattice-Boltzmann simulations will be used to estimate permeability in these systems and determine the appropriate scaling laws.

The components of this study include:

1. Synthesis and characterization of compositionally relevant silicate-sulfide partial-melts.
2. Perform x-ray microtomography on recovered samples and relate the 3D melt structure to transport properties.
3. Perform electrical conductivity measurements on the partial-melts at controlled conditions.
4. Use the results to constrain models of melt segregation and core formation.

Results and developed techniques apply to many physical problems including evaluating mechanisms of planetary core formation. The results will be used to test the hypothesis that non-wetting melt compositions can be extracted on timescales constrained by geochemistry to form metallic cores in planetesimals.

Results: We have examined the microstructural evolution of a two-phase composite (olivine+Fe-Ni-S) during large shear deformation, using a newly developed high-pressure x-ray tomography microscope (HPXTM). Two samples were examined: a load-bearing-framework- (LBF-) type texture, where the alloy phase (Fe-Ni-S) was present as isolated spherical inclusions, and an interconnected-network-type texture, where the alloy phase was concentrated along the silicate grain boundaries and tended to form an interconnected network. The samples, both containing about 10-vol% alloy inclusions, were compressed to 6 GPa, followed by shear deformation at temperatures up to 800 K. Shear strains were introduced by twisting the samples at high pressure (P) and temperature (T). At each imposed shear strain, samples were cooled to ambient temperature and tomographic images collected. The three-dimensional tomographic imaged were analyzed for structural evolution. Alloy inclusions served as markers, allowing us to track changes in their shape and spatial distribution as shear strain increased. We found that in both samples, Fe-Ni-S, which is the weaker phase in the composite, underwent significant deformation. The resulting lens-like shape lies subparallel to the shear plane and has a laminated, highly anisotropic interconnected-weak-layer (IWL) texture. Scanning electron microscopy showed that many alloy inclusions became film-like, with thicknesses less than 1 μm, suggesting that Fe-Ni-S was highly mobile under nonhydrostatic stress, migrated into silicate grain boundaries, and propagated in a manner similar to melt inclusions in a deforming solid matrix. The grain size of the silicate matrix was significantly reduced under large strain deformation. The strong shape-preferred orientation thus developed can profoundly influence a composite's bulk elastic and rheological properties. High-P-T tomography not only provides quantitative observations on textural evolution but also can be compared with simulation results to derive more rigorous models of the mechanical properties of composite materials relevant to Earth's deep mantle.

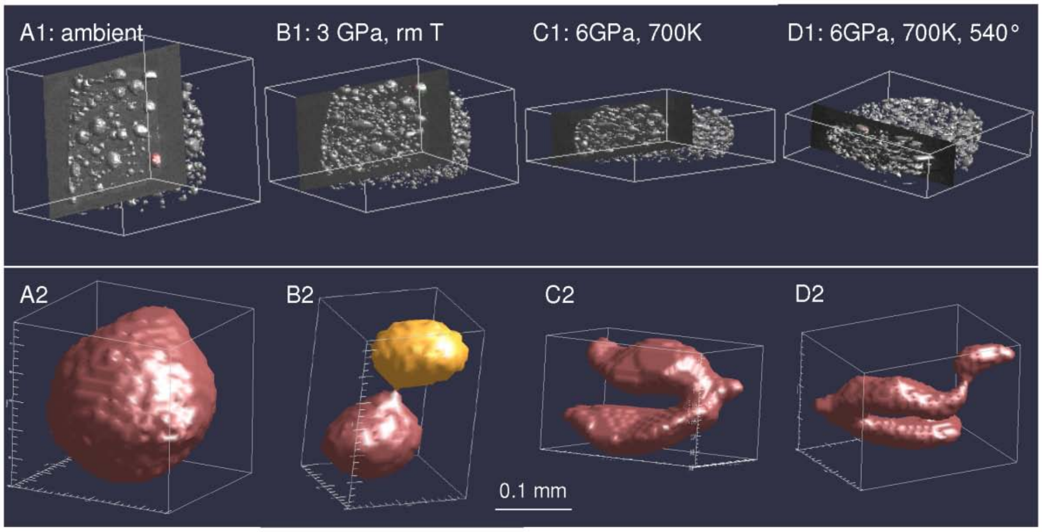

Fig. 1. Fe-Ni-S inclusions extracted from a series of tomographic images using Blob3D. Top row shows complete images of the sample when the silicate matrix is removed; bottom row shows examples of the inclusions extracted and the shape evolution. Fig 1(a): ambient sample before compression; 1(b): sample loaded to 3 GPa, at room temperature; 1(c): sample loaded to 6 GPa after heating to 700 K; 1(d): sample twisted by 540° at 6 GPa and 700 K. For each pair, the upper image (e.g., (a1)) is the 3D view of the

entire sample with one plane highlighted, and the lower image (e.g., (a2)) is the selected image of individual inclusions extracted.

Geochemical Imaging with the NanoSIMS

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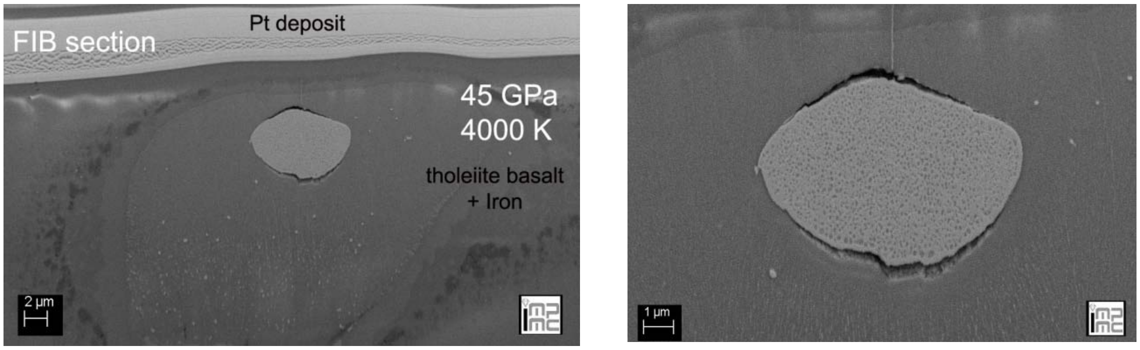
Objectives: The objective of the project is to develop the operating procedures and fundamental parameters required for the routine application of the NanoSIMS, the latest development in elemental and isotopic microanalysis, to geochemical problems, by addressing issues that require its analytical sensitivity and spatial resolution.

Project Description: The NanoSIMS is a recently developed secondary ion mass spectrometer (SIMS) with lateral spatial resolution as good as 50 nm. Coupled with its high transmission, the instrument has the potential to address a number of geochemical problems that were heretofore intractable, essentially taking trace element and isotopic analysis to a spatial scale approaching that of transmission electron microscopy (TEM). The performance and applicability are only now being developed for geochemical applications. This project will contribute to the development of geochemical imaging in three applications to natural and experimentally produced materials that are related by the need for high-resolution imaging. Current efforts are focused on the partitioning of moderately siderophile elements between core-forming metallic liquids and silicate melts. The work takes combines more conventional measurements using piston cylinder and mulit-anvil apparatus with measurements in the laser heated diamond anvil cell.

Results: Superliquidus metal-silicate partitioning was investigated systematically for a large number of elements normally regarded as moderately siderophile (Mo, As, Ge, W, P, Ni, Co), slightly siderophile (Zn, Ga, Mn, V, Cr) and refractory lithophile (Nb, Ta). To constrain separately the effects of temperature, oxygen fugacity and silicate melt composition, isobaric (3 GPa) experiments were conducted in piston cylinder with temperature between 1600 and 2600ºC, relative oxygen fugacity between IW-1.5 and IW-3.5, and silicate melts from basaltic to peridotitic in composition. The individual effect of pressure was investigated through a combination of piston cylinder and multi-anvil isothermal experiments from 0.5 to 18 GPa at 1900ºC. Oxidation states of siderophile elements in the silicate melt as well as effect of carbon saturation on partitioning are also derived from these results. We correct partitioning coefficients for solutes interactions in the metal and provide parameterization to extrapolate partitioning behaviors at conditions of Earth's core formation. For some elements (e.g. Ga, Ge, W, V, Zn), we find notably that temperature dependency does not define trends parallel to the free energy data as assumed in some previous works. Our experimental results are used to test the validity of a single-stage core formation model. Assuming a core only made of Fe, it is possible to establish the abundances of several siderophile elements (Ni, Co, Cr, Mn, Mo, W, Zn) in the mantle for core-mantle equilibration at pressures from 32-42 GPa along the solidus of a deep peridotitic magma ocean (~3000 K for this pressure range) and an oxygen fugacity relevant to the FeO content of the present mantle. However, these P-T-fO_2 conditions cannot produce the expected abundances of Ga, Ge, V, Nb, As and P. For more reducing conditions, the single P-T solution domain is subsolidus and still cannot account for the abundances of Ge, Nb and P. Regardless the oxygen fugacity path considered during accretion, continuous core formation models cannot account for the depletions of Ga and Ge in the Earth's mantle. Other investigations have arrived at similar conclusions regarding the behavior of Se, Te, Os, and Ir, and invoke the addition of a "late veneer" of chondritic composition to reconcile observed mantle abundance patterns. The effects of light element incorporation, especially oxygen, on the mixing properties of metallic liquids is not well constrained, however, and we are using a combination of the LH-DAC, focused ion beam extraction along with analytical TEM and the NanoSIMS to obtain data under more extreme conditions.



Secondary electron image of a FIB section extracted from a tholeiitic basalt-Fe metal sample synthesized at 45 GPA, 4000K in a LH-DAC. The upper surface of the sample was in contact with the diamond during heating. The metal blob is composed of Fe metal with FeO exolved on quench. The sample is doped with Ni, Co, Mn, V, Cr and Nb

GreenHouse Gas Information System (GHGIS)

PI: *Doug Rotman, (925) 422-7746, rotman1@llnl.gov*

Objectives:

The FY10 LLNL objectives in the 4-lab (LLNL, LANL, SNL, and NASA/JPL) GHGIS scoping study include:

1. Goals and Requirements: Develop a set of Monitoring, Analysis, and Reporting goals and a requirements framework that would permit GHGIS to (1) monitor, quantify and report on global GHG concentrations, (2) help assess compliance with treaty obligations on appropriate space and time scales, (3) provide Earth science data in support of climate and carbon-cycle science, and (4) provide data for other purposes.

2. Ground-based observations: Evaluate ground-based (land) sensors and observations, including vertical (atmospheric) profiles using ground-based instrumentation, for top-down GHG emission verification and attribution.
3. Model-prediction uncertainty quantification: Identify computer models and analysis tools to propagate data-uncertainty quantification to model-prediction uncertainty quantification of anthropogenic GHG emissions.

Project Description:

The study aims to scope a GHGIS that will: (1) support monitoring national emissions-reduction and the efficacy of renewable-energy programs; (2) provide information on compliance with existing emissions agreements; (3) assist in the negotiation of and provide actionable information on compliance with future emissions and climate agreements; (4) provide Earth-science data presently not available at adequate space and time scales, on a sustained and traceable basis; and (5) provide data for many other purposes.

Results:

To deliver the most comprehensive and well informed GHGIS scoping study, our work in FY10 has focused on engaging key scientists and technologies across the national laboratory and academic system. Our interactions have crossed monitoring technologies for remotely sensing carbon dioxide to modeling studies of particular carbon processes in the ecosystem.

LLNL has taken a leadership role in coordinating the input from across our partners to define a set of requirements that will drive the system design and capabilities of the monitoring and modeling activities. We are at the mid-point of those discussions, but we have focused on integrating across self reported data along with monitoring/modeling data into metric of detecting changes in emission rates at the 95% certainty range within a short timescale. The group is still discussing and fine tuning the exact metrics and timescale of attainment.

The land team has evaluated the existing land systems – including those working climate and carbon cycle science (e.g., Ameriflux) and those for other purposes (e.g., IMS for the CTBT). They show a relatively robust network across the United States while thinly spaced observation points on other areas of the globe. The analysis is also examining how the inclusion of meteorological data at these ground sites could enable a much improved modeling inversion of emissions given a ground observation dataset; and, cooperative measurements of non-GHGs that could help in detection of anthropogenic fossil fuel emissions.

Our analysis of the modeling and uncertainty quantification has focused on examining the error budgets in current inversion simulations and the sources of these errors through particular atmospheric boundary layer transport and physics packages. The team has also demonstrated a multi-faceted ground observation network design that can help optimize deployed observation networks to minimize uncertainties in inversion simulations.

LOS ALAMOS NATIONAL LABORATORY

CONTRACT: NA25396

PERSON IN CHARGE: D. Janecky

Nonlinear Elasticity in Rocks

PI: *Paul Johnson, 505-667-8936, paj@lanl.gov;*

Co-Is: *Bill Carey, Pierre-Yves LeBas (LANL)*
Robert Guyer, Tim Darling (University (University of Nevada, Reno)
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Website: www.lanl.gov/source/orgs/ees/ees11/geophysics/nonlinear/nonlinear.shtml

Objectives: This work is focused on addressing a new parameter space of elastic nonlinear behavior. The new parameter space is the elastic (nonlinear) response of geomaterials to instantaneous or progressive mechanical "damage", and geochemical change that is manifest by mechanical damage or alternatively, material healing. Another portion of the parameter space is understanding the role of fluid in elastic nonlinear behavior as well as developing new methods to determine nonlinear coefficients.

Project Description: Characterization of material change, including mechanical and chemical change, is a challenging, fundamental problem in geoscience, as well as in many other areas including nondestructive evaluation (NDE) of materials, and materials science in general. *Specifically, how does one discern if mechanical and/or chemical change has taken place, and how does one determine the nature of that change*? The nature of the change may manifest itself in an increase in mechanical damage, for instance. We are studying the geomaterial response to progressive or catastrophic thermo-mechanical and chemical change, by employing dynamic nonlinear-elastic experimental investigation. Elastic nonlinear material response is due to material damage at scales ranging from the micro to the macro. The elastic nonlinear response is the most sensitive measure in existence for probing the material mechanical damage state. We are currently conducting laboratory studies of progressive material change due to chemistry changes. In particular, we are studying the effects of supercritical CO_2 on carbonate and non-carbonate sedimentary rocks. Predicting behaviors at field-scales for problems such as those mentioned above will ultimately be addressed by modeling and comparative field data sets. Impact areas include scientific questions related to volcanism and metamorphism, CO_2 sequestration, reservoir drilling, as well as direct application to monitoring of materials, such as material aging in the nuclear stockpile.

Results: We have a number of topics and results to present from this year's efforts. Work includes basic research exploring pressure, temperature, humidity, and the effects of supercritical CO_2 on carbonate-rich rock.

(1) We developed a pressure/temperature cell and the associated data collection to study primarily temperature and humidity effects on the elastic nonlinear behavior of rocks. Both temperature and humidity have been explored in regards to the nonlinear behavior, but never in extreme conditions. No one has ever isolated the elastic nonlinear response of the matrix in a rock from the influence of water. We knew from previous work that fluids have an enormous influence on nonlinear response. We first took samples to 800 degrees C in air in order to test the vessel. We then studied the effects of fluid on the elastic nonlinear response of rock by measuring the linear and non-linear elastic properties of lab-sized samples over the range of ultra high vacuum. Removal of both water to partial pressures below 10^{-8} Torr changes, but does not remove the essential nonlinear behavior of the rock, meaning that at the lowest humidity ever measured, the elastic nonlinearity is strong. Water modulates, but is not responsible for, the elastic nonlinear behavior of Earth and other solids.

(2) We developed a second pressure vessel measurement system in order to subject rock samples to supercritical CO_2 while applying nonlinear diagnostics. In experiments completed this year, we found that a carbonate-rich sandstone exposed to supercritical CO_2 in the presence of water shows significant changes in both its linear wavespeed and nonlinear elastic response. We infer that that there is dissolution and redistribution of the carbonate phase in the form of precipitation of the carbonate phase (including some mass loss). The elastic nonlinearity decreases indicating that the microcracks and bonds, responsible for the elastic nonlinearity, strengthen—a healing process. We find further that exposure to CO_2 when no liquids are present (excluding the monolayer fluids contained in the sample), the same effect takes place—healing. Our goal is that, under field conditions of supercritical CO_2 injection/sequestration, changes in permeability networks and fracture healing could potentially be examined and quantified by similar nonlinear acoustic, geophysical methods.

Summer of Applied Geophysical Experience (SAGE)

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Website: www.sage.lanl.gov

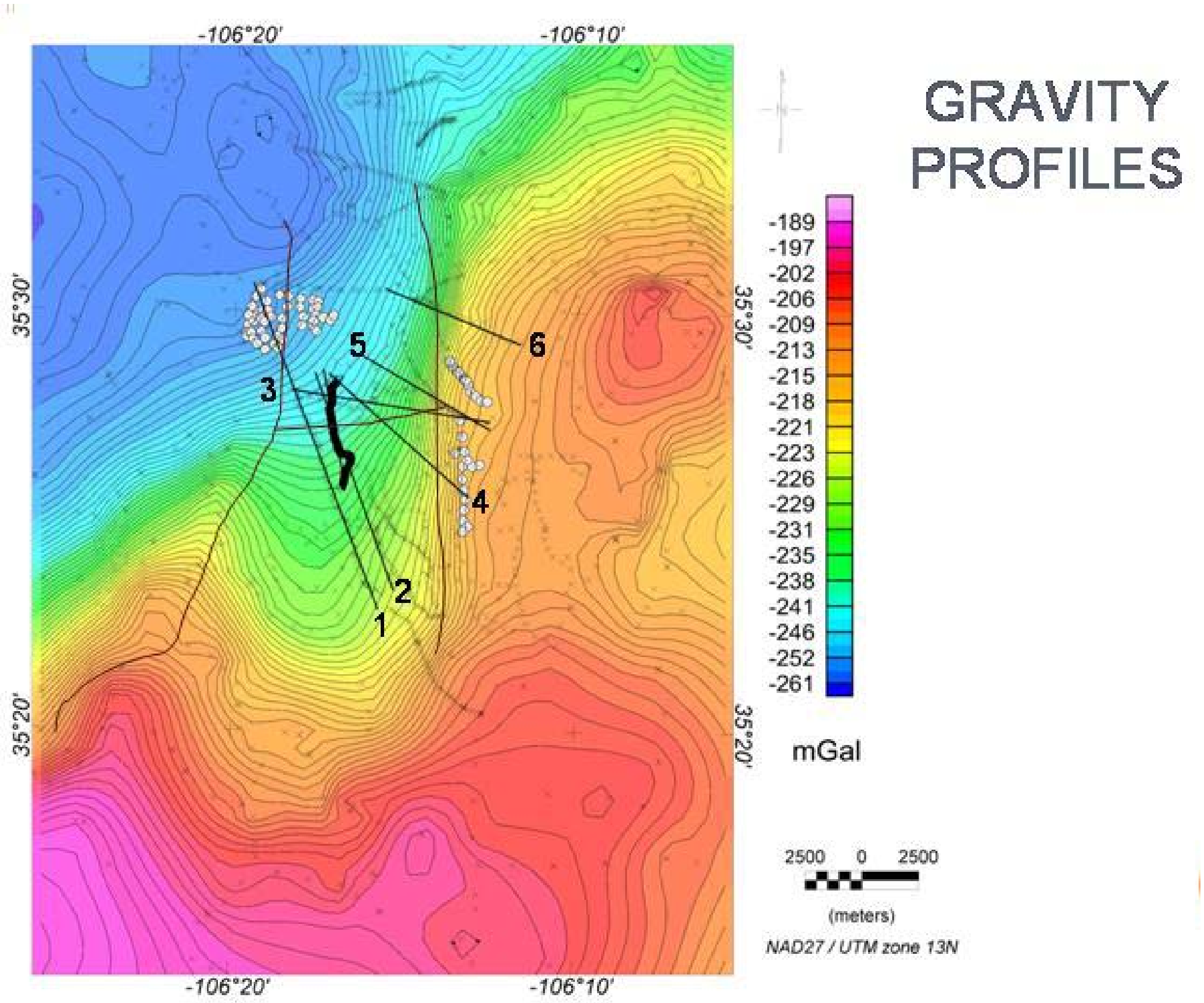
Objective: Objectives of SAGE 2010 included: (1) providing hands-on training and research experiences in basic and applied geophysics for 25-30 students graduate- and undergraduate students, (2) conducting innovative research with students on a variety of important Earth science problems, and (3) introducing students to a range of career choices and opportunities in geophysics. Research results are expected to make significant contributions in a number of national security area, such as development of new energy sources, nuclear and non-nuclear waste disposal, environmental remediation, groundwater resources, and carbon sequestration. In addition, results will impact basic research related to the structure and tectonics of continental extension.

Project description: SAGE 2010 conducted research on two related topics. In the northern Albuquerque basin of the Rio Grande rift, SAGE conducted several concurrent and partially co-located geophysical surveys to examine basin depth and the role of connected and overlapping faults in accommodating deformation. This study furthers understanding of how individual faults link into deformation zones that form a boundary of a major, active continental rift. A second project was undertaken to identify and characterize mainly subsurface, man-made structures at an archaeological site, one of the largest pre-Columbian cities of the American Southwest. Although interesting in its own right, the study also evaluated tools and techniques applicable to smaller-scale environmental-restoration and waste-disposal sites, for which it served as a proxy.

The geophysical techniques used included: seismic reflection and refraction, gravity, time-domain electromagnetics and controlled-source (active) magnetotellurics, magnetics, and ground-penetrating radar; and integration with existing industry seismic data, aeromagnetic data, surface geological mapping, and borehole information. SAGE full- and part time faculty from LANL, several local and national universities, the U. S. Geological Survey, and companies, each expert in different fields of geophysics, instructed and supervised the SAGE participants.

Results: Twenty six new students from 22 universities, and several former SAGE students, participated in SAGE 2010. The quality and quantity of new data acquired by participants was again excellent, thanks in part to strong and committed participation by industry partners. Several industry visitors led teaching exercises or teams of students in the field. Our surveys at the archaeological site extended to new areas of the ca. 60 acre site, mapping floors and stone footings underlying former adobe walls. Magnetic and EM surveys mapped Spanish-era (now buried) smelting debris. Our work constitutes an unprecedented and valuable synoptic view of this major site.

SAGE 2010 also undertook gravity, seismic, and EM surveys of new areas of the rift basin, extending and augmenting data collected in previous years. High-quality, high-resolution seismic reflection and refraction data were acquired along 8 km of line on Santo Domingo Pueblo across the hanging wall of a major rift-bounding fault, not well exposed at the surface. We were able to estimate offset on this fault, along with thickness of the adjacent syn-rift sediments. Our work will inform mechanisms of transferring offset between faults and along boundaries of the rift. In addition, active-source magnetotellurics, imaging the resistivity of sedimentary fill of the rift, extends our information on depth to, and quality of, groundwater in this area.



Caption: Complete Bouguer gravity anomaly map of part of the SAGE field area in the Rio Grande rift, 25 km southwest of Santa Fe, New Mexico. Blue indicates areas of thicker sediments in the Santo Domingo structural basin of the rift. Warm colors indicate of thinner sedimentary rocks or crystalline rocks outside of the rift. Light lines are major faults, heavy line is a SAGE seismic profile.

^{230}Th-^{238}U Disequilibrium Measurements

PIs: *Michael T. Murrell, 505-667-4845, mmurrell@lanl.gov*
S.J. Goldstein, 505-665-4793, sgoldstein@lanl.gov

Objectives: The goal of our work is to use improved U-series analytical capabilities to provide unique information on the behavior of U-series members in the geologic environment. The emphasis is on processes that modify and alter the physical and chemical state of earth materials.

Project Description: The key issue for U-series studies is often to quantify and validate the interpretation of closed vs. open processes or equilibrium vs. nonequilibrium in natural systems.

One approach to such evaluations is concordance between related isotopic systems. A complementary approach is micron-scale sampling. Knowledge of chemical and isotopic variation at the micron scale provides insights that are critical to the proper evaluation of the sample environment, and its influence on the measured age. A critical need for future in situ micron-scale U-series analyses is the development of well-characterized solid standards and reference materials.

We are working to 1) assemble and characterize U-series isotopics in a suite of reference materials for use with laser ablation multi-collector ICPMS (LA-MC-ICPMS), 2) evaluate the new capabilities provided by femtosecond laser ablation (FS-LA), and 3) examine U transport in waters and U-rich fracture-filling samples.

Results:

Glass Standards – We have successfully determined U-Th concentrations and isotopics from a suite of naturally sourced glass reference materials from the USGS and the Max Plank Institute. These results have been accepted for publication by Geostandards and Geoanalytical Research.

Femtosecond Laser Ablation – We have successfully completed the sourcing, purchasing, installation, and acceptance of a FS-LA system for our laboratory. As shown in the Figure, this next step in laser ablation delivers reduced elemental fractionation with less dependence on matrix matched standards.

U Transport – Our results for waters from Pena Blanca have recently been published in two journals. Our groundwater studies indicate that retardation factors for the long-lived U-series nuclides in the saturated zone range from 10^3 to 10^7 and decrease in the order $^{239}Pu \sim {}^{230}Th >> {}^{238}U \sim {}^{226}Ra$. Based on our estimate of groundwater flow rates in the saturated zone of ~10 m/yr, U-series nuclide transport rates range from 1 cm/yr to 1 μm/yr. These data from Peña Blanca indicate that U-series mobility is generally quite low, and that laser ablation techniques are needed to resolve the fine-structure of U-series transport in fractures. We have also provided U-series measurements for waters from Mongolia with extremely high concentrations of uranium in order to study the geochemical evolution of surface waters and subsurface water samples from Rocky Flats to follow transport of uranium post site closure.

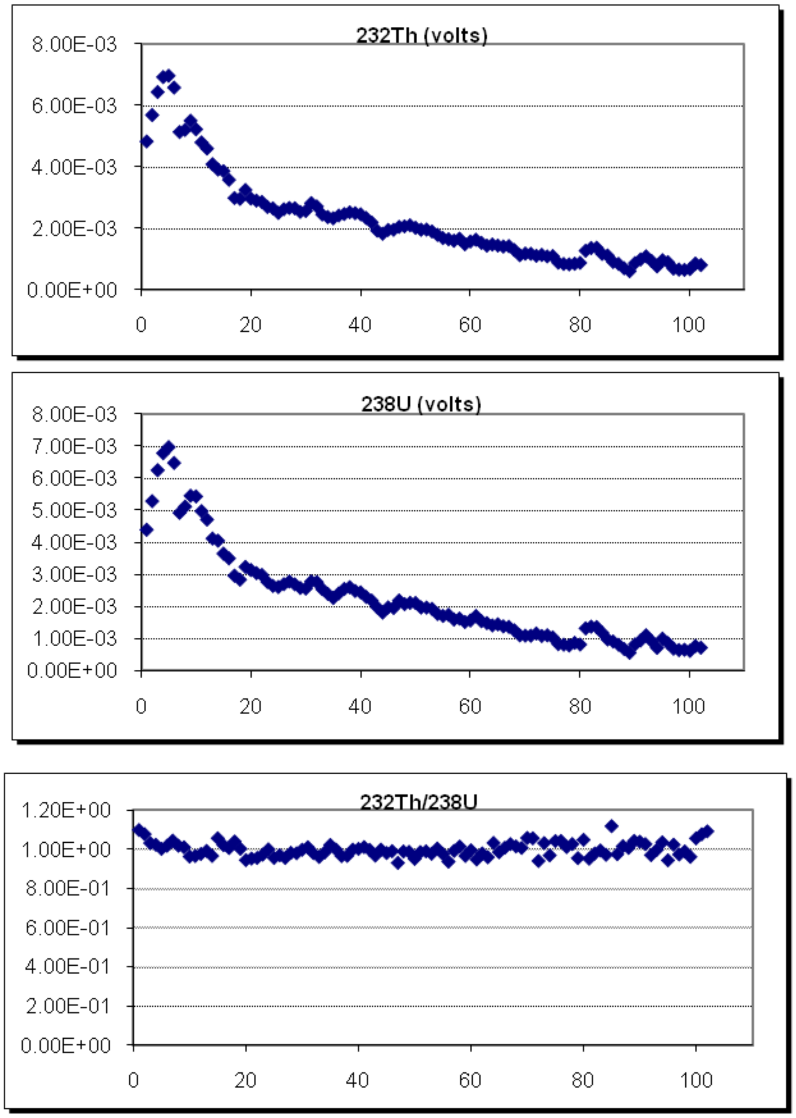


Figure 1. LA-MC-IPCMS data obtained using LANL's femtosecond laser ablation system. Results are shown for Th (top) and U (middle) signals in two Faraday cups collected simultaneously while drilling a single pit of ~ 30 μm diameter. The data were collected in one second integrations over a two minute period. The signal in volts is shown on the y- axis and time in seconds is shown on the x-axis. The bottom plot is the Th/U atom ratio over the two minute period of data collection. These plots show the raw data with no correction for instrumental fractionation. These uncorrected ratios are in good agreement with the nominal Th/U ratio of 1 for this NIST glass.

Greenhouse Gas Information System (GHGIS)

PI: Karl K. Jonietz, 505-663-5539, kjonietz@lanl.gov

Objectives:

The FY 10 objectives of LANL's participation in the 4-lab GHGIS effort include: (1) Conducting appropriate briefings for DC policymakers and others to better define the GHGIS study; (2) Organize appropriate teams at each of the project laboratories; (3) Structure the study in a manner that will both allow for the most informed contributions across the subject areas; and (4) Define a plan and begin to solicit the inputs of the wider climate community.

Project Description:

The GHGIS project is well underway and approximately on target. The current project plan calls for mid-term briefings in November, the distribution of the study for comment in January, and the delivery of the final version in February, 2011.

Results:

The GHGIS team has conducted numerous briefings aimed at better defining the content, goals, and limitations associated with the framework study. LANL leads the airborne and data uncertainty quantification chapters. Chapter assignments have been finalized, and input is being solicited widely. Individual teams have held information and early drafting sessions.

The Airborne chapter team has solicited representatives from all four key labs, as well as others who have had experience in airborne sampling. Discussions have taken place with NASA, NOAA, and others regarding their current airborne sampling campaigns. Telephone discussions have involved the European IAGOS group, and a LANL-led team is planning face-to-face discussions with the Coordinator and Deputy Coordinator of IAGOS in Europe in October, in conjunction with the annual International Conf. on Airborne Research for the Environment (ICARE) conference.

The Data Uncertainty Quantification team has also come together and is planning an initial face-to-face session in Boulder also in October. The team has already held discussions related to data sources, precision and accuracy, as well as quality control mechanisms.

Overall, the GHGIS leadership is working toward a mid-course brief to be available for presentation in mid-November. Additional coordination meetings are taking place with both data contributors and potential system users.

OAK RIDGE NATIONAL LABORATORY

CONTRACT: OR22725

PERSON IN CHARGE: D. Wesolowski

Nanoscale Complexity at the Mineral/Water Interface

PI: *D.J. Wesolowski, (865) 574-6903; Fax (865) 574-496, wesolowskid@ornl.gov*

Objectives: We seek a complete understanding of the complex, nanoscale domain where covalently-bonded crystalline minerals (oxides, silicates) interface with aqueous solutions, over wide ranges of temperature and solution composition. Our goal it to quantitatively link atomic-scale structure and dynamics of interfaces with their macroscopic manifestations, including surface charging, ion adsorption, supercooling of interfacial fluids, dissolution and precipitation kinetics and nanoparticle stability and transport.

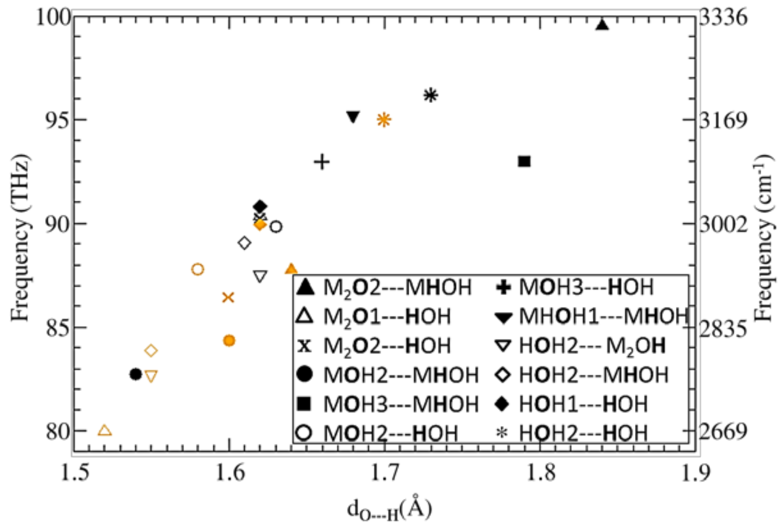
Project Description: A multidisciplinary, multi-institutional effort (ORNL, Argonne National Laboratory, Vanderbilt University, Pennsylvania State University, University of Illinois) is working toward a quantitative understanding of the mineral-solution interface by coupling synchrotron X-ray and neutron scattering probes of atomic-level structure and dynamics; quantum mechanical and classical molecular dynamics simulations; macroscopic experimental studies of surface protonation, ion adsorption, electrophoretic mobility and dissolution/precipitation kinetics; and macroscopic models of reactions at the charged interface over wide ranges of solution composition and temperature. These highly-integrated efforts have been focused in recent years on the interface between aqueous solutions and the (110) surfaces of the isostructural minerals rutile (α-TiO_2) and cassiterite (α-SnO_2), which exhibit modest differences in bulk structures, but very different bulk dielectric properties, related to the polarizability of the valence electrons of the crystalline substrate (rutile is much more polarizable). We are continuing these studies and expanding them to the more reactive and geologically-relevant mineral quartz (α-SiO_2), which is even less polarizable than cassiterite. These properties of the substrate are hypothesized to exert a fundamental influence on the nature of ion adsorption and interfacial structure, dynamics and reactivity, and we hope to link these fundamental properties with macroscopic studies of heterogeneous reaction kinetics.

Results: An extensive collaboration with Drs. Susan Brantley and Karl Mueller at Penn State culminated in the successful defense and publication of Dr. Michael Davis' Ph.D. thesis studies conducted in our laboratories. The dissolution and precipitation rates of quartz in dilute NaCl brines at pH 8-9.5 and 125-200°C at saturation states (free energies of reaction) within 1 kiloJoule/mole of the equilibrium solubility were rationalized in terms of reaction at Q_1 sites very near equilibrium, and at Q_2 sites farther from equilibrium. This notation refers to the number of oxygen atoms of the quartz surface bonded directly to the central atom of the Si-O_4 tetrahedron, where dissolved silicic acid, H_4SiO_4, is defined as a Q_0 species, $\equiv O$-$Si(OH_3)$ is a Q_1 site at the surface, etc. Q_1 and Q_2 detachment rates follow a transition-state-theory relationship ($R = k(1-\exp\{\Delta G_r/RT\})$) and the rate constants follow an Arrhenius temperature dependence, with the Q_1

detachment rates significantly lower than Q_2 detachment rates. Extrapolation of the $Q_1 + Q_2$ dissolution rates to far-from-equilibrium conditions are close to, but systematically lower than, published far-from-equilibrium dissolution rates. We postulate that this is a result of additional reaction at Q_3 sites (silanol groups at the mineral surface) under far from equilibrium conditions. Under this model, very near equilibrium dissolution and precipitation is related to attachment and detachment of isolated Q_1 species on terraces, Q_2 reaction is related to step-edge advance and retreat, and Q_3 reaction relates to etch pit or growth hillock initiation, consistent with reaction models published by Dove and co-workers, Brantley and co-workers and others.

Significant progress was made in developing molecular dynamics models of the quartz-water interface. A periodic Density Functional Theory (DFT) study was completed of water structure and molecular orientation at the quartz (101) surface, revealing the details of hydrogen bonding of water molecules with surface silanol ($\equiv O_3Si\text{-}OH$) groups and the formation energy of a Q_2 center from a Q_3 center (+70 kJ/mol), which is in the range of experimental activation energies for quartz dissolution under far-from-equilibruim conditions. A detailed comparison was also made among 3 classical force fields (Lopes, ClayFF and CHARRM/CWCA), *ab initio* molecular dynamics simulations and synchrotron X-ray reflectometry studies of interfacial water structure at the quartz (101) surface in contact with bulk and bulk-like water. All classical molecular models gave reasonable water interfacial structures, while ClayFF was shown to give the best agreement with the *ab initio* molecular simulations, indicating that ClayFF best treats hydrogen bonding in the interfacial region. We are currently collaborating extensively with Dr. Adri Van Duin of Penn State, the developer of the ReaxFF code, a classical force field that is capable of accurately treating chemical reactions (i.e. covalent bond making and breaking) by evaluating and re-adjusting the bond order for each atom in the simulation at each time step. ReaxFF is 'trained' using experimental and *ab initio* input, and we are working directly with Dr. Van Duin and his research associates to improve the model for treating quartz-water-ion interactions. We consider this reactive force field development critical in making a direct link between molecular models and macroscopic experimental studies of mineral dissolution, precipitation, and charging phenomena. We are also beginning to explore metadynamics, rare event methods and reactive flux approaches for treating large time and length scales of interfacial reactions.

We are continuing with our studies of TiO_2 (rutile) and SnO_2 (cassiterite) interfaces as model oxides for exploration of the relationship between mineral chemistry, surface structure, and fluid reactivity at the mineral-water interface.



Relationship between O-H stretching frequency and H-bond length of water and surface O-H groups that accept or donate hydrogen bonds within the interfacial region at the rutile (110)-water interface from *ab intio* molecular dynamics simulations.

Neutron scattering has emerged as a powerful tool for validating the dynamics of water and ion interactions with mineral surfaces obtained from molecular models, and conversely, the molecular models are critical in identifying individual species' contributions to the overall scattering signal. During this period, we have conducted deep-inelastic neutron scattering (DINS) studies of water at low hydration levels on rutile and cassiterite nanoparticle surfaces, which indicate strong proton tunneling among surface water and hydroxyl groups. We are now attempting to link these observations with atomistic models of interfacial reactivity and surface bond-breaking. We have also linked our *ab inito* molecular dynamics simulations of hydrated rutile and cassiterite surfaces with inelastic neutron scatterings studies to validate the vibrational density of states of surface species. The figure above shows a detailed analysis of the O-H stretching frequencies and hydrogen bond lengths of surface hydroxyls and sorbed water molecules at the interface for rutile, showing that the first layer of sorbed water exhibits a wide range of stretching frequencies and shortened hydrogen bond-lengths. Such information is critical in the identification of those sorbed water moleculars most likely to participate on Si-O-Si bond hydrolysis, the first step in dissolution of the mineral surface.

Atomic- and Molecular-Scale Structures of Geologic Fluids and Minerals

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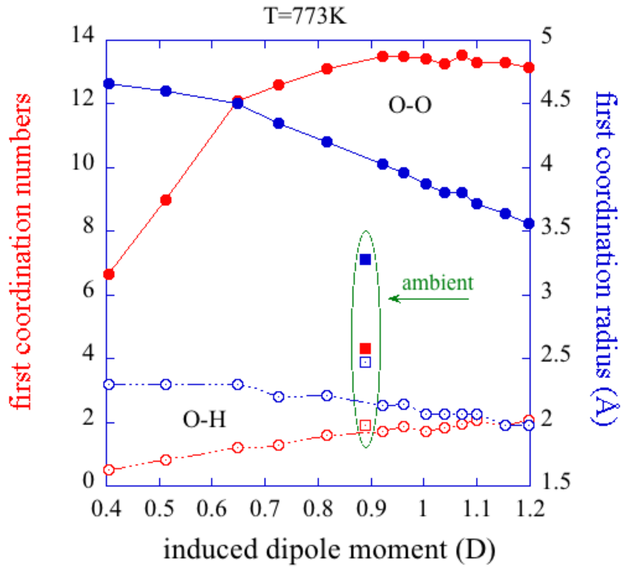
Co-I: *A. A Chialvo*

Objectives: The objective of this project is to advance our fundamental and quantitative understanding of the structure of earth materials, both fluids and minerals, at multiple length scales (atomic to molecular; short- to intermediate- to long-range), over a wide range of pressures and temperatures encountered in near-surface and deep-earth conditions.

Project Description: Geologic fluids (*e.g.*, water) with various short-range structures start to exhibit long-range ordering with increasing pressure (and density), and even crystalline minerals become more disordered in a short-range with increasing pressure and temperature. In order to obtain a fundamental understanding and to build predictive models of the dynamic behaviors and evolution of varied geological systems over a wide range of temperature and pressure, synergistic studies are conducted of: (a) atomic- and molecular-level investigations of hydrogen-bonding in water and hydrous mineral (brucite) by means of high-pressure neutron diffraction and advanced molecular-based simulations, and (b) detailed atomic environments and order-disorder status of ionic-bonding in sedimentary minerals (iron oxides and carbonates), using a total neutron scattering technique. A concerted effort is emphasized between neutron scattering, molecular simulation/modeling, and laboratory experiments toward a more complete understanding of properties and processes of earth materials under diverse environments.

Results: It is now accepted that water (including H and OH) are far more abundant than previously thought in various mantle rocks (possibly as much as contained in Earth's oceans), including both hydrous and nominally anhydrous minerals. Brucite, $Mg(OH)_2$, serves as a simple, yet useful analog for more complex, hydrogen-bearing oxide and silicate minerals of the deep-earth. Our recent neutron diffraction experiments to 9 GPa show that the lattice parameter (c axis along the O-H bonding direction) and unit-cell volume of brucite, both of which decrease with pressure, are systematically smaller for $Mg(OD)_2$ than $Mg(OH)_2$. However, the errors of our data are still large, due to a high background from the incoherent scattering of H. Also, the Paris-Edinburgh high-pressure cell used for neutron diffraction at ORNL's SNS was limited to about 10 GPa. To acquire unit-cell data of normal and deuterated brucite at even higher pressures, we have recently completed systematic and accurate determinations of the lattice parameters and unit-cell volumes of $Mg(OH)_2$ and $Mg(OD)_2$ at room temperature and at pressures up to 20 GPa by means of synchrotron X-ray diffraction. $Mg(OH)_2$ and $Mg(OD)_2$ were simultaneously loaded into a diamond anvil-cell (DAC) with Ne as a pressure medium to maintain hydrostatic pressure. A motor-driven gearbox was used to facilitate the acquisition of multiple, small-increment pressure points from ambient pressure to 20 GPa. Our results show that, in agreement with our neutron diffraction data, the c-axis and unit-cell volume of $Mg(OD)_2$ are consistently smaller than those of $Mg(OH)_2$. However, the differences appear to slowly diminish with increasing pressure between 10 and 20 GPa. These high-precision data from high-pressure X-ray synchrotron diffraction suggest that H-D substitution effects on the lattice parameters of brucite decrease with increasing pressure, which is consistent with our crystal modeling.



Predicted induced dipole dependence of the first coordination numbers for the O···O and O···H interactions as well as their corresponding coordination radii. The induced dipole moment increases with the system density (pressure).

Fundamental studies of the properties of water using molecular modeling methods were extended. We have characterized the polarization behavior of bulk water under geologically-relevant extreme pressure-temperature environments as described by the Gaussian charge polarizable (GCP) classical force field model, and interpreted this behavior in terms of two precisely defined orientational order parameters (i.e. the so-called tetrahedral order q_T and the bond order Q6 parameters), and their connection with the magnitude of the average induced dipole moment of water. This analysis was aimed at addressing relevant questions regarding a conjectured link between the nearest-neighbor distribution (parameter 1) and the magnitude of the average induced dipole moment of water (parameter 2). In that quest we showed that (a) while water exhibits a dramatic microstructural transformation from an open four-coordinated hydrogen-bonded network at normal conditions to a quasi-close-packed coordination at very high pressure and temperature, it still preserves a significant degree of hydrogen bonding; (b) the frequently invoked tetrahedral order parameter provides an incomplete picture of the first nearest-neighbors' ability to hydrogen bond the central water molecule, while the magnitude of the average induced dipole moment becomes a natural and more appropriate (cause-effect) measure for the hydrogen bonding strength. As shown in the figure above, as the induced dipole moment increases (with increasing density or pressure) the average coordination number for the O···O (top red curve) intermolecular interactions goes from four (ambient conditions) to about 13 at 25GPa-773K. Yet, the hydrogen bonding (HB) network, represented here by the O···H (bottom red curve) coordination number, indicates HB strength comparable to those at ambient conditions (green oval).

Evolution of Complex Structures and Reactivity at Mineral/Fluid Interfaces

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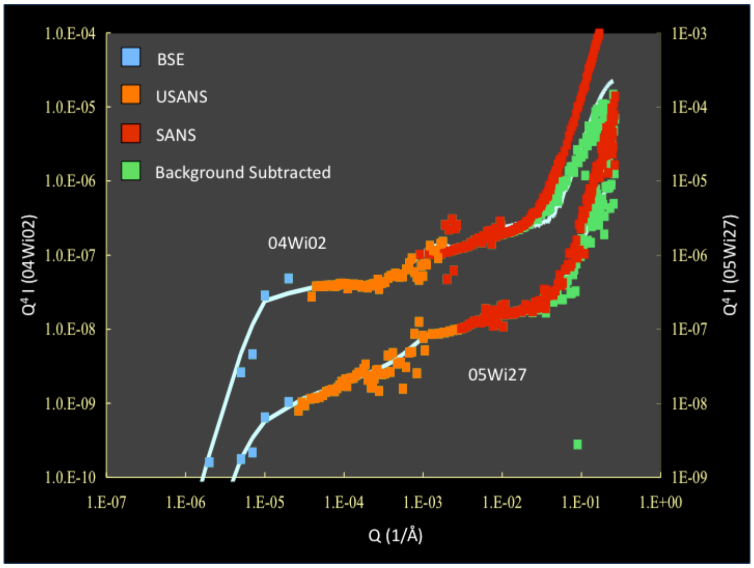
Co-I: *D. J. Wesolowski*

Objectives: The purpose of this subtask is to develop a quantitative understanding of the speciation and transport of fluid-derived-species into reactive minerals, generation of nanoporosity and altered surface layers during fluid/mineral reactions, and the effect of nanoscale confinement on fluid properties and reactivity at conditions representative of those encountered in near-surface and shallow crustal environments.

Project Description: Despite a considerable effort to understand complex mineral dissolution/precipitation and transformation reactions, there are still significant gaps in our understanding of how reactions initiate on a surface, where this occurs, and what happens to the substrate and fluid-derived species as reaction proceeds. The specific aims of this subtask are to: assess the formation of, and chemical communication cross, leached layers and reaction zones with an emphasis on behavior of H-bearing species, characterize the nature of porosity generation and its role in fluid transport and confinement in mineral reaction zones, and probe the structure and dynamics of fluid species present in nanoscale pores. We use advanced chemical and isotopic imaging approaches (e.g. secondary ion mass spectrometry, neutron scattering, and transmission electron microscopy) coupled with modeling and simulation. Knowledge gained from all three aims contribute to a more complete understanding of equilibrium and disequilibrium processes preserved in mineralogical record resulting from water-rock interaction.

Results: We used a combination of Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Small and Ultrasmall Angle Neutron Scattering, (U)SANS, to investigate the nanoscale features of porosity in a number of experimental and natural systems covering the gamut from low temperature weathering to high temperature contact metamorphism. Backscattered electron imaging (BSE) was also used to extend the data to larger length scales and to analyze multifractal behavior. For example, one project involved analysis of samples of buried quartz arenites from the St. Peter Sandstone from S.W. Wisconsin. These samples contain significant porosity, modified by quartz overgrowths, and neutron scattering results (figure below) show significant sub-micron porosity. While previous scattering data from sandstones suggest scattering is dominated by surface fractal behavior over many orders of magnitude, careful analysis of our data shows both fractal and pseudo-fractal behavior. The scattering curves are composed of subtle steps, modeled as polydispersed assemblages of pores with log-normal distributions. In some samples an additional surface-fractal overprint is present, while in others there is no such structure, and scattering can be explained by summation of non-fractal structures. Samples are currently being obtained from Dr. John Valley of the University of Wisconsin for a follow-on study analyzing burial diagenesis of the Mt. Simon sandstone.



Combined BSE, USANS and SANS maps out the scattering from grain boundaries and pores in samples of the St. Peter Sandstone, S.W. Wisconsin at length scales ranging from >60 microns (BSE) to <6 nanometers (SANS).

The analysis of sandstone diagenesis was further enhanced by a series of experimental studies in which pieces of two samples from the St. Peter with different initial porosities were exposed to silica-saturated solutions at 100 and 200°C for up to 7.5 months. Carbonates have also been experimentally recrystallized *in-situ* in vacuum and in pure CO_2 and H_2O/CO_2 environments and analyed by (U)SANS. Both sets of experimental data indicate complex fluid/solid interactions changing pore structures at the nano-to meso-scale. Additional experiments are planned in cooperation with Dr. Valley, who plans to send one of his students to ORNL for similar experiments on samples from the Mt. Simon. In addition, in collaboration with Prof. Susan L. Brantley and her students, we investigated porosity evolution during the weathering of basalt, granite and shale. SANS and USANS results indicate the presence of micropores (d<2 nm) and mesopores (2-50 nm) with the former exhibiting surface fractal features whereas the latter exhibit mass fractal features. In the case of weathered shales, scattering patterns are anisotropic suggesting that cylindrical pores were developed along a certain orientation, probably parallel to the water flow path.

Experimental, analytical and computational techniques have been used to assess the interactions of olivines with water. Single crystal and powder experiments, combined with SIMS and XPS depth profiling have shown significant changes in the mineralogy and buffered pH during water/forsterite reactions. A technique has been devised for synthesis of nano-forsterite suitable for quasielastic neutron scattering analysis of the dynamics of water on the forsterite surface, and a similar technique is being devised to synthesize fayalite. In collaboration with Dr. James Kubicki and Christin Morrow at Penn State the mechanisms and rate of Mg^{2+} release from forsterite have been successfully modeled by integrating experimental data and *ab-initio* results. The reaction mechanisms and barrier heights of the hydrolysis of $Mg–O_{br}–Si$ sites were investigated, and the hydrolysis of the protonated, neutral, and deprotonated states proceeds through a two-step mechanism where the breaking of the Mg–O_{br} bond corresponds to the step which releases Mg^{2+} to solution.

In collaboration with Dr. Alberto Striolo and Dimitrios Argyris at Oklahoma University all-atom molecular dynamics simulations were employed to interrogate the structure and dynamics of aqueous electrolyte solutions within slit-shaped silica nanopores of width 10.67 Å at ambient temperature. All simulations were conducted for 250 nanoseconds to capture the dynamics of ion adsorption and to obtain the equilibrium distribution of multiple ionic species (Na^+, Cs^+, and Cl^-) within the pores. The results clearly support the existence of ion-specific effects under confinement, which can be explained by the properties of interfacial water. Cl^- strongly adsorbs onto the silica surface. Although neither Na^+ nor Cs^+ are in contact with the solid surface, they show ion-specific behavior. The differences between the density distributions of cations within the pore are primarily due to size effects through their interaction with confined water molecules.

Center for Nanoscale Control of Geologic CO_2

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Co-Is: *D.R. Cole, A.A. Chialvo, L.M. Anovitz, G. Rother, L. Vlcek*

Objectives: The overarching goals of this LBNL-led (Dr. Donald DePaolo, Director) Energy Frontier Research Center are to (1) establish, within 10 years, novel molecular, nanoscale, and pore-network scale approaches for controlling flow, dissolution, and precipitation in deep subsurface rock formations with a specific focus on CO_2 bearing fluids, and (2) develop predictive capability for reactive transport of CO_2-rich fluid that is applicable for 100 – 1000 years into the future.

Project Description: The research addresses fundamental science challenges related to far-from-equilibrium systems, nanoscale processes at interfaces, and emergent phenomena. Essential knowledge gaps are the effects of nanoscale confinement on material properties, flow and chemical reactions, the role of nanoparticles, mineral surface dynamics, and microbiota in regulating mineral dissolution/precipitation and fluid flow, the dynamics of fluid-fluid and fluid-mineral interfaces, and quantitative macroscale models based on nano- to pore-scale process descriptions. Carefully integrated experiments using DOE/BES national user facilities plus modeling and simulation approaches will be used to evaluate essential molecular and nanoscale processes, and to treat the transition from the nanoscale to pore scale. Multiscale computational models and lab-scale experiments will be used to understand the emergence of macroscale properties and processes.

Results: Researchers in the Chemical Sciences Division of Oak Ridge National Laboratory utilize world-class computational, experimental and neutron scattering capabilities to investigate the atomistic and molecular-level processes attendant with the interaction of CO_2-rich solutions with mineral surfaces relevant to subsurface environments. The ORNL effort is synergistically linked to the thrust areas of the Center – controlling carbonate nucleation and growth, structure, dynamics and transport of fluids in nanopores and thin films, and emergent processes and properties at the pore scale, leading to unprecedented predictive capability of complex fluid-mineral interactions under high CO_2 loadings.

Thermophysical Properties: This effort utililizes vibrating tube densimetry (VTD) for the first time to measure the total amounts of fluids adsorbed in mesoporous solids. The principal advantages of this method are; a.) its unique capability to directly deliver the total amount of fluid contained in the pores even at high densities, in contrast to conventional manometric-volumetric and gravimetric techniques which are only capable of measuring excess adsorption; and b.) the ability to readily vary temperature, pressure and fluid composition over wide ranges without significantly perturbing the nanoporous substrate.

Measurements of the density of pore-confined fluid and detection of adsorbate condensation in silica aerogel were first demonstrated using relatively inert propane at subcritical and supercritical conditions (35, 70, 92, 95, and 97 °C, pressure from 0 to 55 bar, and density to 0.36 $g\cdot cm^{-3}$) . The isotherm of total adsorption of CO_2 on the same solid was measured at 35 °C to 120 bar (maximum fluid density 0.767 $g\cdot cm^{-3}$). The densities of helium and argon adsorbed in the same porous solid were also measured at 35 °C to provide a means for direct comparison with relative adsorption isotherms obtained gravimetrically. Since the relationship between mass of a vibrating tube and the square of the vibration period is very close to linear, calibration with a pair of reference fluids leads to the most accurate VTD results. All adsorption /desorption isotherms showed monotonic increase/decrease of the total fluid content in the pores with the density (pressure) of bulk fluid.

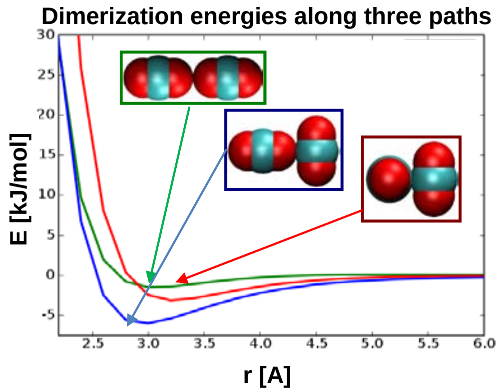
Neutron probes of fluid-matrix interactions: A fundamental understanding of the behavior of supercritical CO_2 and its mixtures with water in nanoscopic pores and fractures is critical to quantifying fluid uptake capacity in reservoir rocks, its flow and migration, and capillary trapping processes. Neutron scattering techniques play a key role in the study of structure and dynamics of fluids in pores and at interfaces because they are uniquely sensitive to hydrogen and other light elements, and neutrons penetrate deeply into dense matter, enabling *in situ* studies at high pressure and temperature. Our ongoing neutron activities for the NCGC project include: (i) sorption of CO_2 and mixtures of CO_2 and water in pores, (ii) calcite precipitation in pores, and (iii) measurement of fluid density profiles at atomically flat surfaces. We have performed a number of experiments and built and tested new equipment critical to the more advanced experiments scheduled for years two and beyond. We use Small-Angle Neutron Scattering (SANS) to measure the nano-scale structure of pore fluids. We have developed a method to measure the density and volume of the sorption phase of pure fluids in pores using SANS. Using our Adsorbed Phase Model (APM) in combination with neutron transmission we measured, for the first time, the density and volume of the sorption phase. SANS data have been measured for carbon dioxide and deuterated propane confined in silica aerogel with 7 nm nominal pore size. From these data, excess, absolute, and total adsorption were calculated. These new and interesting results complement those obtained from the vibrating tube densimeter, which measures total adsorption, and high-pressure gravimetric sorption experiments, which measure excess adsorption.

Molecular-level simulations of interfacial processes: A key ingredient underlying the CO_2 sequestration is its aqueous solubility, not just in bulk, but more importantly, within nano-confined environments. Thus, our overarching goal is the detailed microstructural and dynamical molecular-based characterization of CO_2-aqueous solutions at mineral surfaces and under extreme confinement, by reliable and precisely defined intermolecular models. We have derived and applied a synergistic approach between statistical mechanics developments and

Gibbs ensemble Monte Carlo simulation to calibrate the CO_2-H_2O van der Waals interactions so as to predict accurately and simultaneously the compositions of the two phases in liquid (water rich)-liquid(CO_2 rich) equilibrium at realistic reservoir conditions; and (b) we set up and executed a molecular dynamics protocol that allows the simultaneous study of the fluid behavior at interfaces and within confinement between mineral surfaces, while the fluid remains in equilibrium with its bulk counterpart at isobaric-isothermal conditions.

We have also used MD and Monte Carlo approaches to simulate the structure of amorphous silica surfaces and the adsorption of near-critical CO_2. The study of flat surfaces provides information about the influence of surface roughness on the excess adsorption which can be directly compared to the results of neutron reflectivity (NR) measurements. The effect of surface geometry and topology on the adsorption of CO_2 in porous silica was studied on an aerogel sample and was directly motivated by recent small angle neutron scattering (SANS) experiments on this system. The 3D structure of aerogel is reconstructed using reverse Monte Carlo-style simulations mimicking the physical generating process and using SANS and transmission electron microscopy (TEM) images as the experimental source of information. We also used classical DFT to determine near-critical CO_2 condensation confined in a model porous system resembling aerogel.

Aqueous carbon dioxide in the environment of a sequestration site will experience polarization by strong electric fields due to interaction with water dipoles, and undergo both homogeneous and heterogeneous chemical reactions. These multibody effects influence mutual solubility of water and CO_2, nucleation of carbonates, and reactions of the wetting-phase with reservoir and caprock minerals. Such reactions are not properly represented by existing classical models. To address some of these issues, we are using experimental data and *ab initio* results to develop the Gaussian Charge Polarizable Model (GCPM) of CO_2 and optimized it to reproduce thermodynamic and structural properties of the substance. We are currently working with Dr. Adri Van Duin of Penn State University to parameterize the ReaxFF reactive classical force field for accurate treatment of CO_2 carbonation reactions.



CO_2 dimerization energies from Gaussian Charge Polarizable Model (GCPM).

Mineral Transformations in Supercritical CO_2-Dominated Fluids: Impact on Caprock Integrity

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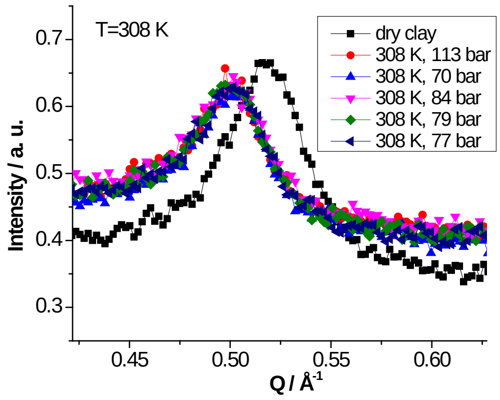
Objectives: This Single-Investigator/Small-Group (SISGR) Research project lead by Pacific Northwest National Laboratory (Dr. K. Rosso) aims to understand the physical and chemical processes taking place at mineral surfaces in contact with carbon dioxide (CO_2) + water mixtures. The project addresses fundamental science questions relevant to the long-term caprock integrity of carbon sequestration sites.

Project Description: The modest ORNL-led portion of the project concerns the study of the pristine and reacted minerals (e.g. olivine, muscovite) and the properties of the density of the sorption phase formed at the mineral grain surfaces in contact with high-CO_2 fluids for different conditions of temperature, pressure and fluid composition. Small angle neutron scattering (SANS) experiments carried out at the neutron sources at ORNL and NIST (Gaithersburg) measure the surface area and fractality of different minerals found in caprock formations (i.e. phyllosilicates and orthosilicates) in pristine and reacted states to gain insight into the effect of fluid-rock interactions on reservoir porosity and permeability. The second subtask studies the fluid interfacial properties of mixtures of CO_2 and water (H_2O/D_2O) at pristine and reacted mineral surfaces. The combined analysis of neutron scattering and sorption data will feed into new models for quantitative description of the sorption behavior of binary mixtures at mineral surfaces. The ORNL effort will be synergistically linked to the overall project, leading to a novel understanding of complex geo-fluids in natural environments.

Results: A neutron diffraction experiment to study the variation of the interlayer spacing of montmorillonite clay with CO_2 loading was performed at the Berlin membrane diffractometer. This instrument has a unique range of momentum transfers that makes it ideal for the study of length scales of interest for that system (Angstroms to tens of Angstroms). We studied the effects of CO_2 pressure and temperature on the clay interlayer spacing. An increase of the interlayer thickness from 12.15 Å for pure dry clay to 12.59 Å was found as a result of addition of CO_2 fluid. Interestingly, neither the density of CO_2 nor temperature had an impact on the diffraction peak shift (see figure). This observation has important implications for both caprock integrity in sequestration environment, and permanent mineral-trapping of sequestered CO_2.



Neutron diffraction patterns for dry clay as a function of CO_2 pressure, T=35^{o}C.

PACIFIC NORTHWEST NATIONAL LABORATORY

CONTRACT: RL01830

PERSON IN CHARGE: A. Felmy

Molecular Mechanisms of Interfacial Reactivity in Near Surface and Extreme Geochemical Environments

PI: *Andrew R. Felmy, 509-371-6356; ar.felmy@pnl.gov*

Objective: The Basic Energy Sciences (BES) Geosciences Research Program managed at PNNL is designed to advance our fundamental understanding of molecular processes to determine the mechanisms that control interfacial reactivity in near surface to extreme geochemical environments.

Project Description: Research activities within the program are focused on 1) unraveling the dynamics of mineral interfacial reactions and the changes induced in mineral surface chemistry by electron conduction/transfer reactions, 2) determining the impact of oxidation/reduction reactions on the transformations of multivalent metal solutes/adsorbates at mineral surfaces, with a special emphasis on determining reaction intermediates, 3) developing a mechanistic understanding of solvation, hydrolysis, and mineral/acid base chemistry including reactions at high temperature and pressure, and 4) developing both new experimental and computational approaches for interrogation of reaction mechanisms at mineral and nanoparticles interfaces. The research program provides a fundamental molecular level understanding of macroscopic mineral-water and more complex rock-water interactions which is critical for accurately predicting the consequences of geologic disposal of the byproducts of energy production activities.

In FY10 research focused on unraveling electron conduction and the influence of surface specific potentials on redox transformations of the iron oxides (subtask 1), the impact of the local chemical environment on stabilizing the U(V) reaction intermediate (subtask 2), the development of new *ab initio* molecular dynamics methods for simulation of metal ion hydrolysis and oxide surface reactions (subtask 3), the influence of microbial biochemical reductants on the transformation of iron oxides (subtask 4), and the impact of oxide shell structure and organic coatings on the reactivity of iron nanoparticles (subtask 5). Each of these research areas is described below with an emphasis on the specific research conducted in FY10.

Subtask 1: Couple Surface and Solid-State Charge and Ion Transport Dynamics at Mineral/Water Interfaces: Redox Transformation of the Iron Oxides

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Objectives: This project provides fundamental insight into spatially remote interfacial electron transfer reactions coupled to each other by solid-state charge transport for semiconducting minerals.

Project Description: Select redox transformations of Fe(III)-(oxy)(hydr)oxide minerals involving Fe(II)-catalyzed interfacial electron exchange are being investigated in detail because of the semiconducting nature of these minerals, the unique opportunity to probe the relationship between surface specific potential and bulk current flow, and because of their high geochemical relevance. Well-defined single crystal surfaces are used so microscopic and spectroscopic observations can be linked to molecular-scale details of surface structure and charge accumulation. Electrochemical methods, scanning probe microscopy, and surface analytical characterization are being used to build up a first-ever picture of the electrostatic potential distribution across crystallographically specific interfaces as a function of degree of surface perfection, pH, ionic strength, and the presence of various organic ligands. Molecular dynamics (MD) simulations are being used to predict free energies of aqueous Fe(II) adsorption and electron exchange with specific surfaces, and to calculate major features of the electrical double layer. Monte Carlo (MC) methods are being used to simulate the kinetics of pH titration, and to test mechanisms of coupled electron and iron atom exchange with and without bulk charge transport enabled. Surface complexation modeling is being used to compute surface charge accumulation and inner-Helmholtz potential development. Collectively this project is providing major new conceptual advances with broad application to understanding redox processes on semiconducting mineral surfaces.

Results: In FY10 this project produced manuscripts on electrochemical measurement and molecular-level simulation of hematite single-surface potentials as a function of pH, ionic strength and the presence of organic ligands, microscopic and Mossbauer-based characterization of hematite redox transformation catalyzed by Fe(II), molecular simulation of electron and iron atom exchange mechanisms and kinetics for Fe(II)/goethite interaction, and developed new computational molecular models for pH-dependent single crystal surface charge accumulation kinetics and thermodynamics. For example, inner-Helmholtz electric potentials of the hematite (001) surface measured as a function of pH and ionic strength showed that the pristine surface is predominantly charge-neutral in the pH 4-14 range, and develops a positive surface potential below pH 4 due to protonation of μ-OH^0 sites. The associated Stern layer capacitance (0.62 F/m^2) is smaller than typical values of powders, and arises from a lower degree of surface solvation possible on a perfect surface. Acid-promoted or ligand-assisted dissolution roughens the surface and increases the density of -$OH_2^{0.5+}$ sites, thereby yielding a propensity for larger surface potential. In the presence of oxalate, potentials are strongly negative from metal-bonded interactions. The surface was also found to acquire negative potentials in the pH 7-11 range due to surface complexation and/or precipitation of trace iron species (0.003 Fe/nm^2) produced from acidic conditions. All measurements were successfully interpreted in terms of a thermodynamic model that can now be used to predict potentials of hematite electrodes of various surface expression. Measurements on four other surface planes are ongoing, and will yield values for the electrical bias that drives bulk current through the solid over a wide range of conditions.

Coupled Fe(II)-Fe(III) electron and atom exchange processes recently reported for acicular goethite rods were simulated entirely from MD and MC to test for the role of bulk conduction. This included comparative models for the exchange process with and without bulk charge transport enabled, where in one model the kinetics of mixing was treated as facilitated exclusively by random thermal fluctuations in surface growth/dissolution for uncoupled crystal terminating surfaces, and in the other model surface-specific energetic requirements for Fe(II) adsorption (Fig. 1), electron injection into the goethite solid, and interior migration of electron equivalents from one surface to the next were explicitly evaluated. The former model shows that room temperature dynamics of surface growth/dissolution at equilibrium alone is sufficient to explain observed isotopic mixing rates in the goethite solid but is inconsistent with lack of observable change in crystal size or shape upon 100% exchange. The latter model shows strong preferential Fe(II) adsorption at rod end faces relative to rod side faces and relatively weaker tendency for electron injection at crystal ends relative to sides. Electron injection and migration across rod widths is mildly uphill but more likely than along rod lengths. The molecular-level picture that emerges is consistent with the bulk charge transport model first laid out from this project in a 2008 Science paper, and more recently invoked as a basis to explain complete Fe(II)-catalyzed iron atom exchange in goethite within 30 days. Our ongoing modeling work endeavors to refine the predictions of both mechanistic models for quantitative comparisons to the observed rate.

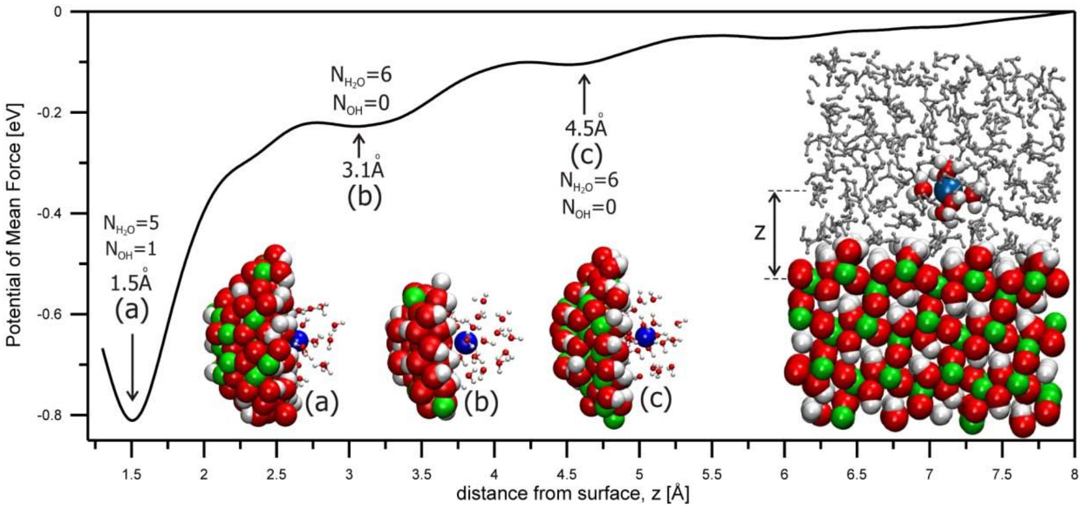

Figure: Free adsorption energy profile for Fe(II) on the (101) goethite/water interface from molecular dynamics simulation. The Fe(II) ion coordination due to surface hydroxyl groups is indicated by N_{OH}, whereas due to the water molecules by N_{H2O}.

Subtask 2: The Influence of Reaction Pathways on the Reduction of U^{VI} to U^{IV}: The Role of the Intermediate U^{V} Species

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Co-Is: *Dr. Andrew R. Felmy, Dr. Sebastien Keresit (PNNL)*
Dr. Paul S. Bagus (University of North Texas)

Objectives: To better understand electron transfer reactions between Fe^{II} in minerals and sorbed polyvalent metals such as U^{VI}. To develop *ab initio* models for the XPS and XANES metals in order to help elucidate information on oxidation states and bonding environments.

Project Description: We are exploring the influence of U coordination environment on the reduction of U(VI) to U(V) to U(IV) at the ferrous mineral-fluid interface. Key techniques used are electron microscopy, x-ray photoemission spectroscopy (XPS), and x-ray adsorption near edge structure (XANES). The project includes complementary theoretical efforts to quantify the effect of coordination environment on the relative stabilities of the different oxidation states of U as well as to help interpret XPS and XANES spectra.

Results: An important development in Task 2 during FY10, was the discovery that U(VI) reduced to U(IV) on the (111) surface of a single crystal magnetite. This contrasts with earlier results using nanocrystalline magnetite where U(VI) reduced to U(V), but not U(IV). The conditions for the two types of experiments were very different; the single crystal experiments were consistently undersaturated with respect to Fe and U phases and maintained nearly constant pH = 5, whereas the nanocrystalline experiments drifted from low pH (3.2-4) to high pH causing U(Fe) phases to precipitate. U(V) appears to be incorporated in those U(Fe) precipitates in a uranate coordination scheme, whereas U(IV) appears to be present as UO_2 associated with defects on the single crystal surface. These results conform to our central hypothesis that reduction of U(VI) to U(IV) might be hindered if U cannot obtain 8-fold coordination and that uranate coordination stabilizes U(V).

The experimental work has been complemented with ab initio calculations on the effect of U coordination environment on the reduction of U(VI) to U(V) and U(IV) by Fe(II)-Fe(III, II)-U(VI) trimers, and atomistic simulations of U(IV, V, VI) in different Fe-(hydr)oxide structures. In the former, U(VI) was most stable in uranyl coordination, whereas the stability of both U(V) and U(IV) increased with the loss of the short trans-dioxo bond and a shift to uranate coordination. U(IV) stability was further enhanced by increasing U coordination from 7 to 8. Within the confines of the model, it was only possible to reduce U(VI) to U(IV) if U(IV) was in 8-fold coordination and U(V) maintained uranyl coordination, otherwise U(VI) was reduced to U(V). This, too, is consistent with our central hypothesis. The atomistic simulations provided rapid screening of potential coordination structures for U(VI, V, IV) in Fe-(hydr)oxides. The results were compared to published results for EXAFS of U incorporated in Fe-(hyrd)oxides. The combination of simulations and experiment proved a powerful constraint on likely incorporation sites (i.e., octahedral, tetrahedral, or interstitial) and charge compensation mechanisms (i.e., deprotonation, Fe(III) reduction to Fe(II), or vacancy formation).

We have improved the efficiency of our programs for simulating bonding environment effects in the XPS spectra of actinides as well as any other heavy element of interest. In particular, we reduced the time for calculating spectral intensities by over an order of magnitude. In other developments, we have shown that covalent mixing of metal and ligand orbitals to form bonding and anti-bonding orbitals yield additional many-body effects and may provide a unified understanding of the XPS of metal compounds. This is a major advance beyond semi-empirical models which treat metal and ligand orbitals separately (i.e., as atomic orbitals), and only consider charge transfer configurations (i.e., transfer of an electron from a pure ligand orbital to a pure metal orbital) in the screening of the core hole created during the photoionization process. Another significant advance in understanding the XPS of metal compounds is our recent discovery that vibrational excitations in the final state make major contributions to the broadening of individual multiplet peaks. The previous paradigm was that differential broadening of XPS peaks arise from core-hole lifetimes and inhomogenieties in the sample. Advances in simulating XPS spectra for heavy element compounds are described in greater detail in the Summary of the Co-PI, Paul S. Bagus (UNT).

Subtask 3: Development and Application of Next-Generation Parameter-Free Petascale Simulation Technology for Solution Species, Nanoparticles, and Geochemical Interfaces under Extreme Conditions

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Co-I: *Eric Bylaska (PNNL)*

Objectives: The development and application of next-generation parameter-free petascale simulation technology for solution species, nanoparticles, and geochemical interfaces under extreme conditions. New parameter-free methods of simulation that exploit the full capabilities of emerging massively parallel computers and allow the simulation of new classes of materials are developed and applied to complex geosciences problems.

Project Description: To address the problems associated with future energy strategies a much more quantitative, parameter free interpretation of elementary geochemical processes will be required. In this program new 1st principles simulations methods are being developed and applied to the study of the chemical behavior of metal ions, their counter ions, their oxo-hydroxo hydrolytic polyions in aqueous solutions. The understanding of the aqueous chemistry of these species is essential to the interpretation of processes such as, the formation of minerals, the sequestration of CO_2, the storage of nuclear waste, and the transport of toxic materials. The 1st principles-based simulation methods that are being used and developed allow the parameter-free prediction of the properties of these chemically complex materials over the wide range of conditions encountered in geological applications and will utilize the rapidly expanding power of leadership class computers.

Results: The formation of $Al^{3+}Cl^{-}$ ion pairs in aqueous solutions: 1st principle free energy simulations have been used to investigate the possibility of the formation of an $Al^{3+}Cl^{-}$ ion pair in water. The $AlCl_3$ salt is commonly assumed to be completely dissociated in solution. However, there is recent experimental evidence suggesting that other similar 3+ charged ions form chloride ion pairs. The presence of an $AlCl^{2+}$(aq) species would have significant consequences in the interpretation of Al^{3+} distribution and transport in natural waters. Our calculated free energy of along the linear dissociation path of the aluminum-chloride ion pair shows a pronounced minimum at a distance $r_{Al\text{-}Cl}$ = 2.3 Å suggesting (contrary to present interpretations) the presence of a contact ion pair with a free energy barrier of 11.14 kcal/mol. Two local minima assigned (solvent separated ion pairs) are also present. The positions of the minima coincide with the hydration shell interval of the aluminum cation (dotted line lower figure) suggesting that the Cl^- ion is most stable in regions of low water particle densities. The electronic structure of the system was also investigated using the method of maximally localized Wannier functions. The dipole moment of the water molecules inside and outside the 1st hydration shell of Al^{3+} and the dipole moment of the Cl^- ion are calculated as a function of the separation of the Al^{3+} and Cl^- ions. There are major changes in the average dipole moment of the hydrating waters as the Cl^- is moved out of the 1st hydration shell (e.g., the average 1st shell water dipole is 3.85D when Cl^- is in 1st hydration shell of Al^{3+}, 4.42D when the 2nd shell and 4.07D when in the bulk).

The prediction of an ion pair species in the $AlCl_3$-H_2O system is quite controversial and illustrates the importance of 1st principle simulations to support the proper interpretation of solution structure. To ensure that the simulations are providing accurate free energies we have extended equilibration times for each constrained step. These results are still being analyzed.

Inclusion of Exact Exchange in AIMD using force calculations at the MP2 level: The inclusion of exact exchange corrections to DFT in our AIMD algorithm (forces calculated at the DFT+gga+exact exchange level) provides a significant improvement over the gradient corrected DFT for our simulation program. However adding exact exchange in the calculation greatly increases the cost per step. In this period we have developed a new parallel implementation strategy that scales very well. Scaling results for this algorithm are illustrated in Figure 1. We note that the time step for a 160 atom Hematite supercell (544 spin up electrons and 544 down spin electrons) has been reduced to an acceptable 15 sec per step. This is an acceptable time step for a dynamical simulation considering that this is a very difficult system to treat with 1st principle methods.

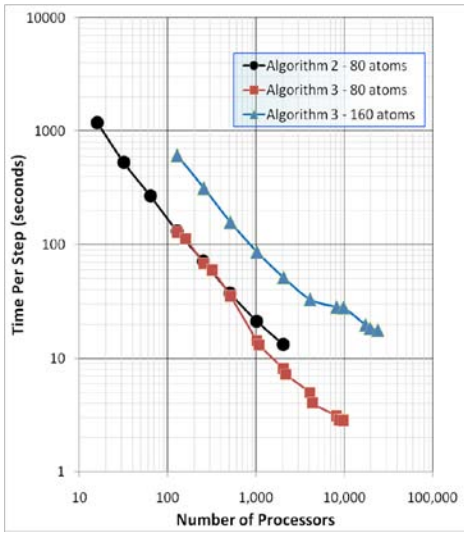

Figure: Scaling of *ab-initio* molecular dynamics step DFT + gga+exact exchange. Note the near linear scaling and the final step time of 15 seconds per step for a 160 atom Hematite supercell.

However, it is well known that DFT+gga+exact exchange, while provide a major improvement over the usual DFT+ gga level of solution still has accuracy issues for electronic structure calculations. Problems that are particularly important to geochemical applications include: the prediction of lower solvent coordination numbers than higher-level methods (e.g., underestimates the contribution of associative mechanisms) and the prediction of lower barrier to proton transfer.

Possibly the most reliable level of solution to the electronic structure problem that can still be efficiently implemented for systems with large number of atoms is the MP2 approximation. This method is based on many-body perturbation theory and does not have the problems found in DFT based methods. However, it is even more expensive to calculate. We believe that the compute time for this method can also be greatly reduced by our parallel strategies. In FY10, we have begun to extend our plane-wave exact exchange AIMD method with free-space boundary conditions to the MP2 level. Our current implementation is similar in spirit to localized MP2 methods. However, instead of using localized basis sets we are using plane-waves. We expect our initial implementation to be finished in the fall of 2010.

Subtask 4: Reductive Mineralization of Fe(III) Oxides Promoted Through Biogeochemical Fluxes of Fe(II): A Molecular and Microscopic Study

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Co-Is: *J.K. Fredrickson; Z. Shi; L. Shi; K. M. Rosso; and S. Kerisit*

Objectives: Research is evaluating the kinetic mineralization pathways of lepidocrocite and ferrihydrite promoted by $Fe(II)_{aq}$, and by sorbed Fe(II) generated by heterogeneous electron transfer reactions of different rates and stoichiometry. We speculate that the molecular stoichiometry of electron transfer is an important variable controlling the nature of mineral transformation.

Project Description: Laboratory studies are using static and dynamic-flow through experimental systems with $Fe(II)_{aq}$ and a series of biochemical reductants that exhibit a range of electron transfer stoichiometry [reduced anthraquinone disulfonate (AH_2DS), flavin mononucleotide ($FMNH_2$), and multi-heme cytochromes (plus a physiologic electron donor NADH)] to investigate the rates and products of Fe(II) induced recrystallization and transformation of ferrihydrite and lepidocrocite. Reaction kinetics are determined by monitoring electron donor use and Fe(II) generation in response to changes in experimental variables (electron donor to acceptor ratios, presence and absence of bicarbonate and phosphate), and structural features of the transformation products. Variable temperature Mossbauer spectroscopy, conventional and synchrotron x-ray diffraction, micro-XANES spectroscopy, scanning and transmission electron microscopy, and atomic force microscopy are applied to identify reductant induced changes to the Fe(III) oxides, and to identify the nature and properties of the product phases. Large-scale, semi-atomistic model simulations (kinetic Monte Carlo) of coupled Fe(II)-enhanced surface dissolution and precipitation are being performed to provide insights on biologic and abiotic controls on mineralization pathways, precipitation kinetics, and final phase assemblages.

Results: Kinetic mineralization experiments in FY 2010 have investigated the $Fe(II)_{aq}$-, AH_2DS-, and $FMNH_2$- FH/L systems as we work out details for more complex experiments with cytochromes of different heme contents. The $FMNH_2$-FH/L system has been our primary focal point, as $FMNH_2$ is postulated to be and important reductant of microbial origin in geochemical systems and credible literature reports on the reactivity of this compound do not exist. The $FMNH_2$ system has shown surprising experimental difficulty in terms of unexpected analytical challenges, back reactions, and complexation affinity for both Fe(II) and Fe(III). These challenges have been resolved, and we now have the system under complete experimental control. The first documented artifact-free kinetic studies of $FMNH_2$ reaction with FH and L have been completed where electron transfer stoichiometry (2:1) has been confirmed (Figure 1). These have revealed a very rapid electron transfer reaction between $FMNH_2$ and the Fe(III) oxides that are compete within 10 minutes for L and 30 minutes for FH. The reaction rates derived from this data are much faster than observed for AH_2DS. Curiously however, the two reductants differ markedly in the reductive mineral phases that they produce after reaction [e.g., Fe(II) generation] with AH_2DS producing magnetite as a primary product and $FMNH_2$ yielding and Fe(II)-enriched amorphous phase. These differences appear to result from the adsorptivity of the oxidized biochemical product and the molecular environment and reaction pathway of "sorbed", reaction product Fe(II). Ongoing experimental and kinetic Monte-Carlo modeling studies seek to understand the mechanisms involved in these differences; particularly the relationship between the electron transfer and mineralization reactions that appear linked but that proceed over markedly different time scales.

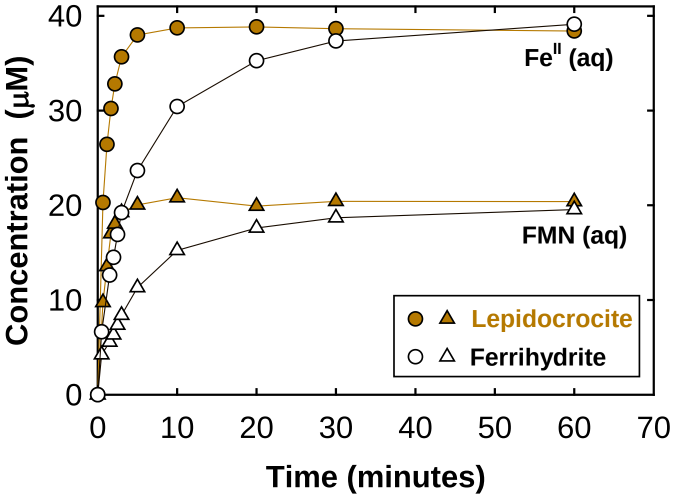

Figure: Reductive dissolution of 50 μM lepidocrocite or 50 μM ferrihydrate by 20 μM $FMNH_2$. Suspensions contained 30 mM PIPES buffer (pH 7.0). Fe^{II}(aq) was analyzed by ferrozine assay, and FMN(aq) was analyzed using UV-Vis spectrophotometer in glovebox. Note that the electron transfer reaction can be formulated as follows for lepidocrocite: $2FeOOH + FMNH_2 + H^+ \leftrightarrow 2Fe(II) + FMN + 2H_2O$.

Subtask 5: The Reaction Specificity of Nanoparticles in Solution: Interactions between Iron Core/Shell Nanoparticles, their Coatings, and the Environment

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P. G. Tratnyek, J. T. Nurmi, A. S. Salter (OHSU)

Objectives: The objective of this project is to obtain fundamental information about the physical and chemical transformations that occur on and within mineral oxide nanoparticles (NPs), with emphasis on electron-transfer reactions and interactions involving surface coatings.

Project Description: This project is focused on geochemically mediated transformations and how they alter NP reactivity, electron availability, and particle mobility. Natural particles and synthesized model particles are being used to study their transformations, interfacial reaction products, particulate reactivity.

The work is organized around four major activities: 1) synthesis of well-defined NPs, 2) characterization of their surface and bulk composition as well as physical and electronic structure (before and after reaction measurements) characterization of their surface and bulk composition as well as physical and electronic structure (before and after reaction measurements) using a range of tools including those available in the Environmental Molecular Sciences Laboratory (EMSL), 3) *in situ* real-time and batch measurements of NP properties and reactivity in vacuum and solution, and 4) theory and modeling work that helps identify reaction mechanisms and reaction intermediates. The project integrates the results of these four activities to accomplish the major objective.

Results: Important questions identified by earlier work involve the impact of solution composition on the transformation (aging) of NPs and the role played by surface coatings—including those involving organic matter—in the reactions of NPs with solution components. Specifically, we have examined the impact of inorganic anions, natural organic material, and model organic surfactants on the oxidative aging and reactivity of iron NPs. Natural organic material decreases both the oxidative aging and the reactivity of particles with a probe oxidant like CCl_4, which simultaneously alters the overall structure of the oxide shells (see figure) on the NPs and facilitates the transport of particles through a soil column. Phosphate destabilizes the particles increasing the overall aging rate of NPs while chloride ions have little impact. The details of many of these effects can be understood in terms of changes in the relative solubility of the surface phases that can form as the reacting solution evolves towards higher pH and H_2(g) levels.

A combination of model experimental and theoretical studies was undertaken to assist fundamental understanding of reaction pathways for the interaction of solution species with NPs. The model experiments examined the reaction of zero-valent iron atoms and clusters with chlorinated methanes and water and demonstrated that reaction proceeds via the formation of insertion complexes where the iron atom inserts between the C and Cl atom or the H and O atom, forming C-Fe-Cl and H-O-Fe-H species respectively. The experiments also reveal that these insertion complexes are highly stable with respect to further reactions. Reactions proceeding via formation of these insertion complexes were modeled using density functional theory electronic structure calculations to provide fundamental understanding of factors affecting reactivity of nano iron particles with substrates. These calculations also demonstrate the stability of these insertion complexes. Taken together these experimental and theoretical results provide new mechanistic understanding of reactions which were previously thought to proceed via atom abstraction.

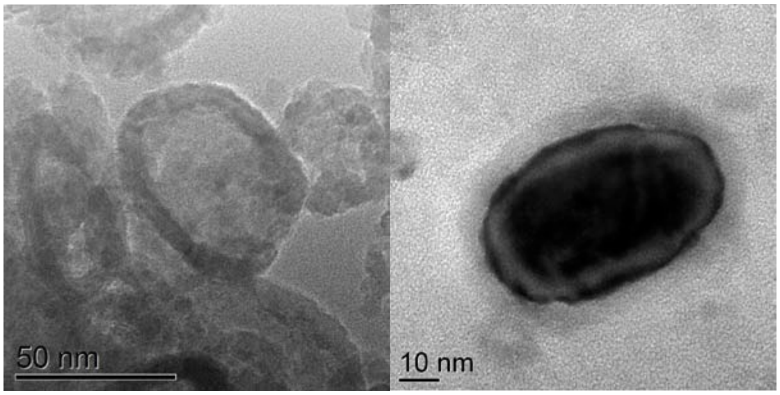

Figure: When iron metal-core oxide shell nanoparticles are exposed to solutions containing natural organic material (NOM) for 24 hours both hollow oxide shells and intact particles (with metal cores and oxide shells) are observed by electron microscopy measurements. The hollow shells are not observed without the presence of the NOM, which interacts with the particles, changing the structure and time evolution of the oxide shells. The hollow shells occur as the metal core is removed from the particle during oxidation, but (when sufficient NOM is present) an oxide shell remains.

Mineral Transformations in Supercritical Carbon Dioxide-Dominated Fluids: The Role of Interfacial Processes in Mineral Transformations in Wet Supercritical Carbon Dioxide

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Objectives: The primary objective of this project is to unravel the molecular mechanisms governing the reactivity of supercritical-CO_2 ($scCO_2$) of variable water content with mineral phases important in the geologic sequestration of CO_2.

Project Description: This project is a comprehensive experimental and theoretical investigation of the role of interfacial water and CO_2 on the energies, mechanisms, and rates of reactivity of a series of orthosilicate and phyllosilicate minerals in contact with $scCO_2$ containing variable H_2O. The molecular mechanisms for carbonation reactions, as well as the distribution of H_2O between $scCO_2$ and mineral surfaces, will be followed using molecular simulations and surface spectroscopy as a function of T, P, mineral composition and structure, and water activity. The theoretical studies will be coupled with *ex situ* and *in situ* high-resolution spectroscopic measurements (e.g., IR/FTIR, NMR, and Small Angle Neutron Scattering (SANS)) to investigate the formation and structure of water layers at mineral surfaces and in the interlayer region of phyllosilicates, and identify potential interfacial carbonate and silicate species. The proposed research will provide new insights into mineral transformations under extreme conditions and help establish a basis for assessing the effectiveness of CO_2 sequestration in geologic disposal sites.

Results: This project was initiated at the end of FY09. Research during FY10 has focused on both *ex-situ* and *in-situ* FTIR/NMR studies of the role of interfacial water in the reactions of forsterite with supercritical CO_2/H_2O mixtures.

Our *ex-situ* studies of forsterite reactivity at 80°C in supercritical CO_2 ($scCO_2$) were conducted in the presence of different amounts of liquid water and the reaction products examined using a combination of solid state NMR (^{13}C SP-, CP-MAS, ^{29}Si SP-, CP-MAS), XRD, TEM and XPS. No reaction was observed in the absence of water. However, in the presence of an aqueous solution we identified the initial reaction products as hydrated/hydroxylated magnesium carbonate phases (e.g., dypingite) which transformed to amorphous silica and magnesite with reaction time. Studies conducted over a broad range of water content showed that forsterite surfaces reacted even at water contents below the levels needed to saturate the $scCO_2$ with water. The reaction products consisted of a complex mixture of partially hydrated/hydroxylated magnesium carbonate species and a variety of hydroxylated surface silica species. These initial reaction products were mainly in an amorphous state, forming a thin layer on the forsterite surface. At high water contents forsterite was converted into magnesite, and an amorphous SiO_2 reaction product dominated by Q4, and to a lesser extent by Q3 silica coordination. The formation of these anhydrous phases (magnesite and/or amorphous silica) effectively liberates water that can induce further reactivity. The importance of this catalytic role of water is illustrated in Figure 1 which shows the large differences in extent of forsterite reaction with small changes in initial water content. The figure on the left illustrates the impact of the formation of intermediate species (hydrated $MgCO_3$ phases and hydrolylated Si species) which consume water and halt reaction progress after a short initial period. If however, if sufficient water is present for the reaction to proceed to the formation of the anhydrous phases (magnesite and amorphous silica) then water is regenerated and the reaction proceeds for long time periods consuming most of the added forsterite.

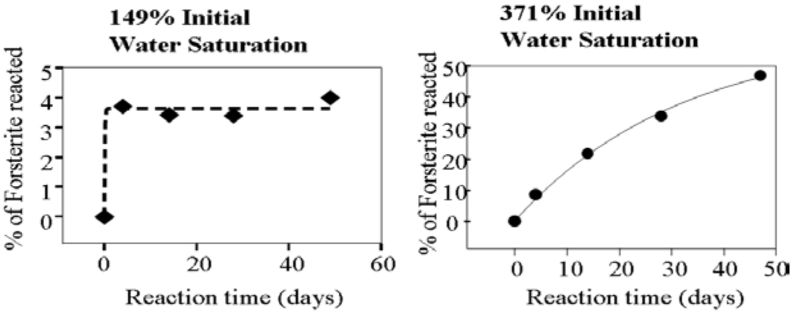

Figure 1. The percentage of Mg_2SiO_4 conversion as a function of reaction time determined from the ^{29}Si SP-MAS spectra. (a) 149 % initial H_2O saturation (b) 371% initial H_2O saturation.

In order to further define the role of interfacial water in forsterite reactivity *in-situ* mid-infrared spectroscopy studies were conducted that examined the dynamics of water film formation on forsterite surfaces with wet $scCO_2$ at 50°C and 180 atm, using water concentrations corresponding to 0%, 55%, 95%, and 136% saturation. Results show a dramatic dependence of reactivity on water concentration and the presence of liquid water on the forsterite particles. At 55% and 95% water saturation, a liquid-like thin water film was detected on the forsterite particles and only 1% of the forsterite transformed. At 136% saturation, where an (excess) liquid water film approximately several nanometers thick condensed on the forsterite, the carbonation reaction proceeded continuously for 24 hr with 10% to 15% transformation. Our collective results suggest constitutive links between water concentration, water film formation, reaction rate and extent, and reaction products in wet $scCO_2$.

During FY10, we also assisted in the development of a new *in situ* optical platform and a unique *in situ* high pressure MAS NMR capability. The *in situ* optical spectroscopic platform integrates a $scCO_2$ generation and manipulation system with optical spectroscopy techniques including UV-visible, IR, Raman and laser fluorescence spectroscopy. Our initial results indicated that IR spectra of H_2O/D_2O in the range from 700 cm-1 to ~ 2900 cm-1 can be used for *in situ* qualitative and quantitative analysis. Molecular simulations of the vibrational spectra were also conducted to help interpret the experimental data. The high pressure MAS NMR capability, consists of a high pressure MAS rotor, a high pressure loading/reaction chamber and a MAS probe. The high pressure MAS rotor has been tested for successfully maintaining $scCO_2$.

SANDIA NATIONAL LABORATORY/ALBUQUERQUE

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Geochemistry of Interfaces: From Surfaces to Interlayers to Clusters

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Co-Is: Louise J. Criscenti, Jeffery A. Greathouse, Kevin Leung, May D. Nyman (SNL)
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Summary:

The mineral-water interface provides the critical setting for many geochemical processes in the environment. The surface properties of the mineral substrate and the modified behavior of water molecules near the interface relative to bulk water, remain difficult to characterize despite the best efforts of modern analytical methods. Although the science of interfacial chemistry has seen significant advances in recent years, there remains a significant gap in our knowledge of structure, reactivity, dynamics, and molecular-level mechanisms of mineral surfaces and interfaces (including the confined interlayers of clay minerals), and nanoscale molecular clusters that are dominated by surfaces comprised of oxygen, hydroxyl, and water ligands.

This project combines theoretical, computational, synthetic, and spectroscopic tasks to examine the nature of complex geochemical interfaces. Specific tasks include the analysis of surface speciation, adsorption phenomena, surface complexation modeling, ion pairing, interlayer structures, parameterization of edge surfaces of clay minerals, and synthesis of molecular clusters as well as the structure and reactivity of their surfaces sites. Theoretical efforts emphasize the use of large-scale molecular dynamics simulations, *ab initio* molecular dynamics, and related density functional theory and classical methods to address structure and thermodynamics of mineral-water systems. A task to develop a second generation classical force field for large-scale simulations of interfacial phenomena in mineral-water systems is also included. A variety of experimental and spectroscopic work complements the theoretical effort. These tasks incorporate nuclear magnetic resonance, X-ray absorption, second harmonic generation, sum frequency generation, infrared and Raman vibrational, small-angle X-ray scattering, and inelastic neutron scattering spectroscopies as well as more conventional characterization methods to understand the key molecular processes and help validate the modeling studies.

Task One: The Nature of the Mineral-Water Interface: A Molecular Simulation and Spectroscopic Investigation

Objectives: Development of computational tools for the accurate simulation of environmental processes, specifically those involving aqueous interactions with layered nanomaterials that are difficult to evaluate using conventional analytical methods. Classical and quantum simulations, along with synchrotron and specialized diffraction methods, are used to evaluate interfacial structure and dynamics of selected oxide, hydroxide, and aluminosilicate systems.

Project Description: In coordination with analytical and spectroscopic methods, we are investigating the atomistic behavior of the mineral-water interface. Specifically, we are examining layered mineral systems which have received special scientific interest and widespread technological application because of their enormous surface area and strong interactions with aqueous phases and solutes. Basal and edge surfaces provide contrasting internal and surface environments that affect mineral reactivity and hydration. We are developing a second-generation energy force field for classical simulations of interfacial phenomena in mineral-water systems. These improvements will aid in the interpretation of vibrational spectra and related spectroscopies, including second harmonic generation which we use to discriminate adsorption of solutes onto basal and edge surfaces of single crystals of muscovite.

Results: Development of bonded force field parameters for edge site species (M-O-H where M = Si, Al, Mg, etc) of layered minerals has been the primary effort for the first year of the project. The preliminary force field development is being done in collaboration with Andrey Kalinichev (Michigan State University and Ecole des Mines de Nantes). Molecular models have been prepared for hydroxylated surfaces of cristobalite, gibbsite, and brucite, and their aqueous interfaces. Average molecular parameters (M-O and O-H bond lengths, M-O-H angle) from classical simulations have been compared with corresponding density functional calculations. New and refined force field parameters will be validated with energy optimization and molecular dynamics simulations of edge sites and incorporated into CLAYFF. We have also continued our combined molecular dynamics simulation and inelastic neutron scattering (INS) experimental study of water vibrational behavior in clay minerals. This task expands our recent analysis of fibrous clays (palygorskite and sepiolite). We have collected INS spectra of montmorillonite and beidellite clays at LANSCE for samples exchanged with various alkali and alkaline earth cations. Results indicate a difference of librational and aluminol behavior for Na-, Cs-, Mg-, and Ba-exchanged samples, especially for the interlayer Mg cation which maintains a strong hydration shell of water molecules and weakly interacts with the clay surface.

Task Two: Ion Pairing at Oxide/Water Interfaces

Objectives: The objectives of this task are to develop an approach for predicting the types of metal surface complexes that form on mineral surfaces by focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models to predict adsorption behavior.

Project Description: We combine the use of several analytical tools including Raman spectroscopy, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, vibrational sum frequency generation (VSFG) spectroscopy, and X-ray absorption spectroscopy (XAS) with classical and *ab initio* molecular dynamics simulation techniques to understand fundamental adsorption processes at the molecular level. In concert with the collection of molecular-level data and modeling, we continue to collect bulk adsorption data and attempt to improve our ability to fit these data with continuum surface complexation models such as the CD-MUSIC model and the TLM. Molecular-level studies provide insight on key variables that may presently be absent in the continuum models. In turn, the failure of continuum models to fit certain types of adsorption data helps us target our molecular-level studies to address the most critical questions.

Results: This year, the SNL team studied the behavior of water on two distinct goethite surfaces using classical and *ab initio* molecular dynamics (MD). If goethite is defined according to the *P*nma space group, then the surfaces studied are the (100) and (101) crystal faces or cleavage planes. These surfaces are the most thoroughly investigated by experiments and modeling. The surfaces are characterized by different numbers and types of surface sites. The (100) surface is characterized by 5-fold Fe atoms, Fe_2O_IH and Fe_3O_{II} surface sites, and the (101) surface has four different types of surface sites including Fe_3O_{II}, Fe_3O_IH, $Fe_2O_{II}H$ and $Fe_1O_{II}H$ where the subscript after Fe indicates how many Fe-O bonds link the Fe atom to the bulk crystal structure, and O_I and O_{II} represent hydroxylated and unhydroxylated oxygen atoms within the goethite structure (Venema et al. 1998). Classical MD simulations show that the first layer of water near the (100) surface is strongly structured due to hydrogen bonding between the water and surface hydroxyl groups. Water layers immediately above the (101) surface are not as well ordered. Atomic density profiles of 0.1M NaCl solutions about the (100) surface compare well with results from Kerisit et al. (2006) who performed comparable simulations with a different force field. On both surfaces, the Na^+ ions are always adsorbed as inner sphere ions and the Cl^- ions form outer sphere complexes. Our next step is to investigate the effect of electrolyte type (NaCl, Na_2SO_4) and concentration on interfacial water structure on both of these surfaces.

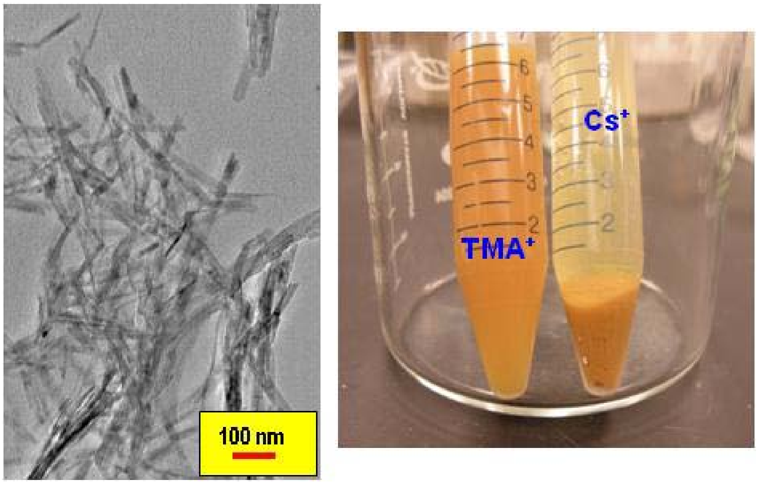
Ab initio MD (AIMD) simulations were also performed to investigate the acid-base behavior of hydroxyl groups on the (101) surface. According to the MUSIC model (Venema et al. 1998), these hydroxyl groups exhibit first and second deprotonation pK_a values ranging from -0.2 to 11.7. AIMD simulations have been applied successfully to predict pK_a values for silica-water interfaces (Leung et al. 2009). We implement the same method to reinvestigate pK_a predictions on goethite. At zero temperature, transferring a proton to form a $Fe_IO_{II}H_2^+/Fe_3O_{II}^-$ neighboring pair from $Fe_IO_{II}H/Fe_3O_{II}H$ only costs 1 kcal/mol (~0.7 pH unit). This suggests that the pK_a of these hydroxyl groups should not differ by the 4 pH units suggested by the MUSIC model. However, AIMD simulations were also performed with added explicit water molecules and several initial configurations with either $Fe_IO_{II}H_2^+/Fe_3O_{II}^-$ or $Fe_IO_{II}H/Fe_3O_{II}H$ neighbors. Within the AIMD simulation time (~10 ps), these two proton configurations do not exchange, suggesting there is a substantial barrier between them. Our future work involves performing AIMD potential-of-mean-force calculations which will enable calculation of the barrier and the free energy difference between the two states, which will readily yield the pK_a difference between the two OH groups.

Task Three: Molecular Clusters: Structure and Reactivity towards Understanding Nanoscale Reactions in Aqueous Geochemistry

Objectives: In this new task on the Sandia Geochemistry BES project, we are focused on the synthesis, characterization, and aqueous reactivity of metal oxide clusters relevant to earth systems. There is a paucity of clusters that fit the definition of "geochemically relevant", and expanding this suite of clusters is in itself is a huge challenge.

Project Description: The geochemical relevance of these clusters means they largely contain metals that are abundant in the geosphere including Fe, Al, Si, Ca, Na, K, Mg; or close chemical analogues of these. The clusters also have water-based ligands including H_2O, OH^-, and O^{2-}, for instance, which renders them water-soluble. Since such metal-oxide clusters are discrete, well-defined, and water-soluble, they are excellent models for experimental and theoretical studies of aqueous-metal-oxide interfaces in the environment. These studies include, for instance, understanding colloidal transport of inorganic, organic and microbial contaminants, adsorption of ionic species (contaminants, common ions, etc.) on surfaces, growth, and dissolution of oxide surfaces at the aqueous interface. We are focusing our synthetic efforts in particular on 1) the aluminum polycations with substitution of heterometals, 2) silicate and aluminosilicate anionic clusters, and 3) ferric clusters.

Results: With aluminum polycations, we are attempting to replace the tetrahedral Al central to the cluster with alternative metals that would alter the cluster aqueous behavior. We have learned that certain heterometals stabilize (Ga) and destabilize (Ge) the cluster and, thus, respectively, improve adherence to anionic contaminants (i.e. phage) and diminish adhesion to anionic contaminants. In ongoing studies, we are attempting to synthesize Zn(II)-centered aluminum polycations to stabilize and diminish aqueous reactivity even further. This affords a new window of ligand reactivity to document; and, furthermore, it should be rendered a potent reagent for water-treatment technologies. For aluminosilicate clusters, we have synthesized two cubane octamers: $[Si_8O_{20}]^{8-}$ and $[Al_4Si_4(OH)_4O_{16}]^{8-}$. We are investigating the reactivity of these clusters in solution. We are currently carrying out experiments with the clusters to form new isolated species with different sizes and geometries, as well as clusters that contain other heterometals. Finally, for ferric-based clusters, we are currently synthesizing and characterizing iron-containing nanoparticles of spinel analogues and goethite. We can control the solubility of these clusters with surface-association of cations (see figure). These nanomaterials are essentially composed of cluster building-blocks; i.e. the ε-Keggin ion in the spinel. Therefore, we are working towards isolating the cluster precursors.



Left**:** TEM image of goethite nanoparticles; Right: surface cations control aggregation and suspension of goethite nanoparticles.

Pore Network Evolution and Chemo-Mechanical Coupling in Mudstones

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Objectives: This project investigates coupled mechanical and chemical dynamics of mudstones. Central questions are – can macroscopic properties like membrane efficiency, permeability and swelling responses be reconciled with nano- and pore-scale observations? How do microscopic changes driven by chemistry influence macroscopic mechanics? How do macroscopic swelling displacements partition at the pore scale? How are mudstone mechanical properties and anisotropy scale-dependent, and influenced by fluid chemistry?

Project Description: This research involves 5 specific tasks – these are (1) Measure influence of fluid chemistry on mudstone pore network evolution via permeability and electro-osmotic (semi-permeable membrane properties) effects; (2) Acoustic measurements of changes in mudstone anisotropy, poro-elastic properties and swelling/contraction associated with pore fluid chemical changes; (3) Measure influence of elevated temperature, phase changes, and compaction/creep on mudstone permeability and membrane efficiency; (4): Quantitative three-dimensional imaging of organic distribution and pore networks in mudstones; and (5): Modeling mudstone geomechanics and pore network evolution. Methods involved in this research include moderate pressure and temperature flow through experiments, large sample flow-through experiments with acoustic emissions, microscopic visualization experiments with a sapphire cell, load frame and laser scanning confocal microscopy (LSCM), dual beam SEM/Focused Ion Beam (FIB) imaging of pore structures, and pore scale modeling.

Results: Task 4 work focused on 3D FIB/SEM image acquisition, analysis and modeling of pore networks from range of depositional facies and geologic ages. Analysis yielded a mudstone pore type classification scheme, pore-scale statistics and flow property compilation. One paper accepted for publication and another submitted. Collaborated with Dr. Navarre-Stichler and colleagues (CSM) on Small-Angle Neutron Scattering pore statistics; results presented at GSA and upcoming AGU meeting. For Task 5, we developed a FIB method for producing micron-scale micropillars for uniaxial compression testing of mudstones and ran tests, comparing these to core-scale triaxial tests for upscaling of elasto-plastic behaviors. We began Lattice Boltzmann (LB) modeling of single phase flow in pore networks, including nested grids. New LB algorthim is under development for variable water properties. Task 2 efforts include acoustic data acquisition code for velocity/anisotropy measurements. Work continues on an algorithm for acoustic tomography, and we ran several experiments testing new software. For Tasks 1-3, we acquired a dedicated creep vessel for flow-through and acoustic measurements. A new dedicated lab space was developed for confocal microscopy and high pressure high temperature flow-through visualization experiments. Additionally, we ran a Theme Session last year and this year at Fall AGU meetings on “Mudstone Multiphysics”.

PART II: OFF-SITE

THE UNIVERSITY OF ALABAMA

Department of Chemistry, Box 870336, Tuscaloosa AL 35487

Grant: DE-FG02-06ER15764

Molecular Basis for Microbial Adhesion and Geochemical Surface Reactions: A Study Across Scales

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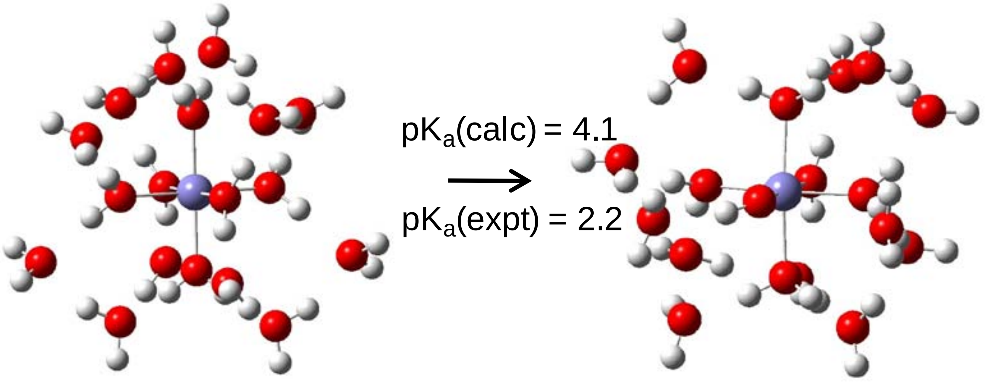
Objectives: The goal is to develop a molecular level description of the interactions of microbial membranes with subsurface materials. We are developing a molecular level view of microbial metal binding, microbial attachment to mineral surfaces, and, eventually, oxidation/reduction reactions (electron transfer) that can occur at these surfaces and are mediated by the bacterial exterior surface.

Project Description: The focus is the interaction of the outer microbial membrane, which is dominated by an exterior lipopolysaccharide (LPS) portion, of *Pseudomonas aeruginosa* with minerals and with solvated ions in the environment. It is a combined computational and experimental project (PNNL) that will enable us to generate new insights into the mechanisms of microbial attachment and validate the molecular models and computational approaches. The theoretical modeling capability will allow the transfer of the necessary fundamental information across the needed series of spatial scales, and will include molecular level simulations of small molecular clusters, molecular dynamics investigations of large biomolecular systems, and predictions of macroscopic geochemical reactions using thermodynamic models. This capability is used to gain a fundamental understanding of the processes controlling the LPS structure and function, metal uptake and transport within the outer microbial surface, and the binding of LPS functional groups to specific sites on mineral surfaces. The ability to predict bacterial attachment and detachment to/ from mineral surfaces will provide information critical for the understanding and modeling of bacterial transport in subsurface systems.

Results: There is significant interest in the acidities of various biological groups and the subsequent ability of the anions to bind cations. The study of gas phase proton transfer reactions provides unique insights into the structures and energetics of such groups. We have extended our work on the acidities of the amino acids to predict those of the glycine and alanine di and tripeptides. Anions were created by deprotonating the parent molecule at specific sites along the backbone, including both the N- and C-termini. Conformational searches of the neutrals and anions were performed with density functional theory with the B3LYP functional. The resulting optimized structures were used as starting guesses for the G3MP2 calculations. The freedom afforded by skeletal bond rotation allowed intramolecular hydrogen bonding to play a key role in stabilizing conformations. The acidities of the backbone C-H and N-H bonds were much stronger than expected due to the formation of enolate anions and show that the protein backbone can be deprotonated. Work is ongoing to calculate the pKa's in aqueous solution using self consistent reaction field approaches.

The pKa's of metal complexes in aqueous solution are critical to understanding how metal ions in nuclear waste aggregate and are transported in the environment. The gas phase acidities of $M^{2+}(H_2O)_n$ clusters for M = Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Fe^{2+}, Zn^{2+}, and Cd^{2+} among others have been predicted using density functional theory, MP2 perturbation theory and coupled cluster CCSD(T) theory with correlation-consistent basis sets. The specific number of attached water molecules were determined by calculations with varying n to determine the optimal $M(H_2O)_n$ structure for each metal. A self-consistent reaction field model using the COSMO parameterization was used to predict the pK_a's in aqueous solution. Good agreement with the experimental pKa is found when the appropriate value of n is used. This enables the correct prediction of the size of the first solvation shell, which provides critical speciation data for the metal ions in solution. A second solvation shell is needed for the prediction of the pK_a of +3 ions and this has been tested for Fe^{3+}.



$[Fe(H_2O)_6(H_2O)_{12}]^{3+}$ $[Fe(H_2O)_5OH(H_2O)_{12}]^{2+}$

ALFRED UNIVERSITY

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Grant: DE-FG-02-10ER16128

Computational and Experimental Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interfaces

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Objectives: The main objective of this joint research effort with Michigan State University is to improve our molecular-scale understanding of the structure, dynamics, and reactivity of geochemically important fluids, fluid-mineral interfaces, and confined fluids using computational modeling and experimental methods sensitive to molecular-scale behavior, principally nuclear magnetic resonance spectroscopy.

Project Description: Molecular scale knowledge of the structure and dynamics of aqueous fluids, how these fluids are affected by mineral surfaces and molecular-scale nano-confinement, and how water molecules and dissolved species interact with mineral surfaces is essential to understanding the fundamental chemistry of a wide range of geochemical processes relevant to energy geoscience, and is one of the most important cross-cutting fundamental research issues in effectively addressing the ***Grand Challenges*** in basic energy sciences. We develop general principles for understanding and predicting these behaviors on length scales from ~0.1 nm to ~10 nm and on time scales from picoseconds to nanoseconds and longer by combining computational studies, performed through the sister grant at Michigan State University, R. James Kirkpatrick P.I., and experimental studies of carefully selected material systems. The specific Alfred University project objectives are to perform a comprehensive molecular scale investigation of the structure and dynamics of amorphous calcium carbonate (ACC) formation and to investigate the structure, dynamics and energetics of Ca^{2+} and Na^{+} exchanged clay minerals using nuclear magnetic resonance (NMR) spectroscopy.

Results: In the first eight months of the current grant, multiple synthetic routes to the hydrous crystalline calcium carbonate polymorphs (monohydrocalcite and ikaite) and hydrous amorphous calcium carbonates were developed, leading to an improved understanding of the poorly defined transformations between these phases and their thermodynamic stabilities. Experiments are currently in progress to further refine our results by characterizing in detail the extent of Mg incorporation, the effects of Mg^{2+} concentration and CO_3^{2-} addition rate on hydrous carbonate formation, the structure of intermediates, and then to generate ^{43}Ca-enriched versions of these materials. A series of supporting periodic DFT calculations using the CASTEP code (Segall et al., 2002, *J. Phys Condens. Matter* **14***:* 2717) show that it is feasible to characterize these materials using natural abundance ^{43}Ca NMR since they exhibit NMR parameters similar to those of many inorganic phases already analyzed in the literature.

We have also characterized the Na^+ structure and dynamics in two sodium-saturated smectite minerals under various levels of hydration using ^{23}Na variable temperature NMR. Our preliminary findings show that 60% by mass D_2O:clay pastes made with Na-saturated hectorite and Na-saturated montmorillonite are dominated by a dynamically averaged signal indicating rapid exchange of sodium in interlayers and on the external surfaces with a bulk liquid-like environment between -80°C and 55°C (Figure 1). There is also evidence of a small but increasing fraction of rigidly bound Na^+ below -20°C as the temperature is decreased, suggesting that some sodium exists as inner-sphere complexes that lack sufficient energy to exchange with the more rapidly moving outer-sphere/bulk liquid sodium population at these temperatures, in agreement with our ^{39}K NMR results published previously (Bowers et al., 2008, *J. Phys. Chem C* **112:**6430-6438). The same sodium-saturated clays equilibrated in a ~45% relative humidity D_2O environment (producing a 1-layer hydrate) exhibit multiple sodium resonances that differ between the two clays and show a clear association with the mineral interlayer and external surfaces. These sites experience different dynamics and a much greater interaction between mobile Na^+ and the mineral surfaces than in the paste samples.

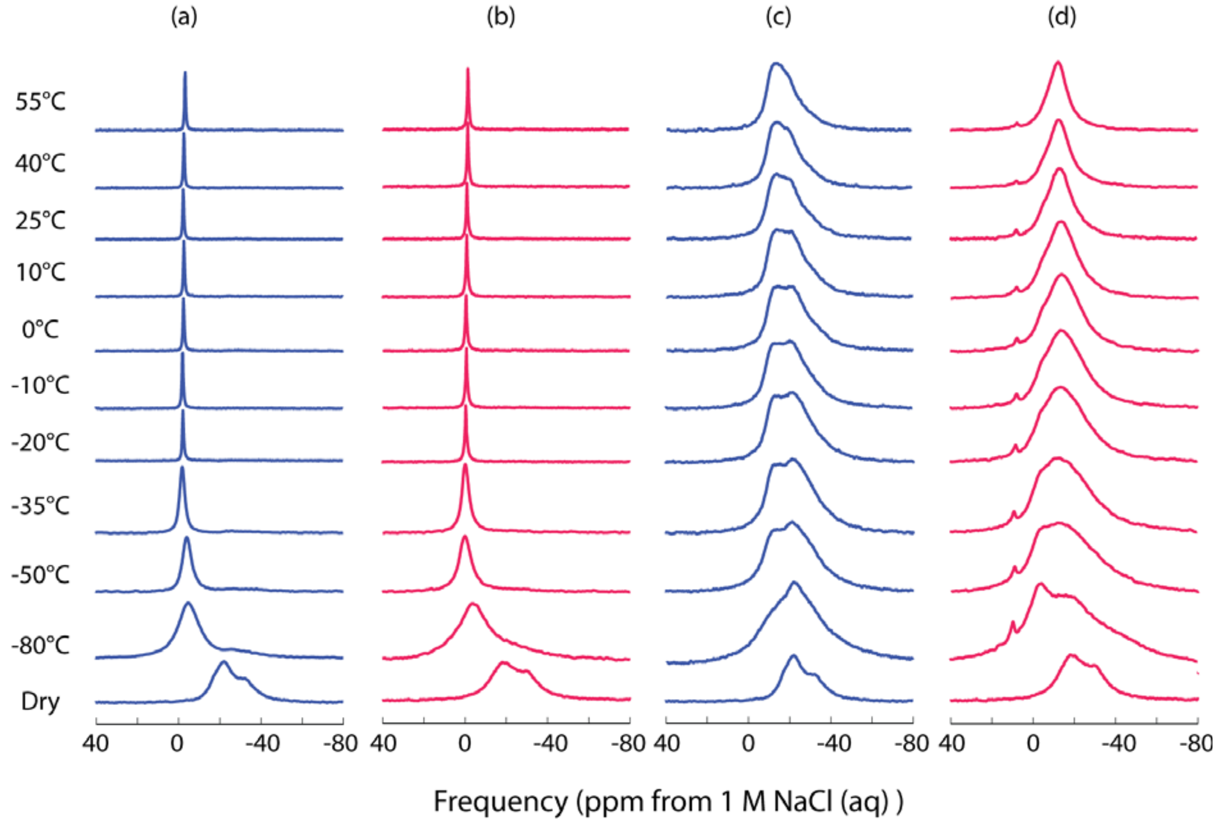

Figure 1. ^{23}Na variable temperature NMR results for the sodium-saturated 1:1.5 by weight hectorite/D_2O paste (a), montmorillonite/D_2O paste (b), ~45% RH equilibrated hectorite (c), and ~45% RH equilibrated montmorillonite (d).

BOSTON UNIVERSITY

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Grant: DE-FG02-95ER14498

Failure of Rock Masses from Nucleation and Growth of Microscopic Defects and Disorder: A Statistical Physics Approach to Understanding the Complex Emergent Dynamics in Near Mean-Field Geological Materials

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Introduction: Our primary objective in this proposal is to employ computational simulations and statistical field theories for nucleation dynamics to 1) Develop statistical physics models including fully interacting defect and damage fields leading to correlated dynamics of systems with long range elastic interactions and near mean field dynamics; 2) Determine the stability phase fields for deformation of these near mean field materials; 3) Compute correlation and response functions as an aid to understanding the emergent failure modes and space-time patterns of defects, damage and fracture for geological materials under load; and 4) Develop methods to compute the lifetime of the material under load (the average time until failure) as well as the physical origin and dynamics of correlated statistical fluctuations and variability.

Rocks are, in fact, an example of complex systems. Observations of rock masses over a range of spatial scales indicate that these failure modes, such as fracture, demonstrate scale invariant deformation, or power law behavior, are characteristic of complex non-linear systems. These are observed in both laboratory settings in acoustic emission experiments, as well as in large scale field settings associated with tectonic faults (Gutenberg-Richter magnitude-frequency relation; Omori relation for aftershocks). One important reason for this behavior is that driven threshold systems of rock masses in which defects interact with long range interactions display near mean field dynamics and ergodic behavior. This result, which was first proposed on the basis of simulations and theory, was subsequently observed in field observations on scales of 100 km to 1000 km. The projects where the lead investigator was at Boston University are summarized below.

Phase Transition Kinetics: The catastrophic failure process associated with damaged materials has the characteristics of a phase transition. Understanding the kinetics of the transition is an essential ingredient in understanding the damage process. Many damaged materials of interest to the DOE have a crystalline order and the kinetics of the phase transitions in these systems is not well understood. We have studied both the nucleation process and the evolution of unstable states in transitions with a spatial symmetry change and elastic forces.

A: Unstable State Evolution: We studied the early time behavior of the evolution of an unstable state with a non-uniform spatial symmetry. The main results are: First: The symmetry of the unstable phase couples with the Fourier modes that are evolving so that the exponentially growing states are not simple Fourier modes as in the standard Cahn-Hilliard-Cook theory but are eigenvectors of an evolution matrix obtained from the Langevin equation that describes the dynamics. Second: The initial phase of evolution is non-linear. This gives way to a stage in which the evolution is described by a linear theory where the exponentially evolving objects are eigenvectors rather than Fourier modes as described above. There is then a third stage in which the Fourier modes are growing exponentially and finally another non-linear evolution. The surprise in this form of evolution is the initial non-linear growth which is contrary to all previous theories of unstable state evolution. We show this to be a consequence of the spatial symmetry change. Briefly, the drift term in the Langevin equation is symmetry preserving. This then implies that any symmetry breaking associated with the change in phase must come from the noise term. Since the noise in systems with elastic forces is reduced the initial evolution involves a symmetry preserving dynamics that is intrinsically non-linear.

B: Nucleation:

a. Nucleation from a metastable liquid near the liquid solid spinodal was shown several years ago by Klein and Leyvraz (KL) to be non-classical. That is, the droplet need not have the symmetry of the stable phase. To the contrary KL showed that the droplet could have a bcc symmetry or consist of stacked parallel planes with a hexagonal in plane symmetry independent of the symmetry of the stable phase. We have recently shown that there is another possible symmetry for these spinodal nucleation droplets: a spherical symmetry and an oscillatory variation of the density in the radial direction. We are now exploring the ramifications of these droplets for the catastrophic fracture process.

b. Effect of Damage on Nucleation. Nucleation of spall for example originates on defects or grain boundaries, i. e. damage. We explored the affect of damage on the nucleation process in simple models. Our conclusions are 1) The presence of damage changes the character of the critical droplet. It appears to be denser and more classical near the spinodal than the droplets that appear in the undamaged system at the same values of the thermodynamic parameters. 2) Even simple damage at low densities affects the nucleation rate so that nucleation is always facilitated even if the damage is vacancies. The reason for this is not known.

C: Models: A focus of our research during the past year has been on defining simple models of damage that are analytically tractable and that can be easily simulated in the computer. We have introduced a new model which is a modified form of a model introduced to study earthquakes. In one limit the model is a fiber bundle model and in another limit it can be used to study models in which the stress is tensorial. We have used simulations and scaling arguments to obtain the following results. 1) Equilibrium methods that can be used to describe the model without damage cannot be used once damage is introduced. We have shown that the introduction of damage destroys ergodicity. 2) The nature of catastrophic failure depends on the range of stress transfer R. If R is large catastrophic failure appears to be nucleation or a classical crack. Where as, if R is small catastrophic failure appears to be fractal in nature. Measurement of the fractal dimension of the percolation cluster associated with the catastrophic failure (non-classical crack) indicates that the associated percolation problem is in a different universality class than non-meanfield random percolation. 3) For large R with no damage the model runs near the meanfield spinodal which is responsible for the Gutenburg Richter (GR) scaling. As damage is introduced the model runs further from the spinodal and the data appears to be fit by a power law with an exponential cutoff. However, if we sum the data for models with all degrees of the damage we obtain excellent scaling with a new exponent. This is similar to what one sees in real earthquake fault systems and would seem to indicate that fault damage plays an essential role in GR scaling. We have also seen in the models that increased damage increases the ability to forecast catastrophic events in the models. We are investigating the relation of the model physics to that of real earthquake faults.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Division of Geological and Planetary Sciences, Pasadena CA 91125

Grant: DE-FG02-06ER15773

Experimental Petrology and Geochemistry of Volatile-Bearing Silicate Melts

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Objectives: The focus of this project is the application of experimental petrology and geochemistry to problems in petrology and geochemistry, with particular emphasis on understanding the behavior and properties of the principal volatile components, H_2O and CO_2, and trace elements such as P in magmatic systems.

Project Description: The goal of Part 1 is the definitive determination of the diffusion coefficient for water ($D_{\mathrm{H_2O}}$) in basaltic, andesitic, and rhyolitic melts in order to understand its compositional dependence, especially with respect to water content. Profiles of water concentration in hydration and diffusion couple experiments have been analyzed by Fourier transform infrared spectroscopy and secondary ion mass spectrometry. $D_{\mathrm{H_2O}}$ values were determined from the analyzed profiles using both direct calculations (i.e., Boltzmann-Matano methods) and models assuming specific relationships between diffusivity and water content. Part 2 is the study of the zonation of P and other elements in olivines. Using electron microprobe, we have characterized the complex (and often oscillatory) phosphorus zoning in natural olivines from basalts, andesites, dacites, komatiites, and igneous meteorites. We generated similar P, Al, and Cr zoning in olivines grown experimentally at 1 atm with cooling rates of 1-30°C/hr in a synthetic Hawaiian basalt. We have also begun measuring Al and P chemical diffusivities in olivine.

Results: *Part 1:* We have concentrated our experimental work this year on understanding the dependence of water diffusivity ($D_{\mathrm{H_2O}}$) on total water concentration ($C_{\mathrm{H_2O}}$) from experiments with very low water concentrations. This study follows from the results of our experiments on diffusion experiments with very small gradients in $C_{\mathrm{H_2O}}$. These are hydration and couple experiments with the extremes of the water concentrations differing by less than ~1 wt. %. By combining the results from multiple experiments with different $C_{\mathrm{H_2O}}$, we are building up the $D_{\mathrm{H_2O}}$ - $C_{\mathrm{H_2O}}$ using direct calculations (including modified Boltzmann-Matano techniques) from the diffusion profiles. When we compare these results to functional relationships between $D_{\mathrm{H_2O}}$ and $C_{\mathrm{H_2O}}$ (including $D_{\mathrm{H_2O}}$ proportional to $C_{\mathrm{H_2O}}$ and $D_{\mathrm{H_2O}}$ an exponential function of $C_{\mathrm{H_2O}}$), and a speciation model in which $D_{\mathrm{H_2O}_{\mathrm{molecules}}}$ is constant and hydroxyl groups are treated as being immobile, we find that results from our experiments (with $C_{\mathrm{H_2O}}$ ranging from 0.2-5.9 wt.% for haplobasalt and 0.2-3.8 wt.% for haploandesite) cannot differentiate among these three relationships. However, these relationships diverge at very low and high $C_{\mathrm{H_2O}}$. Therefore we are now focusing efforts on the very low $C_{\mathrm{H_2O}}$ region, because knowing these diffusivities is important for understanding the evolution of volatiles during fire fountaining in Hawaii and on the moon and for inferring initial $C_{\mathrm{H_2O}}$ prior to eruption. Motivated by the work of Saal et al. (2008, Nature 454, 192-195) we are presently working on measuring the diffusion of water in a lunar glass composition at low total water contents (several 100 to <100 ppm H_2O) in order to confirm this behavior for this important natural composition. At these low total H_2O contents, the dominant dissolved species in a silicate melt is OH and not molecular H_2O, as is the case when total C_{H_2O} reaches weight percent levels. Thus D_{H_2O} should be much lower than at high total C_{H_2O} since $D_{OH} << D_{H_2O_{molecules}}$. Our experimental approach is quite simple: we made a synthetic, alkali-free, lunar yellow glass composition from oxides and carbonates and have been equilibrating 60-80 mg samples suspended from Re wire loops in a Deltech gas mixing furnace with a H_2-CO_2 gas mix at iron-wüstite (IW)+1. At 1350°C (~10°C above the liquidus temperature of our composition) and IW+1, the P_{H_2O} of the gas is ~0.3 atm. In agreement with water-solubility models, we have found ~300 ppm water dissolved in the melt. The key to our experimental approach is that by changing the gas mix from H_2-CO_2 to CO-CO_2 (all at IW+1) we can change the P_{H_2O} from ~0.3 to near zero atmospheres. The results are surprising. During dehydration experiments, the experimental runs are always homogeneous in water content, with lower C_{H_2O} than the starting material but with no gradient as would be expected from simple chemical diffusion. In contrast, hydration does produce diffusion profiles, but this process is much more rapid than dehydration, with hydration producing homogeneity across 3-4 mm diameter samples in less than 10 minutes. In order to evaluate whether H_2, produced by interaction with Fe in the synthetic lunar melts, might be affecting diffusion, we are running similar experiments in an analogous haplobasalt composition. However, the results in the Fe-bearing composition indicate that the problem of diffusive water loss from lunar basalts during eruption is more complex than has been considered thus far.

Part 2: Our 1-atm experimental attempts to produce olivine diffusion couples with relatively high and low concentrations of P, Cr, and Al have hit a fortuitous snag. Over 300-400 hours, an olivine sphere placed at the bottom of the silicate melt bead (hanging on a Fe-Pt wire loop), evolves from the original sphere into a watch-glass form. This transformation is reproducible and presumably reflects very small (<1°C) thermal gradients over the ~3–4 mm height of the silicate bead. Although such charges cannot be used for diffusion experiments, the extremely slow dissolution/re-precipitation process suggests that the runs have closely approached equilibrium and thus, given the relatively large size of the re-crystallized olivine, we can obtain equilibrium distribution coefficients for a wide suite of highly incompatible elements (the silicate melt is the USGS rock standard BHVO-2 plus dissolved olivine). We are currently working to analyze these experiments using the Caltech Cameca 7f ion microprobe. We continue to perform 1-atm controlled cooling rate experiments on a Hawaiian basalt in order to develop a better understanding of substitution mechanisms for minor elements in olivine and to explore the conditions under which oscillatory zoning of P and other elements can be produced. We have collected a fairly complete suite of X-ray maps (P, Cr, Al) of olivine microphenocrysts from our Kilauea Iki lava lake samples. All of the olivines show P bands except one sample, also unique in that the olivine contains abundant plagioclase inclusions. P-associated zoning of Cr and Al appears to be absent for 150-181 and 275-295 ft samples from the drill hole and generally present at intermediate depths, suggesting that factors in addition to time-temperature history may influence the evolution of the zoning. We have also obtained extensive data on olivines from Gorgona komatiites. Al-Cr plots reveal strong correlations suggesting substitution in a 2:1 ratio. In addition, we recently discovered olivine-hosted melt inclusions from Siqueros that are zoned in major and minor elements due to late-stage growth of olivine. We intend to invert these profiles to constrain the thermal histories of these rapidly quenched samples.

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Extracting Geological Stresses and Anisotropy from Rocks by Means of Neutron and Synchrotron X-ray Diffraction

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Objectives: A quantification of structural and textural characteristics of sedimentary rocks is essential in the context of hydrocarbon reservoirs and carbon sequestration. X-ray and neutron scattering data, obtained at National Laboratories, are the basis for developing comprehensive models, relating elastic properties, especially their anisotropy, to microstructures.

Project Description: A basic challenge in the earth sciences is to develop comprehensive models that describe stress-induced effects on rocks of varying composition and microstructures. Such models are available for igneous and metamorphic rocks and make it possible to predict rock properties at depth. For sedimentary rocks, microstructural information is much more limited and thus models more qualitative and empirical. This project uses observations of microstructures and textures in rocks, obtained by time-of-flight neutron and synchrotron X-ray scattering and electron microscopy to understand formation processes and to establish models that link the internal microstructure to macroscopic physical properties. The focus is on shales which comprise over 75% of rocks in sedimentary basins. Sedimentary shales are compared with fault gouge of similar composition (e.g. from the SAFOD project) and metamorphic schists, where phyllosilicate alignment was produced by recrystallization.

Results: Macroscopic elastic properties that can be measured with ultrasound techniques depend on mineral composition, microstructure, pore structure and mineral alignment. The latter is significant for elastic anisotropy which is high in rocks containing phyllosilicates such as schists and shales. Diffraction methods, particularly neutron scattering (at LANL), synchrotron X-rays (at APS and ALS) and electron microscopy have been developed. For the complex data analysis the Rietveld method MAUD has been refined to provide information on phase proportions, preferred orientation and grain size for shales with up to 10 components. Figure 1a shows an X-ray diffraction spectrum and the corresponding least squares fit.

An important ingredient is the 3D microstructure that can be captured with tomography. Also here synchrotron X-rays are advantageous and we are now reaching a resolution of <1μm for microstructures in shales and particularly porosity by using the most advanced experimental and analytical procedures at SLS, APS and ALS. The microtomography will be extended into the nano scale where transmission electron microscopy documented considerable porosity with 5-20nm sizes.

An interpretation of macroscopic anisotropy requires information single crystal elastic properties of clay minerals and we have used first principles calculations to determine stiffness coefficients for illite-smectite and kaolinite. Currently we are developing a comprehensive model to predict properties of aggregates and then compare results with macroscopic velocity measurements on the same samples.

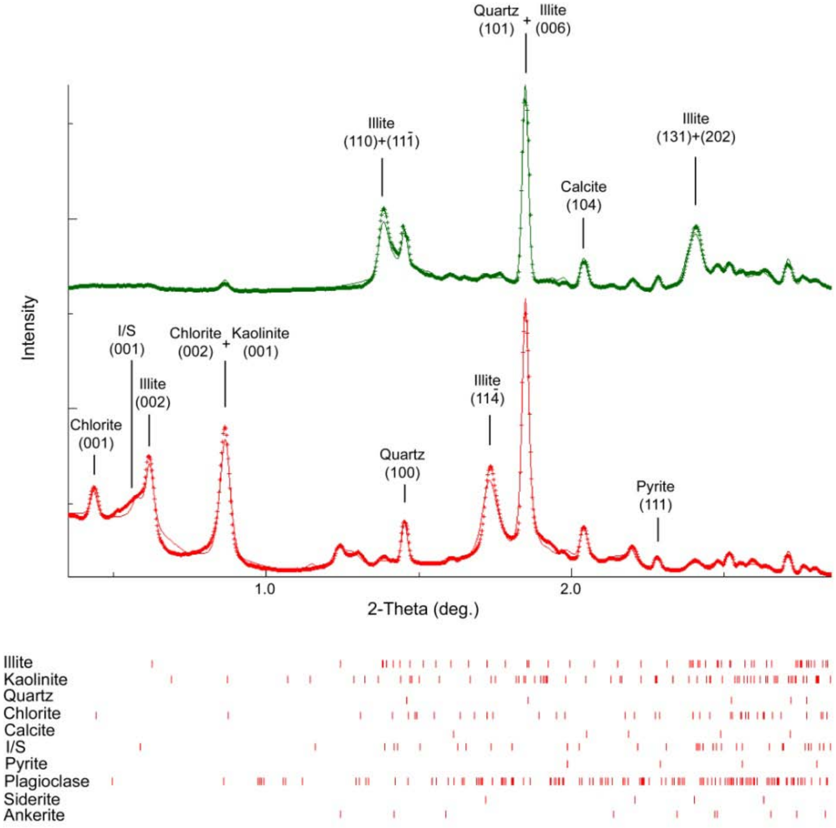

Figure 1. Two XRD diffraction spectra of shale composed of 10 phases perpendicular (top) and parallel (bottom) to the bedding. Intensity differences are due to preferred orientation. Dots are measured values and line is Rietveld fit.

UNIVERSITY OF CALIFORNIA, DAVIS
Department of Chemistry, Department of Geology, Davis CA 95616

Adding Reactivity to Structure---Oxygen-Isotope Exchanges at Structural Sites in Nanometer-Size Aqueous Clusters

Grant: DE-FG-02-05ER15693

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Objectives: Our goal is to establish reliable methods of estimating reactive properties of structural oxygens in metal-oxide materials water.

Project Overview: Geochemically important reactions often involve a bonded atom or functional group being replaced with another. We probe these reactions at the molecular scale, in both experiment and simulation, in order to establish reliable methods for predicting rates that cannot be experimentally studied. Much research in the last period emphasized materials that are both geochemically interesting and also have applications at water-splitting catalysts for energy production.

Results: The structures on which we worked included several sets of oxide molecules of nanometer-size scale, but included a brucite-like cobalt-oxide cluster that is among the most exciting materials for splitting water into oxygen and hydrogen. We showed via Electron Paramagnetic Resonance (EPR) that the structure reached Co(IV) in the catalytic cycle; this result was highlighted in *Chemistry and Engineering News* and other general science venues. Similarly, the result of collaboration with Dr. May Nyman (Sandia National Laboratory) on aluminum-hydroxide clusters, or Keggin molecules, was also highlighted in *Chemistry and Engineering News*. In this work, a substituted version of one of the aluminum cations was shown to be particularly effective in water purification and had antibiotic features. Additional results on the niobate molecules were chosen as the cover article for the *J. Amer. Chem. Soc*, and we were invited to write a review article reprising all of this work for *Nature Materials (see http://chemgroups.ucdavis.edu/~casey/)*.

Much of our time was dedicated to study of a series of niobate molecules with single-atom substitutions. With these, we probed the extents to which the functional groups in isotope-exchange reactions could be treated as isolates. We found that entire cluster dynamics are important at the molecular scale; pH dependencies, for example, could be inverted completely with a single-atom substitution of Ti(IV) for Nb(V). These results have implications for geochemical modeling of reactions at oxide mineral interfaces where the functional groups are treated as independent of one another and a small molecular fragment is used to represent a much larger structure. An example would be the use of a silicate dimer to represent the quartz surface. Although it is likely that structural sensitivity becomes muted as the molecules grow beyond the ~40 atom clusters we studied, clusters of nanometer size are exactly at the same scale used in calculations of electronic structures and transition states using electronic-structure methods.

That the rates of isotopic exchange are so sensitive to details of the structure was previously unappreciated and important.

We also worked to examine the kinetics of reactions in brucite-like layers, which are key building blocks for clays [Figure]. Geochemists have long speculated about the reactivity of clay edges such as these brucite-like moieties shown below in talc. We have adapted methods to study these brucite-like structures as they are made stable in solution by large tungstate ligands. The result is a large anion that has four Co(II) arrayed in edge-shared polyhedra, but that exists stably in solution so that we can apply the methods of NMR to understand the reactivities. These molecules are well known in the polyoxometalate community as oxidation catalysts but are interesting to us because of their similarity to brucitic moieties, and also because we can substitution cleanly other metals into the sandwich. We are currently looking at the effect on ligand-exchange rates at the bound waters of a Co(II) tetrameric sandwich, and plan to make other substitions (e.g., Ni(II)) for one of the metals and to oxidize the Co(II) to higher valence states. The effects on rates of ligand exchanges of these simple substitutions are completely unknown.

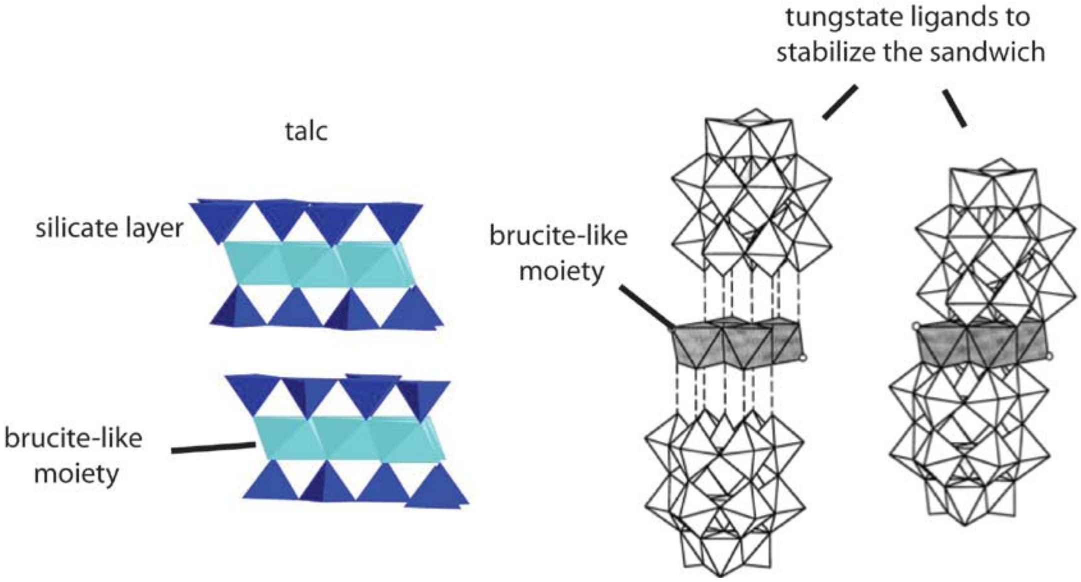

Figure: Elementary reactions such as ligand exchanges affecting minerals can be characterized by isolating the key structures using ligands that make them soluble in water. The mineral talc, for example, has a brucite-like layer **(left)** that is thought to control the reactivities of the functional groups at clay edges. The brucite-like structures are difficult to study in minerals but the key feature can be made stable by bonding it to two large tungstate anions (**right**) that allow detailed ^{17}O-NMR solution spectroscopy. We unexpectedly found that the rates of ligand exchanges at the key bound waters are very similar to the simple monomer ion, which makes simulation easy.

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Grant: DE-FG02-97ER14749

Thermodynamics of Minerals Stable Near the Earth's Surface

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Collaborator: Peter A. Rock (Thermochemistry Laboratory, UC Davis)

Objectives: Using specialized calorimetric techniques, we obtain thermochemical data for bulk and nanoscale minerals and apply the findings to geochemical problems in the Earth‘s critical zone.

Project Description: Minerals at or near the Earth's surface have complexity of structure, metastability, hydration, and variable crystallinity. They are carriers of and sinks for pollutants. This project measures, systematizes and interprets the thermodynamic properties of a variety of complex mineral phases using oxide melt solution calorimetry and related techniques. Systems currently under study include hydrated sulfates, iron oxyhydroxides, hydrotalcites, other phases related to acid mine drainage, phosphates, arsenates, and heavy metal containing minerals.

Results: We have been focusing on the oxidation-reduction energetics of iron oxides at the nanoscale and on the energetics of iron-containing spinel solid solutions. Surface energy alters redox equilibria and phase stability of transition metal oxide nanoparticles. Using extensive calorimetric data on surface energies in the cobalt - oxygen system and additional data in the iron - oxygen, manganese - oxygen, and nickel - oxygen systems, we present evidence that spinels (M_3O_4) commonly have lower surface energies than metals (M), rocksalt oxides (MO), and trivalent oxides (M_2O_3) of the same metal. Thus, the contraction of the stability field of the divalent oxide and expansion of the spinel field appear to be general phenomena. Using tabulated thermodynamic data for bulk phases to calculate redox phase equilibria at the nanoscale can lead to errors of several orders of magnitude in oxygen fugacity and of 100 - 200 K in temperature. Using our new values for surface energies and thermodynamic data for the bulk Fe - O system, the phase equilibria involving metal Fe, wustite $Fe_{0.947}O$, magnetite Fe_3O_4 and hematite α-Fe_2O_3 were computed and are shown in Fig. 1. The redox chemistry is altered drastically at the nanoscale, with the elimination of $Fe_{0.947}O$ as a stable phase, substituted by direct equilibrium between Fe and Fe_3O_4. $Fe_{0.947}O$ has a low temperature stability limit of 850 K relative to Fe and Fe_3O_4 in the bulk. At the nanoscale, this temperature greatly increases. The calculations imply that $Fe_{0.947}O$ nanoparticles are unlikely to form below 100 nm in size, as the lowest temperature, at which they would be stable with respect to Fe_3O_4 + Fe, about 1000 K, is high enough that coarsening would be rapid. Particles below about 16 nm in diameter would not be stable up to the melting point of bulk $Fe_{0.947}O$. Redox and dissolution reactions of iron and manganese oxides provide energy sources for microbial communities. For example, Fe (II)-rich mineral dissolution is usually accompanied by oxidation, which supports Fe-oxidizing microorganisms. Shifts in thermodynamics at the nanoscale will change the free energy of such reactions. It is conceivable that organisms tailor particle size to optimize both the kinetics and the free energy change available to them. It is also possible that nanoparticle redox reactions, with energetics different from the bulk, may have played a role in chemical processes leading to abiotic organic synthesis and the origin of life on the early Earth. Other ongoing work includes calorimetric studies of magnetite - maghemite spinel solid solutions, manganese oxides to separate the thermodynamic effects of surface energy, polymorphism, and oxidation-reduction, and calcium phosphates and related minerals.

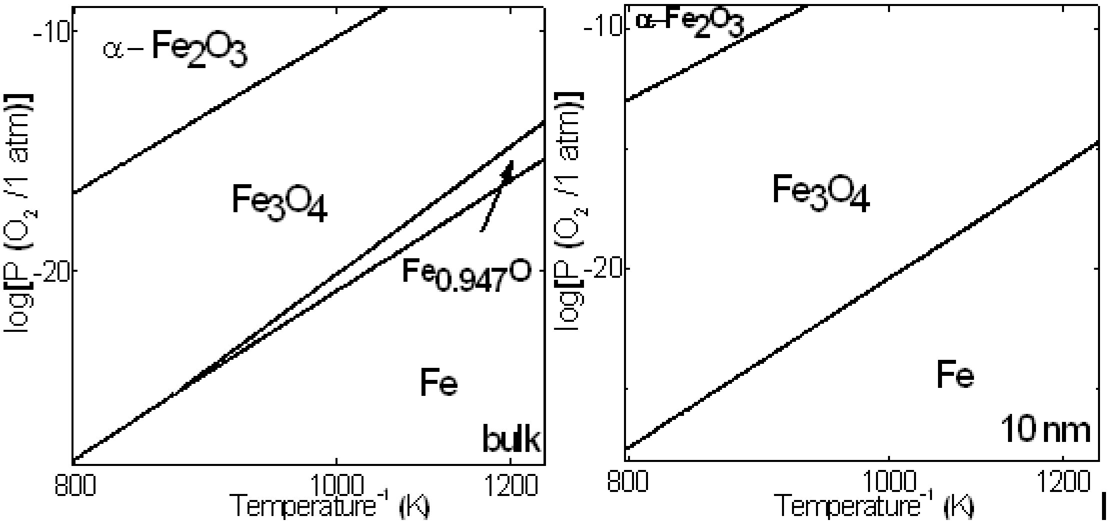

Figure **1:** Calculated phase diagrams for the iron-oxygen system.
(left) Fe-O (bulk); (right) Fe-O (anhydrous 10 nm particles).

UNIVERSITY OF CALIFORNIA, DAVIS

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Collaborative Research: Failure of Rock Masses from Nucleation and Growth of Microscopic Defects and Disorder

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Objectives: To employ computational simulations and statistical field theories for nucleation dynamics to 1) Develop statistical physics models including fully interacting defect and damage fields leading to correlated dynamics of systems with long range elastic interactions and near mean field dynamics; 2) Determine the stability phase fields for deformation of these near mean field materials; 3) Compute correlation and response functions as an aid to understanding the emergent failure modes and space-time patterns of defects, damage and fracture for geological materials under load; and 4) Develop methods to compute the lifetime of the material under load (the average time until failure) as well as the physical origin and dynamics of correlated statistical fluctuations and variability.

Project Description: Storage of nuclear waste, oil recovery and earthquakes are examples of how the structure and failure of rock masses affect processes of interest to the DOE. Each of these processes involves the multi-scale physics of geological materials at shallow depths. Observations of rock masses over a range of spatial scales indicate that the failure modes of these systems, such as fracture, demonstrate scale invariant deformation, or power law behavior, characteristic of complex non-linear systems. These are observed in both laboratory settings in acoustic emission experiments, as well as in large scale field settings associated with tectonic faults (Gutenberg-Richter magnitude-frequency relation; Omori relation for aftershocks). One important reason for this behavior is that driven threshold systems of rock masses in which defects interact with long range interactions display near mean field dynamics and ergodic behavior. This result, which was first proposed on the basis of simulations and theory, was subsequently observed in field observations on the tectonic scale.

Results: In this year's research, we have studied the physics of progressive material damage under load using two models that incorporate both failure thresholds and load sharing. Models of this class include fiber bundle models, two of which we have studied this year. In both models, external loads are applied to a load plate to which each of the fibers is attached. Fully interacting fields of defects and damage are generally not included in most current models for material deformation, however our models include such effects.

In the first problem, the *Time to Failure* model for damage involves the idea that fibers or materials under stress will weaken and fail under any load, however small. One constructs a lattice (d = 2) of side length L in which n_0 cohesive sites or fibers interact within some range R, so that the number of fibers with which each fiber interacts is $(2r+1)^2$ -1. The fibers can be considered to be attached to plates at their ends. A stress $\sigma = F/n_0$ is applied to the end plates and consequently the fibers experience a load. The force F is held constant until failure of the entire grid occurs. This is a problem with a *constant quench depth*.

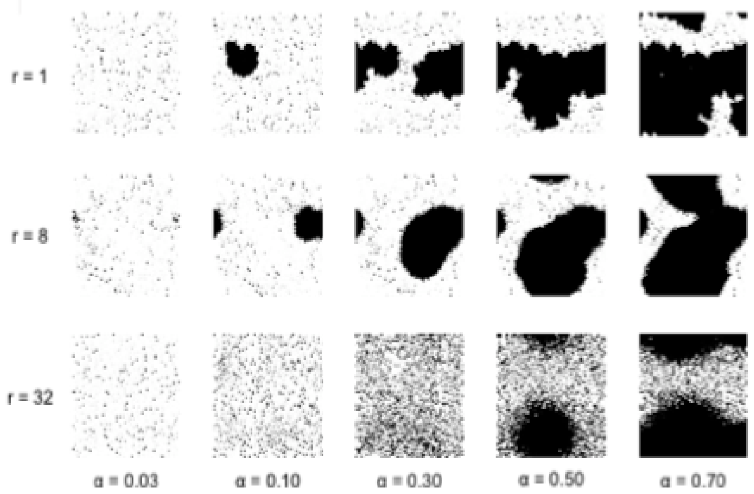

Figure 1. Accumulation of damage. Broken fibers in black.

To determine the time of failure, it is often assumed that the rate of failure is given by Poisson statistics. As the load increases, the damage also accumulates through the action of a hazard rate with exponent ρ. The damage $\alpha(t)$ evolves according to a Langevin equation. Under these equations, it can be shown that for any applied force F, damage will accumulate and the system must inevitably fail macroscopically. The value of the exponent ρ determines a number of properties of the failure mode. Examples of the accumulation of damage during the failure process are shown in figure 1 for various ranges of interaction r.

The second problem is the *Weibull Strength* model, which has a different dynamics. Physically, we again work with cohesive elements (“fibers”) each of which has a distinct failure strength that is chosen from a Weibull distribution of strengths. Elements again interact throughout a range of stress transfer or interaction R, and a damage variable is defined as before.

The dynamics of this problem is enabled by raising the stress σ until it equals the strength of the weakest fiber. This fiber is allowed to fail, its stress is redistributed within the range of stress transfer, and the process is repeated. In this problem, a constant quench rate is assumed, that is, the load increases linearly with time. The process is continued until catastrophic failure of the entire lattice results. A damage variable is defined in the same way as previously. We find that this model captures a variety of simple behaviors in damage and fiber bundle type models, in particular, the general characteristics of the time to failure as observed in laboratory experiments.

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The Impact of Carbonate on Surface Protonation, Electron Transfer and Crystallization Reactions in Iron Oxide Nanoparticles and Colloids

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Co-I: Jean-François Boily, Pacific Northwest National Laboratory

Objectives: This project addresses key issues of importance in the geochemical behavior of iron oxides and in the geochemical cycling of carbon and iron.

Project Description: We are studying the influence of carbonate on electron transfer reactions, solid phase transformations, and the binding of carbonate to reactive sites on the edges of iron-based particles. The emphasis on carbonate arises because it is widely present in the natural environment, is known to bind strongly to oxide surfaces, is reactive on the time scales of interest, and has a speciation driven by acid-base reactions. The geochemical behavior of carbonate strongly influences global climate change and CO_2 sequestration technologies. Our goal is to answer key questions with regards to specific site binding, electron transfer reactions, and crystallization reactions of iron oxides that impact both the geochemical cycling of iron and CO_2 species. Carbon dioxide has a substantial impact on the environment due to the combustion of fossil fuels. A consensus has emerged that increasing levels of CO_2 in the atmosphere from anthropogenic sources correlate with higher global temperatures. A key constraint on atmospheric CO_2 is the solubility of CO_2 in the oceans. A specific focus of the work is the development of a molecular level description of carbonate chemistry in solution. This work is also needed for the development of reliable models for the geological sequestration of CO_2.

Results: In addition to the isotopic composition of carbonate trapped in goethite, another key climate proxy is based on the isotopic composition of trace amounts of boron trapped in calcite growing in seawater. Effective use of this proxy requires knowledge of the equilibrium constant for boron isotope exchange between boric acid and borate ion in seawater. Recent computational studies had cast some doubt on the early empirical value of this equilibrium constant. It was subsequently shown, by our *ab initio* molecular dynamics simulations, that the vibrational spectrum of borate had been improperly assigned, leading to an incorrect force field, and erroneous prediction of the equilibrium constant. Experimental values for this equilibrium constant are now available, however, it is clear that computational studies will be useful for computing fractionation factors that are not yet known experimentally, such as, for example the $^{10}B/^{11}B$ fractionation factor between aqueous species and boron trapped in calcite. Previous computational studies of the aqueous fractionation factor had been done at a relatively low level of theory, so we wanted to ascertain how the predicted fractionation factor changed as a function of the DFT exchange-correlation functional, the representation of the aqueous solvent, the size of the basis set used to represent the one-electron space. The results of our calculations are summarized in Fig. 1 below:

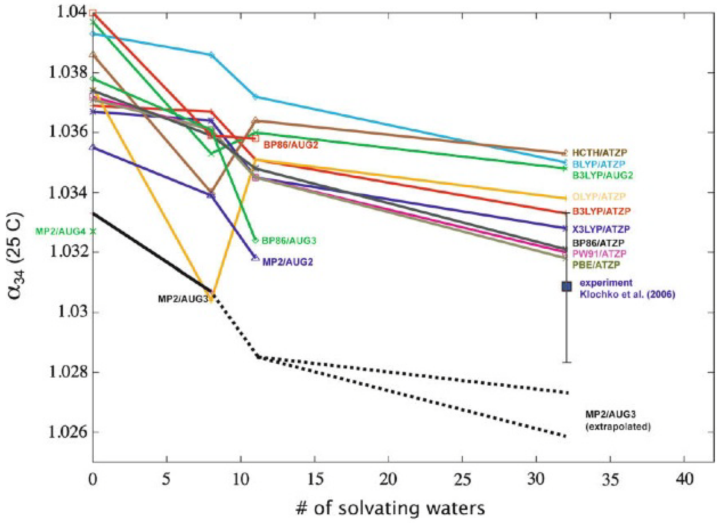

Fig. 1. Predicted α_{34} as a function of the number of solvating waters for the DFT and MP2 calculations. Experimental values are taken from Klochko et al. (2006) (where error estimates are given as two standard deviations). The entries at 11 and 8 involve the borate $n = 11$ and $n = 8$ clusters, both reacted with the $n = 6$ cluster for boric acid. Dashed lines represent extrapolated values for MP2/aug-cc-pVTZ. The upper dashed line represents extrapolation using the lowest drop in α_{34} between the $n = 11$ and $n = 32$ clusters (OLYP). The lower dashed line is based on the largest drop (BP86).

Through a series of DFT and MP2 calculations on hydrated boric acid and borate clusters, $B(OH)_3 \cdot nH_2O$ (n = 0, 6, 32), and $B(OH)_4 \cdot nH_2O$ (n = 0, 8, 11, 32), we provide an extrapolated value of the equilibrium constant a34 for the isotope exchange reaction,

$$^{10}B(OH)_3(aq) + {}^{11}B(OH)_4\ (aq) = {}^{10}B(OH)_3(aq) + {}^{11}B(OH)_4\ (aq).$$

The predicted value of of the equilibrium constant, expected to be close to the MP2 complete basis set limit, is 1.026–1.028. We find that DFT methods overestimate the equilibrium constant by about 10-15 percent relative to MP2, although, if a small basis set is used, the DFT methods artifically give equilibrium constants close to the MP2 predictions. Our calculations strongly suggest that improving the accuracy of the estimates provided here would require calculations at the MP2/aug-cc-pVTZ level for on the order of 10 uncorrelated conformations of $B(OH)_3 \cdot 32H_2O$ and $B(OH)_4 \cdot 32H_2O^-$. Until such calculations become possible, DFT calculations on large 32-water boric acid and borate clusters at the aug-cc-pVTZ level would allow a more thorough evaluation of the extrapolation procedure employed here.

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Multiphase Fluid Flow in Deformable Variable-Aperture Fractures

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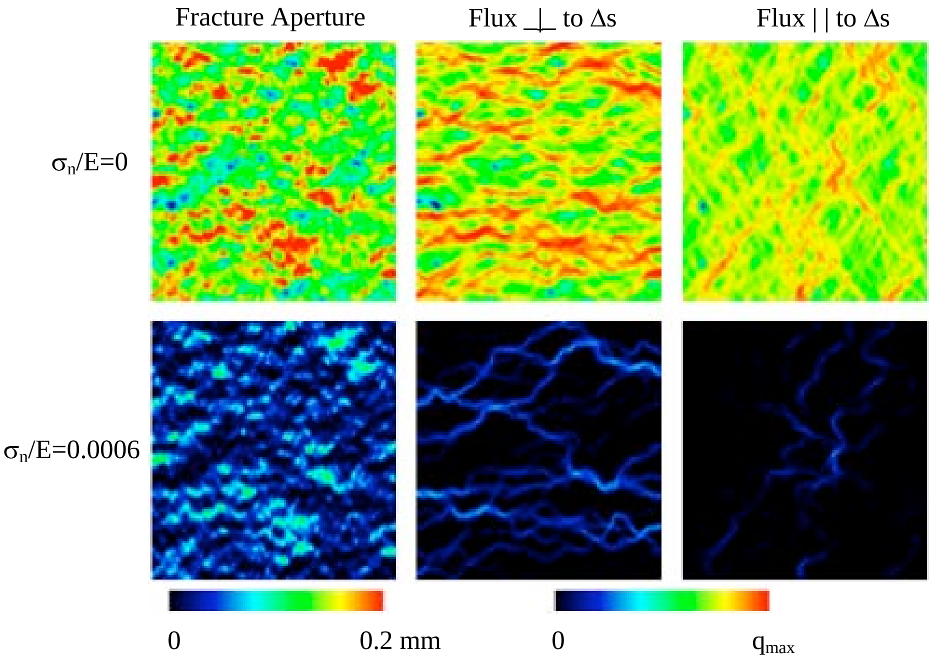
Objective: The objective of this project is to develop a quantitative understanding of the mechanisms that control two-phase fluid flow in variable aperture fractures under conditions where physical and/or chemical processes deform fracture apertures over time.

Project Description: We are integrating systematic laboratory experimentation and fracture-scale computational modeling to clarify the interaction of different permeability-altering mechanisms. Experiments utilize an experimental apparatus that allows application of a steady confining stress to transparent analog fractures while simultaneously quantifying changes in fracture aperture and fluid phase distribution within the fracture. This allows direct, nondestructive measurement of fracture apertures and fluid phase distribution during experiments. Results from systematic experiments will support the development of mechanistic computational models that explicitly couple mechanical deformation, two-phase flow, and chemical alteration within a single variable aperture fracture. The resulting model will provide a tool for evaluating the relative importance of the different processes on the alteration of fracture transport properties.

Results: Two experimental campaigns have been carried out to date: 1) saturated fractures subjected to a constant normal stress and flow of a chemically under-saturated fluid (i.e. net dissolution) and 2) partially saturated fractures subjected to flow of a chemically under-saturated fluid while the fracture surfaces were maintained at a fixed displacement. In the past year, efforts have focused on developing mechanistic models to simulate these potentially coupled processes.

An interesting observation from experiments in fractures subjected to a constant confining stress was that dissolution of fracture surfaces led to the weakening of contacting asperities and cyclic inelastic collapse causing closure of the fracture. We have modified a micromechanical model of elastic deformation of contacting fracture surfaces to include irreversible damage when local stresses exceed the strength of individual asperities. Results from the new model compare favorably with the limited available experimental measurements that show irreversible closure of fractures subjected to cyclic loading cycles.

A second effort involved using the elastic micromechanic deformation model to complete a parametric study of the relationship between applied normal stress and transmissivity in fractures consisting of two contacting self-affine surfaces. Surfaces with different Hurst exponents (H) were offset laterally through a sequence of steps (Δs) corresponding to small shear displacements of the surfaces. Results support previous observations that shear displacement of well-mated fractal surfaces leads to transmissivity anisotropy, with larger transmissivity perpendicular to the offset direction. In addition, our results show the importance of normal stress on quantifying both decreases in fracture transmissivity and the potential for more than an order of magnitude change in the anisotropy ratio (_|_b_{eff}^3 / | | b_{eff}^3) at large applied normal stresses.



Fracture aperture for a fracture created by mating two identical self-affine surfaces with H=0.8, a lateral offset of 3.2 mm and a Young's modulus (E) of 60 GPa. Flux fields calculated perpendicular (_|_) and parallel (| |) to the offset direction. In addition to a significant reduction in flow at larger confining stress (σ_n), it is clear from the flux fields that flow parallel to the offset direction is much less than flow perpendicular to the offset direction.

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Grant: DE-FG02-10ER16136

Stable-Isotope Probe of Nano-Scale Mineral-Fluid Redox Interactions

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Objectives: Our goal is to study how electron transfer processes at a reactive interface fractionate stable isotopes and apply our findings to understand isotope signatures arising from redox processes in a wide variety of natural environments.

Project Description: Stable isotope signatures can be used as a marker for a variety of geochemical processes, but only if the physical mechanisms underlying fractionation are understood and quantified. Based on theories describing stable isotope geochemistry and electrochemical kinetics, we hypothesize that electrochemical processes can generate mass-dependent isotopic fractionations in all systems that undergo a redox (electron transfer) reaction, with an isotope signature that is dependent on the thermodynamic driving force—the extent of disequilibrium and the equilibrium fractionation factors between product and reactant. In addition, mass transport and chemical speciation changes can both contribute to the overall observed isotopic signature during interfacial reactions. Measuring isotope fractionation during electrodeposition as a function of temperature provides one way to delineate different mechanisms generating isotope signatures.

Results: Our latest studies of isotope fractionation during electrodeposition as a function of temperature show very different behavior depending on the kinetic regime. The isotopic composition of metal deposits on planar electrodes and on rotating disc electrodes show opposite trends as a function of temperature (Figure 1). On planar electrodes, where diffusive mass transport of reactant to the electrode is the rate limiting step, the stable isotope fractionation of iron and zinc metal deposits increases with increasing temperature (Figure 1A), a trend counterintuitive to equilibrium stable isotope theory. However, on a rapidly rotating disc electrode, which enhances the flux of material to the electrode surface, the observed isotope fractionation decreases with increasing temperature (Figure 1B).

To interpret these observed trends, we modeled both the overall temperature-dependent kinetics and the predicted isotope signatures of electroplated material under different kinetic regimes, and with different mass fluxes to the electrode. The three scenarios are depicted in Figure 2. When the activation energy for diffusion (E_D) is less than or equal to that of the chemical reaction (E_R) (Figure 2 left and middle, respectively) then the predicted isotope fractionation always decreases with increasing temperature, at all mass fluxes. However in the case $E_D > E_R$ where diffusive flux to the electrode is rate-limiting (Figure 2 right side), at low mass fluxes, the predicted fractionation increases with increasing temperature while at high mass flux, the fractionation decreases with increasing temperature. This model provides an explanation of our results shown in Figure 1, and shows that the use of the rotating disc electrode can be used to control kinetic regime for these experiments, and ultimately eliminate these diffusive limitations.

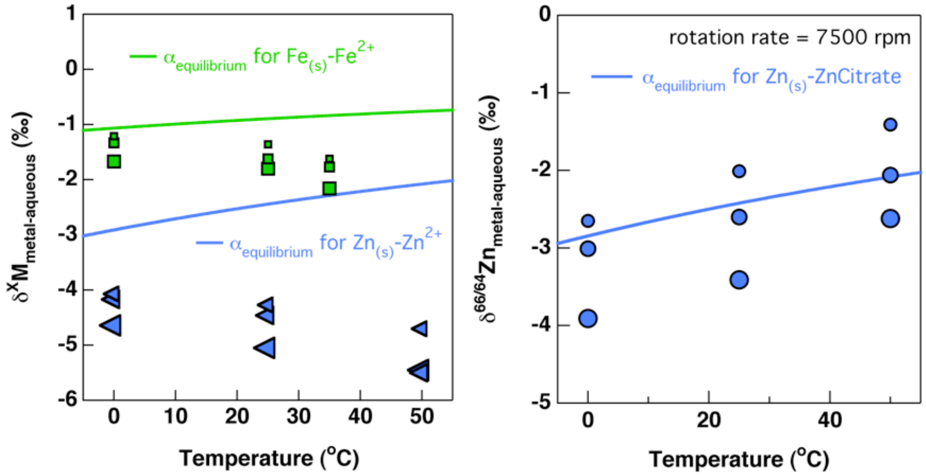

Figure 1. *Stable isotope composition of electroplated iron and zinc as a function of temperature on planar glassy carbon electrodes (left); and a rotating disc electrode (right).*

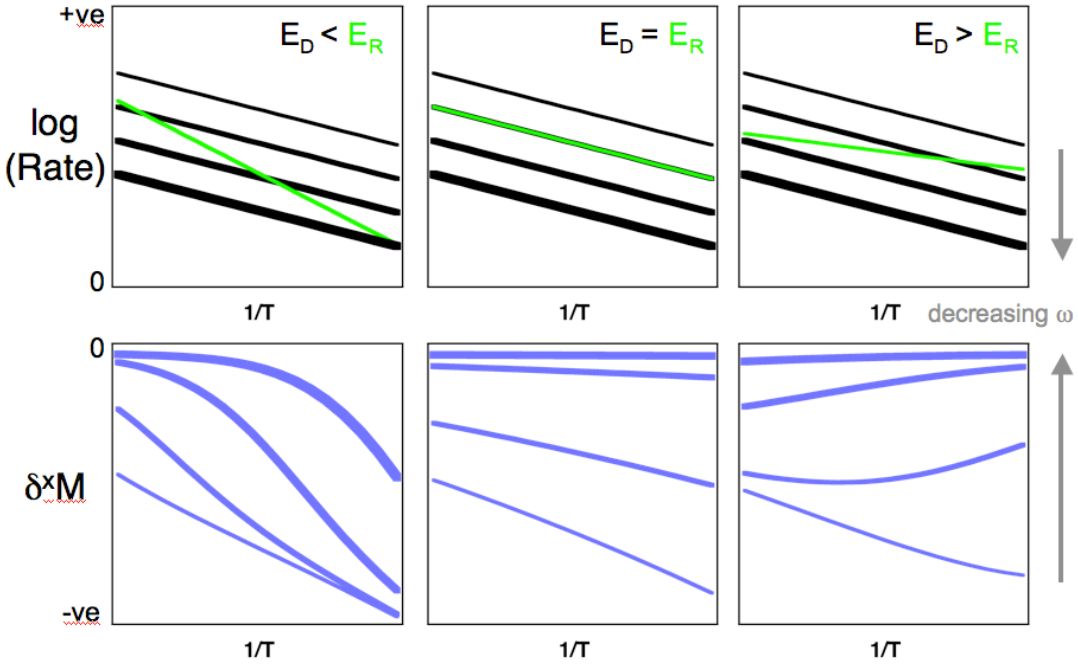

Figure 2. *A comparison of isotope fractionation behavior during electroplating for the case where diffusion to the electrode is rate limting (left side), where electron transfer is rate limiting (right side) and where the two rates are similar (center). The top three plots show relative rates of reactions for electroplating rate-limited by diffusion kinetics (black lines) and electron transfer kinetics (green lines). The bottom three figures show corresponding calculations for temperature-dependent isotope fractionation. Calculations as a function of decreasing mass flux to the electrode surface (controlled experimentally by lowering the rotation rate of the rotating disc electrode) are indicated by the gray arrows on the right hand side of the figure.*

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Grant: DE FG02-06ER15767

First Principles Simulation of the Temperature, Composition and Pressure Dependence of Natural Fluids: Collaborative Research Program with Pacific Northwest National Laboratories

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Objectives: To address the problems associated with future energy strategies a much more quantitative, parameter free interpretation of elementary geochemical processes will be required. In this program new 1st principles simulations methods are being developed and applied to the study of the chemical behavior of metal ions, their counter ions and their oxo-hydroxo hydrolytic polyions in aqueous solutions. The understanding of the aqueous chemistry of these species is essential to the interpretation of processes such as, the formation of minerals, the sequestration of CO_2, the storage of nuclear waste, and the transport of toxic materials. The 1st principles based simulation methods that are being used and developed in this program allow the parameter free prediction of the properties of these chemically complex materials over the wide range of conditions encountered in geological applications. Because of the 1st principle nature of these methods they have very general application to the interpretation of many complex materials of interest to the BES community. In this program special effort is being made to develop new simulation methods that will be able to exploit the full capabilities of emerging massively parallel computers and allow the simulation of new classes of materials.

Project Description: The results of this research will contribute to the molecular level understanding of the chemistry of processes such as ore formation, toxic species transport, mineral solubility, and absorption on mineral surfaces for sub-critical to supercritical conditions as well provide for the more detailed analysis of the new classes of experiments such as, high resolution NMR, X-ray absorption fine structure, sum frequency vibrational spectroscopy, high resolution x-ray and neutron scattering, photoelectron spectroscopy etc. that are being used to study fundamental geochemical processes at the molecular level. Since for many of these problems the appropriate simulation methods and implementations are not yet available, an important strength of this program is our ability to develop and efficiently implement new parameter free methods of simulation. The metals included as application targets in this research, Al^{3+}, Fe^{3+}, Cr^{3+}, Ca^{2+}, and Ni^{2+}, are chosen because of their geochemical importance and because they display a wide range of properties such as very different hydrolysis constants, ligand residence times, formation of oxo-hydroxo hydrolytic polyions. In this research we endeavor to relate the properties of the ions to their chemical behavior in geological applications. The program is carried out through the very close collaboration of researchers at PNNL (co-PI Eric Bylaska) and UCSD (PI John Weare). The researchers in these two institutions collaborate in both the methods development and application aspects of the program. Collaboration is enhanced by the frequent visits of the PIs and their co workers, the graduate students and postdoctoral students in the program to both institutions. While the closeness of the collaboration makes it difficult to assign tasks, there is more emphasis on methods development at PNNL and on chemical application at UCSD. However, every student in the program will participate in some aspect of methods and software development and in application simulation.

Applications Results: High TP ion pair formation at High TP; Reactions with labile ions have been extensively studied by Eigen and others. The putative general mechanism (Eigen-Wilkens mechanism, EW) for these reactions follows *Scheme 1*,

$$\mathrm{M}^{m+} + \mathrm{L}^{x-} \underset{k_{10}}{\overset{k_{01}}{\rightleftarrows}} \mathrm{M} \bullet \mathrm{OH}_2 \bullet \mathrm{OH}_2\mathrm{L}^{(m-x)+} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \mathrm{M} \bullet \mathrm{OH}_2\mathrm{L}^{(m-x)+} \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} \mathrm{ML}^{(m-x)+} .$$

Scheme 1: **A** **B** **C** **D**

In *Scheme 1,* **A** represents the reactant ligand in the bulk water (Cl^{-} (yellow and green in Fig.1 right) separated by at least two waters (Fig1 right), **B** represents the ligand coordinated to the 2nd shell separated from the ion core by two waters (not seen as stable in high T trajectory), **C** represents the ligand in the second shell separated by a single water from the ion core in an outer sphere complex (Fig.1 right) and **D** represents the contact pair product in a inner sphere complex (Fig.1 right) of the reaction. TS is a transition state between the C and D states.

At room temperature $CaCl_2$ is largely dissociated in aqueous solutions. Results for water exchange at 298^{o}K were given in last year's report and the mechanism is in remarkable agreement with EW. At high temperatures ions associate to form $CaCl_2$ contact ion pairs as studied in this project. In Fig. 1 results from AIMD simulations at 650^{o}K of $CaCl_2$ in 64 waters are shown. The results are in qualitative agreement with the EW mechanism. For this 650^{o}K simulation the Cl^{-} initially in the bulk water (not in the hydration region of the ion) quickly formed $CaCl_2$ contact ion associated species. The axial placement of the Cl^{-} ions, the four fold coordination of the hydrating waters, and the bond distances in this structure are all in excellent agreement with the available EXAFS data (Fig. 1 left, e.g., R_{CaCl}=2.698 Å (AIMD), 2.677 Å (EXAFS), T=400^{o}C) (FULTON et al., 2004). The regions of the high TP trajectories (Fig 1 right) that might be associated with events in the EW mechanism as in *Scheme 1* are noted on the trajectory, Fig. 1. right. For this temperature the structure in 2nd shell is very fluxional and the mechanism for formation of the ion pair species should best be described as diffusion controlled and only qualitatively related to the EW mechanism.

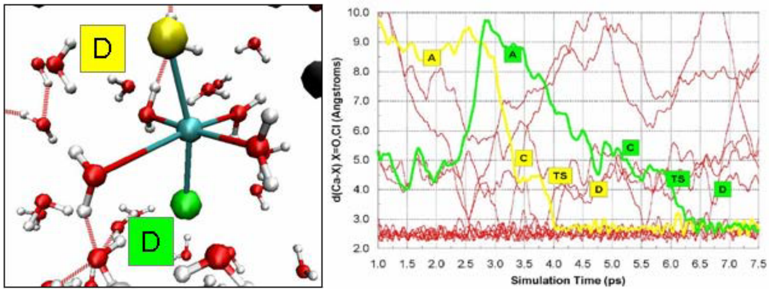

Figure 1. Diffusion-controlled high PT ion pair formation.

Methods Developments Results: (please see PNNL Report)

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

Department of Earth Science, Santa Barbara CA 93106

Grant: DE-FG02-96ER14620

Physiochemical Evidence of Faulting Processes and Modeling of Fluid Flow in Evolving Fault Systems in Southern California

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Objectives: This is a collaborative study to quantify basinal fluid flow, submarine methane migration and diagenetic effects within deforming faults in a transpressional setting that is seismically active. The emphasis is faulted basins in California.

Project Description: We have mainly targeted active faults and young (Tertiary strata) petroleum fields in southern California for study. Faults include the Refugio Fault in the Transverse Ranges, the Ellwood Fault in the Santa Barbara Channel, and the Newport-Inglewood in the Los Angeles Basin. Subsurface core and tubing scale samples, outcrop samples, well logs, reservoir properties, pore pressures, fluid compositions, and published structural-seismic sections are being studied to characterize the tectonic/diagenetic history and geochemical signatures in carbonate that characterize rapid CO_2 degassing. These data provide constraints for finite element models that are being developed to predict fluid pressures, flow patterns, rates and patterns of deformation, subsurface temperatures and heat flow, and geochemistry associated with large fault systems.

Results: Our studies of the South Ellwood fault, which bounds the north edge of the south Ellwood field, have given us direct evidence of connectivity between the sea floor and producing wells in the field from changes in gas seep rate to the sea floor. We estimate permeability on the fault of about 30 Md. We have recently documented sea water incursion down the fault into the reservoir from oxygen, deuterium and sulphate composition. Sr isotopes, however indicate the possibility of deeper fluids coming from below the main reservoir. We are currently evaluating the chemical composition of deeper fluid sources in this area.

In the LA basin we have recently completed a preliminary Sr isotopic study of formation waters in the Long Beach field. The results indicate the Sr values are highly radiogenic and significantly great than expected Tertiary marine values. There appears to be significant differences across the field. The purpose of this study is to establish background water composition to evaluate possible upward fluid movement associated with fault related thermal anomalies observed in the field. The Long Beach field is the area that Signal Hill Petroleum is planning a drill hole and core within the Newport-Inglewood fault zone. A recent 3-D survey of the prospective drill area is currently being evaluated and the current plan is to drill a test hole adjacent to the fault followed by drilling and coring through the fault zone.

In conjunction with collaborators at the University of Toronto, we are conducting a laboratory study of the effects of crystallization rates on calcite stable isotopic compositions. These experiments will be used to explain the extremely light oxygen isotopic composition of calcites we have observed in rapidly degassing environments such as well tubing scales. We are also continuing to document carbonate isotopic compositions in rapidly crystallizing environments such as geothermal areas.

In conjunction with collaborators at Tufts University, Boles is providing geological constraints and hydrogeologic parameters for large-scale mathematical models of the Los Angeles Basin that document and test various working hypotheses for the effects of faults on petroleum migration and accumulation in one of the world’s largest/richest petroleum provinces. Recent models have shown that slightly overpressured sections of the Miocene strata provided rich source kitchens for petroleum generation, and lateral carrier beds and major faults like the Newport-Inglewood facilitated rather rapid transport of petroleum to shallower parts of the stratigraphic sequence where it was structurally trapped.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA
Departments of Mechanical Engineering and Computer Science, Santa Barbara CA 93106

Grant: DE-FG02-08ER15991

Multiscale Investigation and Modeling of Flow Mechanisms Related to CO_2 Sequestration in Geologic Formations

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Objectives: Our objectives are to investigate the relevant physical mechanisms at the microscopic and mesoscopic scales with the help of detailed experimentation and high accuracy numerical simulations, as well as to carry out effective modeling of such mechanisms at the geologic scale based on the probability density function (PDF) approach.

Project Description: Our approach is to develop the missing link between the fundamental physics of multiphase flow at the pore-scale and the phenomenological representation of dynamic behaviors across a hierarchy of geologic scales. We will use the problem of CO_2 sequestration in geologic formations as a prototypical application of multiphase flow in porous media. We take this approach not only because of the lack of understanding of the sequestration process and its immense potential for environmental impact, but also because the process involves a wide range of fundamental physical mechanisms that arise in a host of other applications, such as, contaminant transport and remediation as well as enhanced oil recovery.
Our approach will be to develop novel numerical methods for interface problems, for the Navier-Stokes equations, for stochastic multiscale methods as well as to develop innovative experimentation and visualization techniques for micromodels. The proposed research will, in general, make it possible to make reliable predictions regarding geologic flows. In particular, it will significantly improve the understanding of hydrodynamic mechanisms and will allow the development of physically accurate macroscopic models in order to provide improved predictability and management capability for CO_2 sequestration and other geologic flows.

Results: Our computational efforts to date have been focused on the design and implementation of a numerical method for solving two-phase Navier-Stokes on Octree grids, a data structure that is optimal in terms of memory storage (see figure 1). A hallmark of our approach is that the ratio between grid cells is unconstrained. In addition, the interface between phases as well as the boundary of the porous structure (rocks) is implicitly captured. This has the benefit of greatly simplifying mesh generation and allows for Cartesian meshes to be used.

We have worked on several fronts in order to design an efficient three-dimensional solver:

- We have developed an efficient approach for solving the Navier-Stokes equations on arbitrary geometries. The method is second-order accurate and can handle large ratio of viscosity between phases.

- We have developed a numerical method to impose general boundary condition on arbitrary domains. This method uses novel discretization of the Dirac delta and Heaviside functions that are robust to perturbation of the interface on the grid. This part is significant because it leads the way to imposing boundary conditions on moving boundaries in a robust and efficient way.

- We have developed a multigrid solver for the solution of the pressure component on arbitrary geometry as well as the solution of the stress tensor. This multigrid solver leverages the specific sampling of solution on the Octree data structure and is significantly faster than standard Conjugate Gradient methods.

- We have implemented a level-set based numerical methodology for tracking moving contact lines along solid/fluid interfaces. The key challenge of dealing with the force singularity at the contact line was addressed by implementing a Navier-slip condition that accounts for essential contact line hysteresis effects. The numerical approach has been validated via comparisons with boundary integral method results in the limit of small Reynolds numbers, and with other numerical data in the limit of large viscosity ratios. For the simple geometry of a plane channel, we are now conducting parametric studies, in order to evaluate such properties as front velocity, film thickness and contact line motion as functions of the capillary number, the viscosity ratio and the Reynolds number.

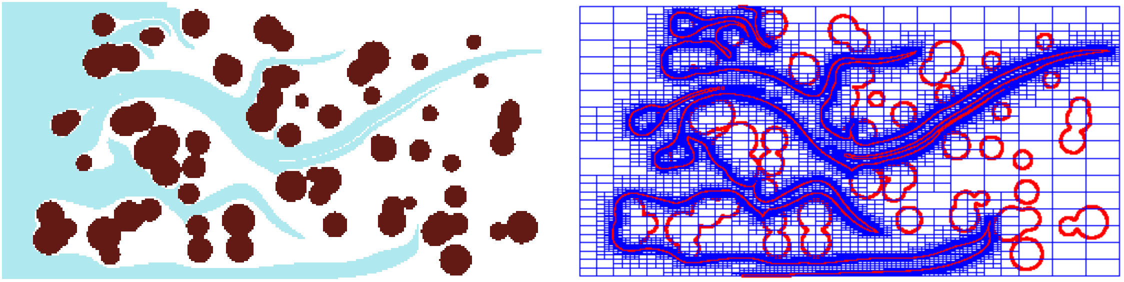

Figure 1: Simulation of a two-phase flow in porous media. The left picture depicts the two phases and the right picture depicts the interface tracking along with the octree adaptive mesh.

UNIVERSITY OF CHICAGO

Center for Advanced Radiation Sources, 5640 S. Ellis Avenue, Chicago IL 60637

Grant: DE-FG02-92ER14244

Synchrotron X-ray Microprobe and Microspectroscopy Research in Low Temperature Geochemistry

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Objectives: The project focuses on low temperature geochemistry applications of the x-ray fluorescence microprobe on beamline X26A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The microprobe can be used to determine the composition, structure, oxidation state, and bonding characteristics of earth materials with trace element sensitivity and micrometer spatial resolution.

Project Description: Instrumentation for the following techniques is provided for earth and environmental science research: (1) microfocused x-ray absorption spectroscopy, (2) fluorescence microprobe analysis, (3) microdiffraction, and (4) x-ray fluorescence computed microtomography. Research areas include the geochemistry of toxic metals and metalloids in contaminated sediments and particulates, efficiencies of contaminant remediation strategies, studies of how bio-accumulation processes affect the distribution of trace toxic metal species in soils, using iron oxidation states determined by XANES to infer the geochemical states of magmatic systems, and mineral surface controls on metal partitioning.

Results: Research results included the following (collaborators and affiliations in parentheses): (1) Titanium K-edge x-ray absorption near edge structure (XANES) measurements demonstrated that Ti^{4+} substitutes for Si^{4+} on fourfold tetrahedral sites in quartz at temperature between 700 to 940 °C and pressure between 5 and 20 kbars. These results set the foundation for use of the P-T dependencies of Ti-in-quartz solubility as a thermobarometer (J. Thomas, E. B. Watson, F. S. Spear, P. Shemella, S. Nayak, Rensselaer Polytechnic Institute); (2) The chemical and mineralogical forms of As, Pb, Cr, and Cd were studied in a metal-contaminated organic soil (Histosol) that received runoff and seepage water from a site that was once occupied by a lead smelter. The complex oxide and sulfide mineralogy observed in these samples has important implications for risk assessment and the design of in-situ remediation strategies for this and similar metal-contaminated sites (X. Gao and D. Schulze, Purdue University). (3) High-precision micro X-ray absorption near-edge structure (μ-XANES) calibrated for natural basalt compositions was developed for application to the direct, in situ microanalysis of $Fe^{3+}/\Sigma Fe$ in primitive, undegassed, natural magmatic liquids yielding a precision of ±0.0045 in $Fe^{3+}/\Sigma Fe$ for glasses with $Fe^{3+}/\Sigma Fe > 8\%$, which is comparable to the precision of wet chemistry. This method was applied to natural basalts covering a range of plate tectonic settings and the results indicated a direct link between mass transfer from the subducted plate and oxidation of the mantle wedge (E. Cottrell and R. Fischer, Smithsonian Institution; K. Kelley, University of Rhode Island); (4) The role of particle size on the oxidation, bioavailability, and adverse effects of manufactured Cu nanoparticles (NPs) in soils was investigated. X-ray absorption spectroscopy and scanning X-ray fluorescence microscopy were used to characterize changes in chemical speciation and spatial distribution within earthworms exposed to a series of concentrations of commercially produced NPs in artificial soil media. The results suggests that oxidized Cu NPs may enter food chains from soil but that adverse effects in earthworms are likely to occur only at relatively high concentrations (>65 mg Cu kg^{-1} soil) (J. Unrine, O.Tsyusko, S. Hunyadi, J. Judy, and P. Bertsch, University of Kentucky).

UNIVERSITY OF CHICAGO
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Grant: DE-FG02-94ER14466

GeoSoilEnviroCARS: A National Resource for Earth, Planetary, Soil and Environmental Science Research at the Advanced Photon Source

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Objectives: GeoSoilEnviroCARS is a national consortium of earth scientists whose goal is to design, construct and operate, as a national user facility, synchrotron radiation beam lines at the Advanced Photon Source, Argonne National Laboratory.

Project Description: Instrumentation for the following techniques is provided for earth and environmental science research: (1) x-ray absorption fine structure spectroscopy; (2) fluorescence microprobe analysis, (3) microtomography; (4) powder, microcrystal and surface diffraction; (5) high-pressure crystallography with diamond anvil cells and multi-anvil presses, and (6) radiography at high pressure in the multi-anvil press. Research areas include phase transitions in mantle minerals; the properties of the Earth's core; migration and remediation of toxic metals and radioisotopes in contaminated sediments; structure, reactivity and sorption at the mineral-water interface; the chemical nature of hydrothermal fluids and magmas; and flow dynamics of fluids and solids.

Results: Two-hundred eighty-three (283) beam time proposals were received, 348 unique users conducted experiments, and 43 papers were published. Results included the following (collaborators and affiliations in parentheses). (1) The hydrated goethite (α-FeOOH) (1 0 0) interface structure consisted of a double hydroxyl, double water terminated interface with significant atom relaxations (G. Waychunas, LBNL; T. Trainor, U. Alaska – Fairbanks); (2) The surface structure of unreacted α-Fe_2O_3 (0 0 0 1) consisted of two, chemically distinct, structural domains: an O-layer terminated domain and a hydroxylated Fe-layer terminated domain. After exposure to aqueous Fe(II), the surface structure of both co-existing structural domains was modified due to adsorption of Fe at crystallographic lattice sites of the substrate, resulting in six-coordinated adsorbed Fe at the surface (K. Tanwar, S. Petitto, T. Trainor, U. Alaska – Fairbanks); Spatial variation in wettability of porous media surfaces has a significant impact on pore-scale characteristics of residual NAPL blobs in saturated porous media systems (R. I. Al-Raoush, Southern University and A&M College; In a study of packing of granular polymer chains, it was found that long chains pack into a low-density structure and on compaction, randomly oriented, semi-rigid loops form along the chain. Close similarities between the packing of chains and the glass transition in polymers were uncovered (L.-N. Zou, X. Cheng, H. Jaeger and S. Nagle, University of Chicago); The results of a study on removal of hexavalent chromium from wastewater showed that the product of the reaction of Cr(VI) with Fe(II)-

faujasite is primarily a poorly order $Cr_xFe_{1-x}(OH)_3$ mixed phase similar to previous investigations of the reaction of Cr(VI) with Fe^0 and not solely Cr(III) bound directly to zeolite cation exchange sites (J. Kiser and B. Manning, San Francisco State University); The form of solid phase U after Fe(II) induced anaerobic remineralization of ferrihydrite in the presence of aqueous and absorbed U(VI) was investigated. The prevalence of site specific U incorporation under both abiotic and biotic conditions and the fact that the produced solids were resistant to both extraction and oxidation suggest the potential importance of sequestration in Fe oxides as a stable and immobile form of U in the environment (P. Nico, LBNL; B. Stewart, Montana State University; S. Fendorf, Stanford University).

UNIVERSITY OF CHICAGO
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Grant: DE-FG02-09ER16092 (DE-SC0002580)

Canted Undulator Upgrade for GeoSoilEnviroCARS Sector 13 at the Advanced Photon Source

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Objectives: GeoSoilEnviroCARS (GSECARS), a multi-user, synchrotron radiation research facility dedicated to earth, environmental and planetary science (Sector 13, Advanced Photon Source, Argonne, IL), is implementing a canted undulator upgrade.

Project Description: The canted undulator upgrade will provide (1) a unique sub-micron resolution microprobe in a dedicated enclosure for detailed speciation and compositional research on light (as low as sulfur) and heavy elements in systems of geochemical, environmental and cosmochemical significance; (2) an optimized high energy insertion device to advance the quality of surface and high pressure diffraction data; and (3) the doubling of undulator beam time to open up the capabilities of GSECARS to more investigators than currently possible. Because of the wide-ranging science program at GSECARS, the upgrade project is being supported through a division of costs involving programs at DOE, NSF, and NASA. The Advanced Photon Source is providing the accelerator-associated components (undulator and front-end components) for the upgrade.

Results: Staged modifications to experimental station ID-C are underway which allow the station to be run normally during operations periods while the construction is in progress. New labyrinths have been installed to allow for the necessary cabling and utility access. Personnel safety system (PSS) and utility wiring have been modified and/or rerouted. The PSS panel has been relocated and modified in preparation for split-off of the new, independent ID-E station. The new access door for ID-E has been installed. Installation of most of the ID-C interior wall has taken place during the September 2010 maintenance shutdown.

In a cost-saving effort, existing beamline components (e.g., slits, collimator, monochromator and mirror assemblies) are being modified where possible, rather than designing and building all completely new components. For example, modifications to our existing 400 W pinhole, which helps to restrict the total power that is transmitted down the 13-ID-C/D beamline, will be made to allow the second undulator beam to pass. Major progress has been made in this design effort and the procurement order for the slit modifications and additions has been let.

The required accelerator-associated upgrades by the APS are on schedule. The 3.6-cm undulator magnets procurement package has been completed and award of the order is imminent. The order for the 3.0-cm undulator magnets has been awarded and delivery is expected in Jan. 2011. The poles for both the 3.0-cm and 3.6-cm undulators are in fabrication and delivery is expected in Dec. 2010. The canting magnets were received in Sept. 2010. All front end components are ordered and will be received by Jan. 2011. The vacuum chamber and end boxes

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Department of the Geophysical Sciences, Chicago IL 60637

Grant: DE-FG02-01ER15254

Kinetic Isotope Fractionation by Diffusion in Liquids

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Objectives: The overall objective of our research effort is to document and quantify kinetic isotope fractionations during chemical and thermal (i.e., Soret) diffusion in liquids (silicate melts and water) in both laboratory experiments and in natural settings.

Project Description: Isothermal diffusion couples are used to measure major element isotopic fractionation by chemical diffusion in natural composition melts using starting materials made from Mid-Ocean Ridge Basalt juxtaposed with a natural rhyolite glass or from rock powders from a coeval felsic and silicic magmatic systems in coastal Maine. The field component of our work involves finding natural analogues of isotopic fractionations seen in the laboratory and interpreting these in terms of dominant chemical transport mechanism (molecular diffusion versus magma mixing) in the natural system. A separate set laboratory experiments involves quantifying thermal isotope fractionations that arise when a temperature gradient is maintained across an initially homogeneous fluid for a sufficient length of time. Both silicate liquids such as molten basalt and water with dissolved salts are used for these thermal fractionation experiments. Numerical models reproducing the kinetic elemental and isotopic of dissolved salts in water have been developed to provide insight into what control the magnitude of such kinetic effects in water.

Results: *Kinetic isotope fractionation in laboratory experiments:* We have extended out earlier laboratory experiments on the thermal fractionation (also referred to as Soret diffusion in the geochemical literature) of the major elements (Si, O, Mg, Ca, and Fe) except for Al in molten basalt to now include the alkalis potassium and lithium. We find the alkali elements to be less fractionated by temperature differences than the major elements because of their faster chemical diffusion, which counterbalances the thermal effects. We are carrying out Soret diffusion experiments in water where we are reproducing Soret's original experiments for the thermal diffusion of dissolved salts (NaCl and KCl) and will measure associated isotopic fractionation of potassium.

Kinetic isotope fractionation in natural settings: We have completed a study of magnesium isotopic fractionations associated with chemical diffusion of magnesium between melts of different composition exposed in Vinalhaven Igneous Complex, Maine. Laboratory diffusion couples were made using rock powers from various rock types exposed in the complex to quantify the magnitude of magnesium isotopic fractionation by diffusion between these compositions when juxtaposed as melts. When the results of the laboratory experiments are compared to the magnesium isotopic fractionation associated with magnesium concentration gradients in the natural system we find cases where the lab and field results are virtually identical while along other profiles there is no measurable magnesium isotopic fractionation associated with the magnesium concentration gradient. The degree of magnesium isotopic fractionation along a concentration gradient can thus be used to determine the relative importance of transport between melts by diffusion (which fractionates isotopes) and by mechanical mixing that does not fractionate isotopes.

Analytical developments: We have completed and submitted a study documenting the magnitude of matrix effects associated laser ablation inductively coupled plasma mass spectrometer (LA-ICPMS) measurements over a broad range of compositions ranging from rhyolite to basalt. Our results provide guidelines as to how closely one has to bracket samples with unfractionated standards in order to remove matrix effects to a given level of precision or when it would be better to measure isotopic compositions on solutions that have been purified by passing then through ion exchange columns.

CLARK UNIVERSITY

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Grant: DE-FG02-02ER15367

Physics of Channelization: Theory, Experiment, and Observation

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Objectives: We seek a fundamental understanding of the physical processes that erode channels and create drainage networks, by integrating theoretical models, laboratory experiments, and field observations. We focus on channels incised by groundwater flow, and seek to quantitatively relate mechanisms of channel growth to channel shape and network geometry.

Project description: Our studies of channel shape concentrate on the growth and form of elevation contours and longitudinal profiles. Our investigations suggest that the focusing of groundwater at the channel head selects predictable forms. We seek to better understand how these forms are selected. The mechanisms that induce bifurcation or "tip-splitting" of the channel head are of particular interest.

At scales much larger than an individual channel, headward erosion, side-branching, and a succession of tip-splitting instabilities create channel networks. These processes are closely related to the ways in which subsurface water is attracted to channel heads. We seek a simple theoretical representation of the subsurface flow and attempt to relate it to sediment flux.

Our investigations involve physical reasoning, mathematical modeling, laboratory experimentation, and observations of kilometer-scale channels. Our field investigations, performed at the Apalachicola Bluffs and Ravines Preserve, near Bristol, Florida, emphasize quantitative tests of our theoretical predictions.

Results: In FY2010 we studied the focusing of groundwater into channel heads and the resulting channel growth. Figure 1a shows the predicted shape of the water table and the resulting aggregation of water in the streams. We find that, for moderate sediment transport intensities, the force balance on the scale of a sand grain determines the width and the depth of a channel at a given slope and water discharge. Conservation of mass then requires that the discharge be proportional to the inverse-square of the channel slope. We test this prediction by comparing the stream discharge determined from simulation to the slope of the stream bed, as measured from a high-resolution map of the study site. Figure 1b shows that the predicted force balance is found in the streams of Bristol. From this constraint, we predict the equilibrium shape of streams and find it to be consistent with observation (Figure 1c).

We have also developed a physical understanding of the bifurcation of a growing valley head. We find that the angle between bifurcating tips in the field site is consistent with the predicted value of 72°.

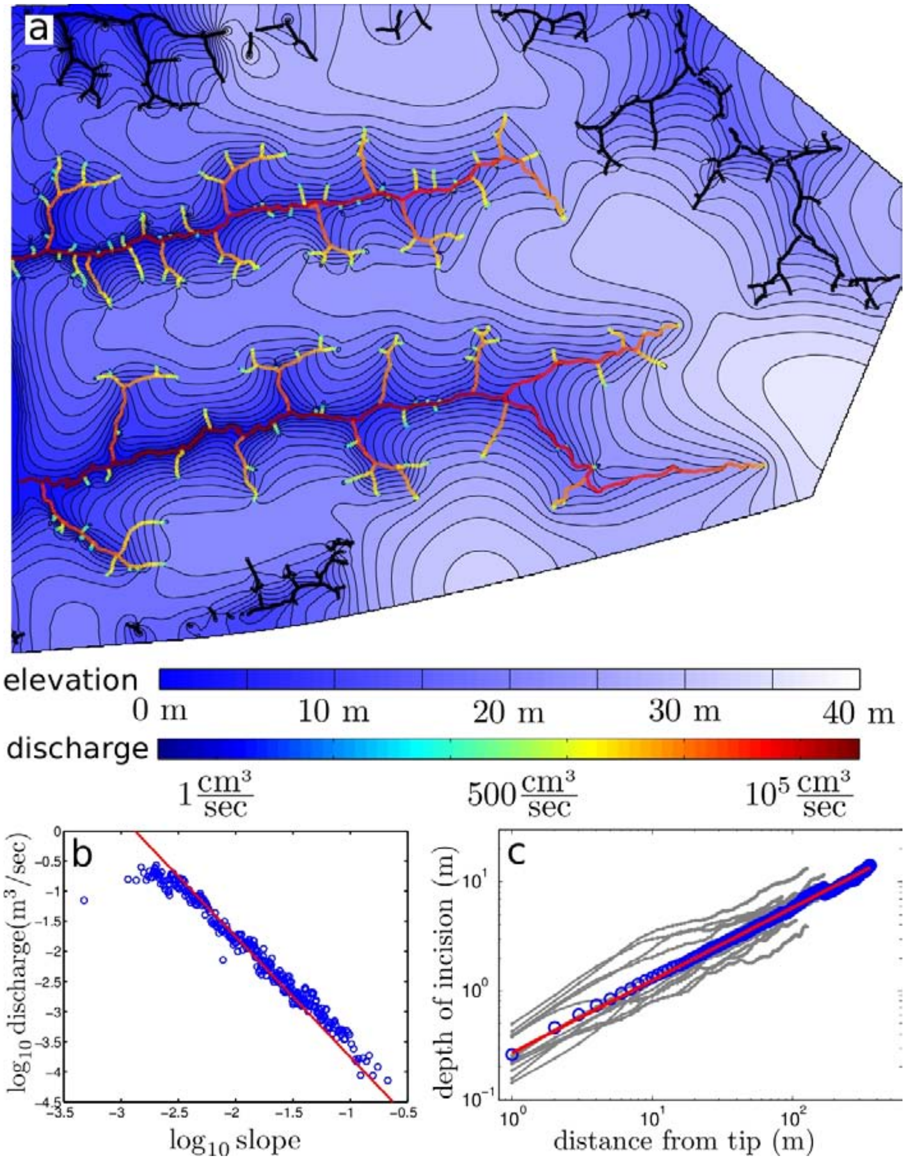

Figure 1: The geometry of seepage valleys represent a balance between the focusing of groundwater and the transport of sediment. (**a**) The predicted shape of the water table around the river networks and the resulting discharges in the stream. (**b**) At equilibrium, the discharge through the stream is balanced by the slope of the stream. Measurements from the field (blue circles) are consistent with the predicted relation (red line). (**c**) From the equilibrium hypothesis, we predict the longitudinal shape of a stream near the spring. The profiles of 10 representative streams (gray lines) are averaged (blue circles) and found to be consistent with prediction (red line).

COLORADO SCHOOL OF MINES

Colorado Center for Advanced Ceramics, Department of Metallurgical & Materials Engineering
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Grant: DE-FG02-10ER16125

Kinetics and Mechanisms of Calcite Reactions with Saline Waters

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Objectives: This project will investigate the rate limiting effects of intermediate phases on calcite precipitation and dissolution reactions in saline waters using laboratory synthesis and a suite of nanoscale characterization techniques.

Project Description: The general objective of the proposed research is to determine the kinetics and mechanisms of calcite reactions with saline waters over a wide range of saline water composition, $p\text{CO}_2$, and modest ranges in T and P. This will be accomplished by studying both reaction rates and solubility from changes in solution chemistry, and making nanoscale observations of calcite precipitate surface morphology and composition at the micro-to-nano-scale to provide an understanding of controlling reaction mechanisms and pathways. The specific objectives necessary to reach the general objective are: a) determination of how $p\text{CO}_2$, Ca^{2+}, ionic strength and “foreign” ions influence reaction rates; and b) investigate the influence of these parameters on apparent kinetic solubility from dissolution and precipitation reactions. This information will clearly be central to the construction of reliable reaction-transport models to predict reservoir and formation response to increased CO_2 in saline waters.

Results: Electron microscopy investigations of laboratory grown carbonate overgrowths indicated that a previously undetected, < 100 nm thickness, sub-stoichiometric layer of amorphous calcium carbonate (ACC, see figure 1) is present in calcite precipitates grown under certain conditions. This layer, along with other metastable carbonate polymorphs such as vaterite may be the causes of anomalous reaction kinetics of carbonates in saline water. Future work in this recently initiated program will utilize µ-Raman spectroscopy, scanning electron microscopy, transmission electron microscopy, electron spectroscopy, and atom probe tomography to analyze the structure and composition of carbonate overgrowths produced under a variety of saline conditions.

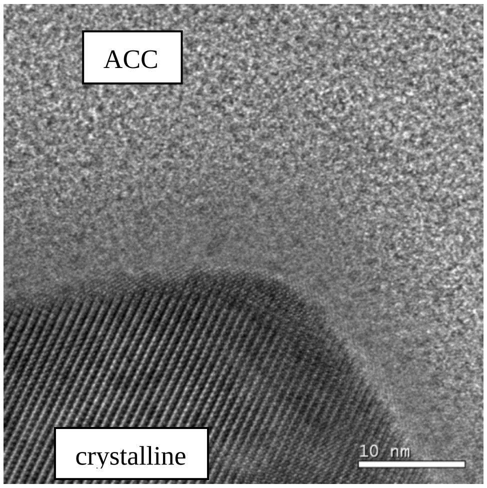

Figure 1. High Resolution Transmission Electron Microscopy image of a crystalline carbonate overgrowth / amorphous calcium carbonate (ACC) interface. The presence of an ACC phase between the crystalline growth and the saline environment may suggest that metastable phases are responsible for anomalous carbonate dissolution and precipitation kinetics.

COLORADO SCHOOL OF MINES
Department of Physics, 1500 Illinois Street, Golden CO 80401

Grant: DE-FG02-09ER16018

Characterization of Electrical and Elastic Properties of Rocks at the Sub-Millimeter Scale

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Collaborators: Nathan S. Greeney, Alex Yuffa, Daniel Gibson

Overview: Here we describe our progress to date in measuring the submillimeter-scale elastic and mechanical properties of rocks. Electrical characterization is done using a near-field method developed and described in our original proposal. In the past year, we have developed a novel laser ultrasound technique that allows us to map the travel time of pulses over short distances through the sample; we couple this with laser scans at high spatial resolution. We have also developed new image processing techniques for speckle interferometry images. These techniques are crucial in going from speckle interferograms to quantitative strain measurements.

High resolution laser ultrasound results: Figure (1-left) shows the laser ultrasound setup, which uses high-power pulsed infrared laser to generate ultrasound via thermoelastic expansion, and a laser Doppler vibrometer, which measures surface particle velocity. The IR laser has a repetition rate of 3kHz, allowing rapid averaging of the signal to reduce noise. A single lens is used to focus the IR beam to a point on the rock's surface. The vibrometer uses a low-power stabilized Helium-Neon laser to illuminate a spot on the rock directly opposite the source. By mixing the transmitted and reflected beams the particle velocity is retrieved from the Doppler shift.

The Tektronix oscilloscope has an ethernet port, which makes it easy to retrieve data using open source software tools. We've written Python code to retrieve the traces (averaged already on the scope) and perform data processing. This code also controls two linear, motorized stages that can be positioned with sub-micron precision. By moving the sample at small increments and taking a measurement at every location, we obtain a map of the time it takes for the ultrasonic waves to traverse the thin sample. The velocity of the ultrasonic waves is proportional to the elasticity of the material that the wave is traveling through. For a given thickness, the elastic moduli will be proportional to the time that it takes to go through the sample. To keep the data processing simple, we use the first peak and are only concerned with the changes in this peak as a function of space. In principle this should give us the perturbations in the compressional modulus as a function of space. These can then be added to the bulk or average modulus to get the absolute modulus at each point.

As a first test, we scanned a plate of aluminum vertically (Fig. 1). After demonstrating measurement consistency for a homogeneous sample, we moved on to a medium grained granite sample we have used previously. The optical scan in the top of Figure shows the main constituents of this granite sample.

The bottom of Figure (2) shows the time mapping of the sample with respect to the average time of the sample. Correlating the optical and the time map it is apparent that the red and yellow colors (larger travel times, slowest propagation) correspond to the feldspar. The greenish color (slightly faster than average) correspond to quartz. The bluish color (shortest travel time) correspond to biotite.

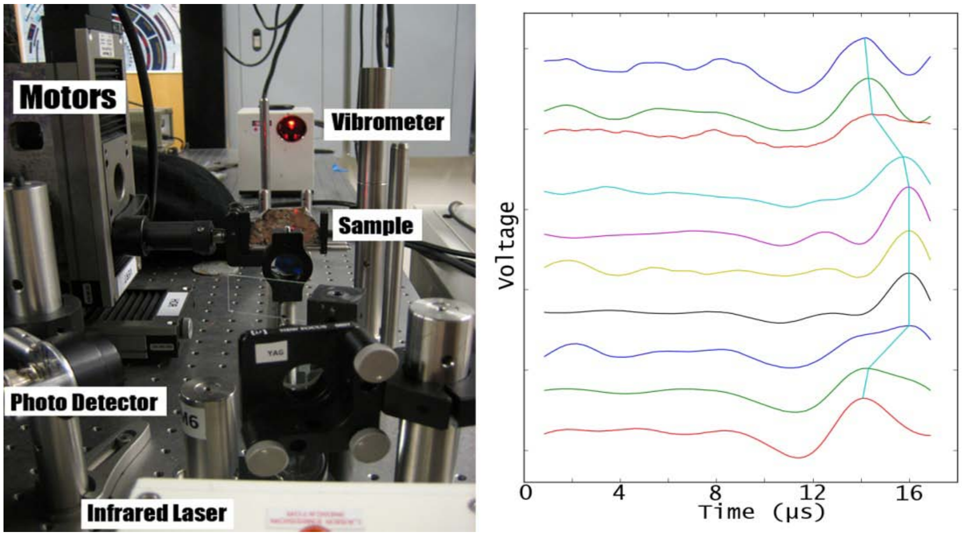

Figure 1: On the left we show the ultrasonic scan setup from infrared laser view point looking towards vibrometer. On the right we show the Time-Voltage scan of Aluminum Sheeting. Each line is the output voltage from the vibrometer with the location of each line being 1 mm apart vertically from each other. The semi-ertical line marks the first peak off each measurement. The fact that the vertical line is constant except near the top and bottom suggests that we have a consistent measurement except near the edges.

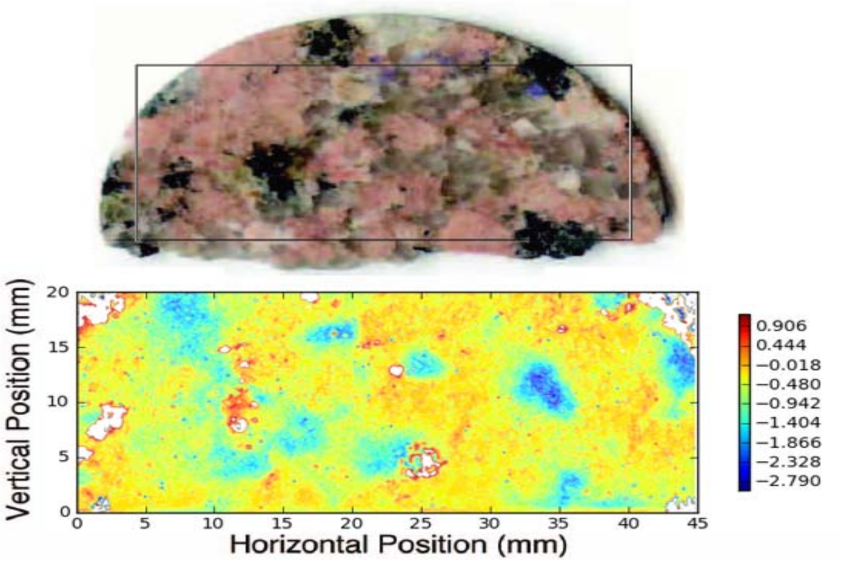

Figure 2: Ultrasonic time contrast map of granite (black grains are biotite, gray are quartz, pink are feldspar crystals). Shown here is the time for an ultrasonic wave to travel through a 2.13mm thick granite sample (below) and an optical scan of the granite sample (above). Changes in the time relate to the changes in the elastic properties of granite. Granite image made using a flatbed scanner.

Previously, with the same granite sample, we spatially scanned it with millimeter waves generated from a millimeter wave vector network analyzer (MVNA; AB Millemetre of France). This setup generated millimeter waves focused using a Teflon cone. The waves moved through the sample into a second Teflon cone and then into a receiver that measured the change in phase of the electric field at 150 GHz (2 mm wavelength in free space). Then using a motor controller and motors that held the sample we were able to spatially scan over the sample. The phase change of the transmitted wave is important due to it being proportional to the index of refraction. (For more details see [1]).

Figure (3) shows the optical scan (top) and phase map (bottom) of the medium grain granite from the millimeter wave scan. Correlating the colors of the phase map to the optical scan we can see that the red colors (large positive phase perturbations) correspond to quartz. The green color (zero relative phase) corresponds to feldspar. The bluish color (large negative perturbation) corresponds to biotite. Finally we put the figures together in Figure (4) to show correlations.

Reference

[1] Nathan S. Greeney and John A. Scales. Dielectric microscopy with submillimeter resolution. Applied Physics Letters, 91(22):222909, 2007.

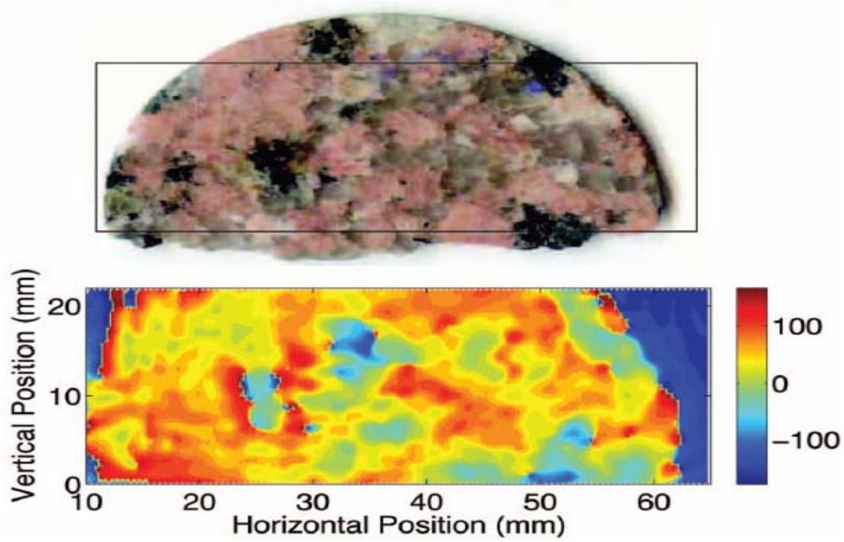

Figure 3: MM wave phase contrast map of granite. Shown here is the phase of z-component of the electric field at 150 GHz transmitted through a 2.13 mm thick piece of granite (below) and an optical scan of the granite sample (above). Changes in the phase relate to the changes in the dielectric properties of granite.

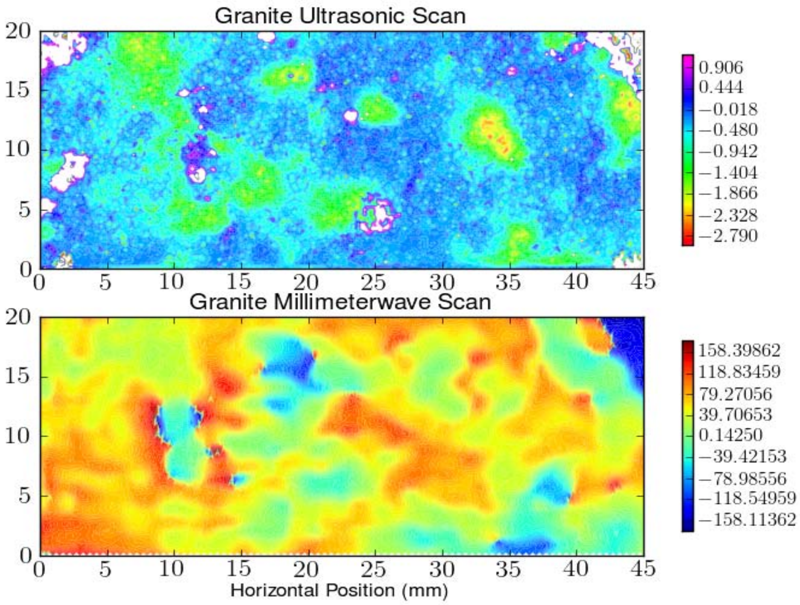

Figure 4: Comparison of time map in microseconds (top) and phase map in degrees (bottom) of the medium grain granite sample. The similarities between the two show there it a relationship between the two leading to a relationship between the dielectric and elasticity.

UNIVERSITY OF CONNECTICUT

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Grant: DE-FG02-95ER14528

Air-Derived Noble Gases in Sediments: Sites and Mechanisms for Trapped Components

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Lawrence Berkeley National Laboratory

Objective: This project seeks to improve the application of noble gas isotope studies to multiphase fluid processes in the Earth's crust by (1) identifying the important noble gas carrier phases in sediments to address the processes that have led to the observed enrichment/depletion patterns in sedimentary rocks and fluids, (2) examine the mechanisms by which such noble gas patterns are acquired, trapped and subsequently released to mobile crustal fluids, and (3) evaluate the time and length scales for the transport of noble gas components, such as radiogenic ^{4}He, through the continental crust.

Project Description: Sedimentary rocks and oil field gases typically are enriched in heavy noble gases: Xe/Ar ratios of ~10-10,000 times the ratio in air have been observed that can not be explained by adsorption hypotheses. Laboratory experiments designed to isolate sedimentary phases for noble gas analysis are conducted to identify the carrier phase(s). It has been observed that radiogenic ^{4}He accumulates in confined aquifer waters at rates that exceed the rate of local production and approaching the whole crustal production rate. A literature evaluation of ^{4}He, ^{3}He crustal fluxes is being conducted to evaluate crustal scale mass transport in terms of the rate, mechanisms, temporal and spatial variability and the role played by tectonic processes.

Results: The laboratory study has concentrated on noble gas abundances in a variety of sedimentary silica samples. We have found that, in general, samples of inorganic silica have noble gas abundances that are consistent with occlusion of air-saturated water in fluid inclusions and lack requisite enrichment/depletion factors needed to explain the noble gas inventory in oil field fluids. However, numerous replicate analyses of noble gases extracted from silica spicules from live sponges (Calyxnicaeensis) show significantly enriched Ar, Kr, and Xe concentrations ($[^i\mathrm{Ng}]_{sample}/[^i\mathrm{Ng}]_{asw} > 1$), but with very little if any mass dependence in the acquisition and trapping of Ar, Kr and Xe. Noble gases in silica samples from the (diatomaceous) Monterey Formation (Elk Hills oil field, CA) and an Atlantic box core were found to be somewhat depleted with respect to the sponge spicule, fractionated in a fashion favoring the heavy noble gases, and approach the compositions that have been observed in bulk deep sea sediments. We suspect that the differences in noble gas absolute and relative abundances between the sponge spicule samples and the more evolved diatomaceous samples are related to either (1) fundamental differences in the biologically controlled mineralization or (2) post-depositional effects related to the progressive crystallization of amorphous silica (e.g. opal-A) to more ordered structures. Laboratory cultured diatoms and box core sea sediment samples collected as a function of depth within the sediment column have been processed for analysis of the silica phases to address these questions.

Through a statistical evaluation using a global data base covering many geologic environments, we have determined that the log normal mean of the radiogenic ^{4}He flux across the Earth's continental crust is 4.18 x 10^{10} ^{4}He atoms m^{-2} s^{-1}. Furthermore, it was found that the range of the continental ^{4}He degassing flux increases with decreasing time and space scales. The statistics can be interpreted as reflecting natural variability and suggest that the mechanisms transporting the crustal helium degassing flux contain a high degree of both spatial and temporal variability. This estimate of the log normal mean of the continental degassing flux of ^{4}He is approximately equivalent to the radiogenic production rate for ^{4}He in the whole crust. Large scale vertical mass transport in continental crust is estimated as scaled values of the order 10^{-5} cm^2s^{-1} for helium (over 2Byr and 40km vertically) vs. 10^{-2} cm^2s^{-1} for heat. This rate of mass transport requires not only release of He from the solid phase via diffusion, fracturing or comminution; but also an enhanced rate of mass transport facilitated by some degree of fluid advection. This further implies a separation of heat and mass during transport.

UNIVERSITY OF FLORIDA

Chemical Engineering Department, PO Box 116005, Gainesville FL 32611

Grant: DE-FG02-98ER14853

Multiscale Modeling of Dissolution in Rough Fractures

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Website: http://ladd.che.ufl.edu/research.dissolution/dissolution.htm

Current Objectives: We are using a variety of numerical and analytical methods to investigate the dissolution of a single fracture. The knowledge obtained from these investigations will be used to construct a model for the change in fracture permeability during dissolution. Our goal is a model that incorporates the key feature of fracture dissolutions – namely, its strong spatial inhomogeneity – in a sufficiently simple way that it can be used to improve the accuracy of Discrete Fracture Network models at the reservoir scale.

Description: Discrete fracture network models do not include the possibility that spatially localized dissolution can take place within an individual fracture in the network. However, in fractured carbonates there is a *universal* instability in the dissolution front, which can reduce the breakthrough time in an individual fracture by orders of magnitude, thereby completely changing the hydraulic properties of the global fracture network. It is therefore important to develop a model of evolving fracture permeability that includes the inherent heterogeneity of the dissolution process. In this project we are developing a multiscale analysis of the evolution of fracture permeability, using numerical simulations and linear stability analysis.

Our main focus this year has been on the development of a linear stability analysis for an initially smooth fracture. 2D numerical simulations suggested that, contrary to expectations, a smooth fracture (with aperture variations less 0.01%) will eventually transition from a smooth front into a few regions of highly localized dissolution. It has long been recognized that the development of channels of dissolution (or wormholes) has a profound effect on fracture breakthrough times, but it has not been previously recognized that such behavior is inevitable on geophysical scales. A linear stability analysis was originally developed by Prof. Szymczak to check the surprising predictions of the numerical simulations, but the analysis has now developed into a critique of one-dimensional models of karst formation (speleogenesis). Such models assume that the dissolution front is uniform transverse to the flow and in such cases non-linearity in chemical kinetics is essential to explain the deep penetration of reactant. However, our analysis and supporting simulations show that chemical kinetics is secondary to the instability dynamics in promoting long conduits in the dissolving fracture. The most interesting aspect of this analysis is that it predicts a strong wavelength selection for the instability, as illustrated in Fig. 1. Thus for a given flow rate and reaction rate (or Damkohler number) there is a specific wavelength to the instability, proportional to the initial fracture aperture. The long-time evolution of the fracture permeability is dominated by the interaction between the growing channels. Results of this analysis have been submitted for publication to Earth and Planetary Science Letters.

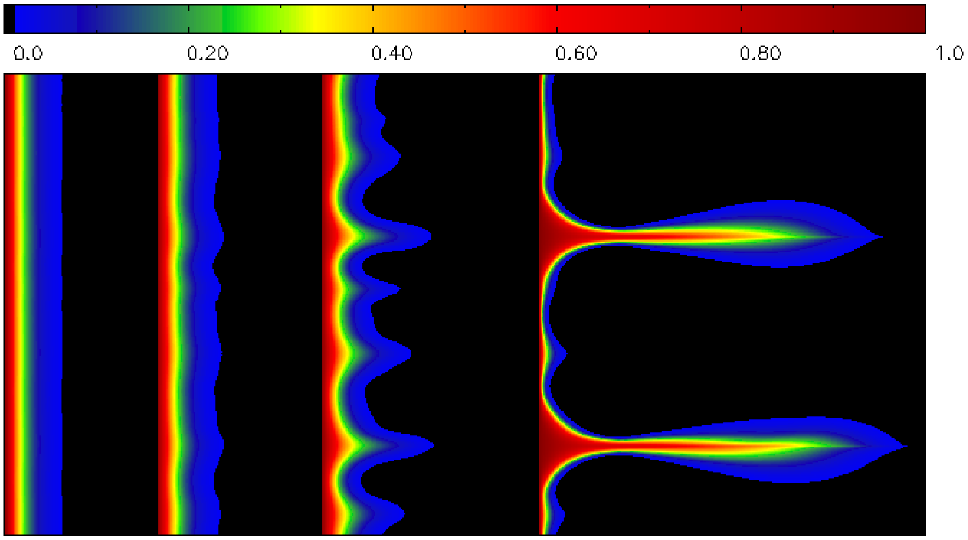

Figure 1. **Evolution of the concentration field in a smooth fracture at equally spaced time intervals.**

GEOCHEMICAL SOCIETY
Washington University in St. Louis
Earth and Plantary Sciences
One Brookings Drive, CB 1169
St. Louis MO 63130-4899

Grant: DE-FG02-10ER16160

Support of Graduate Student Travel Support Program for the 2010 V.M. Goldschmidt Conference, Knoxville, TN, June 13-18, 2010

PIs: Juske Horita; Tel. (806) 742-3109, juske.horita@ttu.edu
Seth Davis; Tel. (314) 935-4131, seth.davis@geochemsoc.org

Website: http://www.geochemsoc.org/programs/goldschmidttravelgrants/2010stg/

Objective: To provide exemplary graduate students with (1) the opportunity to present their own work, either as a talk or as a poster, (2) a professional environment to learn and network, and (3) experience that positively influences their research and career plans for the future.

Project Description The project collected applications for travel funds from students planning to attend the 2010 V.M. Goldschmidt Conference in Knoxville, TN. The applications where then reviewed and ranked with the top students receiving funding. Those students were then asked to complete an online post-conference survey to assess the effectiveness of the program.

Results: The top 11 students of 93 applications were approved for funding of up to $1000 each for a total support of $10,000. The eleven students were from eight different institutions: Arizona State University, Case Western University, Florida International University, Harvard University, Penn State University, University of Maryland, University of Minnesota, and Woods Hole Oceanographic Institution.

<u>POST-CONFERENCE SURVEY</u>: A post conference survey was administered to the 11 students who were funded by the DOE grants funding. Of those, 7 completed the survey. The questions and answers are provided below.

Did you present a poster or a talk?
- Talk - 5
- Poster - 2

What did you learn from the sessions you attended?
- I learned about the current research endeavors of my colleagues and groups across the world.
- I learned what are the front edges of those topics.
- I learned a lot about trace element geochemistry, and how it signifies origin and melting history. Also there is some question as to rather or not the moon originates from a large meteoritic impact event. There is a competing theory that is gaining some ground that the

moon was produced during a fusion event during early Earth accretion and this may be able to describe differences observed in geochemical composition observed in terrestrial and lunar samples. Also I talked to a volunteer from UT about his work on phosphorous bands in olivine from meteorite samples viewed in SEM. These reveal growth rates and directions, which is indicative of cooling history.

- I learned a lot about what other colleagues in my field are working on and had the opportunity to talk to them about there research. Not sure if specifics are needed but I found out a lot about neutrophilic nitrate dependent iron oxidation for one.
- Interesting things I can apply for my research
- Many things- In particular, I learned more about some geochronology techniques (mostly U-series) which I am applying in my own thesis research.
- Updated on some of the more recent findings on deep Earth related topics.

Were you able to establish new connections while attending the conference?

- Yes.
- Yes, I made new connections.
- Yes, certainly. I am currently seeking a postdoctoral position. I originally decided to apply for the travel grant in order to have the opportunity to meet with a potential employer. A job interview stemmed from our lunch meeting. I was also able to meet another potential employer at the meeting as well.
- I met many new colleagues during the meeting. I was able to meet and talk to many people in my field and was able to use what they said to focus the rest of my research. A lot of people had good things to say about the talked and thought it had the potential to be high impact.
- Definitely
- Definitely- the best part was that I received several informal postdoc offers. I will follow up on these as I graduate next year.
- Yes and to renew old contacts.

How did this meeting influence your research plans for the future?

- Collaborations were forged and ideas were nucleated.
- It really brought me some new ideas, and let me know what should I do in the future.
- I learned what is possible with cutting edge techniques in geochemistry. I learned how my research in the deep Earth (300-700 km) can help constrain related fluid-mineral interactions from shallower depths (100-200 km). This will significantly improve my dissertation and manuscript on olivine-ringwoodite transformation kinetics.
- As mentioned above there was a lot of really great input from colleagues about my talk and possibly places to go from here. I have already used that input to focus my research goals.
- I applied for post-doc positions
- I have partially re-designed my U-series geochronology and made connections with potential postdoc supervisors. I also changed a section of a paper I am writing as a result of long discussions with a co-author. These discussions are so much easier to have in person rather than over email.
- Opportunity to present my research is always a good idea.

GEORGE WASHINGTON UNIVERSITY

Department of Chemistry, 725 21st St., NW, Corcoran Hall, Washington, DC 20052

Grant: DE-FG02-02ER15366

Interface Induced Carbonate Mineralization: A Fundamental Geochemical Process Relevant to Carbon Sequestration

PI: H. Henry Teng; Tel. (202) 994-0112, hteng@gwu.edu

Objective: To examine the crystallization process of nesquehonite ($MgCO_3 \cdot 3H_2O$) in aqueous solutions. Specific goals are (1) understanding the kinetics of nucleation and growth; (2) determining the energetic of nucleation.

Project Description Mineral carbonation is one of the proposed strategies for carbon sequestration and can be applied to regions where underground storage is unavailable or where suitable feedstock abounds near large carbon sources. To date, effort in mineral sequestration is largely concentrated on Mg-silicates but is hindered by the slow kinetics and associated high cost. A potential alternative is the carbonation of brucite which has not been a focus because of the mineral's limited natural abundance. However, the much higher reactivity of $Mg(OH)_2$ towards CO_2 points to the application of this mineral to, e.g. flue gases scrubber systems, much like $CaCO_3$ used for desulfurization. In the previous funding period, we conducted brucite carbonation experiments in aqueous environment and elevated pCO_2 conditions and showed that nesquehonite was the chief product. The intent of this year's research was to examine the crystallization process of nesquehonite and gain a better understanding of its potential as a carbon storage phase.

Results: Nesquehonite crystallization experimental was carried in solutions made by mixing reagent grade $MgCl_2$ and Na_2CO_3 at room temperature and ambient pCO_2. Based on the results of our previous study, we chose to fix the solution supersaturation aΩ= IAP/Ksp = 1.97. The nucleation and growth are monitored *in situ* by a laser diffraction size analyzer. Experimental results show that the first solid particles detected by the laser had a radius about 60 nm. These nuclei particles grew quickly from ~100 to 200 nm in diameter to 600 – 800 nm within 10s of seconds (Fig 1). Meanwhile, the particle count dropped rapidly following the decrease in solution supersaturation. For particle larger than 2 μm, however, we found an increase of both particle size and particle count after the initial surge in particle count (within the next 2-3 minutes), marking the post nucleation growth stage where more and more nuclei grew into stable and large crystals. If we assume the first particles detected by the laser are the critical nuclei, then their size can be used to compute the surface energy of the nesquehonite-water interface. Estimated value, 1264 mJ/m^2, compares pretty well with the literature data of 1200 mJ/m^2 for periclase MgO, but is significantly higher than that of magnesite or dolomite (84 and 165 mJ/m^2, respectively). This makes sense because nesquehonite is much less stable thermodynamically than magnesite and dolomite. Kinetic data show a non-linear growth of particles up to approximately 10 -12 μm in diameter, with an average growth rate of 60 -70 nm/s.

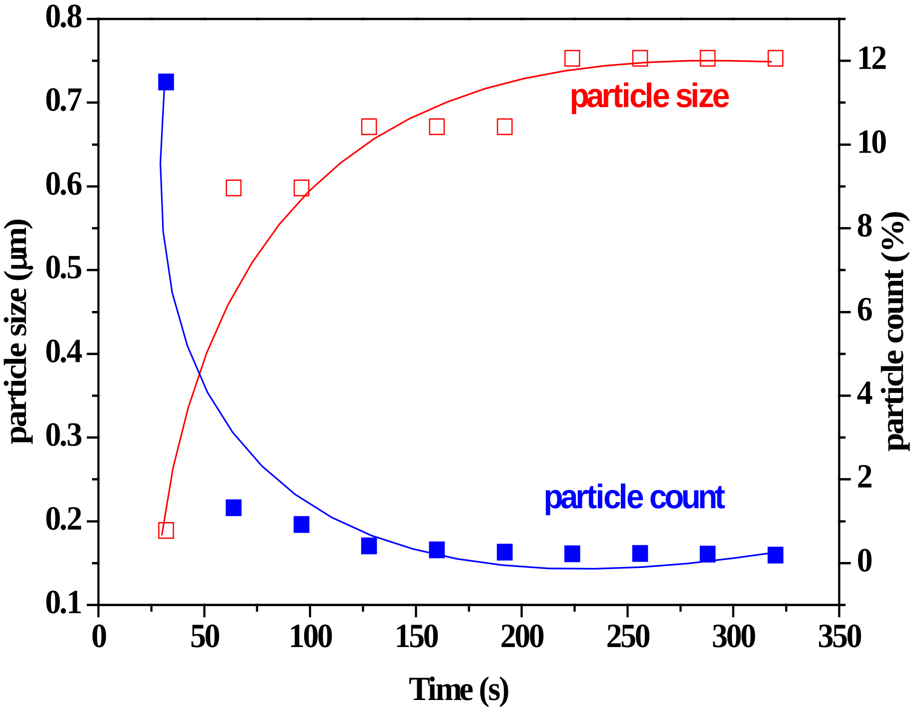

Figure 1. Consumption of nuclei by the rapid initial post-nucleation growth.

GORDON RESEARCH CONFERENCE

Administratrive Office: Tel. (401)-360-1508; 512 Liberty Lane/ West Kingston, RI 02892

Grant: DE-SC0004405

Environmental Bioinorganic Chemistry Gordon Research Conference

PI: Rachel Narehood Austin; Tel. (207) 786-6295, raustin@bates.edu
Bates College, Chemistry Dept, 5 Andrews Rd. Lewiston ME 04240

Co-PI: Ariel Anbar (Co-Chair)
Arizona State University, School of Earth & Space Exploration and
Dept. of Chemistry & Biochemistry

Co-I: Al Crumbliss (Vice-Chair)
Duke University, Department of Chemistry, Durham NC

Website: http://www.grc.org/programs.aspx?year=2010&program=envbiochem

Objective: Our objective for this conference is to understand the roles in biotic processes of inorganic compounds and ions at scales from the molecular to the global.

Project Description: A group of approximately 100 scientists who study bioinorganic chemistry at different scales of biological organization (molecular to ecosystem) using diverse tools met for 5 days in an intense meeting environment to discuss the latest research on the role of selected inorganic elements in key biologically-mediated processes in the environment. The meeting opened with a keynote address connecting the molecular and cellular and global dimensions of our subject. There were seven sessions covering metal ions in photosynthesis, metallomics, bioinorganic chemistry and public health, imaging the distribution of metals in cells, bioinorganic chemical oceanography, bioinorganic chemistry of the ancient earth and other planets, and environmental metallomics. Poster sessions before dinner each day gave afford all registrants the opportunity to discuss their science with each other. The conference closed with a lecture presenting novel research on the role of manganese in living systems. This conference is unique in deliberately bringing scientists with diverse perspectives together to make connections among bioinorganic processes across spatial and temporal scales and to foster discovery of common and disparate patterns in such processes across the Periodic Table. The conference attendees were diverse with a high proportional of young scientists. The gender balance among participants, speakers and discussion leaders was excellent. Participant enthusiasm for the conference and the high quality of the science was high, as judged by survey responses and unsolicited comments.

GORDON RESEARCH CONFERENCE

Administratrive Office: Tel. (401)-360-1508; 512 Liberty Lane/ West Kingston, RI 02892

Grant: **DE-SC0004474**

Rock Deformation Gordon Research Conference

PI: David Prior; University of Liverpool, davep@liv.ac.uk
As of January 2011: University of Otago (New Zealand)
http://www.otago.ac.nz/geology/people/prior/index.html

Website: http://www.grc.org/programs.aspx?year=2010&program=rockdef

Objectives: To hold the Rock Deformation Gordon Research Conference to highlight the latest research and future trends in brittle and ductile rock mechanics, with experimental, field and theoretical contributions.

Project Description: To explore the theme "Transient and transitional behavior in rock deformation: moving away from steady-state". To use this forum to shape the scientific debate and provide inspiration for young researchers and to fill the still extensive gaps in our knowledge of how the Earth deforms. This is one of the few conferences in a busy conference schedule where young researchers have open access to all levels of the scientific community, so that they can talk face-to-face with leaders in their chosen field about their research. To this end DoE Funding was directed to early career researchers and the programme was designed with a high proportion of younger researchers and female researchers to encourage wide and representative participation from early career researchers.

Results: Formal evaluations are not yet available. However it is clear that this GRC was a great success. The participation level was among the highest seen at a GRC in rock deformation with 130 registered participants. The demographic was skewed towards early career researchers with 90 of the registrant being early-career researchers including 50 graduate students. Informal feedback suggests that the early career researchers benefited significantly from the experience. One graduate student sent the following email (extract) after the meeting: "that was one of the best conferences I've ever been to. I hope this isn't awkward for me to mention, but it was noticeable that you had made a serious effort to diversify both the attendees and the speaker line up. I have been to conferences where this was not the case and where I found it much more difficult to speak up and participate in discussion".

UNIVERSITY OF HAWAII

Department of Geology and Geophysics, Honolulu HI 96822

Grant: DE-FG02-06ER15831

Development of New Biomarkers for Surficial Earth Processes

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Website: http://www.soest.hawaii.edu/GG/FACULTY/jahren/research/bygrant.html

Objectives: To quantify the carbon isotopic fractionation between plant tissue and the atmosphere at $p\mathrm{CO_2}$ levels up to 1791 ppm (~6x), which encompasses the entire range of projections for the Cenozoic, in order test the use of plant tissue to determine $\delta^{13}\mathrm{CO_2}$ across the highly fertilizing environment of the last ~65 million years.

Project Description: The δ^{13}C value of fossil terrestrial plant tissue is increasingly used as a biomarker of paleoenvironment. In 2000, we proposed that $\delta^{13}\mathrm{CO_2}$ can be calculated from the δ^{13}C of terrestrial land plants ($\delta^{13}C_p$) based on the strong linear correlation between $\delta^{13}\mathrm{CO_2}$ and C3-$\delta^{13}C_p$ values [r^2=0.91; 519 measurements on 176 species] seen in the ecological literature. In order to expand the application, we wished to test plants grown across a large range in $\mathrm{pCO_2}$ levels (i.e., levels similar to those seen through the last 65 million years) in order to evaluate the relationship between $\delta^{13}\mathrm{CO_2}$ and $\delta^{13}C_p$ values under enhanced growth. We grew *Raphanus sativus* L. (common radish) under $p\mathrm{CO_2}$ levels ranging from that of today's atmosphere (389 ppm) to 6× that of today (1791 ppm). During the 47-day experiments, plants were supplied with excess water, nitrogen, phosphorus and other nutrients. Upon harvest, the $\delta^{13}C_p$ value was determined for both above- and below-ground biomass; during growth the $\delta^{13}\mathrm{CO_2}$ value of each experimental chamber was monitored.

Results: In keeping with the majority of the previous studies on $\mathrm{CO_2}$ fertilization, we observed *R. sativus* grown to maturity under elevated $p\mathrm{CO_2}$ levels to have greater total biomass than those grown under ambient atmospheric conditions; during the final year of this grant we endeavored to analyze biomass augmentation using methods commonly employed by ecologists. Within our experiments, the plant-to-plant biomass variability did not exceed what is commonly observed for plant experiments in general. Total-biomass variability for each set of growing conditions (measured as the standard deviation of the ln-transformed biomass data) averaged 0.29, which is nearly identical to the median variability in total biomass determined by Poorter and Navas* (2003) for 700 herbaceous plants (0.28). We analyzed our biomass data in terms of a hyperbolic response, as routinely invoked for modeling $\mathrm{CO_2}$ and light responses of photosynthesis in single leaves and whole plants (Lloyd and Farquhar, 1996; Nowak *et al.*, 2004). In order to perform a direct and specific quantitative comparison to lower $p\mathrm{CO_2}$ experiments, the data were plotted and fitted to a two-parameter rectangular hyperbola, after the method used by Hunt *et al.*, (1991; 1993) for assessing the trajectory of the biomass response for 36 herbaceous species grown under $p\mathrm{CO_2}$ levels ranging from 365 to 812 ppmv:

$$y = \frac{abx}{a + bx} \qquad (1)$$

where y is the plant-yield variable (i.e., biomass); x is the $p\mathrm{CO}_2$ level; a is the asymptote; and b is the slope at $y = x = 100$ ppmv, the value used for CO_2 compensation point of dicotyledons (Ludlow and Jarvis, 1971; after Hunt *et al.*, 1991). Hunt *et al.* (1991; 1993) defined the value b as an overall index of CO_2 responsiveness: at low b values the function approaches the asymptote slowly, at high b more rapidly. Because the function is non-linear, fitted estimates of a and b were obtained by iterative optimization to maximize the correlation coefficient (r):

$$r = \sqrt{1 - \frac{\sum_{i=1}^{n} (y_i - yf_i)^2}{\sum_{i=1}^{n} (y_i - \overline{y})^2}} \qquad (2)$$

where y_i is the average biomass value at each $p\mathrm{CO}_2$ level, yf_i is the fitted biomass value at each $p\mathrm{CO}_2$ level, and $\overline{y}$ is the mean biomass value for all $p\mathrm{CO}_2$ levels. While the above-ground response ($b = 0.23$) was similar to the mean value of responsive (i.e., total biomass, $b < 1$) angiosperms ($b = 0.38$; $n = 23$) (Hunt *et al.*, 1991, 1993), the below-ground response was remarkable ($b = 0.07$).

Percent biomass increase across the full spectrum of $p\mathrm{CO}_2$ levels, calculated from the fitted biomass values, showed that the total biomass increase we observed for *R. sativus* at $p\mathrm{CO}_2$ levels up to 760 ppmv was consistent with the average percent increase observed in ten experiments on *R. sativus* grown at ambient (330-386 ppmv) and elevated (600-761 ppmv) $p\mathrm{CO}_2$. Maximum biomass augmentation, however, occurred in below-ground tissues, which will likely have a major impact on the distribution of biomass within the plant. An increase in root-to-shoot ratio is a common observation in experiments that elevate $p\mathrm{CO}_2$ to ~700 ppmv (Rogers *et al.*, 1994; Rogers *et al.*, 1996) resulting from increased root size (length, diameter, and dry weight) (Rogers *et al.*, 1992), and has been observed in *R. sativus*, specifically (Overdieck *et al.*, 1988; Barnes and Pfirrmann, 1992; Chu *et al.*, 1992; Wong, 1993; Jablonski, 1997). The percent biomass increase was up to 58 % and 279 % for above- and below-ground tissues, respectively. Much of the net increase (38 % for above- and 53 % for below-ground biomass) occurred above 700 ppmv, *i.e.,* above the average $p\mathrm{CO}_2$ estimates for 2100 (Houghton *et al.*, 1992) and most commonly used elevated $p\mathrm{CO}_2$ level in two-point experiments (Poorter and Navas, 2003).

For above-ground tissues, the trajectory of percent biomass increase observed in our experiments up to ~1800 ppmv is identical to the trajectory of Hunt et al. (1991; 1993) for lower $p\mathrm{CO}_2$ experiments (< 800 ppm). The trajectory that we observed for below-ground biomass increase was extremely high compared to other herbs, causing the trajectory for total biomass to similarly exceed extrapolation based on previous experiments. If we compare the fertilization trajectory we observed to the results of two-point studies on root crops, we see that the data for lower $p\mathrm{CO}_2$ studies is within the range of our study for both above- and below-ground tissues, and for very high $p\mathrm{CO}_2$ levels, below-ground fertilization increases significantly. Other workers have shown that below-ground tissues for root crops may increase significantly more than non-root crops under slightly elevated $p\mathrm{CO}_2$ levels (Idso *et al.*, 1988); our work suggests that this effect will continue to augment at very high $p\mathrm{CO}_2$ levels (> 750 ppmv).

Note: *A full list of references cited herein is available upon request.*

UNIVERSITY OF ILLINOIS AT CHICAGO

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Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source

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Objectives: The objective of this program is to advance the basic understanding of rock-fluid and soil-fluid interactions through experimental studies on atomic-scale processes at the mineral-fluid interfaces. This is crucial to establishing the relation between atomic-scale processes and macroscopic geochemical transport in natural systems.

Project Description: The principal approach is to observe single-crystal mineral surfaces in situ during chemically controlled reactions with fluids using high brilliance synchrotron radiation. Experimental techniques include high resolution X-ray scattering (X-ray reflectivity, x-ray standing waves, resonant anomalous X-ray reflectivity) as well as X-ray absorption spectroscopy. Phenomena of interest include mineral-water interface structure, adsorption/desorption of ions and organic molecules, dissolution, precipitation and growth. Experiments are performed on common rock- and soil-forming minerals under conditions representative of geochemical environments near Earth's surface. A fundamental understanding of the molecular-scale processes is obtained through direct observations of interfaces before, during and after reaction.

Results:

Recent research focused on resolving mineral-water interface structure and reactivity with ~Å-resolution and sensitivities. The primary emphasis of these studies has been on understanding the reaction of mineral surfaces with solution species, including interfacial structure, ion adsorption, and the role of natural organic matter and ionic strength in mediating ion-mineral interactions and growth/dissolution processes. Additional efforts were made in the development of interfacial X-ray based analytical techniques needed to answer fundamental questions in geochemical research.

Ongoing studies of silicate dissolution processes used in-situ X-ray reflectivity (XR) to probe the dissolution of orthoclase(001) surfaces at 85°C and pOH=2. We observed that the addition of 2 *m* NaCl increases the overall dissolution rate by a factor of ~5, and leads to a rougher surface than found in the absence of NaCl. Parallel ex-situ measurements were made using X-ray reflection interface microscopy (XRIM), a new surface imaging tool developed by this program. Reacted surfaces were imaged revealing that orthoclase initially dissolves heterogeneously at these high saline conditions, leading to micron-scale regions with locally increased roughness.

These XRIM results complement the in-situ XR observations by providing information on the *lateral* variation of interfacial reactivity. At the same time, and these results demonstrate for the first time the ability of XRIM to image interfacial reactivity using this non-invasive X-ray microscopy. This establishes XRIM as a new approach for imaging interfacial processes, complementing existing imaging approaches (e.g., atomic force microscopy).

Following up on the development of ex-situ XRIM capability, a prototype flow-through apparatus was developed for in-situ XRIM and tested under conditions of low pOH and varying solution ionic strength. Apparent beam-induced surface damage caused by roughening in the beam spot was observed, and attributed to surface reactions with photolysis products of water dissociated in the beam path. The time constant of apparent beam-induced roughening decreased with increasing ionic strength of the solution.

UNIVERSITY OF ILLINOIS, URBANA-CHAMPAIGN

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Grant : DE-FG02-08ER15961

Aqueous Geochemistry at High Pressures and Temperatures

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Objectives: The goal of this study is to further our understanding of deep subduction zone processes that involve aqueous fluids, including halide and CO_2-bearing fluids. This will be achieved through equation-of-state measurements of H_2O- and CO_2-rich fluids at high pressures and temperatures, and by X-ray and neutron scattering experiments.

Project Description: Convergent margins are critical for understanding the global geochemical cycles of volatiles such as hydrogen (as H_2O) and carbon (as CO_2). Despite the essential role of deep fluids in subduction zone processes, the absence of experimental thermodynamic data precludes quantitative modeling of reactions and mass transfer in this setting. The vast majority of aqueous geochemistry studies have been conducted at pressures below ~0.3 GPa, and the widely-used Helgeson-Kirkham-Flowers equations of state for aqueous species are applicable to ≤ 0.5GPa (~ 15km depth). The aim of this project is to determine the sound velocities, equations of state (EOS), and atomic-scale structures of model fluid systems to the high pressures and temperatures appropriate to subduction zones. Brillouin scattering measurements of velocities and EOS on aqueous fluids will be performed to at least 10 GPa and 700° C, and X-ray and neutron scattering experiments will be performed to constrain the atomic-scale structures of the same solutions.

Results: Over the past year, we have emphasized synchrotron-based measurements of the sound velocities and phase diagram of water, and the equation of state of H_2O ices. Experiments were performed at the Sector 13 (GSECARS) of the Advanced Photon Source, using the facility that the UIUC group built for simultaneous Brillouin scattering and synchrotron X-ray diffraction (XRD) (Ref.1). The importance of such measurements is that pressure is measured using X-ray diffraction from an inert Au flake or the Au liner of the sample chamber containing the supercritical fluid (H_2O in this case). We avoid contamination from other sample markers such as ruby, which dissolve and contaminate the sample at high temperatures. Our results show that the melting curve of water-Ice VII above P=4 GPa is higher than previously reported (Datchi et al.). At the highest pressure studied of P=12.5 GPa, our melting curve is higher by over 150°C. We believe that these major differences in the phase diagram of water are due to dissolution of the pressure medium in the water sample (that is, contamination), and the lack of accurate temperature calibration of the DAC. Work by our Livermore co-PI's have accurately calibrated the temperatures in our membrane diamond cells using standard materials indicate that our uncertainties in temperature are ~10°C at 800°C. Such careful temperature metrology has not been reported before on internally-heated diamond cells. We have also performed experiments on the equation of state of Ice VII, for which previously reported bulk moduli vary by over a factor of two. At all PT points in Fig 1 we have measured the sound velocities of water and ice by Brillouin, placing constraints on their equations of state.

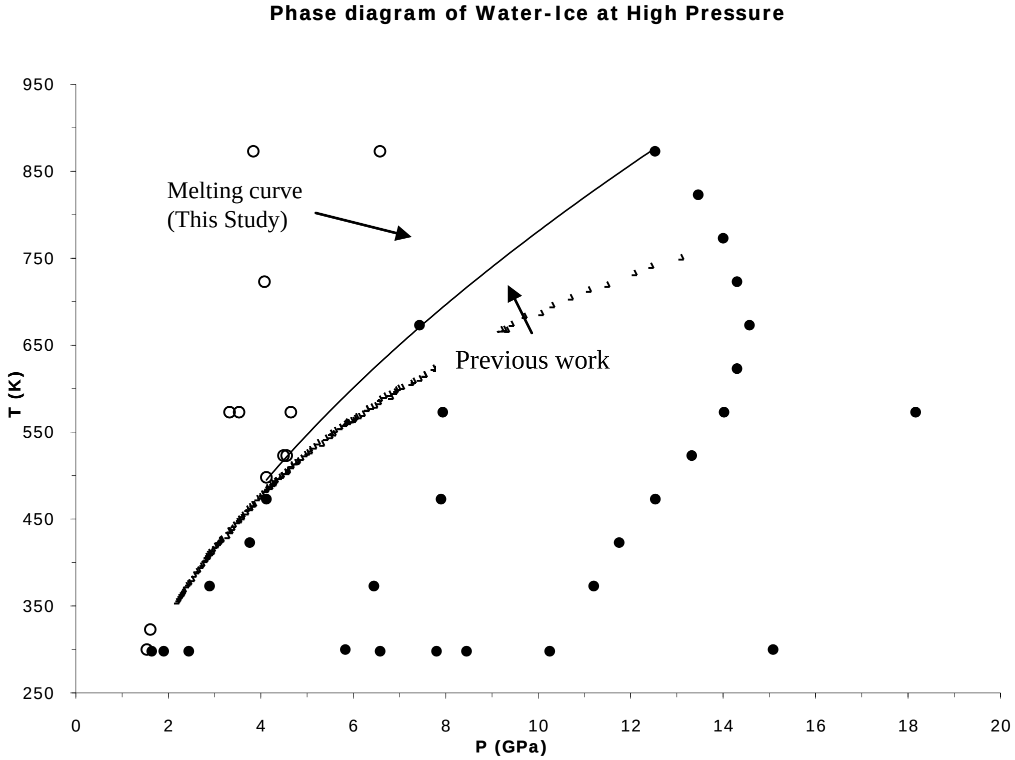

Figure 1 : The phase relations of water and Ice VII from this study and from ref. 2. Solid circles are Ice VII (this study), open circles are water (this study), and triangles are from ref. 2.

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[2] Datchi, F., Loubeyre, P., LeToullec, R. (2000) Extended and accurate determination of the melting curves of argon, helium, ice (H_2O), and hydrogen. Phys. Rev. B 61, 6535-6547.

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Integrated Field, Laboratory, and Modeling Study of Microbial Activity in Pristine Aquifers

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Objective: The goal of this project is to develop, using techniques of molecular biology and on the basis of rigorous quantitative analysis, an improved understanding of the relationship between the chemical composition of groundwater in an aquifer and the microbial community there. Key questions to be addressed by this research include: 1) In what ways does microbial activity affect the chemical composition of groundwater? 2) How does groundwater composition affect the structure of the microbial community? What kinetic and thermodynamic factors in the subsurface control the rate of microbial activity? 3) How do the methods available to sample and observe the microbial community affect our knowledge of its nature? 4) What can reactive transport models tell us about the chemical evolution of groundwater flowing through biologically active aquifers?

Project Description: The study will use advanced techniques in molecular biology (specifically, quantitative reverse transcriptase PCR), combined with *in-situ* sampling of attached microorganisms and dissolved gas concentrations, to address the relationship between the chemical composition of groundwater and its microbial community for the Mahomet Aquifer, the regional water supply for central Illinois. The study will integrate benchtop column experiments, field study, and numerical modeling to address a number of specific questions of current interest: 1) Which microbial populations are active, and at what specific rates? 2) What is the distribution of activity between microbes suspended in the groundwater and those attached to sediments? 3) To what extent do dissolved gas concentrations and volatile fatty acid (VFA, e.g. acetate) concentrations in the groundwater reflect the activity of specific groups of microbes? Results of the study will help establish use of advanced techniques of molecular biology to define not just the identities of microbial populations in the subsurface, and in experiments, but the specific activities of those populations. The results will help reveal the relationship between microbial activity and groundwater quality.

Results: Previously, we performed a comprehensive analysis of how the communities of attached and suspended microbes in an aquifer vary depending on the concentrations of sulfate and ferrous iron. A statistical comparison of the community profiles revealed systematic similarities and differences in the bacterial communities between sites with high and low sulfate concentrations. We found no relation between ferrous iron or sulfide concentrations to community composition in the aquifer, even where iron reducers were predominant. Sulfate reducing bacteria (SRBs) also occurred in both low and high sulfate wells, with different taxa being present in each type of environment. In a collaborative related project with Dr. Jorge

SantoDomingo at EPA in Cincinnati, more 16S rRNA gene clones, including the Archaea, have been sequenced from the DNA extracted from attached microbial communities. The EPA interest relates to understanding background microbial community composition in an aquifer prior to influence by elevated CO_2 due to carbon sequestration. The results benefit our project by adding more power to our molecular ecological analysis of processes in the Mahomet aquifer.

To obtain real rate data, we have focused on bacterial mediated sulfate reduction, specifically on the quantitative relation between the RNA gene transcripts (mRNA) of the dissimilatory sulfite reductase (*dsr*A) gene associated with the rate of that sulfate reduction. Using a novel bioreactor design, we quantified this relation at sulfate reduction rates 300 times lower than previously tested using *Desulfovibrio vulgaris* and found that the relative *dsr*A transcript per cell decreases proportionally with the rate of sulfate reduction (Fig. 1). We are continuing this with Mahomet aquifer isolates.

To facilitate the frequency of groundwater biogeochemical data collection, we developed a passive sampling approach to analyze for gas and aqueous ions. Using this method we demonstrated that wells in the Mahomet can be monitored for spatial and temporal variation in groundwater chemistry without being pumped. We found that monitoring wells near municipal production wells show large variations in dissolved gas concentrations, with partial pressures ranging in a single well from < 0.05 atm to 0.8 atm (data not shown).

We have developed numerical models of the origin of microbiological zoning in groundwater flows, based on principles of thermodynamics, kinetics, and population ecology. The modeling shows neither thermodynamic nor simple kinetic interpretations explain the mechanism by a microbial population excludes others from a zone. Instead, microbes in the models exclude competitors by maintaining conditions under which growth of other populations is insufficient to replace cells lost to decay and predation. The models show that communities assumed to be dominated by a single functional group may in fact be areas of mixed metabolism, and that zones containing iron-rich groundwater may be dominated by sulfate reducing bacteria, rather than iron reducers.

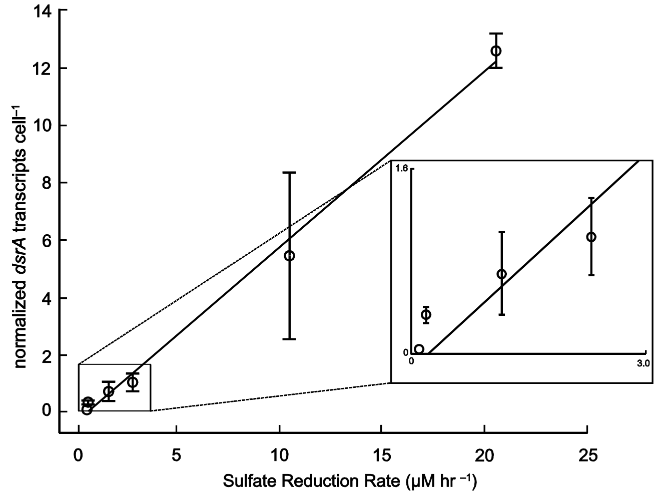

Figure 1: Relationship between the relative *dsrA* mRNA transcripts expressed per cell and the sulfate reduction rate maintained in the reactors. The symbols represent the means ± standard deviations of samples taken from duplicate cultures, two reverse transcription reactions, and triplicate QPCR reactions per sample. The regression equation is $y = 0.6097x - 0.125$ ($R^2 = 0.99$).

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Grant: DE-FG02-96ER14616

Predictive Single-Site Protonation and Cation Adsorption Modeling

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Objectives: The overall goal of this research is to develop a predictive model of adsorption processes at the mineral-water interface that can advance a fundamental understanding of the role of mineral-surface chemistry in the chemical evolution of shallow and deep groundwaters, the fate of contaminants in groundwaters, and the storage of carbon dioxide in the subsurface.

Project description: The research is aimed at generating a comprehensive, internally consistent, quantitative description of the interactions of natural waters with mineral surfaces for both well crystallized and poorly crystalline materials and both inorganic and organic species. The model is being developed to integrate all the available experimental information on adsorption with spectroscopic results for the nature of surface species. By so doing, it will facilitate the comparison of experimental data from different investigators and enable interpolation and extrapolation to conditions not yet studied experimentally. This provides a basis for analysing the role of surface complexation in natural and contaminated environments. It will help lead to predictive models of the behavior of nuclear waste in the subsurface, the migration of subsurface carbon dioxide, and the behavior of nanoparticles interacting with contaminants.

Results: We focussed on describing carbonate adsorption on mineral surfaces and the competitive adsorption of carbonate and arsenate. Although carbonate adsorption on goethite has been well documented, little is known about carbonate adsorption on other geologically important minerals. After carrying out a detailed surface complexation model analysis of carbonate adsorption on goethite we obtained thermodynamic equilibrium constants that can be used in more complex systems. In addition, we used Born solvation theory to help develop a linear free energy correlation for oxyanion species including carbonate and our published results for sulfate and oxalate. This enables prediction of carbonate adsorption on many minerals over a wide range of environmental conditions. In this way, results for inorganic and organic systems can be generalized in a predictive framework.

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Grant: DE-FG02-89ER14074

Crystal Chemistry of Toxic Metal Sequestration

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Objectives: This project involves development and application of integrated imaging and spectroscopic methods to uranium contaminated soils. Specific objectives this year have included investigation of a newly discovered, nanoscale zirconium (oxyhydr) oxide at the Hanford 300 Area and detailed investigation of the crystal chemistry of uranyl phosphates.

Project Description: The project centers on the crystal chemistry of minerals that host toxic metals in contaminated environments. The current focus is investigation of uranium sequestration by adsorption on surfaces and incorporation within mineral hosts using TEM, FIB, neutron scattering, and synchrotron-based techniques.

Results: We have extended our investigation of solid hosts for uranium in samples of vadose-zone sediments from the Hanford 300 Area. The newly discovered zirconium (oxyhydr)oxide phase has proven particularly interesting. We are using an integrated FIB, TEM-based EELS and electron microprobe analysis (EPMA) approach to investigate and characterize this phase and have shown that it sequesters a significant portion (16%) of the U in the shallowest vadose zone samples. The phase is intimately intergrown with phyllosilicates in fine-grained coatings found on lithic and mineral fragments in the shallow portion of the vadose zone. EELS reveals a P:Zr atomic ratio of ~0.2, suggesting the phase is either intergrown with minor amounts of a Zr-phosphate or has adsorbed a significant amount of phosphate. Preliminary synchrotron-based x-ray microprobe reveal details of spatial distribution. MicroXRD and electron diffraction show the material is amorphous. MicroXAS data were collected and EXAFS modeling has begun that suggests the phosphate is, indeed, a sorbed species.

A second area of focus involves structural and chemical investigation of meta-autunite group minerals including metatorbernite [$Cu(UO_2)_2(PO_4)_2{\cdot}8H_2O$] which is found in grain coatings at Hanford. Metatorbernite comprises autunite-type sheets of corner-sharing uranyl square bipyramids and phosphate tetrahedra with interlayer Cu^{2+} and molecular water (Locock and Burns, 2003). Its hydration state varies with temperature and water activity (Burns, 2005). Understanding the formation and abundance of autunite/meta-autunite minerals is fundamental to geochemical understanding and remediation efforts for many soils contaminated with uranium in both natural and anthropogenically contaminated environments (e.g. our recent work in Stubbs et al., 2009 and refs therein).

We have investigated dehydration in metatorbernite from 31.5-315 ˚C using continuous heating during synchrotron x-ray powder diffraction (Stubbs et al, 2010) and identified four phases characterized by distinct basal spacings of 8.7 Å, 8.3 Å, 6.9 Å and 5.4 Å. These phases correspond to metatorbernite (8 interlayer H_2O) and unnamed lower hydrates (4, 2 and 1 H_2O) identified by Suzuki et al. (2005). Using powder XRD and Rietveld methods we have successfully refined the structures of the 8.7 Å, 8.3 Å, and 6.9 Å phases in space groups P4/n, P4/n and $P2_1$ respectively. These results are the first refinements for hydrates lower than the 8.7 Å phase. Important results include identification of previously unsuspected distortions in the uranyl-phosphate sheets of the 8.3 Å phase and a complete reconstruction in the 6.9 Å phase to uranophane-type sheets of edge-sharing uranyl pentagonal bipyramids linked by sharing edges and vertices with phosphate tetrahedra. The discovery of this transformation is particularly exciting and explains how the structure overcomes steric constraints on minimum possible basal spacing while maintaining Cu in the interlayer. The discovery of these significant changes in sheet structure suggests major reassessment of the identification and geochemical behavior of uranyl phosphates in a variety of experimental and environmental settings. We are currently analyzing neutron powder diffraction data collected on the HiPPO diffractometer at the Los Alamos Neutron Science Center (LANSCE). This is the first neutron diffraction investigation of metatorbernite and is designed to resolve issues of interlayer Cu occupancy, details of oxygen positioning and location of the interlayer waters that coordinate the Cu and form the basis of the hydrogen bonding network. We have also collected inelastic neutron scattering data from the Fourier Difference Spectrometer (FDS) at LANSCE and are working to detail the interlayer H-bonding network.

UNIVERSITY OF MARYLAND

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Grant: DE-FG02-07ER15916

Collaborative Research: Evolution of Pore Structure and Permeability of Rocks under Hydrothermal Conditions

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Objective

The transport properties of rocks can be altered by diagenetic, metamorphic, and tectonic processes. Such changes are critically important to understanding of industrial applications including resource recovery, carbon-dioxide sequestration, and waste isolation, and natural processes, including metamorphism, fault mechanics, and pressure solution. Here, we propose to investigate the changes of permeability and pore geometry owing to inelastic deformation by solution-transfer, brittle fracturing, and dislocation creep in fluid-filled quartz and calcite rocks and to investigate the effects of loading configuration on porosity and permeability under hydrothermal conditions. We will perform laboratory experiments, numerical calculations, and observations of microstructure. The experiments provide mechanical and transport data under conditions designed to isolate each particular mechanism. Simultaneous measurements of pore volume, permeability, axial and volumetric strain rates will be made under isostatic and conventional triaxial loading. Temperatures (T) up to 800 K will be used, while confining pressure (P_c) and pore pressures (P_f) are maintained independently up to 500 MPa. Microstructure observation made with micro-CT, scanning electron microscopes, and laser confocal scanning optical microscopes, will be used to quantify changes in surface roughness, porosity, and pore dimensions. The data will be used in network, finite-difference and other numerical models to elucidate relations between permeability and other rock properties.

Current Results: Progressive Microscopic Damage and the Development of Macroscopic Fractures in Porous Sandstones

We continue the quest to obtain quantitative relationship between microcrack damage and fault development during brittle failure in porous rocks. A new loading configuration, called lateral relaxation compression, was designed to investigate the interaction between progressive microscopic damage and macroscopic failure. In conventional triaxial tests, the effective mean stress increases as the deviatoric stress increases, whereas in lateral relaxation compression tests, the effective mean stress decreases as deviatoric stress increases. Darley Dale and Berea sandstones with initial porosity of 13% and 21% respectively were deformed using this loading configuration. Dilatancy and strain softening were observed in all of the deformed samples. The critical stress at the onset of shear-induced dilation obtained under lateral relaxation compression is comparable to that reported for the conventional compression tests, but brittle failure during lateral relaxation loading was more stable, allowing us to investigate fault nucleation and growth and to measure quantitatively stress increment, strain softening, and dilatancy. A suite of samples were deformed and subsequently unloaded at different post-failure stages, before macroscopic faulting occurs. Quantitative characterization of crack damage indices, crack density, grain size distribution, and porosity reduction provides characteristic failure patterns. We have developed a MATLAB code to quantify crack density along orientations varying from 0 to 180 degrees with respect to the maximum principal stress. Characterization of the progressive microstructural damage is on-going.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Grant: DE-FG02-07ER15839

Rheology of the Earth's Interior: Experimental Investigation to Pressures of 15 GPa Using the Deformation DIA

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Objectives: The focus of this study is to quantify the rheological behavior of mantle rocks under simulated mantle conditions including high temperature, high pressure, and the presence of fluid phases (i.e., water and melt). The goal of our research is to assure that the flow laws determined in the lab are sufficiently robust to provide a basis for geodynamical models of mass and heat transport in Earth's mantle.

Project Description: We have carried out a series of creep experiments on mantle rocks, with emphasis on the minerals olivine and garnet, using a deformation-DIA (D-DIA), a solid-medium apparatus with the capacity of performing high-pressure triaxial deformation experiments.

Experiments are conducted at temperatures from 673 to 1573 K and pressures from 3 to 10 GPa. Advanced synchrotron x-ray techniques enable *in-situ* measurement of pressure, differential stress, and strain as a function of time. These data are used to quantify the flow properties of mantle rocks in terms of the dependence of creep rate on deformation conditions including stress, pressure, temperature, water fugacity, and melt fraction. We work in close collaboration with David L. Kohlstedt and Shenghua Mei at the University of Minnesota.

Results: To determine the flow behavior of olivine under lithospheric conditions, we carried out a series of experiments on the steady-state creep behavior of polycrystalline olivine at high pressures (~4 to 9 GPa), relatively low temperatures (≤ 673 $T \leq 1273$ K), and anhydrous conditions using a deformation-DIA (D-DIA). Experimental results yield a flow law for low-T plasticity of olivine. Our results yield a Peierls stress of $s_P = 6.2 \pm 0.2$ GPa and activation energy of $E = 290 \pm 60$ kJ mol^{-1}. Our low-temperature plasticity flow law predicts a strength at 873 K and 10^{-14} s^{-1} of ~600 MPa for anhydrous lithospheric mantle.

We have also experimentally investigated the creep behavior of garnet at high pressures. Samples are cold-pressed from a garnet powder and deformed at constant displacement rates ranging from 1.1 to 2.6×10^{-5} s^{-1} at high temperatures (1273 -1473 K) and high pressures (2.4 - 4.1 GPa). Our results provide a measure of the dependence of creep rate of garnet on temperature with an activation energy of ~280 kJ/mol and on pressure with an activation volume of ~10×10^{-6} m^3/mol. Determination of the influence of pressure on viscosity of garnet is critical for extrapolating laboratory results to geological conditions.

Furthermore, we investigated the creep contrast between olivine and garnet, the two major constituent minerals of Earth deeper upper mantle. In this study, samples of olivine and garnet were stacked together, separated by a nickel foil disk. Experiments were carried out at 1373 - 1573 K and pressures of 3 - 5 GPa. At our experimental conditions, samples of olivine deform only a factor of ~1.5 faster than samples of garnet of similar grain size, indicating that there is no significant rheological contrast between samples of olivine and garnet under anhydrous conditions. This result, which is the first direct comparison of the rheological behavior of olivine and garnet, provides a solid basis for modeling the rheological structures of subducted lithosphere.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Grant: DE-FG02-97ER14760

Collaborative Research: Evolution of Pore Structure and Permeability of Rocks under Hydrothermal Conditions

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Objectives: The broad objective of this proposal is to study interrelationships among permeability, mechanical properties, and pore structure of rocks under hydrothermal conditions, with and without metamorphic reactions. We have worked with Prof. W.-L. Zhu, the PI on a collaborative grant to Univ. Maryland, College Park, and occasionally with others, this year including Prof. M. Li, of Southwest Petroleum University, Chengdu, China and Dr. A. Maineult, IPGP, Paris, France.

Project Description: We are studying the changes in transport properties of rocks that result from mechanical deformation, structural heterogeneities, and low-temperature metamorphism using both laboratory and numerical experiments. Conventional triaxial mechanical tests are done at temperatures up to 700°C, and confining and pore fluid pressures up to 400 MPa. Simultaneous measurements of permeability are done during the mechanical tests; and some experiments will also investigate the effects of concurrent metamorphism. Characterization of the pore space is done using SEM, confocal microscopy (LSCM), and CT microtomography. Numerical modeling using finite-element and finite-difference techniques also provides a powerful set of tools to understand variations in pore structure caused by compaction, diagenesis, and cementation.

Results: In recent work, we investigated the effect of pore size heterogeneity and pore connectivity on permeability using simulations of pipe networks with different coordination numbers and different radius distributions. Following a method widely used in percolation theory, we sought "universal" relationships (i.e., independent on lattice type) between macroscopic properties such as permeability k and porosity f, and, pore geometry attributes such as hydraulic radius r_H, coordination number z, and so forth. Our main result was that, in three-dimensional simple cubic, FCC and BCC networks, permeability obeyed "universal" power laws, k µ $(z-z_c)^b$, where the exponent b is a function of the standard deviation of the pore radius distribution and $z_c = 1.5$ is the percolation threshold expressed in terms of the coordination number. Most importantly, these power law relationships hold in a wide domain, from z close to z_c to the maximum possible values of z. A permeability model was inferred based on the power laws mentioned above. It was satisfactorily tested by comparison with published, experimental and microstructural data on Fontainebleau sandstone. We are now applying the same technique to investigate the relationship between permeability and the electrical formation factor.

We continued our work on the effective pressure law (EPL) for permeability. The main problem is that the EPL for permeability is usually significantly non-linear, i.e., if we express it as $p_{\mathrm{eff}} = p_c - \mathrm{k}\ p_f$, where p_c and p_f are the confining and fluid pressures, respectively, then the coefficient k is not a constant but varies with p_c and p_f. The occurrence of a non-linear EPL for permeability has important implications for modeling the pressure dependence of permeability of reservoir rocks and predicting the reservoir evolution during production of oil or gas. In the case of non-linear EPL's, we must distinguish between secant and tangent EPL coefficients (denoted k_s and k_t, respectively). In our previous work, we measured the tangent coefficient k_t for a set of tight sandstones from China. However, the secant coefficient k_s must be included in the relation mentioned above: $p_{\mathrm{eff}} = p_c - \mathrm{k}_s\ p_f$, and we devised a special method to determine it based on the measured values of k_t. To test the method, we applied it to a second set of cores from the E-bei gas reservoir in China.

We are extending our work on pressure solution from numerical modeling of deformation at single contacts to that occurring within a random packing of contacting spheres. This work, now in progress, also aims to compute the time evolution of porosity and permeability within the aggregate. The calculation will incorporate a more realistic set of Hertzian forces at the grain contacts, rather than assuming constant or linearly varying normal stress, as is common in most models. Deformation rates can then be examined as a function of grain-size distribution, temperature and confining pressure; importantly, one may also examine the extent of transient deformation rates.

Recently, we initiated a new set of experiments to measure the effect of low-temperature metamorphism on the permeability of thermally fractured periodite. Experiments were done at 185 °C, 200 bars (20 MPa) pore fluid pressure, and 250 bars (25MPa) confining pressure over 24 hours. During the heat-up, the permeability of the cores decreased rapidly by an order of magnitude from the starting permeability of about 10^{-18} m^2. During the next 23 hours, permeability continued to decrease, but much more slowly. The pore fluid used was saline brine saturated with CO_2 and was essentially stagnant during the experiment. One expects the pore fluid chemistry to be quite important, and current work is focused on improving techniques for controlling and monitoring fluid chemistry during the experiment.

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Grant: DE-FG02-99ER15004

Physics of Channelization: Theory, Experiment, and Observation

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Objectives: We seek a fundamental understanding of the physical processes that erode channels and create drainage networks, by integrating theoretical models, laboratory experiments, and field observations. We focus on channels incised by groundwater flow, and seek to quantitatively relate mechanisms of channel growth to channel shape and network geometry.

P:roject description: Our studies of channel shape concentrate on the growth and form of elevation contours and longitudinal profiles. Our investigations suggest that the focusing of groundwater at the channel head selects predictable forms. We seek to better understand how these forms are selected. The mechanisms that induce bifurcation or “tip-splitting” of the channel head are of particular interest.

At scales much larger than an individual channel, headward erosion, side-branching, and a succession of tip-splitting instabilities create channel networks. These processes are closely related to the ways in which subsurface water is attracted to channel heads. We seek a simple theoretical representation of the subsurface flow and attempt to relate it to sediment flux.

Our investigations involve physical reasoning, mathematical modeling, laboratory experimentation, and observations of kilometer-scale channels. Our field investigations, performed at the Apalachicola Bluffs and Ravines Preserve, near Bristol, Florida, emphasize quantitative tests of our theoretical predictions.

Results: In FY2010 we studied the focusing of groundwater into channel heads and the resulting channel growth. Figure 1a shows the predicted shape of the water table and the resulting aggregation of water in the streams. We find that, for moderate sediment transport intensities, the force balance on the scale of a sand grain determines the width and the depth of a channel at a given slope and water discharge. Conservation of mass then requires that the discharge be proportional to the inverse-square of the channel slope. We test this prediction by comparing the stream discharge determined from simulation to the slope of the stream bed, as measured from a high-resolution map of the study site. Figure 1b shows that the predicted force balance is found in the streams of Bristol. From this constraint, we predict the equilibrium shape of streams and find it to be consistent with observation (Figure 1c).

We have also developed a physical understanding of the bifurcation of a growing valley head. We find that the angle between bifurcating tips in the field site is consistent with the predicted value of 72°.

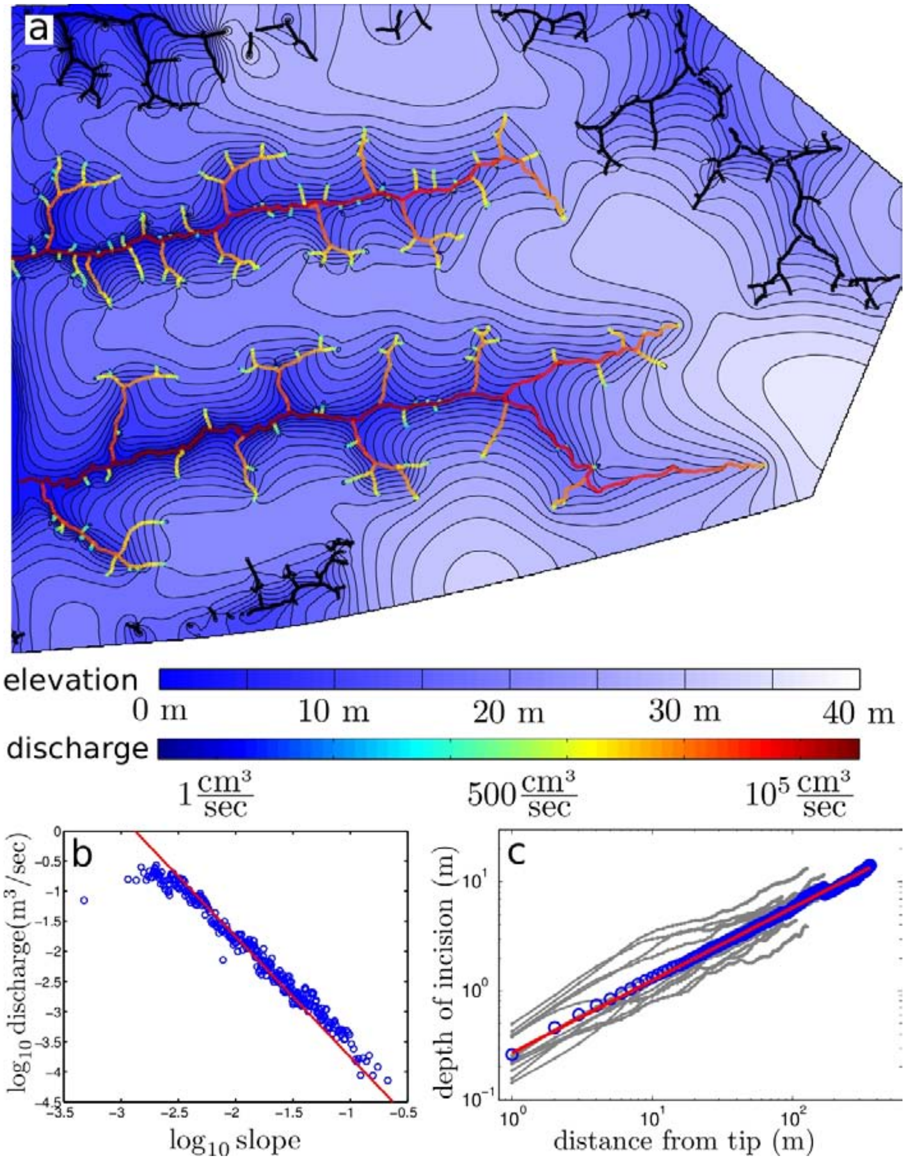

Figure 1: The geometry of seepage valleys represent a balance between the focusing of groundwater and the transport of sediment. (**a**) The predicted shape of the water table around the river networks and the resulting discharges in the stream. (**b**) At equilibrium, the discharge through the stream is balanced by the slope of the stream. Measurements from the field (blue circles) are consistent with the predicted relation (red line). (**c**) From the equilibrium hypothesis, we predict the longitudinal shape of a stream near the spring. The profiles of 10 representative streams (gray lines) are averaged (blue circles) and found to be consistent with prediction (red line).

MICHIGAN STATE UNIVERSITY

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Grant: DE-FG02-08ER15929

Computational and Spectroscopic Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interfaces

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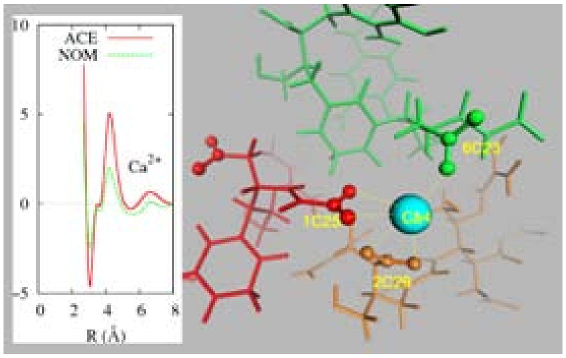
Objectives: The research supported by this grant focuses on development of molecular scale understanding of a range of central issues related to the structure and dynamics of geochemically important fluids, fluid-mineral interfaces, and confined fluids using computational modeling and experimental methods. The work under this grant is closely aligned with the work undertaken under grant DOE DE-FG02-10ER16128 with the same title, Geoffrey Bowers of Alfred University, P.I. The Michigan State efforts are principally computational, and the Alfred University efforts are principally experimental.

Project Description: Molecular scale knowledge of the structure and dynamics of aqueous fluids, how these fluids are affected by mineral surfaces and molecular-scale (nano-) confinement, and how water molecules and dissolved species interact with surfaces is essential to understanding the fundamental chemistry of a wide range of geochemical processes relevant to energy geoscience. These processes include mineral reactivity, dissolution and precipitation, sorption and geochemical transport. Our principal efforts are devoted to continuing development of advanced computational approaches to address these problems, application of these approaches to important geochemical questions, relevant experimental spectroscopic studies, and application of the computational methods to understanding the experimental results. The combination of computational modeling and experimental approaches is proving highly effective in addressing otherwise intractable problems.

Results: In 2010 we completed a series of computational studies of the interaction of the common cations Na^+, Mg^{2+}, and Ca^{2+} with natural organic matter (NOM). NOM is a highly reactive component of natural waters and can interact with and change the solubility and toxicity of many dissolved species. NOM can also form an organic coating on solid surfaces which significantly alters the electrostatic properties of the surface and strongly affects the transport and availability of toxic species. For instance, formation of NOM coatings is a significant factor controlling the stability of viruses in aquatic systems and the performance characteristics of inorganic and polymeric nanofiltration membranes. Common cations are thought to play an important role in the supramolecular aggregation of NOM molecules into colloidal particles, the formation of NOM surface coatings, and the aggregation of mineral particles. The new computational results provide quantitative insight into the structure, energetics, and dynamics of the interactions of NOM molecules with metal cations and the effects of cations on the colloidal aggregation of NOM molecules. Molecular Dynamics (MD) and Potential of Mean Force (PMF) calculations yield a molecular scale structural picture of the metal binding, equilibrium constants describing overall ion association and the distribution of metal cations between different types of binding sites, and the rates of exchange among these sites. The results also demonstrate that the experimentally observed NOM aggregation in the presence of Ca^{2+} is caused by its relatively strong binding to NOM but also by its ability to readily exchange waters of hydration for the O-atoms of the carboxylic groups of NOM. Na^{+} does not bind strongly enough to NOM, and Mg^{2+} can bind strongly but does not readily exchange its hydration waters for the O-atoms of the carboxylic groups. The figure shows the computed potential of mean force between Ca^{2+} and the carboxylic groups of the model NOM molecule and acetate ion in aqueous solution and a structural model illustrating how Ca^{+2} can bridge NOM molecules to form super-molecular clusters.



Potential of mean force between Ca^{2+} and the carboxylic groups of a model molecule of natural organic matter and acetate ion in aqueous solution and a structural model illustrating how Ca^{2+} can bridge NOM molecules to form super-molecular clusters.

We have also completed a comparative quantitative analysis of the quasielastic neutron scattering (QENS) measurements and MD trajectories simulating the librational dynamics of water nano-confined in the highly ordered interlayers of the layered double hydroxide, hydrocalumite $[Ca_2Al(OH)_6]Cl\cdot 2H_2O$. The QENS and MD results both capture the important details of the dynamics of nano-confined water and the effects of the orientational ordering of the interlayer H_2O molecules. Quite unexpectedly, however, the MD simulations also revealed that the dominant mechanism of H_2O reorientation in the interlayers is not the rotation in the plane of the molecule, as we had earlier suggested, but a “flipping” motion in which one hydrogen bond to a neighboring interlayer Cl^{-} ion remains intact, while another H-bond changes its coordination between two other neighboring Cl^{-} ions. The MD simulations also provide the life times of hydrogen bonds formed by the interlayer H_2O molecules.

We have begun a combined experimental spectroscopic (^{43}Ca NMR) and computational study of the structure and formation of amorphous calcium carbonate (ACC) in conjunction with the Alfred University group. That group has successfully synthesized ACC and related crystalline compounds. At Michigan State we have used quantum chemical methods to calculate the ^{43}Ca NMR parameters of these materials. The results are an essential step in our ability to interpret the experimental ^{43}Ca NMR results for ACC. They also demonstrate that it is feasible to characterize these materials using natural abundance ^{43}Ca NMR, since they exhibit parameters similar to those of many inorganic phases already analyzed in the literature.

We have also begun a computational MD study of the structure, dynamics and energetics of interlayer cation in expandable clay minerals with different water contents to help interpret at a detailed molecular level the new ^{23}Na NMR results for hectorite and montmorillonite that the Alfred University group has obtained.

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Grant: DE-FG02-04ER15500

Rheological Properties of Earth's Lithosphere: Experimental Constraints on Low-Temperature Plasticity of Olivine-Rich Rocks at High Pressures

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Objectives: The focus of this study is to quantify the rheological behavior of mantle rocks under simulated mantle conditions including at high temperatures, at high pressures, and in the presence of fluid phases (i.e., water and melt). The goal of our research is to assure that the flow laws determined in the lab are sufficiently robust to provide a basis for geodynamical models of mass and heat transport in Earth's mantle.

Project Description: We have carried out a series of creep experiments on mantle rocks, with emphasis on the minerals olivine and garnet, using a deformation-DIA (D-DIA), a solid-medium apparatus with the capacity of performing high-pressure triaxial deformation experiments.

Experiments were conducted at temperatures from 673 to 1573 K and pressures from 3 to 10 GPa. Advanced synchrotron x-ray techniques enabled *in-situ* measurement of pressure, differential stress, and strain as a function of time. These data are used to quantify the flow properties of mantle rocks in terms of the dependence of creep rate on deformation conditions including stress, pressure, temperature, water fugacity, and melt fraction.

Results: To determine the flow behavior of olivine under lithospheric conditions, we carried out a series of experiments on the steady-state creep behavior of polycrystalline olivine at high pressures (~4 to 9 GPa), relatively low temperatures ($673 \leq T \leq 1273$ K), and anhydrous conditions using a deformation-DIA (D-DIA). Experimental results yield a flow law for low-T plasticity of olivine. Our results yield a Peierls stress of $\sigma_P = 6.2 \pm 0.2$ GPa and activation energy of $E = 290 \pm 60$ kJ mol^{-1}. Our low-temperature plasticity flow law predicts a strength at 873 K and 10^{-14} s^{-1} of ~600 MPa for anhydrous lithospheric mantle.

We have also experimentally investigated the creep behavior of garnet at high pressures. Samples were cold-pressed from a garnet powder and deformed at constant displacement rates ranging from 1.1 to 2.6×10^{-5} s^{-1} at high temperatures (1273 -1473 K) and high pressures (2.4 - 4.1 GPa). Our results provide a measure of the dependence of creep rate of garnet on temperature with an activation energy of ~280 kJ/mol and on pressure with an activation volume of ~10×10^{-6} m^3/mol. Determination of the influence of pressure on viscosity of garnet is critical for extrapolating laboratory results to geological conditions.

Furthermore, we investigated the creep contrast between olivine and garnet, the two major constituent minerals of Earth deeper upper mantle. In this study, samples of olivine and garnet were stacked together, separated by a nickel foil disk. Experiments were carried out at

1373 - 1573 K and pressures of 3 - 5 GPa. At our experimental conditions, samples of olivine deform only a factor of ~1.5 faster than samples of garnet of similar grain size, indicating that there is no significant rheological contrast between samples of olivine and garnet under anhydrous conditions. This result, which is the first direct comparison of the rheological behavior of olivine and garnet, provides a solid basis for modeling the rheological structures of subducted lithosphere.

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Grant: DE-FG02-08ER15958

Evaluation of the Origin and Hydrocarbon Transport Capabilities of Solitary Waves in Fault Conduits with Visco-Elastic Rheologies

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Objectives: The objectives of this research are to investigate the conditions that give rise to the formation of solitary waves in elastic and visco-elastic fault conduits in compacting sedimentary basins like the Gulf of Mexico basin, and to quantify the fluxes of hydrocarbons that they can transport from deep source rocks to shallow reservoirs.

Project Description: Solitary waves are hypothesized to be a mechanism for rapid hydrocarbon reservoir filling in parts of the Gulf of Mexico basin, such as in the Eugene Island minibasin, offshore Louisiana. The solitary waves are manifested as regions of increased fluid pressure within faults that arise where the faults intersect zones of overpressure caused principally by disequilibrium compaction and fluid generation. The project consists of two main parts. One consists of modeling the evolution of the Eugene Island minibasin, coupling the processes of sedimentation, fault growth, heat transport, hydrocarbon generation, multi-phase fluid flow, and fluid pressure evolution. The second part consists of modeling the formation and propagation of solitary waves and the flux of fluid that they transmit based on the fluid pressures that develop along a growth fault that serves as a principal vertical fluid conduit at Eugene Island.

Results: A detailed basin evolution model for Eugene Island has been constructed using the BasinMod2D™ software that calculates fluid pressure and flow patterns as sediments are deposited, buried, and compacted, and as hydrocarbons are generated from organic-rich stratigraphic intervals. The model predicts the development of overpressures in the range of 40 to 60 MPa at depths of about 3 km, caused mainly by disequilibrium compaction, which is in good agreement with present-day observations. A separate numerical model has been developed that solves a conservation of mass equation for single-phase fluid flow in a porous medium in the vertical dimension, where permeability is a strongly decreasing function of increasing effective stress. The results show that for intermediate initial permeability values of order 10^{-12} to 10^{-15} m^2, bulk density and compressibility values of the porous medium of 1525 kg/m^3 and 1×10^{-8} Pa^{-1}, respectively, overpressures of 40 to 60 MPa are sufficient to generate solitary waves that propagate as discrete pulses of elevated fluid pressure over kilometer-scale distances in a petroleum-rich porous medium. Under these conditions, solitary waves were observed to ascend at average velocities of about 0.1 m/yr, about an order of magnitude greater than the background Darcy velocity, showing that they can serve as a mechanism for enhanced fluid transport. The project is currently in its third year and in a one-year no cost extension period.

NATIONAL ACADEMY OF SCIENCES

Board on Earth Sciences and Resources, 500 5th Street, N.W., Washington, DC 20001

Grant: DE-FG02-07ER15915

Board on Earth Sciences and Resources and Its Activities

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Objectives: The Board on Earth Sciences and Resources (BESR) provides a focal point for National Research Council activities related to the earth sciences. Under the aegis of the Board, ad hoc committees provide independent advice to the federal government on a wide range of earth science issues, including research, the environment, natural hazards, resources, data, and education. It also provides guidance related to U.S. participation in international earth science programs.

Project Description: The Board and its five standing committees (Committee on Earth Resources; Geographical Sciences Committee; Committee on Geological and Geotechnical Engineering; Committee on Seismology and Geodynamics; and Mapping Science Committee) hold approximately two meetings each per year. At these meetings, potential studies are discussed and developed. Many of these activities are in response to requests from agencies of the federal government for advice on specific technical or policy issues. Other activities are federally mandated, or initiated by the Board in accordance with its efforts to support the continued health of the solid earth sciences. The Board responds by establishing an ad hoc committee or panel to address the specific issue. The Board continually seeks to provide accurate and timely input to support wise decision-making in government, academia, and industry.

Results: In FY 2010, the Board oversaw 19 studies. Examples of studies underway during FY 2010 are Deep-Time Geologic Records for Understanding Climate-Change Impact; Induced Seismicity Potential in Energy Technologies; Sea-Level Rise in California, Oregon, and Washington; Uranium Mining in Virginia; and Emerging Workforce Trends in the U.S. Energy and Mining Industries. BESR completed eight studies in FY 2010. The results of BESR's studies are published in its peer-reviewed reports. These 2010 studies are: *Precise Geodetic Infrastructure: National Requirements for a Shared Resource; Management and Effects of Coalbed Methane Produced Water in the United States; New Research Directions for the National Geospatial-Intelligence Agency: A Workshop; Understanding the Changing Planet: Strategic Directions for the Geographical Sciences; Understanding Climate's Influence on Human Evolution; Private-Public Sector Collaboration to Enhance Community Disaster Resilience: A Workshop Report; Realizing the Energy Potential of Methane Hydrate for the United States;* and *Landscapes on the Edge: New Horizons for Research on Earth's Surface;*

During this reporting period, the Board held two meetings. The Fall 2009 meeting was held in Tucson, Arizona. The highlight of this meeting was a roundtable titled, "Interdisciplinary Earth Sciences Perspectives on the Future of the Colorado River Basin and Beyond: Confronting

Climate Change." Speakers dealt with ongoing natural and anthropogenic climate change challenges in the Colorado River basin, Colorado River stream flow, abrupt ecosystem changes from draught, and four degrees and planetary boundaries: implications for climate adaption in local, national and international contexts.

The Spring 2010 meeting was held at the Keck Center in Washington, DC. The Board conducted its traditional business in closed session, listened to presentations by Charles M. Vest, President, NAE, and Marsha McNutt, Director, USGS, and held a roundtable on "Science and the Carbon Market."

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK
Benjamin Levich Institute & Department of Physics, New York NY 10031

Grant: DE-FG02-06ER15817

Complex Fluids in Self-Affine Fractures

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Objectives: To understand the dynamics of non-Newtonian liquids and particulate suspensions in self-affine fractures, and in particular how the correlated surface roughness affects permeability, tracer dispersion and sedimentation.

Project Description: Naturally fractured rocks have "self-affine fractal" surfaces which exhibit power-law correlations giving rise to distinctive velocity fluctuations and transport inhomogeneities when fluids or tracers pass through the fracture. The goal of this research is to understand the interplay of diffusion and convection in the hydrodynamic dispersion of non-Newtonian liquids, and the evolution of the fracture surface when (non-colloidal) particulates carried by the fluid deposit on the walls. Both problems are characterized by nonlinear feedback mechanisms, which renders their analysis difficult. In the first case, the velocity variation within a heterogeneous fracture leads to an inhomogeneous shear stress pattern, which in a shear-thinning liquid causes spatial variations in viscosity, which enhances the velocity variation. In the second problem, deposition processes alter the fracture geometry, which in turn alters the velocity and stress fields, which can then promote or discourage deposition in different regions of the fracture. We will employ numerical simulations based on the lattice-Boltzmann method, based on our newly developed codes for shear-thinning liquids and solid particle transport, complemented by effective medium and other averaging techniques. The proposed analytical and numerical work at CCNY will be complemented by a continuing collaboration with an experimental group led by J.-P. Hulin at the Universitè de Paris - Orsay.

Results: We have studied the flow and gravitational sedimentation of a suspension in a fracture channel with a self-affinely rough bottom surface, which in comparison with last year's study of suspension flow in straight channels allows us to elucidate the roughness. If an initially uniform suspension is driven through the fracture channel, at early times three characteristic layers form, clear fluid at the top, flowing suspension in the middle whose characteristics resemble those of flow in a flat-walled channel, and a denser sediment region at the bottom where particle motion is impeded by surface irregularities. Quantitative "local" results on density, fluid velocity and particle velocity and angular velocity profiles across the fracture, and "global" results on fluid and particulate flux as a function of Reynolds and Buoyancy number have been obtained. We have begun to study jamming/obstruction phenomena wherein a local constriction in the channel aperture forms a trap for particles and blocks the flow – the figure below gives an example. We have observed that such a particle jam at a single obstruction is characterized by a peak in the velocity power spectrum, whereas in continuous flow the spectrum is featureless, and that increasing the fluctuations in the pressure gradient is an effective means to unblock the particles. The interaction between multiple jamming sites is now under study.

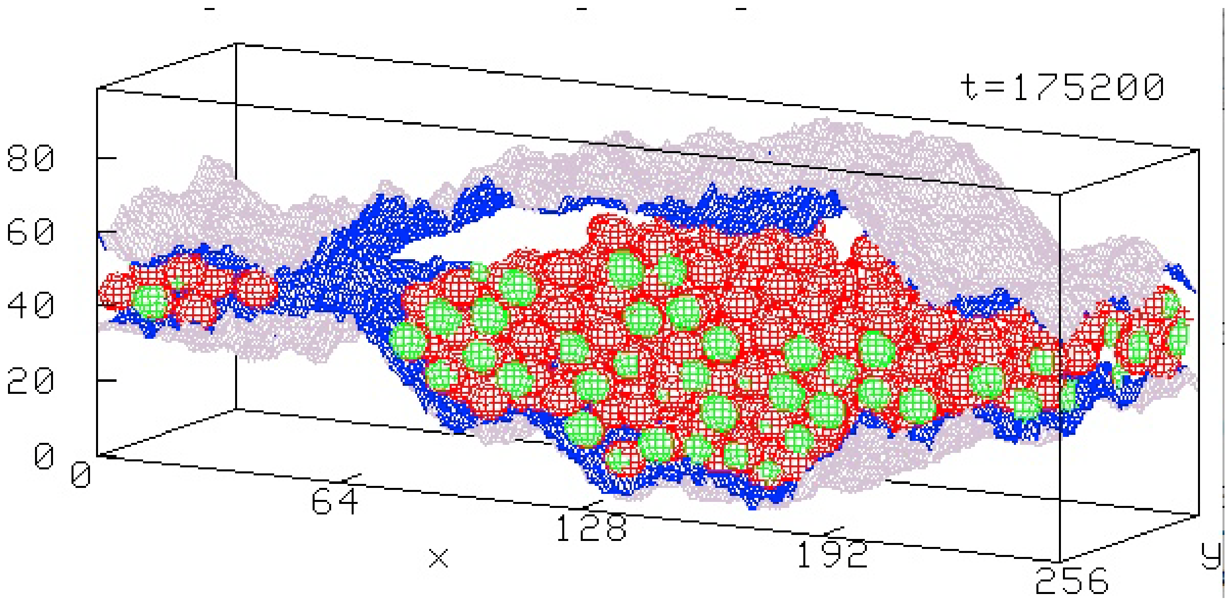

Figure: Example of a jammed configuration. The fracture channel has periodic boundaries in both horizontal directions, and self-affine top and bottom surface shown in blue nearly touch at the left rear position. The particles are displayed as the red spheres, green indicates the faces of particles which cross the periodic boundary, and the suspending fluid is not shown. The particles initially form a slug which occupies half the fracture length and after flowing periodically through the fracture for some time become jammed in the configuration shown.

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK
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Grant: DE-FG02-03ER15458

Studies of Elasticity, Sound Propagation and Attenuation of Acoustic Modes in Granular Media

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Co-Is: David L. Johnson; (617) 768-2348 (Schlumberger-Doll Research)

Website: http://www.jamlab.org

Objectives: The goal of this project is to develop a theoretical and experimental understanding of acoustics and dissipation in granular materials. The merit of this proposal rests on its scientific value and consequent impact on industrial applications. The topic is certainly relevant for identifying and characterizing the underground formation for storage of either CO_2 or nuclear waste material, or efficient production of hydrocarbon. Understanding the basic properties of acoustic propagation in granular media is of importance to the energy industry, as well as the pharmaceutical, chemical and agricultural industries.

Project Description: We employ a set of experimental and theoretical concepts including the dynamic effective mass of granular media, normal modes analysis, statistical mechanics frameworks and numerical simulations based on Discrete Element Methods to develop a study of acoustics and dissipation in granular media. A theoretical statistical approach studies the necessary phase space of configurations in pressure, volume fraction to classify the granular materials. We will develop an experimental and theoretical investigation of the frequency-dependent effective mass, M(w), of granular particles occupying a rigid cavity to a given filling fraction. Effective mass measurements allow us to study the mechanisms of the elastic response and attenuation of acoustic modes in granular media. This method is a sensitive and direct way to measure characteristics of the granular medium causing changes in acoustic properties of structures containing grain-filled cavities. We perform experiments and simulations under varying conditions, including humidity and vacuum, and different interparticle force-laws to develop a fundamental understanding of the mechanisms of damping and acoustic propagation in granular media.

Results: (a) In a collaboration with Prof. J. Jenkins from Cornell University, and Prof. Luigi La Ragione Politecnico di Bari, we are investigating the properties of isotropically compressed dense packings of spheres with the goal of capturing the relevant state variables to develop a theoretical framework for the effective bulk and shear moduli and dissipation in granular packings.

(b) We have studied the structural properties of granular matter that determine the response functions using a statistical mechanics approach based on the volume ensemble for granular materials. A statistical theory of volume fluctuations has been developed based on the calculation of the Voronoi volume of a single particle in a packing. Currently, we are investigating how the micro-structure described by the theory determines the elastic response and the vibrational density of states of the granular packing from the lowest densities of RLP up to crystallization at FCC.

(c) We have analyzed the acoustic response of a structure that contains a cavity filled with a loose granular material from an experimental and theoretical perspective. The inputs to the theory are the effective masses of each subsystem: that of the empty-cavity resonating structure and that of the granular medium within the cavity. This theory accurately predicts the frequencies, widths, and relative amplitudes of the various flexural mode resonances observe with rectangular bars, each having a cavity filled with loose tungsten granules. Inasmuch as the dominant mechanism for damping is due to adsorbed water at the grain-grain contacts, the significant effects of humidity on both the effective mass of the granular medium as well as on the response of the grain-loaded bars are monitored. Here, depending upon the humidity and the preparation protocol, it is possible to observe one, two, or three distinct resonances in a wide frequency range (1–5 kHz) over which the empty bar has but one resonance. These effects are understood in terms of the theoretical framework, which may simplify in terms of perturbation theories.

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Grant: DE-FG02-96ER14633

Reactivity of Iron-Bearing Minerals and CO_2 Sequestration: A Multi-Disciplinary Experimental Approach

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Objective: The primary goal of this research program is to understand the chemistry that results when supercritical CO_2 ($scCO_2$) with H_2S and/or SO_2 in deep saline formations (DFS) contacts iron- bearing minerals. Understanding the complexities the sulfur co-injectants introduce is a critical step in developing CO_2 sequestration as a climate-mitigating strategy. The research strategy is to understand macroscopic observations of this chemistry with an atomic/molecular level view using surface analytical techniques.

Project Description: Research is investigating some of the complexity associated with CO_2 sequestration in DFS. Specifically, research is focused on developing an understanding of the chemistry that will result when $scCO_2$ with varying amounts of H_2S and/or SO_2 comes in contact with iron-bearing sediments common to deep saline formations. A representative suite of well-characterized sedimentary rocks (sandstones, siltstones, marls, and carbonates) will be exposed to $scCO_2$, $scCO_2/H_2S$, $scCO_2/SO_2$ as well as Na-Cl brines equilibrated with these supercritical fluids in a hydrothermal flow-through setup. The experimental system provides for long-term monitoring of changes in sulfur chemistry in the effluent. Complementary spectroscopic studies will use in situ vibrational spectroscopy to examine the interactions under near-field conditions at the molecular level and resolve the interaction of $scCO_2$, $scCO_2/H_2S$, and $scCO_2/SO_2$ with relevant iron mineral phases. These studies will initially concentrate on iron bearing minerals common to sandstone.

Results: The experimental work with pure iron hydroxide and oxide mineral phases conducted in Strongin's research group is complemented by batch experiments and flow-through experiments with various sand stones. Flow-through experiments and batch experiments (75°C) have been conducted to determine the reactivity of crushed, iron-bearing sandstones to $scCO_2$ containing H_2S and/or H_2SO_3. The flow-through experiments are conducted in a newly developed system that allows advection of $scCO_2$ over a column of crushed sandstone. The system has the option to mix an aqueous H_2S or H_2SO_3 into the $scCO_2$ stream before it enters the column. The conditions in these flow-through experiments simulate the conditions near a $scCO_2$ injection point at depth. Batch experiments in which $scCO_2$ coexist with an aqueous phase complement the flow-through experiments. These experiments are conducted by adding dry ice to a small volume of rock slurry contained in an autoclave. Supercritical conditions are reached by heating the autoclave to 75°C. At the conclusion of the experiments the materials are recovered and examined with XRD, TGA, and Mössbauer Spectroscopy. Mössbauer

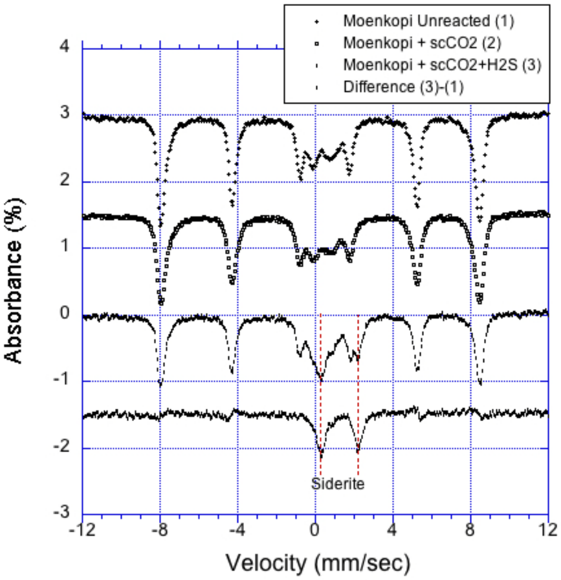

Figure 1. Mossbauer spectrum for reacted and unreacted red sandstone at 75°C in batch experiments. Unreacted (top), reacted with $scCO_2$/water (second down), reacted with $scCO_2$ /aqueous H2S solution (third down), difference spectrum (bottom). Red lines indicated the position of absorption peaks for siderite. Note that exposure to water equilibrated with $scCO_2$ does not lead to significant changes in spectrum.

spectroscopy is particularly useful because it allows one to determine the changes in iron mineralogy, despite the fact that the iron content of most sandstones is less than 1-2 wt%. The Mössbauer spectra were obtained in the laboratory of Dr. Darby Dyar, Mount Holyoke College.

Consistent with the results obtained with pure iron (hydr)oxide phases, the sandstone shows only a change in the iron mineralogy when sulfide is present. Figure 1 shows the sandstone reacted with $scCO_2$ and water as well as with $scCO_2$ and aqueous sulfide solution. The difference spectrum shown in Figure 1 shows a gain in absorbance consistent with the formation of siderite.

Besides the batch and flow-through experiments we have started a series of experiments to determine the partitioning of sulfur dioxide between $scCO_2$ and water and the stability of sulfite in water equilibrated with $scCO_2$. These experiments are necessary to understand the reactivity of aqueous sulfite under conditions relevant to the injection of $scCO_2$ containing SO_2 as co-injectate into an aquifer.

STATE UNIVERSITY OF NEW YORK, STONY BROOK

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Grant: DE-SC0004118

Changes of Porosity, Permeability and Mechanical Strength Induced by CO_2 Sequestration

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Objectives: In the context of CO_2 sequestration, the overall objective of this project is to conduct a systematic investigation of how the flow of the acidic, CO_2 saturated, single phase component of the injected/sequestered fluid changes the microstructure, permeability and strength of sedimentary rocks, specifically limestone and sandstone samples.

Project Description: The project consists of three tasks. The first task involves continuous measurement of permeability versus time on small-diameter core samples as CO_2 enriched brine is flowed through the sample. The kinetics of fluid-rock interaction will be controlled by a number of parameters, including the partial pressure of CO_2, pH and cation concentrations of the brine, temperature and advective velocity. The second task is to correlate these changes to before-and-after changes in the sample microstructure. These changes will be measured via X-ray computed microtomography at an expected spatial resolution of 4 μm. The third task is to characterize the mechanical properties of the limestone and sandstone samples that have been altered by injection and percolation of CO_2, with the objective of understanding how mechanical failure is influenced by modification of the pore space.

Results: This is a new project that began recently. We are on track in setting up the flow and mechanical testing facilities for tackling the above tasks.

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Grant: DE-FG02-09ER16017

Structural Basis for Stabilization and Transformation Behavior of Amorphous Calcium Carbonate

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Objectives: The main goals are to determine short- and medium-range structure in various forms of doped and undoped amorphous calcium carbonate (ACC), and establish the role of structure in stabilization of ACC and in the mechanism and kinetics of its transformation to crystalline forms.

Project Description: This research program combines molecular-scale techniques—synchrotron total X-ray scattering, X-ray absorption spectroscopy, NMR (^{1}H, ^{13}C, ^{25}Mg, ^{31}P), and reverse Monte Carlo refinement—to establish a structure model for hydrated amorphous calcium carbonate (ACC), including samples containing additives that influence its stability and crystallization kinetics. Short- and medium-range order in ACC and the function of additives provide the basis for stabilization and crystallization, and therefore influence formation of calcium carbonate for both biologic and inorganic pathways. A particular focus of the research is evaluation of the effect of inorganic (Mg, PO_4) and organic (amino and organic acids) additives that modify reactivity. In situ study of transformation will identify intermediate phases and operative mechanisms.

Results: Our principal research over the past year involved (1) refinement of a structure model for synthetic hydrated amorphous calcium carbonate, (2) identification of the key structural features associated with medium-range order in ACC, and (3) evaluation of the effect of Mg^{2+} and PO_4^{3-} on short- and medium-range structure in ACC. Our most significant finding, using reverse Monte Carlo refinement of synchrotron X-ray total scattering data, reveals that synthetic ACC consists of a nanoporous Ca-rich framework that supports interconnected channels containing H_2O and CO_3 molecules (Fig. 1). This work resulted from continued collaboration with Drs. Andrew Goodwin and Martin Dove (Cambridge University), who are developing RMC code for application with X-ray and neutron scattering data. The existence of a previously unrecognized nanometer-scale channel network suggests mechanisms of how additives can be accommodated within the structure and provide temporary stabilization, as well as influence the crystallization process. Moreover, while lacking long-range order, the Ca-rich framework in the ACC contains similar Ca packing density to that present in calcite, aragonite and vaterite, yielding clues of how the amorphous material converts into the different crystalline forms.

Medium-range order is found to be associated with Ca-Ca and Ca-O pair correlations within the Ca-rich framework, and corresponds to coordination that is shared among crystalline $CaCO_3$ polymorphs. The nanoporous structure model is consistent with observations by ^{1}H and ^{13}C NMR that show two distinct populations of both water and carbonate groups, differing primarily in the mobility of associated hydrogen. The ^{1}H NMR data show that about one-half of the H occurs in water molecules that exhibit restricted motion on the millisecond timescale at room temperature, which likely occur in the channels. The remainder of the H is primarily in rigid molecular water, except for a small fraction of hydroxyl groups. The presence of both rigid and mobile H is also evident by ^{13}C NMR, which indicates that at room temperature only about one-fourth of the carbonate groups are located near rigid molecular water. There is no evidence for significant motion of the carbonate groups themselves at the millisecond timescale, which suggests that the dynamical effects are mostly related to hydrogen bond reorganization of the water/carbonate network in the Ca-poor channels. These new results provide a starting point for examining the role of structure on crystallization kinetics of amorphous calcium carbonate precursors.

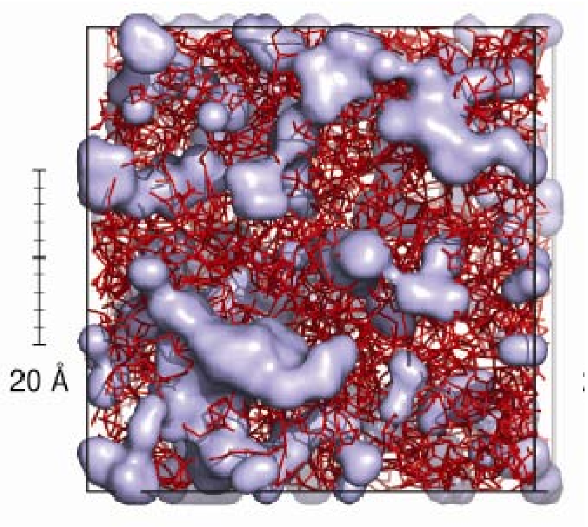

Figure 1. Structure model of ACC from RMC refinement showing the Ca-rich framework in stick representation (red). The H_2O- and CO_3-rich channels (regions of the structure further than 4 Å from any Ca centers) are shown in surface representation (blue) and percolate the structure.

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Grant: DE-FG02-09ER16099

Multiscale Modeling of Multiphase Flow, Transport, and Reactions in Porous Medium Systems

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Objectives: The specific objectives of this project include formulating, closing, and applying three types of multiscale models of porous medium systems: (1) a two-fluid-phase flow model, (2) a two-fluid-phase flow and species transport model, and (3) a three-fluid-phase flow model.

Project Description: Our work is aimed at advancing the thermodynamically constrained averaging theory (TCAT) approach for constructing models of multiphase porous medium systems at a range of length scales. By this method, all variables are expressed in terms of explicitly defined averages of microscale properties; and closure relations are constrained to ensure conditions consistent with the second law of thermodynamics. The results of this approach are models that can be constructed at a range of length scales, explicit definitions of all variables in terms of microscale precursors, hierarchical families of models that vary in sophistication that can be matched to a physical system of concern, and assurance that the models derived are thermodynamically constrained and consistent. This work involves a theoretical component to formulate candidate models, a pore-scale modeling component to guide the formulation of specific closure relations, and a continuum-scale numerical methods component to approximate the formulated macroscale models.

Results: Standard models used to simulate single-fluid, and two-fluid-phase flow are often based on a form of Darcy's law that is expressed in terms of a spatial gradient of fluid pressure. Using TCAT we were able to show that the fundamental form of Darcy's law consists of spatial gradients of potentials. When the commonly used pressure form of Darcy's law is written, we showed that terms related to the averages of fluctuations in microscale quantities relative to their macroscale counterparts arise naturally. These extra terms are non-negligible under conditions in which the porosity or, for the multiphase case, volume fraction of the fluid phase, is spatially variable. The results of this work show relationships between traditional measurements made by Darcy and modern theory, clearly demonstrate errors that exist in common models, and demonstrate how using the theory developed in this work results in a consistent formulation across scales.

While the groundwork for a rigorous two-fluid-phase flow model is in place, a remaining issue is how to formulate the specific closure relations needed to produce a well-posed model. Because this new class of model includes interfaces and common curves, the evolution of the extent of these quantities must be resolved. Evolution equations are not accessible based upon conservation principles alone, so they become a component of the closure relations. This is important and complicated work, which has received some attention in multiple fields of science for various applications. We have formulated evolution equations based upon simplifications to expressions derived using a set of averaging theorems. Evolution equations have been derived for specific interfacial areas and common curve lengths for two-fluid-phase systems. We have clearly shown deficiencies in previous approaches and have performed a preliminary analysis of the new forms derived. Furthermore, we have used these new forms to formulate a complete closed model for two-fluid-phase flow.

We are collaborating with a research group led by Professor Rainer Helmig from the University of Stuttgart on the extension of TCAT to the case of a transition region between fundamentally different physical domains. Such problems arise in land-atmosphere interaction, fuel cells, and many other applications. To fix ideas, consider the situation at the ground surface where on the atmospheric side we have a single fluid, the gas phase, and on the Earth side we have a porous medium system that includes two fluid phases and a solid phase. We are currently working on extending TCAT to this case, which will require dealing with two fluid phase flow and species transport, which is the second type of model that we proposed to work on. This work is opening up another rich set of potential applications based upon our theoretical work.

We are developing a general TCAT model for two-fluid-phase flow and species transport. We are formulating a general set of closure relations to examine the behavior of a two-fluid-phase system in which the non-wetting phase is entrapped by capillary forces and is non-continuous. The general theory will support a much richer set of applications.

We are furthering the development and application of lattice-Boltzmann methods, which we are using to simulate multiphase flow at the pore scale. We are running a large set of simulations to determine the resolution needed to provide grid independent results and the size of the systems needed to yield a representative elementary volume. A finding from this work is that most LB work published to date for multiphase porous medium systems is likely under-resolved. The results of these simulations are being used to derive specific forms of closure relations for a two-fluid-phase TCAT model. To speed these simulations along, we have developed an implementation of our codes on a graphical processor unit (GPU) computing architecture. We have found that the GPU codes can markedly outperform traditional CPU-based codes for certain applications.

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Grant: DE-FG02-04ER15508

The Influence of Mineral Surfaces on Multi-electron Reduction Mechanisms for Polyvalent Metals

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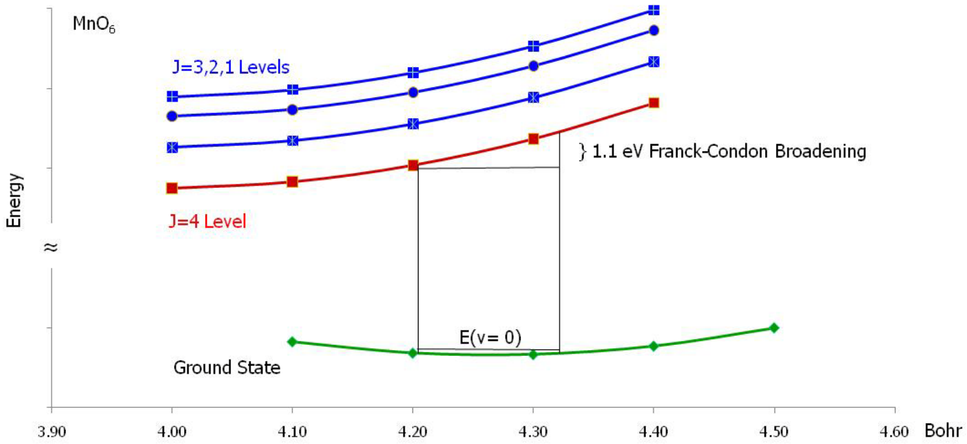
Objectives: To better understand electron transfer reactions between Fe^{II} in minerals and sorbed polyvalent metals such as U^{VI}. To develop *ab initio* models for the XPS and XANES metals in order to help elucidate information on oxidation states and bonding environments.

Project Description: We are exploring the influence of U coordination environment on the reduction of U(VI) to U(V) to U(IV) at the ferrous mineral-fluid interface. Key techniques used are electron microscopy, x-ray photoemission spectroscopy (XPS), and x-ray adsorption near edge structure (XANES). The project includes complementary theoretical efforts to quantify the effect of coordination environment on the relative stabilities of the different oxidation states of U as well as to help interpret XPS and XANES spectra.

Results. A conceptual framework that is standardly used to interpret the X-Ray photoemission spectra, XPS, of ionic materials is one where the orbitals are characterized as being either ligand or metal (cation) orbitals. Then, one describes the inter-atomic many body effects as being single, double, etc. charge transfer, CT, from the ligand to the core ionized atom. Our present work, on transition metal and lanthanide complexes, brings into question whether the concept of CT and the use CT configurations is the most appropriate way to describe the screening of a core-hole. Our results indicate that the covalent mixing of metal and ligand orbitals to form bonding and anti-bonding orbitals that can have different occupations is a fundamental feature of the metal-ligand interaction and that it may provide a unified understanding of different features of the XPS. Furthermore, we have shown that the conceptual framework of natural orbitals, NO's, provide a direct way to understand the bonding and anti-bonding character of a many-body wavefunction. These orbitals are similar to Kohn-Sham DFT orbitals in that they provide the density of a state but they are an improvement over Kohn-Sham orbitals since each natural orbital has a unique occupation number.

We are applying this concept of covalent interactions to study the inherent broadening of the XPS features of oxides and other ionic systems. Although there are occasional exceptions, the XPS peaks for oxides are much broader than the inherent resolution of the photoemission measurement. For example, in our study of the XPS of CeO_2, it was necessary to broaden the calculated features by Gaussians with full width at half maximum, FWHM, of greater than 2.5 eV to have a reasonable match to the widths of the experimental features. However, the measurements were made at a synchrotron with instrumental resolution over an order of magnitude smaller than the observed broadening. Several mechanisms have been suggested for this broadening including core-hole lifetimes and inhomogenieties in the sample. While these mechanisms may contribute to the observed large FWHM's, we have shown that vibrational excitations in the final state make major contributions to the broadening and that this broadening may be different for different states. The vibrational excitations have been analyzed in terms of Franck-Condon broadenings, which provides a transparent way to relate the observed broadening to the character of the interactions between the core-ionized cation and the ligands including the bonding and anti-bonding character of this interaction. Understanding the reasons behind spectral broadening will be important in the interpretation of UO_x XPS spectra.

In the Franck-Condon analysis, one assumes that excitations are possible from all bond distances within the classical turning points of the ground state of the system and one takes excitation from these turning points as estimates of the vibrational broadening in the final state. In the figure below, we show our results for potential curves for the breathing motion of the metal-oxygen distance for the ground state of MnO and for the four multiplet split level for ionization of an Mn $2p^{3/2}$ electron. The minimum of the potential curves for the ionic states is reduced by over 0.25 Å from the distance in the ground state and this directly leads to a Franck-Condon broadening of ~1 eV, precisely the broadening needed to explain the XPS of MnO. Calculations are also being carried out for the main peaks and satellites of other oxides.



Major efforts are also being made to improve the efficiency of our programs for the theoretical simulation of XPS spectra. These efforts are necessary to allow us to accurately simulate the main and satellite XPS peaks of actinides and to apply our newly developed analyses of covalent interactions to these materials. These efforts are being carried out through an EMSL partnership with Dr. DeJong at PNNL. In the first step of this partnership, we have removed the calculation of the spectral intensities as a bottleneck for the simulation of the XPS for our cluster models. Through a major reorganization of the programming algorithms used, we have reduced the time for the intensity calculations by over an order of magnitude. There are two remaining steps in progress. The first involves larger mixings of configurations and two routes for this increase are being tested. Using long integer arithmetic, this enhancement should be straightforward. The second remaining step involves the selection of suitable active orbital and configuration spaces. In our prior work, we have used orbital sets that were optimized for one of the inter-atomic configurations; this has led to a bias in the energetic and intensities in our calculations. We are presently investigating the optimization of orbitals for an average of several different configurations to eliminate this bias.

Experimental results and theoretical modeling of the reduction of U(VI) are described in the Summary of the Co-PI, Eugene S. Ilton (PNNL).

NORTHWESTERN UNIVERSITY
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Grant: DE-FG02-08ER15980

Multiscale Framework for Predicting the Coupling between Deformation and Fluid Diffusion in Porous Rocks

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Objectives: To develop a predictive multiscale framework to hierarchically homogenize the constitutive behavior of fluid-saturated rocks, directly linking the continuum representation with granular processes, in areas of severe deformation, such as deformation banding, where phenomenology breaks down.

Project Description: In this project, a predictive multiscale framework will be developed to simulate the strong coupling between solid deformations and fluid diffusion in porous rocks. We intend to improve macroscale modeling by incorporating fundamental physical modeling at the microscale in a computationally efficient way. This is an essential step toward further developments in multiphysics modeling, linking hydraulic, thermal, chemical, and geomechanical processes. This research will focus on areas where severe deformations are observed, such as deformation bands, where classical phenomenology breaks down.

Multiscale geometric complexities and key geomechanical and hydraulic attributes of deformation bands (e.g., grain sliding and crushing, and pore collapse, causing interstitial fluid expulsion under saturated conditions), can significantly affect the constitutive response of the skeleton and the intrinsic permeability. Discrete mechanics (DEM) and the lattice Boltzmann method (LBM) will be used to probe the microstructure---under the current state---to extract the evolution of macroscopic constitutive parameters and the permeability tensor. These evolving macroscopic constitutive parameters are then directly used in continuum scale predictions using the finite element method (FEM) accounting for the coupled solid deformation and fluid diffusion.

A particularly valuable aspect of this research is the thorough quantitative verification and validation program at different scales. The multiscale homogenization framework will be validated using X-ray computed tomography and 3D digital image correlation in situ at the Center for Quantitative X-ray Imaging (CQI) at Penn State University. Also, the hierarchical computations at the specimen level will be validated using the aforementioned techniques in samples of sandstone undergoing deformation bands.

Results: Pore-scale tomography images with micron resolution have been obtained using the synchrotron at the Advanced Photon Source at Argonne National Lab to quantify topological features of the material that can then be linked to macroscopic properties. Figure 1 shows some micron-resolution images that are used to construct faithful representations of the 3D porous network on samples of Aztec sandstone from the Valley of Fire, NV, where natural compaction bands are found. Preliminary calculations using the lattice Boltzmann method show a contrast in permeability of several orders of magnitude between the inside and outside of compaction bands. These changes are not captured by classical methods, such as Kozeny-Carman. These findings will allow us, for the first time, to directly link the changes imposed on continuum properties due to 3D micromechanical changes.

Currently, we are studying the size effect to identify the smallest representative volume element (RVE) to perform calculations to extract the effective permeability directly from inside and outside of natural compaction bands. Additionally, we are interested in comparing the different topologies of compaction bands formed *in situ* and in the lab. To this end, we have obtained laboratory samples with compaction bands and have scheduled synchrotron time for this fall. By late fall, we will be able to compare directly the 3D microstructure of compaction bands *in situ* and in the lab and quantify their effect on the effective permeability at the macroscale.

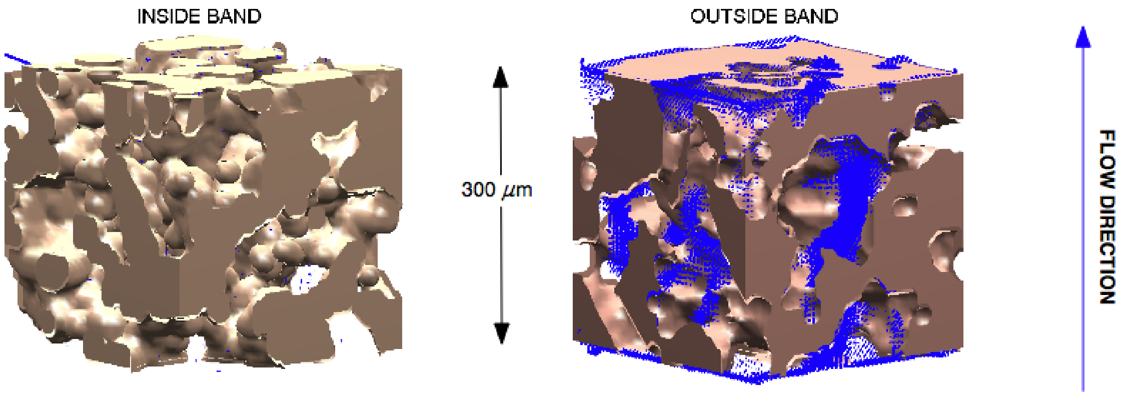

Figure 1. Apparent preliminary results of fluid flow simulations within 3D porous networks using lattice Boltzmann computations inside and outside compaction bands in Aztec sandstones. Blue regions show flow vectors at the grain scale level.

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Grant: DE-FG02-04ER15495

Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale

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Co-I: Louise J. Criscenti (Sandia National Lab)

Co-I: Lynn E. Katz (University of Texas-Austin)

Objectives: The objectives of this research are to develop an approach for predicting the types of metal surface complexes that form on mineral surfaces by focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models to predict adsorption behavior.

Project Description: We combine the use of several techniques including bulk adsorption experiments, X-ray absorption, infra-red, and vibrational sum frequency spectroscopies (XAS, IR, VSFG), and molecular modeling to investigate ion adsorption at mineral surfaces. XAS provides data on how the metal binds to the surface (e.g., monodentate, bidentate), IR provides data on bulk anion adsorption at mineral surfaces from aqueous solution, and VSFG provides surface specific data on anion adsorption at the mineral surface as well as impact of adsorbed metal-anion pairs on water structure at the mineral surface. Molecular modeling is used to guide spectroscopic data interpretation by providing information on water structure around ions in solution and the structure of metal-anion complexes in aqueous solution. In addition, molecular modeling is used to provide insight into water structure at mineral surfaces, the surface sites involved in ion adsorption, and the distribution of ion pairs between aqueous solution and the mineral surface. Our studies have focused on systems involving alkaline earth metal (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and heavy metal (Co^{2+}, Pb^{2+}) cations. The anions we have selected for study include Cl^-, NO_3^-, ClO_4^-, SO_4^{2-}, and SeO_3^{2-}. Ion adsorption and the potential formation of ternary complexes on silica (quartz, amorphous silica), alumina (corundum and gibbsite), and ferric iron (goethite and hematite) oxides are under investigation.

Results (**Allen Lab)**: Research taking place during FY10 primarily focused upon: (1) further characterization of various iron oxide (hematite, maghemite, and magnetite) thin films using Raman and FTIR spectroscopies, (2) attenuated total reflection – Fourier transform infrared (ATR-FTIR) studies of ion adsorption from bulk solution onto the various iron oxides, and (3) VSFG studies of anion adsorption onto iron oxide thin films. Through Raman and ATR-FTIR results, we have shown that utilizing different annealing temperatures during the iron oxide thin film synthesis produces homogenous films of a single iron oxide polymorph. These films were and continue to be used in VSFG adsorption studies. Results from VSFG studies on sulfate anion adsorption at hematite surfaces from near-neutral aqueous solutions (pH~5-6) suggest that sulfate binds with the oxide surface predominantly in an inner-sphere complex. Beyond running VSFG experiments on iron oxide thin films, we are implementing sum frequency scattering (SFS) as a method for probing anion adsorption to colloidal oxide solids.

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Grant: DE-FG02-05ER15675

An Investigation of Roughness and Weathering at the Bedrock-Regolith Interface

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Objectives: We are investigating the interface where weathering occurs in rocks. Understanding the interfacial area in the context of weathering advance rates, timing and chemistry of weathering, mineralogy, and regolith microbiology will teach us how to extrapolate rates of biogeochemical processes across scales.

Project description: We are measuring chemistry, mineralogy, microbiology, and compositions and textures from the mineral surface to the watershed scale to understand changes in the reaction interface during weathering. We are using the data generated to develop models for surface evolution, rind formation, and particle size variation versus depth.

Results: At the mineral surface scale, experiments exposing forsterite to solutions with various concentrations of dissolved Mg and Si allowed for development of steady-state topography of the mineral surface. According to our modeling-based predictions of surface topography, when the rate varies according to so-called TST-like behavior, no spatial correlations exist in the population of reactive surface sites. We are working on a perturbation theory-based proof of this conjecture for the case of a 2-D solid with four nearest neighbors at each lattice point.

In work also at the mineral surface scale, we are also using neutron scattering to probe the interior structure (pores vs. mineral matrix) in rocks during weathering, in features ranging from 10 Å to 10 μm in size. Four common rock types were selected (granite from Puerto Rico and Virginia, USA, diabase from Virginia, USA, basalt from Costa Rica, shale from Pennsylvania, USA). For all four lithologies, the bedrock has low porosity, with most of the pores not accessible for rock-water interaction. During weathering, the surface area, porosity, and connectedness increase.

Neutron scattering also probes the pore geometry and alignment. In our studies, granite and basalt exhibit azimuthally symmetric scattering spectra, as expected for random two-phase systems (pore-mineral matrix). In contrast, scattering patterns obtained from the shale are anisotropic indicating oriented pores. Disappearance of clay minerals leads to a decrease in pore anisotropy with weathering progress.

Similarly, all weathered diabase samples reveal an unusual "asterisk" distribution of scattering intensities, which may be explained by the presence of elongated pores developing anisotropically as a consequence of dissolution. Pore distribution data obtained by neutron scattering is in agreement with μ-computed tomography (μ-CT) measurements, which document plagioclase to kaolinite transformation in weathering granite, and formation of pores within pyroxene grains in diabase (Fig. 1).

As an extension of ongoing neutron scattering work, we investigated three shale sites cross a tectonic and climatic gradient (grey and black Marcellus shale in Pennsylvania, grey shale in Oregon and Taiwan). The production of nano-porosity was controlled primarily by erosion rates and presence of reactive minerals such as pyrite, and secondarily by climate conditions such as temperature and precipitation.

At the clast or hand specimen scale, we are investigating the geometry of the weathering interface in extensively weathered low-porosity granitic or basaltic clasts from Guadeloupe. Weathering profiles across a single basaltic andesite clast collected from the B horizon of a late Quaternary volcaniclastic debris flow on Basse-Terre Island, Guadeloupe show that weathering rinds are thicker and weathering velocity is rapid where the curvature of the clast is greater. Reaction front thickness measured for glass dissolution also increases with curvature, while reaction front thicknesses measured for other minerals do not. This contradiction is attributed to mm-scale roughness of the interface which is related to phenocryst grain size and distribution.

At the watershed scale, we have developed a "weathering conveyor belt" model describing fragment size versus position in the weathering of low-porosity metavolcanic rocks in a Puerto Rico watershed. This model and our previously published spheroidal weathering model for a nearby catchment are consistent with the possibility that steady state regolith can be maintained for some systems where erosion and weathering advance rates are related through a condition on either the size of the fragment exiting the upper surface of the regolith or on the reactant concentration in the porefluid.

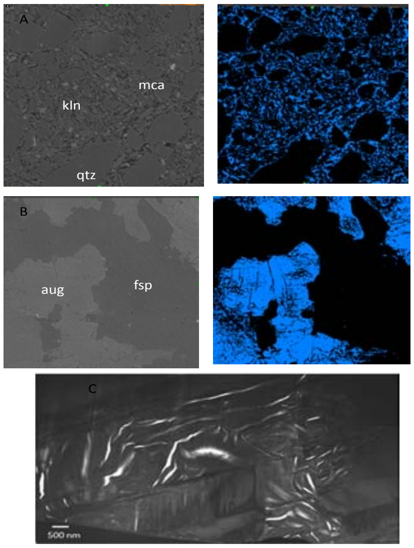

Figure 1. Reconstructed μ-CT image (left) and corresponding segmented binary image showing pore space in blue (right) in A) weathered granite, Davis Run; B) weathered diabase, Davis Run (pore space in black within blue augite grains). C) TEM photomicrograph exhibiting elongated pores developed in weathered pyroxene. Mineral abbrev.: fsp – feldspar, aug - augite, qtz - quartz, mca – mica, kln – kaolinite

Uranium disequilibrium analysis: We are collaborating with Prof Francois Chabaux of Univ of Strasbourg, France for uranium disequilibrium analyses. This collaboration has resulted in understanding how to use U-Th chronometry to constrain the time evolution of weathering. We are currently analyzing isotopic data utilizing U-Th chronometry for a basaltic clast weathering on Basse-Terre Island, Guadeloupe. The U analysis is allowing us to estimate rind production rates in the Guadeloupe clast. These results greatly improve our understanding of the important controls such as climate and landscape on chemical weathering. We are pursuing the use of U disequilibrium analysis also for the Puerto Rico weathering system.

Microbial involvement in weathering: Given that all weathering involves the presence of biota, we are characterizing the microbial biomass and community composition in the Bisley watershed in Puerto Rico to elucidate how bacterial systems are impacting the weathering interface. Field samples were collected from deep saprolite for microbiological analysis. Cell numbers and the presence of iron-related bacteria vs. depth have been determined. DNA has been extracted and 454 sequencing with barcoded 16S rDNA primers is in progress.

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Grant: DE-FG02-09ER16022

The Physics of Swarms in Fracture Networks: Integration of Seismic Characterization and Controlled Micro-Transport

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Objectives: The objective of this research is to determine how to control the injection and retrieval of simulated sensor swarms within fracture networks. This will be the first application of the physics of swarms to fracture networks, and will have important implications for the future use of collaborative sensors to characterize the subsurface.

Project Description: A laboratory study was performed to explore the evolution, maintenance and control of swarms in constrained geometries, i.e. fractures and fracture networks. Because fractured systems are composed of length scales that span several orders of magnitude, we have developed a multi-modal imaging method (optical/seismic) to explore the physics of distributing sensors in fractured media. We have performed laboratory experiments to determine the effect of particle concentration (1%, 2%, 4% by mass), initial swarm volume (2.5 µl - 60 µl), and aperture of a smooth-walled fracture (1 mm – 50 mm, & open tank) on swarm velocity and swarm bifurcations.

Results: For swarm volumes that ranged from 15 µl to 60 µl, the initial swarm velocity was 4 to 60 times the single particle settling velocity. When a particle swarm was released in a fracture, the swarm velocity decreased relative to that in an open tank because of the additional drag from the presence of walls. As a swarm falls in an open-tank of water, it forms a torroidal shape that is stable as long as no ambient currents exist in the water tank (Figure 1a). When a swarm is released into a fracture with an aperture 5 mm or less, the swarm forms a torroidal shape but becomes distorted (Figure 1b). The portions of the torroid closest to the fracture wall experiences more drag that causes the swarm to bifurcate (Figure 1b). In fractures with 2.5 mm apertures, swarms were observed to bifurcate 7-10 times over a distance of 70 mm. The length of the branches in the tree-like structures decreased as the swarm progressed through multiple bifurcations. The bifurcation length is related to the distance swarms can travel along fractures. Understanding swarm bifurcation is important for determining the distances over which sensor swarms will remain coherent in fractures.

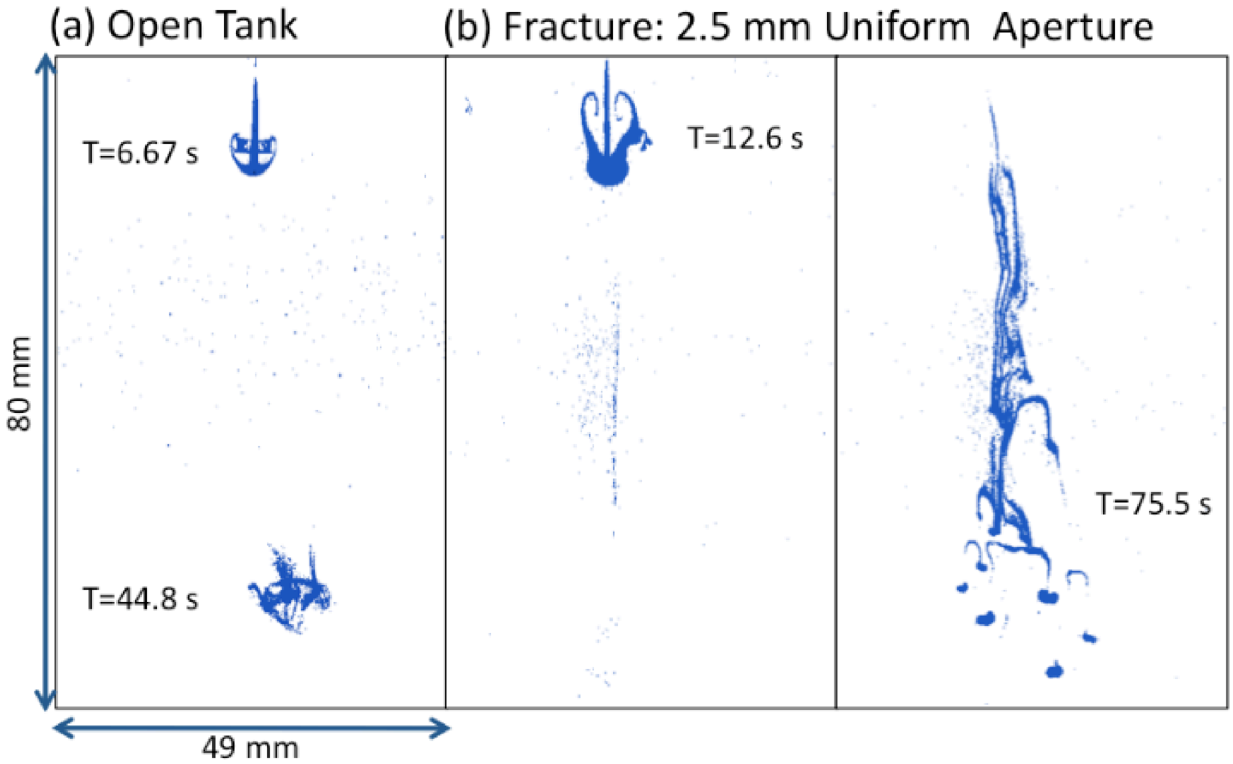

Figure 1. Images of a 30 micro-liter swarm (blue) with 1% concentration by mass of 25 micron glass beads in (a – *left image*) an open tank at times T = 6.67 s and T = 44.8 s; and (b) in a fracture with a uniform aperture of 2.5 mm at (*middle image*) T = 12.6 s and (*right image*) T = 75.5 s.

RENSSELAER POLYTECHNIC INSTITUTE

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Grant: DE-FG02-94ER14432

Grain-Boundary Transport of Incompatible Elements in the Earth

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Objective: To further advance our understanding of mass transport in deep seated regions of the Earth through experimental investigations of diffusion along dry grain boundaries in rocks.

Project Description: During the past year we continued to characterize mobilization and transport of elements along dry grain boundaries. Grain boundaries act as a pathway for rapid transport of components in many crustal and mantle rocks. Natural examples of apparent grain boundary control of bulk-rock transport are found in zoning profiles in garnets and other phases, in metamorphic textures, and in size distributions of porphyroblasts and accessory phases. Many crustal and mantle rocks contain minor or accessory minerals that are enriched in components that are incompatible in the minerals that dominate the rock matrix. From a purely geometrical standpoint, the only available pathway for isolated minor grains to ‘communicate’ with one another in response to changes in P-T is by chemical exchange through the grain boundaries. In a fluid-absent rock, transport of elements must occur by diffusion along pathways composed of dry grain boundaries and grain edges.

Results: We developed the ‘detector particle’ experimental method at RPI to evaluate type-c grain boundary diffusion kinetics along dry grain boundaries, in which the diffusant is incompatible in the dominant matrix minerals of a rock. The detector particle method consists of two parts: synthesis experiments and diffusion experiments. The synthesis experiments are tailored to produce rocks composed mainly of minerals in which the diffusant of interest is incompatible and containing 5-20% of a mineral in which the diffusant is highly compatible as dispersed ‘detector particles’. Two types of rocks were synthesized for use in the detector particle experiments to characterize Fe-Mg interdiffusion along dry grain boundaries. Quartzites containing fayalite (Fe_2SiO_4) detector particles were synthesized by packing Ni capsules with powdered quartz and a mixture of quartz plus fayalite. Pure quartzites were produced by packing capsules with powdered quartz. The rock syntheses were completed by running the components at high P-T conditions in a piston-cylinder apparatus to produce rocks with equilibrium microstructures. In the fayalite-bearing quartzite the fayalite crystals occur as dispersed crystals pinned along quartz grain boundaries. After synthesis experiments, the rock analogs were cut into disks and polished. In the diffusion experiments polished surfaces of the rock analogs were placed against polished slabs of MgF_2. Two different configurations were used for diffusion experiments to evaluate grain boundary diffusion.

Standard-type detector particle experiments were conducted by placing the fayalite-bearing quartzite directly against a polished slab of MgF_2. The juxtaposition of the quartzite containing dispersed fayalite detector particles against an Mg-rich diffusant source caused strong Fe-Mg chemical potential gradients to develop. The only pathway for transport from the diffusant source to the detector particle minerals was along the grain boundaries. The diffusant concentration in the sink minerals will be proportional to the concentration profile of the diffusant in the grain boundaries throughout the bulk sample.

The MgO content of the fayalite detector particles decreases as a function of distance from the quartzite/ MgF_2 interface. The fayalite grains that were within ~10 μm of the interface reacted to form enstatite and contain the highest MgO contents at ~20 wt.%. The longest experiments from a 'time series' do not show significantly greater transport distance, but at any given distance from the interface, the fayalite grains from the longer experiments have higher MgO concentrations. Prior to our ability to successfully model grain boundary diffusion, we did not fully understand why the diffusant was not transported further in the 8 day experiments than in the 2 day experiments. The numerical modeling has revealed that the detector particles that are closest to the diffusant source partition the majority of the diffusant from the grain boundary thereby significantly diminishing the concentration of diffusant in the grain boundary on the 'backside' of the fayalite detector particle. Due to the strong partitioning and large volume of the fayalite detector particle relative to the grain boundary volume, the fayalite crystals nearest the source interface effectively sequester the majority of the diffusant so that the longer duration experiments do not have longer transport distances.

Sandwich-type grain boundary diffusion experiments are composed of monomineralic quartzite slabs sandwiched between MgF_2 and a quartzite containing fayalite detector particles. The only available pathway for Fe-Mg communication between the MgF_2 and the fayalite detector particles was along the grain boundaries in the pure quartzite. The uptake of Mg by the fayalite detector particles in the fayalite-bearing quartzite confirms that Fe-Mg exchange occurred through the dry grain boundaries of the intervening quartzite. The thickness of the intervening quartzite slab and the duration of experiments were varied to constrain Fe-Mg interdiffusion along the quartz-quartz grain boundaries. These experiments suggests Fe-Mg interdiffusivities of $\sim 10^{-10}\ m^2s^{-1}$ at 1100°C and $\sim 10^{-11}\ m^2s^{-1}$ at 700°C, suggesting a low activation energy for Fe-Mg grain boundary diffusion.

During diffusion experiments Mn-rich pyroxene crystallites (up to 5 μm) grew along the grain boundaries of the initially monomineralic quartzite. The new pyroxene crystallites did not exist prior to the diffusion experiments and must have formed as Fe-Mg exchange along the quartz grain boundaries supplied the necessary components to form the new pyroxene crystallites. The Fe and Mg contents of the newly formed pyroxene crystallites vary linearly throughout the intervening quartzite. A time series study shows that steady state interdiffusion is established in <2 days within the intervening quartzite slab. The newly formed pyroxene crystallites have high Mn contents; however, neither the starting materials nor the Ni capsule contain appreciable Mn. We suggest that the Mn occurs as a low concentration impurity in one of the starting materials and is strongly partitioned into the grain boundaries during the diffusion experiments at which time it combines with Fe, Mg and SiO_2 to form the new pyroxene crystallites in the intervening quartzite.

Field emission scanning electron microscope images of grain boundaries show that during Fe-Mg interdiffusion experiments that new pyroxene crystallites form in the initially monomineralic quartzite as 10-200 nm films and blebs along the quartz-quartz grain boundaries. The pyroxene films evolve from a structurally unstable film configuration to lozenge-shaped features as diffusants accumulate to form larger pyroxene crystallites at grain boundary triple junctions. We are currently using a focused ion beam to cut transmission electron microscopy foils that contain the grain boundaries feeding the newly formed pyroxene crystallites.

Transmission electron microscopy and energy dispersive spectroscopy will be used to measure the physical structure and concentration of diffusants along the grain boundaries.

STANFORD UNIVERSITY
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Grant: DE-FG02-03ER15454

Framework for Constitutive Branching in Porous Rocks Undergoing Brittle Faulting and Cataclastic Flow

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Objectives: This project investigates the mechanisms of pore collapse in high-porosity rocks using three levels of mechanical description: specimen scale, mesoscopic scale, and grain scale. Mechanisms of pore collapse to be investigated include crystal plasticity and grain crushing. Bifurcation analyses will be conducted at the mesoscopic scale.

Project Description: High-porosity rocks have the greatest potential to undergo irreversible compaction due to pore collapse instability. Reduction in rock porosity typically occurs from fluid extraction as fluid pressures decrease and loads are transferred as effective stresses into the mineral skeleton. Mechanisms of pore collapse include grain crushing (often termed cataclastic flow) and crystal plasticity in the mineral grains. In this project we propose to develop a mesoscopic scale modeling approach to investigate the interplay between these two fine-scale processes as they impact pore collapse. We will model the solid matrix microstructure using the finite element method with the voids represented by hollow inclusions. Grain crushing will be represented by multiple slip surfaces through the solid matrix, and irreversible deformation in the mineral grains will be modeled using crystal plasticity theory. An extended finite element (FE) formulation will be employed to enable the slip surface to pass through the interior of finite elements while keeping the grid fixed. The grain-scale mechanical processes will be homogenized to represent the overall mechanical response of a mesoscopic element. Based on the homogenized response we will conduct bifurcation analyses at the mesoscopic scale to infer the onset of pore collapse instability at that scale.

Results: The examples below consist of a cubical sample clamped at both its top and bottom surfaces and stretched vertically. The volume is defined by three-dimensional tetrahedral elements each of which represents an f.c.c. crystal. We assume that the crystal orientations are uniform throughout the volume, but they are not aligned with the Cartesian axes. Figure 1 below shows the deformed finite element mesh after imposing 3% vertical stretching. We see that the lateral contraction is greater in the y-direction than in the x-direction, demonstrating the effect of crystal orientation on the deformation response. By comparison, Figure 2 shows a similar simulation result obtained with von Mises plasticity suggesting the deformation patterns to be the same in both the x- and y-directions. The von Mises model smears the plastic deformation within the volume, and so it cannot represent the effect of lattice orientation on the deformation response.

The results presented below have significant implications for the analysis of the deformation and localization responses of crystalline rocks. It is generally recognized that crystal deformation is responsible for some brittle micro-failure processes in these materials, including the loss of cohesion along grain boundaries and across individual crystals, a process called cataclasis. Crystal deformation is also responsible for other mechanical processes such as creep and pressure solution, albeit the actual mechanism for the latter process is not so well understood. The tools currently under development will be used to address some of the above fundamental problems.

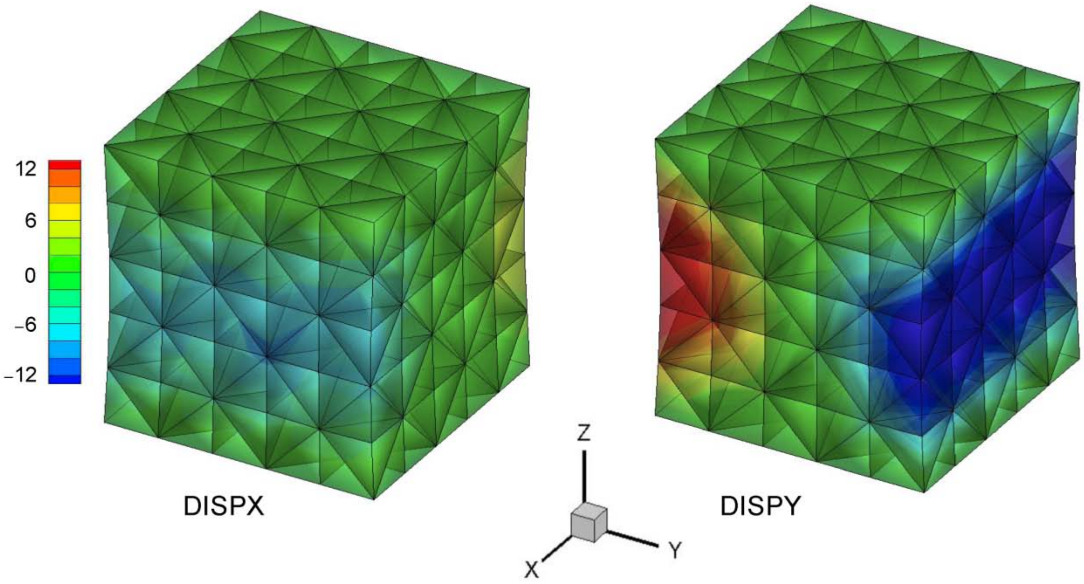

Figure 1. Elastoplastic cube (1x1x1 cubic meters) clamped on top and bottom surfaces and subjected to vertical stretching. The material is modeled as a perfectly plastic f.c.c. crystal with a uniform orientation but not aligned to the Cartesian axes. Note that the lateral contraction is greater in the y-direction than in the x-direction. Color bar is displacement in millimeters.

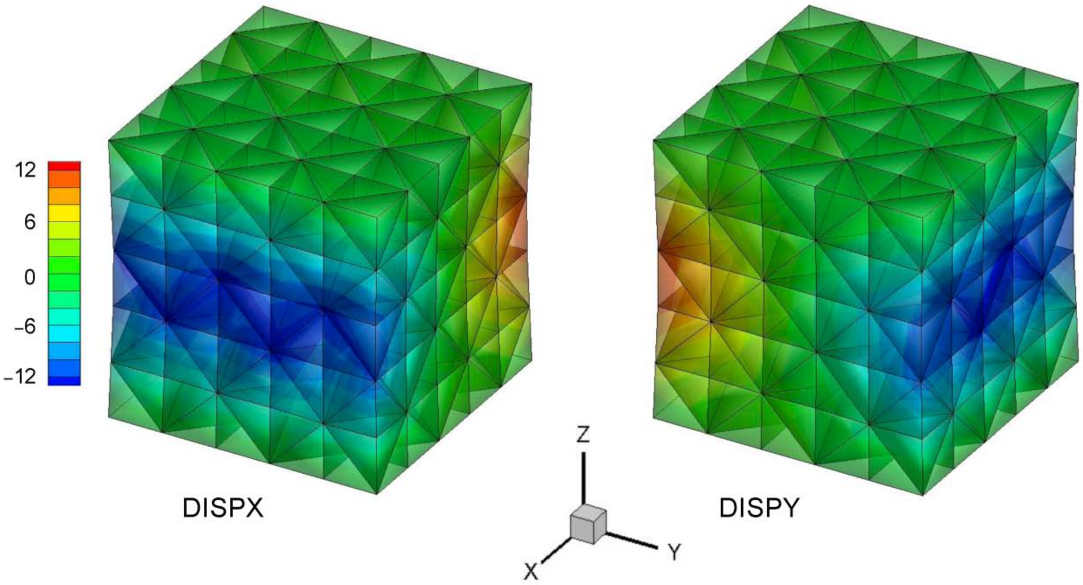

Figure 2. Elastoplastic cube (1x1x1 cubic meters) clamped on top and bottom surfaces and subjected to vertical stretching. The material is modeled as elastic-perfectly plastic von Mises model. Note that the lateral contractions are the same in the x- and y-directions. Color bar is displacement in millimeters.

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Porous Rock with Fluid: Impact of Heterogeneity on Reservoir Transport and Elastic Properties and Application to Unconventional Pore-Filling Materials

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Project Objective and Description: Heterogeneity in rock occurs at all scales. It is often apparent in the thin section where visible variations in texture and porosity occur at a scale as small as a few mm. Basic questions related to this inherent feature of rock are: (a) How important is the pore-scale heterogeneity for macroscopic transport and elastic properties that impact the depletion of and natural flow in reservoirs? (b) Can we ignore the small-scale heterogeneity and if not, what are rational ways of accounting for it when estimating the macroscopic properties? (c) What is the statistical nature of this spatial heterogeneity and is it ergodic, i.e., can we predict the permeability, conductivity, and elasticity of a relatively large "representative" rock sample from their values obtained on many small "subrepresentative" samples? A practical question ensued from these basic problems is: Is it possible (and if it is, how) to use the digital and physical data from small rock samples (drill cuttings and/or fragments of core) to assess the corresponding large-scale properties.

A way of addressing these questions is utilization of digital and physical experiments in exploring the transport and elastic properties of rock with fluid. The emphasis is on the effect of pore-scale heterogeneity on the macroscopic properties via massive numerical experiments based on realistic inputs and verified by physical evidence. We (a) use high resolution CT scans of real rock as starting points for building and altering the pore space; (b) use fast and accurate computational engines to obtain permeability, relative-permeability, capillary pressure, electrical conductivity, and elastic properties; and (c) compare experimental data with the computed results.

Results. We have conducted a large number of computational experiments to quantify the permeability and elastic properties on fragments of rock with these properties measured in the physical laboratory. Specifically, we explored samples of micritic carbonate, Fontainebleau sandstone, Berea sandstone, and dolomite carbonate.

The results indicate that indeed, it is possible to recreate a macroscopic trend from very small fragments of rock. Such trends become less tight as the number of the subsamples of the original digital sample increases and, hence, the size of a subsample is reduced. Nevertheless, such digital trends persist and appear realistic (Figure 1).

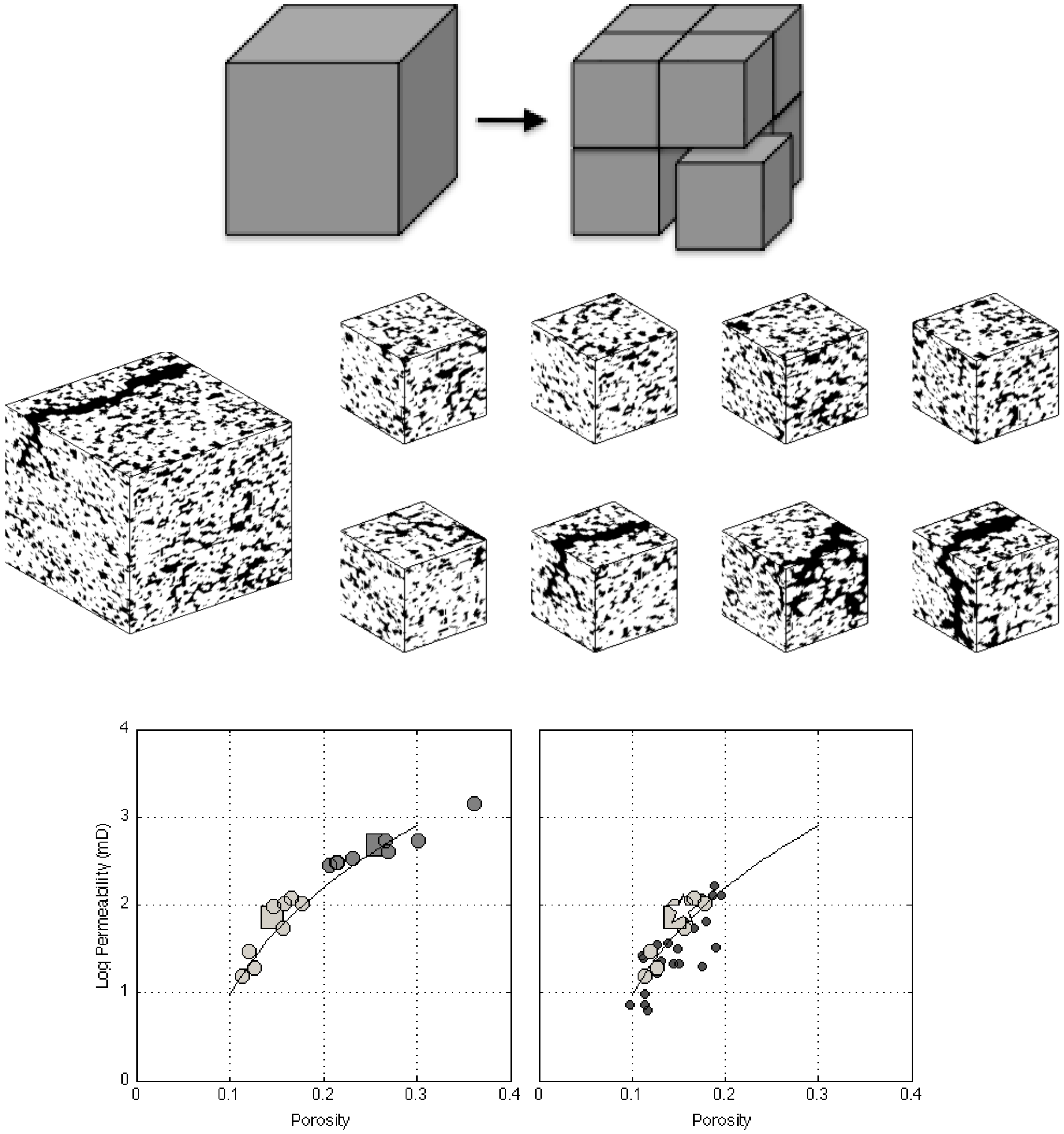

Figure 1. Top: Subsampling procedure (cartoon). Middle: The original 3D oil sand cube (left). The resolution is 8.6 micron per pixel. The size is 150 by 150 by 150 pixels (1.3 by 1.3 by 1.3 mm). Eight sub-cubes of the original cube (right). The size of each sub-cube is 75 by 75 by 75 pixels (0.645 by 0.645 by 0.645 mm). Bottom-left: Permeability versus porosity in Berea sandstone (light square) and oil sand (dark square). Smaller round symbols of the same shade of gray are for the eight subsamples of these two samples. Bottom-right: Berea sandstone with its eight and twenty seven (small black circles) subsamples. The open star symbol is from a physical measurement. A Kozeny-Carman curve (black, same in both plots) is given for reference.

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Structural Heterogeneities and Paleo-Fluid Flow in an Analog Sandstone Reservoir

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Objectives: We are developing conceptual and quantitative mechanical models and predictive tools for understanding the spatial distribution of permeability in sandstone aquifers and reservoirs as determined by structural heterogeneities including faults, joints, sheared joints, shear deformation bands, and compactive deformation bands. These structural heterogeneities significantly influence subsurface fluid flow.

Project Description: We are conducting a broad-based research project to map and characterize structural heterogeneities (deformation bands, joints, sheared joints, and faults) in the Jurassic Aztec Sandstone exposed at the Valley of Fire State Park, Nevada, as an analog for active hydrocarbon reservoirs and groundwater aquifers. Our current efforts comprises two complementary sub-projects: (1) characterization of fault structure, linkage and fluid-flow effects using field mapping and effective medium theory; (2) modeling the evolution of non-planar faults using boundary element methods, contact mechanics, and complementarity algorithms. The integrated approach of the project—combining detailed field and petrographic observation and analysis, process-based mechanical modeling, laboratory experimentation and numerical simulation of fluid flow—serves to illuminate how a complex suite of brittle structures can evolve to affect fluid flow in a typical sandstone aquifer/reservoir at a variety of length scales.

Results: The two sub-projects are summarized below.

(1) Characterization of fault structure, linkage and fluid-flow effects

We have been investigating the geometrical, statistical, hydraulic, and geomechanical characteristics of fault networks including both large (seismic-scale) and small (non-seismic-scale) faults in the sandstone. During the past year, we brought to completion the publication of papers on the segmentation and scaling of strike-slip faults primarily in the study area (de Joussineau and Aydin, 2009), and the analysis of fault growth using effective medium theory together with the field data collected in the previous two years (Aydin and Berryman, 2009; and Berryman and Aydin, 2009). We collaborated with James G. Berryman, a physicist at Lawrence Berkeley National Laboratory, who also is supported by the DOE, Basic Energy Sciences. The results from these efforts allowed us to elucidate lengthening and widening of fault zones as a function of slip and to develop criteria for the linkage of fault segments and the widening of fault rock zones based on the density and intersection angles of the faulting-related fractures.

In addition, we brought to completion a side project that we started a few years back on bed-parallel compaction bands and their petrophysical properties (Aydin and Ahmadov, 2009).

(2) Modeling the evolution of non-planar faults

Our current research focuses on the mechanical behavior of curved faults and geometrically irregular fault surfaces under tectonic loads, which is fundamental to understanding the brittle deformation of rock, and also of practical importance to disciplines such as earthquake science, rock mechanics, and geotechnical engineering. In addition, the opening and closing behavior of curved faults will affect frictional resistance to slip and local fluid flow. We use two-dimensional numerical solutions for quasistatic elastic boundary value problems to investigate both circular arc cracks and sinusoidal wavy cracks under compressive and shear stress as models for faults.

The analytical solution for a circular arc crack has been used widely to study curved crack behavior in an otherwise homogeneous and isotropic elastic material. For certain orientations and magnitudes of the remotely applied loads, portions of the crack will close, causing the analytical solution to fail due to violation of the traction-free boundary condition. Therefore, a two dimensional displacement discontinuity method is combined with a complementarity algorithm to solve the problem for partially closed circular arc cracks with friction based on the code (Mutlu & Pollard, 2008). Taking the arc crack as a model for a fault with curvature, the range of conditions for partial opening has been investigated (Ritz & Pollard, 2009). Opening is spatially associated with the lee side and closure with the stoss side of the fault surface. In general, an increase in friction is found to decrease the length of opening along a curved fault. As an extension of the circular arc crack, the wavy crack problem can be analyzed as linked circular arc segments or a sinusoidal curve using the same numerical method to find the stress and displacement perturbations.

In summary, we find that opening may alter propagation paths, lead to the formation of new fractures in the process zone, and affect fluid flow in and around the fault as a function of its curvature.

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Multiscale Investigation and Modeling of Flow Mechanisms Related to CO_2 Sequestration in Geologic Formations

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Objectives: Our objective is to investigate the relevant physical mechanisms of CO_2 flow and entrapment in brine formations at the microscopic and mesoscopic scales. We use advanced flow visualization techniques and high accuracy numerical simulations.

Project Description: Our approach is to develop the missing link between the fundamental physics of multiphase flow at the pore-scale and the phenomenological representation of dynamic behaviors across a hierarchy of geologic scales. We use the problem of CO_2 sequestration in geologic formations as a prototypical application of multiphase flow in porous media. We take this approach not only because of the lack of understanding of the sequestration process and its immense potential for environmental impact, but also because the process involves a wide range of fundamental physical mechanisms that arise in a host of other applications, such as, contaminant transport and remediation as well as enhanced oil recovery.

Our approach is to develop novel numerical methods for interface problems, for the Navier-Stokes equations, for stochastic multiscale methods as well as to develop innovative experimentation and visualization techniques for micromodels etched with characteristic sandstone pore network patterns.

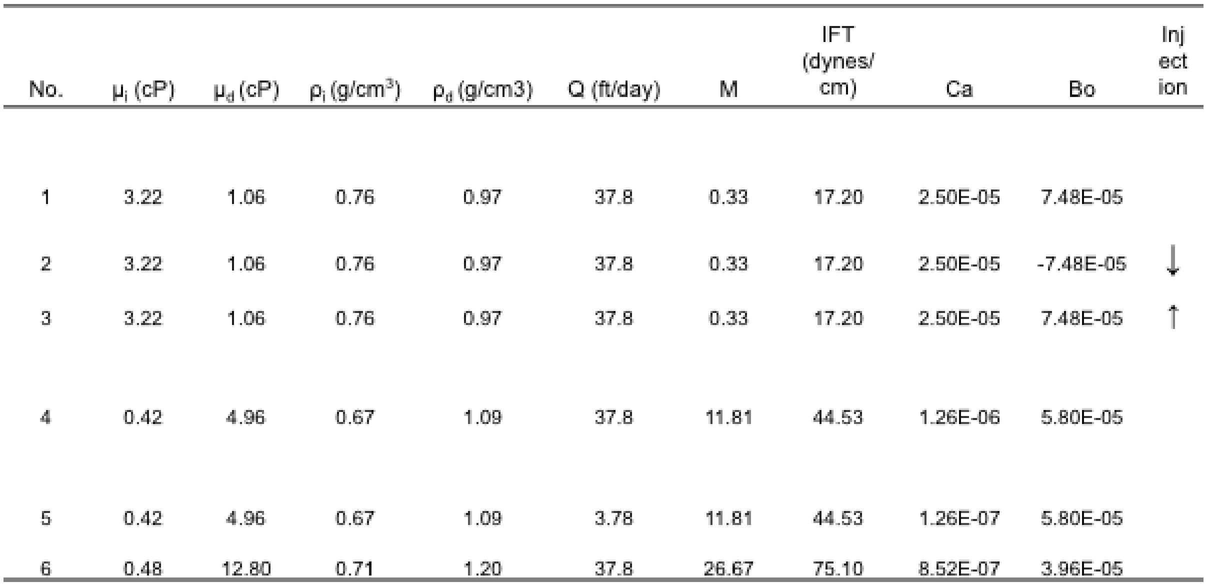
The proposed research will, in general, make it possible to make reliable predictions regarding geologic flows. In particular, it will significantly improve the understanding of hydrodynamic mechanisms and allow the development of physically accurate macroscopic models in order to provide improved predictability and management capability for CO_2 sequestration and other geologic flows.

Results: This project began in Sept. 2008. Our experimental efforts to date have centered upon the selection of a micromodel system, identification of suitable fluids, conducting baseline transient experiments, and conducting a set of drainage displacement under representative conditions. Our micromodels are etched in silicon and feature a 1:1 representation of sandstone pore-network patterns. Although they are two-dimensional in nature, micromodels provide the best method to visualize directly pore-scale, multiphase fluid movement. The overall dimensions of the micromodels are 5 by 5 cm with 25μm etch depth. The model reflects a two-dimensional porous medium of 600 by 600 pores. This number is sufficient to meet the scaling requirements for representative elementary volume. Micromodel porosity and permeability are roughly 0.22 and 900 md, respectively. The micromodel contains four ports allowing fluids to enter and exit along a face of the micromodel. In a macroscopic sense, displacements are linear.

The micromodel is saturated with various two-phase mixtures of water/glycerol/hydrocarbon that are equilibrated. The fluid systems provide a range of viscosity and density conditions. Hence, in combination with the selection of an appropriate fluid injection rate and vertical versus horizontal orientation of the micromodel, we apply a range of capillary number (ratio of viscous to capillary force), Bond number (ratio of gravity to capillary forces), and mobility ratio conditions (ratio of injected phase to resident phase mobility).

We conducted and reported baseline experiments that demonstrate pore-level events occur in a physically accurate manner within the micromodel. In the past year, we conducted a set of unstable drainage displacements under mobility ratio and capillary number conditions that are representative of CO_2 sequestration. These experiments are summarized in Table 1. Micromodels were oriented vertically and horizontally to examine the role of gravity at the pore and network ensemble scale. Images were collected at both scale and we work toward appropriate image analysis of experimental results.

Table 1: Description of experimental parameters. Subscripts "i" and "d" refer to injected and displaced fluids, respectively. Arrows indicate the direction of injection.



No.	μ_i (cP)	μ_d (cP)	ρ_i (g/cm^3)	ρ_d (g/cm3)	Q (ft/day)	M	IFT (dynes/ cm)	Ca	Bo	Inj ect ion
1	3.22	1.06	0.76	0.97	37.8	0.33	17.20	2.50E-05	7.48E-05	
2	3.22	1.06	0.76	0.97	37.8	0.33	17.20	2.50E-05	-7.48E-05	↓
3	3.22	1.06	0.76	0.97	37.8	0.33	17.20	2.50E-05	7.48E-05	↑
4	0.42	4.96	0.67	1.09	37.8	11.81	44.53	1.26E-06	5.80E-05	
5	0.42	4.96	0.67	1.09	3.78	11.81	44.53	1.26E-07	5.80E-05	
6	0.48	12.80	0.71	1.20	37.8	26.67	75.10	8.52E-07	3.96E-05	

Both drainage and imbibition experiments show that as viscosity and density were changed to unfavorable conditions, the displacement pattern becomes unstable at the microscopic level. This observation is consistent with previous research work at larger scale. On the other hand, varying the capillary number did not show a significant change in the flow regime, however, storage rate is increased as the flow rate was decreased. The effect of capillary forces seen in this study does not agree with Frette et al. (2007) conclusion such that the capillary number is more important in determining displacement morphologies at high injection rate. The effect of gravity and buoyancy to drainage displacement is still ambiguous and remains to be further investigated.

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Grant: DE-FG02-96ER14644

Reactivity of Iron-Bearing Minerals and CO_2 Sequestration: A Multi-Disciplinary Experimental Approach

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Objective: The primary goal of this research program is to understand the chemistry that results when supercritical CO_2 ($scCO_2$) with H_2S and/or SO_2 in deep saline formations (DFS) contacts iron bearing minerals. Understanding the complexities the sulfur co-injectants introduce is a critical step in developing CO_2 sequestration as a climate-mitigating strategy. The research strategy is to understand macroscopic observations of this chemistry with an atomic/molecular level view using surface analytical techniques.

Project Description: Research is investigating some of the complexity associated with CO_2 sequestration in DFS. Specifically, research is focused on developing an understanding of the chemistry that will result when $scCO_2$ with varying amounts of H_2S and/or SO_2 comes in contact with iron-bearing sediments common to DFS. A representative suite of well-characterized sedimentary rocks (sandstones, siltstones, marls, and carbonates) will be exposed to $scCO_2$, $scCO_2/H_2S$, $scCO_2/SO_2$ as well as Na-Cl brines equilibrated with these supercritical fluids in a hydrothermal flow-through setup. The experimental system provides for long-term monitoring of changes in sulfur chemistry in the effluent. Complementary spectroscopic studies will use in situ vibrational spectroscopy to examine the interactions under near-field conditions at the molecular level and resolve the interaction of $scCO_2$, $scCO_2/H_2S$, and $scCO_2/SO_2$ with relevant iron mineral phases. .

Results: Research progress in FY2010 has focused on understanding the transformations of iron oxides and oxyhydroxides to siderite ($FeCO_3$) in the presence of $scCO_2$ and aqueous sulfide. Techniques used continue to be *in situ* attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and *ex situ* X-ray diffraction (XRD). In FY2009 we focused on the transformations of the iron oxyhydroxide, ferrihydrite. In FY2009 we focused on the transformations of the iron oxyhydroxide, ferrihydrite. In FY2010 we have concentrated on pure iron oxide phases present in subsurface environments as well as iron-oxide-bearing sandstones.

A majority of the recent studies have focused on hematite with nano-morphologies, denoted by **H1** (~42 nm average particle diameter) and **H2** (average particle diameters of 267 nm) in this progress report. X-ray diffraction (XRD) data obtained before and after the exposure of **H1** and **H2** particle slurries to $scCO_2$ at 70 °C as a function of the aqueous sulfide concentration are shown in Figure 1. In the figure S1 and S2 refer to sulfide concentrations that

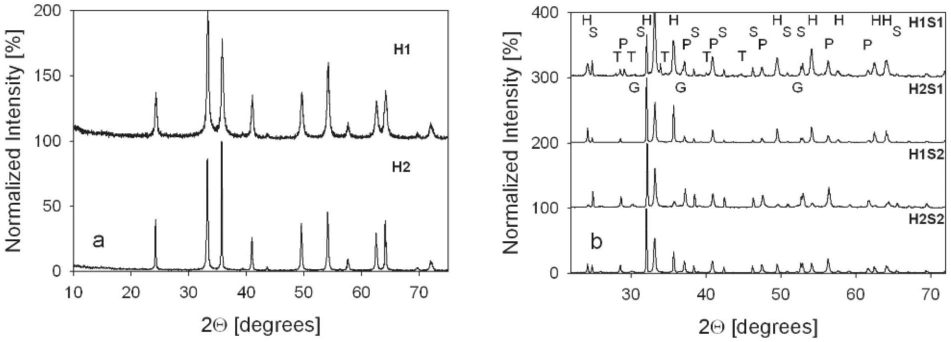

Figure 2: XRD patterns for the a) H1 and H2 starting materials and for b) H1 and H2 after reaction with $scCO_2$ in the presence of 50 mM (S1) or 100 mM (S2) aqueous sulfide (i.e., H1S1, H2S1, H1S2, and H2S2). Labels on the XRD pattern refer to hematite (H), siderite (S), pyrite (P), trona (T), and greigite (G).

are representative of having 2.5 and 5% H_2S in the $scCO_2$. Inspection of the post reaction XRD shows that hematite was partially converted to carbonate and sulfide phases during the exposure to $scCO_2$. All of the experimental conditions resulted in a significant portion of the hematite converting to pyrite and siderite. Analysis of the results reveals that the sulfide concentration affects the amount of hematite conversion. For example, the lower sulfide concentration experiment, **S1**, results in ~30% of the iron being converted to siderite and pyrite, and the use of a higher sulfide concentration, **S2**, results in the conversion of about 76% of the iron in the small diameter hematite (**H1)** to iron sulfide and carbonate product. This same trend can be observed for the **H2** sample, but in this case even at the higher sulfide concentration only ~55% of **H2** iron converted in to pyrite and siderite. These experimental observations suggest that the amount of reduction of ferric to ferrous iron and ultimately the amount of hematite conversion to siderite (for a given starting mass of hematite) at the highest sulfide concentrations is greatest for the small diameter particles. We suspect that the increased conversion of **H1S2** relative to **H2S2** is due to the greater initial surface area associated with **H1** (~53 m^2/g) compared to the **H2** sample (~11 m^2/g). The reason why all the hematite does not convert to siderite and pyrite under any of the conditions used in our study is not known, but it may be that product formation on the hematite particle surface ultimately blocks or prevents the reaction of sulfide with the subsurface region of the hematite particles.

It is important to note that in all cases the reaction with hematite led to equimolar amounts of siderite and pyrite. This particular experimental observation suggests that the following reactions dictate the outcome of the experiment:

$$2Fe^{3+} + 2S^{2-}\,(aq) \rightarrow FeS_2(\text{pyrite}) + Fe^{2+}(aq) \tag{1}$$

$$Fe^{2+}(aq) + CO_3^{2-}\,(aq) \rightarrow FeCO_3(\text{siderite}) \tag{2}$$

In this reaction scheme, every mole of pyrite produced from ferric iron and sulfide produces one mole of ferrous iron that reacts with carbonate to form siderite (reactions 1 and 2).

TEXAS A&M UNIVERSITY

Texas Engineering Experiment Station, Department of Petroleum Engineering, 3116 TAMU
College Station TX 77843

Grant: DE-FG02-00ER15034

Time-Lapse Seismic Monitoring and Performance Assessment of CO_2 Sequestration in Hydrocarbon Reservoirs

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Objectives: Our goal is to examine the viability of time-lapse seismic monitoring using an integrated modeling of fluid flow, including chemical reactions, geomechanical effects and seismic response. A critical aspect here is computational efficiency so that the approach can be suitable for large-scale field applications using high resolution geologic and seismic models.

Project Description: Our work focuses on fully integrating fluid flow and seismic data for monitoring injected CO_2 fronts by developing robust methods for reservoir characterization via coupled seismic and fluid flow modeling and joint inversion of seismic and fluid flow data. For computational efficiency and suitability for large-scale field applications, we are developing streamline-based compositional modeling of CO_2 sequestration including compressibility, stress-sensitivity, compositional and geochemical effects. We perform comprehensive simulations of the gas injection process accounting for the phase behavior of CO_2-reservoir fluids, the associated precipitation/dissolution reactions and the accompanying changes in porosity and permeability. The simulation results are then used to model the changes in seismic response with time. For data integration and uncertainty assessment, we adopt an efficient Bayesian framework using reversible jump multistage Markov Chain Monte Carlo (MCMC) methods.

Results: The effects of heterogeneity in Carbon Capture and Storage (CCS) in saline aquifers have been investigated extensively and are known to have important bearings on the storage capacity of the aquifer. In CCS projects, the time-lapse seismic survey has been proposed as a valuable tool for monitoring of CO_2 movement. However, the potential of the time-lapse seismic data for heterogeneity characterization and geologic model updating has not been fully explored. One of the biggest challenges in the quantitative use of time-lapse seismic data during CCS is the complex movement of the CO_2 influenced by compositional effects, geochemical reactions, phase changes and gravity segregation.

During the past year, our main focus has been to examine the viability of time-lapse seismic data for heterogeneity characterization, particularly in the presence of high gravity segregation as determined by the viscous to gravity ratio. We first introduced compositional streamlines to understand and visualize the flow and transport of CO_2 in the presence of mineral precipitation/dissolution, residual trapping and buoyancy effects. To start with, individual component fluxes are generated by a finite difference fully implicit compositional simulator incorporating all the relevant physics of CO_2 sequestration. The fluxes are then utilized in novel streamline tracing algorithms to generate phase and component streamlines depicting the movement and the trapping of CO_2 in the aquifer. Next, we utilize the compositional streamlines to determine the sensitivity of the time-lapse seismic attributes specifically, interpreted saturation differences, to changes in reservoir properties such as permeability and porosity. The sensitivities are then used in an inverse modeling algorithm to calibrate the geologic model to time-lapse seismic data. The outcome is an improved description of permeability heterogeneity that is consistent with the 4-D seismic response and improved predictions of the CO_2 storage capacity.

We illustrate the effectiveness of the time lapse seismic inversion when there is significant vertical migration of CO_2 using a 3D heterogeneous example. The 3D model consists of 10 layers with 100ft. each. As expected, the injected CO_2 at the center rises vertically because of buoyancy forces. This is clearly visible from the streamline patterns in Fig. 1.

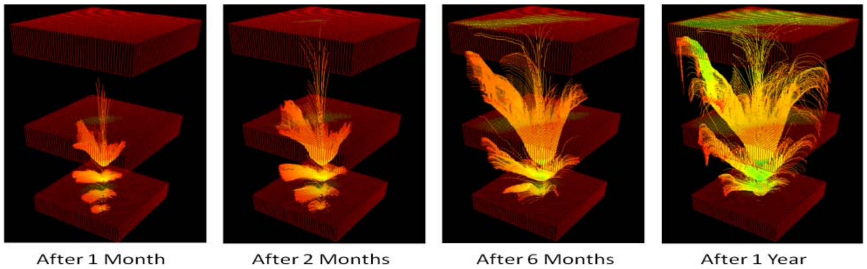

Fig.1 Vertical movement of CO_2 plume as depicted by the streamlines

The streamline methodology to integrate seismic attributes into high resolution models is based on the analytical relationship between the arrival time of a propagating fluid front and the reservoir properties like porosity and permeability. Using an asymptotic solution for the propagation of a two phase front, it is possible to find a self similar variable along the characteristic curves that has the property of transforming the spatial domain from an Eulerian representation to a Lagrangian perspective. This technique is very efficient and requires a single forward simulation to calculate the reservoir parameter sensitivities to time-lapse seismic response. Once the sensitivities are calculated, the data integration is performed utilizing an iterative least squares minimization of the differences in the interpreted saturation of CO_2 between two consecutive seismic surveys.

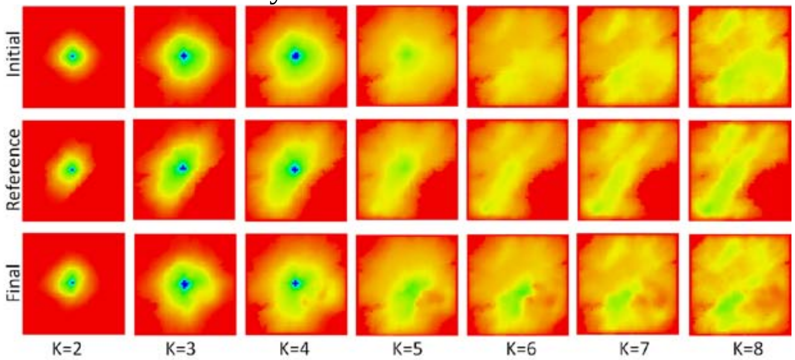

Figure 2 CO_2 front propagation before (initial) and after (final) time lapse seismic data integration.

Fig. 2 shows the evolution of the CO_2 plume in different layers before and after the time-lapse data integration. It can be clearly seen that the time lapse seismic data integration helps in capturing the CO_2 plume movement which now better resembles the reference case.

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Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale

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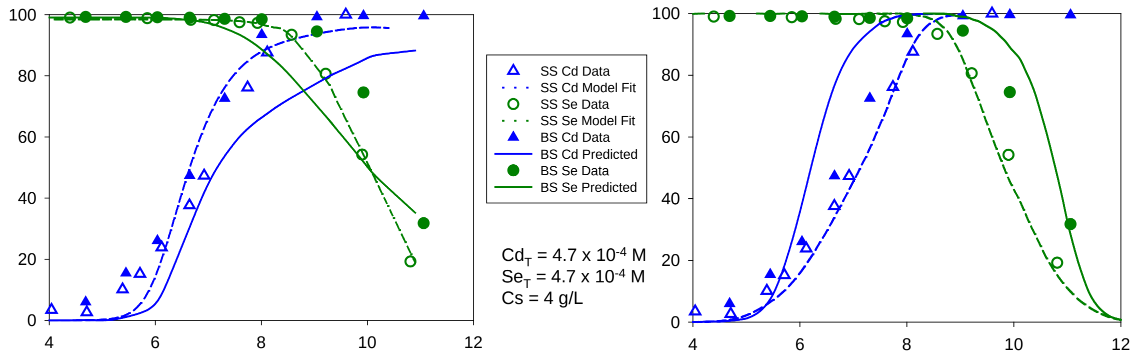
Objectives: The objectives of this research are to develop an approach for predicting the types of metal surface complexes that form on mineral surfaces by focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models to predict adsorption behavior.

Project Description: We combine the use of several techniques including bulk adsorption experiments, X-ray absorption, infrared, and vibrational sum frequency spectroscopies (XAS, IR, VSGS), and molecular modeling to investigate ion-pairing in solution and at mineral surfaces. XAS provides data on how the metal binds to the surface (e.g., monodentate, bidentate), IR provides data on ion-pairing in aqueous solution, and VSGS provides data on the impact of adsorbed metal-anion pairs on water structure at the mineral surface. Molecular modeling is used to guide spectroscopic data interpretation by providing information on water structure around ions in solution and the structure of metal-anion complexes in aqueous solution. In addition, molecular modeling is used to provide insight into water structure at mineral surfaces, the surface sites involved in ion adsorption, and the distribution of ion pairs between aqueous solution and the mineral surface. Our studies have focused on systems involving alkaline earth metal (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and heavy metal (Co^{2+}, Pb^{2+}) cations. The anions we have selected for study include Cl^-, NO_3^-, ClO_4^-, SO_4^{2-}, and SeO_3^{2-}. Ion adsorption and the potential formation of ternary complexes on silica (quartz, amorphous silica), alumina (corundum and gibbsite), and ferric iron (goethite) oxides are under investigation.

Results: This fiscal year, the Katz lab focused on extensive modeling approaches with various systems involving cation and anion adsorption, continuing the efforts from last year's work. In addition, XAS spectra were collected at Stanford Synchrotron Radiation Lightsource for the As(V), Ca(II), and Si(IV) studies that we conducted last year for a diffuse layer modeling (DLM) effort. Our modeling focus this year centered around three contemporary models, the triple-layer model (TLM), the extended TLM (ETLM), and the charge-distribution multisite complexation (CD-MUSIC) model, for Cd(II), Pb(II) and selenite adsorption onto goethite. Because these models describe sorption behavior in more details than the less complicated models (such as DLM) they should provide a better framework for assessing our ability to connect our macroscopic scale modeling efforts to our molecular spectroscopy and molecular modeling and possess a larger number of parameters, especially the CD-MUSIC model. Our approach was to re-parameterize a TLM model to describe the systems mentioned previously using published values of parameters from similar systems for applying ETLM and CD-MUSIC models. In using the existing parameters, the extensibility of these models can be tested and the calibration effort for ETLM and CD-MUSIC can be significantly reduced. By comparing the results to results from a well-calibrated TLM system, we can evaluate the applicability of this approach. Our results showed that ETLM and CD-MUSIC calibrated using one single solute adsorption edge data set successfully predicted adsorption for single solute systems under varying experimental conditions, as well as the developed TLM approach we had applied previously. For cation bi-solute systems (i.e., Cd(II) and Pb(II)), ETLM and CD-MUSIC described the adsorption trend qualitatively, and were no worse than the previous TLM results. However, for the Cd(II) and selenite bi-solute systems, CD-MUSIC underpredicted selenite adsorption at higher loadings, while the TLM was able to predict the trend more accurately. Representative results are shown in Figure 1.



(a) (b)

Figure 1 (a) CD-MUSIC and (b) TLM model predictions for Cd(II) and selenite single- and bi-solute adsorption onto goethite.

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Predicting Fracture Porosity Evolution in Sandstone

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Objectives: Our goal is to understand how fracture growth and diagenetic alteration interact to create and destroy fracture porosity in subsurface sandstones. We are testing the hypothesis that records of fracture opening can be recovered from fractures formed in the subsurface and that along with fluid-inclusion data and diagenetic and geomechanical models these records can help recover the duration and rates at which fractures open and rock properties change.

Project Description: We use SEM-based cathodolumiescence imaging, a diagenetically sensitive geomechanical model, and a diagenetic model that incorporates mechanics to investigate how diagenesis affects development of fracture aperture, length, and spatial arrangement. Our observations and modeling show that important mechanical and chemical feedbacks govern several important aspects of fracture patterning, and that fracture growth patterns, timing, and rate in principle can be recovered from structural diagenetic data.

We are extending a theory of cementation in fractures that predicts fracture porosity evolution as a function of temperature, surface area, and opening history. The model predicts patterns, rates and durations of fracture opening. We take advantage of new automated image collection systems and protocols, fluid inclusion microthermometry, and sandstone petrography to rigorously test predictions. We also track rock property evolution in the context of burial history. We investigate how diagenesis affects fracture growth by conducting numerical experiments that incorporate diagenesis, using both our geomechanical model, a newly developed hybrid numerical code, and by using other modeling approaches. The numerical experiments are helping us formulate specific hypotheses about how any feedbacks work, including processes that generate fracture size distributions and clustering patterns. We test fracture growth hypotheses against natural examples using high resolution fracture opening histories and fluid-inclusion data keyed to opening increments, which allows rigorous comparison with our diagenetic models. We also seek to understand causes of heterogeneous sealing of large, static fractures by carbonate cementation, a widespread phenomenon that seals some large fractures.

Results: Timing of the development and cementation of fracture porosity, as well as the distributed pattern of fractures can strongly influence fluid flow in the subsurface. Natural opening-mode fractures in Piceance Basin sandstones display evidence of multi-step opening by the crack-seal mechanism of deformation from SEM-CL imaging of synkinematic quartz bridge cements. These diagenetic cements are spatially discontinuous within individual fractures, with significant porosity preserved between bridges. These fractures have power-law aperture-size distributions. Scanline data from twelve samples indicate that as fractures widen, the power law slope decreases and approaches a value near -0.5, observed in populations with the largest fractures. This uniform power law exponent could provide a useful tool for fracture intensity prediction using small datasets of fracture size.

Fluid inclusion assemblages (FIAs) hosted in crack-seal cement deposits within quartz bridges record the overall range of pressure-temperature-composition conditions during fracture opening. Homogenization temperatures of aqueous FIAs indicate a thermal history from ~145°C to ~185°C. Analyses from Corcoran Sandstone elsewhere in the basin indicate a thermal history from ~150°C to ~172°C. Aqueous fluid inclusion salinities are low, ranging from 2-3 wt.% NaCl equivalent at all examined sites, and are similar to seawater salinities. Coexisting hydrocarbon gas inclusions indicate these temperatures represent true formation temperatures of fracture opening, and that gas charge occurred coevally with fracture opening. According to burial histories for these strata, the highest fluid inclusion temperatures are the same as maximum burial temperatures, and suggest a maximum timing for fracture opening between ~42 to ~10 Ma.

Raman spectroscopic analyses indicate that vapor bubbles in aqueous fluid inclusions are adequately modeled by a composition of pure methane, confirming that these inclusions were trapped under methane–saturated conditions. We used the CH_4 Raman peak position of the vapor bubble to determine the pressure of the aqueous inclusions at room temperature. Based on integrated microthermometry, Raman spectroscopy, and equation of state modeling, we calculate pressures at trapping for the observed inclusions. Results indicate trapping pressures ranging from ~70 MPa to ~100 MPa, suggesting fracture opening occurred under significant pore fluid overpressures. These approaches have also been applied to several outcrop fracture systems. The fracture/cement model approach was also successfully applied to fractures in dolostone.

A parameter that can be readily measured in natural fracture populations is the opening or aperture, so it is a good attribute to use for constraining fracture mechanics model results. We used a fracture mechanics model to examine the feedback between these aperture propping mechanisms and fracture network growth. Power laws result from diagenesis active during fracture propagation.

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Center for Frontiers of Subsurface Energy Security

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Objectives: Currently humans extract most of the fuel for the global economy from underground. The byproducts of consuming this fuel enter the atmosphere or remain on the surface. This situation is no longer tenable. A critical step toward future energy systems will be the ability to cycle fuel byproducts back to their original home: the Earth's subsurface. Applications of this concept include storing CO_2 in deep geologic formations and securing radioactive materials in appropriately engineered repositories. Our goal is to fill gaps in the knowledge base so that subsurface storage schemes are reliable *from the moment they open*.

Project Description: Recent theoretical and experimental advances have opened previously inaccessible avenues for understanding material properties at scales less than 100 nanometers. The same advances also present opportunities to control material behavior in novel ways. The central theme of this proposal is harnessing these advances to explain reactive transport in geologic systems. The movement and reaction of species in multiple fluid phases through voids in rocks has been studied for decades. Yet our ability to predict large-scale, long-term behavior is not impressive. Nearly every forecast over human scales (decades) requires substantial revision over time. Too often the reason is that our conceptual and mathematical models leave out or misrepresent features that turn out to be crucial. The current knowledge base is therefore inadequate for one of the greatest challenges for 21st century energy systems: the secure sequestration in the Earth‘s subsurface of byproducts from fuel consumption.

Two scientific Grand Challenges contribute to the gap between forecast and outcome in geologic systems. First, byproduct storage schemes will operate in a far-from equilibrium state. Complicated behavior, including self-reinforcing and self-limiting transport, emerges during such processes. Central to the complexity is the coupling between biogeochemical alteration, transport properties, and mechanical loading. Much of this coupling can be traced to phenomena at very fine scales: the cell wall of a microorganism living in a pore, or molecules at a fluid/mineral interface. Consequently we expect that new materials, new methods for characterization at sub-pore scales, and new modeling concepts and tools will enable an urgently needed advance in our understanding of subsurface flow and transport.

The second Grand Challenge is to explain the emergence of patterns and other manifestations of correlated phenomena. Emergent behavior can arise at several length scales even from a single set of processes, so recognizing this behavior is not always easy. Solutions to the unresolved challenge of discerning the causes of emergent behavior and capturing them in a model will have profound implications on 21st century energy systems. For example, the unforeseen emergence of preferential flow paths can defeat an otherwise secure repository. Tailoring the interaction at a fluid/mineral/microbe interface, on the other hand, could render a system self-sealing. To address those two Grand Challenges, CFSES is organized around four focus areas. The first focus area will investigate natural subsurface processes and engineered systems in far-from-equilibrium states at very small scales (molecules to pores). The second focus area will characterize patterns and behaviors of multiphase reactive flow and mechanics that emerge between the pore and the continuum scales. The third focus area will analyze and characterize the coupled mechanics, reactions, flow, and transport that have their sources at the pore and continuum scales and reveal themselves between the continuum and field scales. Finally, the fourth focus area will develop multi-physics, multiscale modeling and simulation schemes that incorporate the findings of the other three tasks. Geological storage of greenhouse gases from pore to continuum scales. Mesoscale CT data versus time can yield residual saturations and relative permeability, revealing behavior not accessible in traditional experiments.

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Physiochemical Evidence of Faulting Processes and Modeling of Fluid Flow in Evolving Fault Systems in Southern California

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Objectives: This is a collaborative study to quantify basinal fluid flow, submarine gas migration and diagenetic effects within deforming faults in a transpressional setting that is seismically active. The field application emphasis is on faulted basins in southern California.

Project Description: We have mainly targeted active faults and young (Tertiary) petroleum fields in southern California for study. Faults include the Refugio Fault in the Transverse Ranges, the Ellwood Fault in the Santa Barbara Channel, and the Newport-Inglewood in the Los Angeles Basin. Subsurface core and tubing scale samples, outcrop samples, well logs, reservoir properties, pore pressures, fluid compositions, and published structural-seismic sections are being studied to characterize the tectonic/diagenetic history and geochemical signatures in carbonate that characterize rapid CO_2 degassing. These data provide constraints for finite element models that are being developed to predict fluid pressures, flow patterns, rates and patterns of deformation, subsurface temperatures and heat flow, and geochemistry associated with large fault systems.

Results: Our latest studies of the South Ellwood fault in the Santa Barbara basin, as described in more detail in the accompanying 2009 Annual Summary report by J.R. Boles, have given us direct evidence of connectivity between the seafloor and producing wells in the field. These results are surprising as the South Ellwood fault is generally considered a seal to the reservoir. The seafloor seepage emanates from a fault zone in underlying siliceous shale of the Monterey Fm., and is monitored by large seepage tent installed on the sea floor near Platform Holly. Using observed changes in seepage rates and the known pressure gradients, we have calculated the effective permeability with respect to gas to be k~30 md (millidarcys), assuming L~0.9 km for the fracture/fault flow path with an average cross section area A~1860 m^2. This estimate is comparable to k~20 md permeability with respect to water along another segment/bounding fault to the same reservoir (Boles and Horner, 2003). This work shows that fault zones can, at least locally, have relatively high permeability (k~10's of md) and communicate on the km scale with shallower levels. In a similar vein, our studies in the Long Beach field of the Los Angeles basin, have recognized thermal anomalies associated with a splay of the Newport-Ingelwood fault zone. These anomalies occur in at least three wells in which the sub-hydrostatic reservoir overlies a hydrostatically pressured section. Within the wells, the thermal anomaly is 11ºC above the normal geothermal gradient (over an interval of about 70 m). The thermal anomalies appear to be transient over time intervals of two years, and we interpret them to represent upward movement of fluids along faults from deeper levels in the basin. The transient nature of the thermal pulse provides constraints on the magnitude of the fluid flux. Our heat transport calculations indicate that a transient fluid-pulse volume V~170 m^3 caused an 11ºC thermal perturbation, based on a fault k~ 20 to 30 md.

Faults can also have profound effects on large-scale fluid migration in tectonically active systems, especially like those of southern California. Based on the estimates of fault permeability derived above, we have constructed numerical simulations to characterize the geofluids history of the LA basin. The numerical model was developed in our lab at Tufts, and is based on a hybrid FEM/FVM method and the so-called IMPES (implicit pressure explicit saturation) algorithm. This numerical approach allowed us model large differentials in fluid saturation, caused by complex geological heterogeneities associated with complex sedimentation and faulting. Our model simulates the compaction-driven flow associated with early subsidence, and later topography-driven flow during uplift of the San Gabriel Mountains. Our two-phase flow models also replicate the formation-scale patterns of petroleum accumulation associated with the basin margin, where deep faults resulted in stacked petroleum reservoirs over multiple sets of interbedded sandstone and shale. Our calculations indicate a long history of transient and episodic flow from the basin center towards the western flank and the Palos Verdes Peninsula. The models also predict a strong preference for focused upward flow along the Newport-Inglewood fault zone, which today clearly hosts deep thermal anomalies.

Figure 1. Large-scale SW-NE profile FEM model of the LA basin, showing flow patterns.

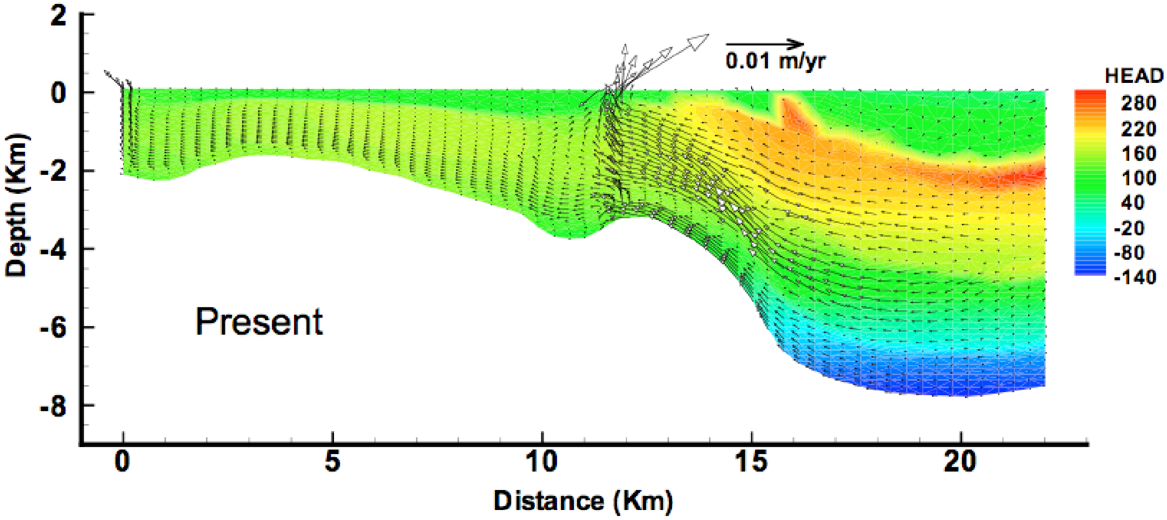
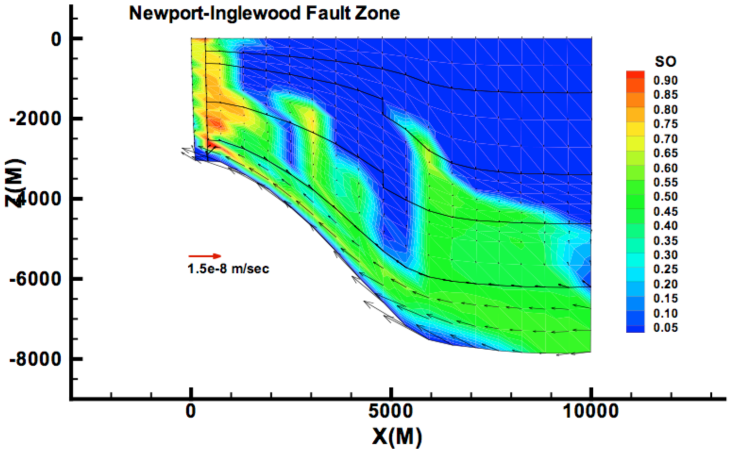


Figure 2. Zoomed view of petroleum saturations and flow patterns near area of discharge.



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Investigation of the Physical Basis for Biomineralization

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Objectives: To determine principles governing interactions of simple protein analogs and key inorganic impurities with carbonate minerals and the resulting structures, polymorphs and signatures that form. Extend this expertise to organic-Si interactions in biosilicification. A long-term goal is to establish the physical basis for biomineralization in Earth systems.

Project Description: The research is focused on developing a mechanism-based picture of controls imposed by Asp-rich polypeptides and biomineralizing proteins on the formation of carbonate minerals by emerging processes that involve clustering and nucleation. Using quantitative molecular-scale techniques, we are also probing the transient events and phase evolution during $CaCO_3$ nucleation at organic templates. Growth studies include: AFM and ToF SIMS studies of Mg and ICP MS studies of Ca-isotopes in calcite grown in the presence of polypeptides and proteins. Nucleation studies include: *in situ* AFM, X-ray absorption spectroscopy, eSEM, *in situ* TEM and molecular modeling of directed $CaCO_3$ nucleation and transformation on SAMs. Investigations into the fundamentals of mineral growth and dissolution utilize *in situ* AFM measurements of kink dynamics, kMC simulations, and development of analytical theories.

Selected results for FY 2010: Over the last year, we have prepared a number of new publications that uncover biomolecule controls on carbonate growth and show thermodynamic versus kinetic controls of their effects on mineralization. Following on our Stephenson et al (Science, 2008) study, we have further investigated biomolecules effects on ion solvation to modulate mineralization rates and potentially direct polymorph selection. This finding has helped us breakthrough several stubborn problems and new studies of ACC are leading to new insights on biomolecule controls on composition. Also, MD simulations are showing exciting results that are in preparation for publication. We also applied new in situ nucleation methods to the amorphous silica system and found that nucleation onto biosubstrates and in solution is favored/disfavored by kinetic factors rather than the long-standing (but untested) perception that thermodynamic barriers control nucleation. To our knowledge, these studies with carbonate and silica are novel to the literature.

Biomolecules influence calcification by controlling magnesium content of amorphous calcium carbonate. *(Wang et al., PNAS, 2009).*

With the realization that many calcified skeletons form by processes involving a precursor phase of amorphous calcium carbonate (ACC), a new paradigm for mineralization is emerging. There is evidence Mg content in biogenic ACC is modulated by carboxylated (acidic) proteins and other macromolecules, but the physical basis for such a regulatory process is unknown. We test the hypothesis that ACC compositions express a systematic relationship with the chemistry of carboxyl-rich biomolecules. By determining the influence of a suite of simple carboxylated organic acids on Mg content, we find that molecules with a strong affinity for binding Ca compared to Mg promote the formation of Mg-enriched ACC with compositions equivalent to high Mg-calcites and dolomite. Measurements show Mg/Ca ratios are controlled by a predictable dependence upon the binding properties of the organic molecules. The trend is rooted in the conformation and electrostatic potential topology of each molecule but dynamic factors may also be involved. The dependence suggests a physical basis for reports that specific sequences of calcifying proteins are critical to modulating mineralization. Insights may also provide a plausible explanation for why some biogenic carbonates and cements in the sedimentary record can contain higher Mg contents than possible by classical crystal growth processes. The findings reiterate controls of micro-environment on mineralization and suggest an origin of compositional offsets, or vital effects.

Kinetics of Silica Nucleation on Carboxyl and Amine-Terminated Surfaces: Insights for Biomineralization. ***(Wallace et al., 2009 J. Amer. Chem. Soc.).*** Biochemical investigations have begun to yield information about structural and chemical properties of organic macromolecules involved in biosilicification processes. However,mechanisms by which molecules mediate biosilica formation remain unclear. This experimental study used a simple model system to emulate key features of biosilica systems in conjunction with a novel AFM-based approach to measure the dependence of amorphous silica nucleation kinetics on the chemical and structural nature of underlying substrate. Model biological surfaces terminated with COOH, NH_3^+, and OH- moieties were generated through the spontaneous adsorption of alkane-thiol self-assembled monolayers onto ultra-flat (111) surfaces of gold. Measurements of surface nucleation rate were conducted under conditions that simulate current views of conditions within silica deposition vesicles of major diatom species (e.g. T = ambient, pH = 5.0, NaCl = 0.1 mol/kg) with variable aqueous silicate levels. Analysis of the data within the framework of nucleation theory quantified the height of the kinetic barrier to silica formation, and the net energy of silica-substrate/solution interfaces. By conducting experiments for COOH, NH_3^+, and OH- functionalized substrates, we determined the kinetic and thermodynamic controls of functional chemistry on heterogeneous nucleation of amorphous silica. These *in situ* measurements are the first their kind and show templating in this system is due to faster nucleation rates brought about by a reduction in the activation barrier rather than minimization of interfacial energy. This novel experimental result is counter to conventional wisdom.

Rethinking classical crystal growth models through molecular scale insights: Consequences of kink-limited kinetics. ***(De Yoreo, Dove, et al, 09, Crys. Growth Des.)*** The classical terrace-ledge-kink' model of crystal growth is widely used to interpret mineral formation in biological and geological systems. A key assumption underlying this model is that thermal fluctuations of steps are sufficiently rapid to produce an abundance of kink sites for attachment of growth units. High-resolution *in situ* AFM studies and kinetic Monte Carlo simulations of step-edge structure and dynamics show this physical picture to be invalid for the common mineral calcite whose steps exhibit low kink density and weak step edge fluctuations. As a consequence, interactions of impurities with calcite step edges cannot be interpreted with traditional *thermodynamic* models based on minimization of the Gibbs free energy. Instead, impurity-step interactions follow a different mechanism determined by the *kinetics* of attachment and detachment. Step advance is unimpeded when the creation of new kinks by attachment of growth units to the step outpaces binding of impurities to the newly created kinks. This kink-*limited* model provides a plausible explanation for reports of ‘kinetic disequilibrium’ of trace element signatures. Moreover, because kink density is tied to crystal solubility, the findings argue for a theory based on weak fluctuations to interpret growth of many crystalline phases in geochemical, biological and technological settings.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

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Grant: DE-FG02-06ER15786

Frontiers in Biogeochemistry and Nanomineralogy: Studies in Quorum Sensing and Nanosulfide Dissolution Rates

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Objectives: Our objectives are (1) to characterize the size, chemical composition, and aggregation state of nanominerals in natural waters and (2) to complement this work by quantitatively measuring the dissolution rates, sorption and catalytic reactivity of nanominerals as a function of size, morphology and aggregation state.

Project Description: Understanding toxic metal transport in the environment is critical for any future remediation efforts of contaminated areas. While nanominerals are omnipresent in environmental systems (natural waters, soils, air) their role in metal transport is not well-understood. Therefore, in our work, we examine nanominerals collected from the mining-contaminated Clark Fork River system (Montana) to determine their impact upon movement of toxic metals in the environment.

To quantitatively understand the behavior of nanominerals in metal transport, as well as other geochemical processes, we are complementing our field-based work with laboratory studies of synthetic nanomaterials (analogs of those present in nature). In particular we are systematically studying the effects of hematite (α-Fe_2O_3) nanoparticle size, morphology and aggregation state upon reductive dissolution rates of hematite and oxidation rates of manganese.

Results: The role of nanominerals and mineral nanoparticles as transporters of toxic trace metals: A case study from the Clark Fork River Superfund Complex. Nanominerals were extracted from river sediments. These samples were analyzed using asymmetrical flow field-flow fractionation (aFlFFF) coupled to multi-angle laser light scattering (MALLS) and high resolution – inductively coupled plasma mass spectroscopy (HR-ICPMS), as well as analytical transmission electron microscopy (aTEM). These methods revealed that the toxic trace metals of concern in this system (lead, arsenic, copper and zinc) were strongly associated with Fe and Ti oxide nanoparticles, demonstrating that nanominerals are likely to play a key role in determining the transport, bioavailability, and toxicity of contaminant trace metals.

The reductive dissolution of hematite nanoparticles as a function of nanoparticle size, morphology, and aggregation. 7 nm and 30 nm hematite nanoparticles were synthesized and subjected to reductive dissolution with ascorbic acid. The dissolution kinetics were tracked by measuring Fe^{2+} in solution via a colorimetric method, and nanoparticles at various stages of dissolution were collected and analyzed with high resolution transmission electron microscopy (HRTEM). The surface area-normalized initial dissolution rate for 7 nm hematite was found to be 2.5 times greater than that for 30 nm hematite, and the steady-state dissolution rates were found to be the same. HRTEM revealed that rough edges and defects were preferentially etched

(Figure 1). It was also determined that there was faster dissolution for non-aggregated nanoparticles.

The oxidation of aqueous Mn in the presence of nanohematite as a function of nanoparticle size, morphology and aggregation. 7 nm and 30 nm hematite nanoparticles were also synthesized for aqueous manganese oxidation in oxygenated water, using the nanohematite as a catalytic surface. We are presently in the process of measuring the rates of Mn oxidation as a function of size, morphology, and aggregation of the nanohematite, and identifying the new Mn phase/phases generated using HRTEM. These new Mn oxide phases are very important in the environment, as they are far more reactive in aqueous metal capture than any known iron oxide, crystalline or amorphous.

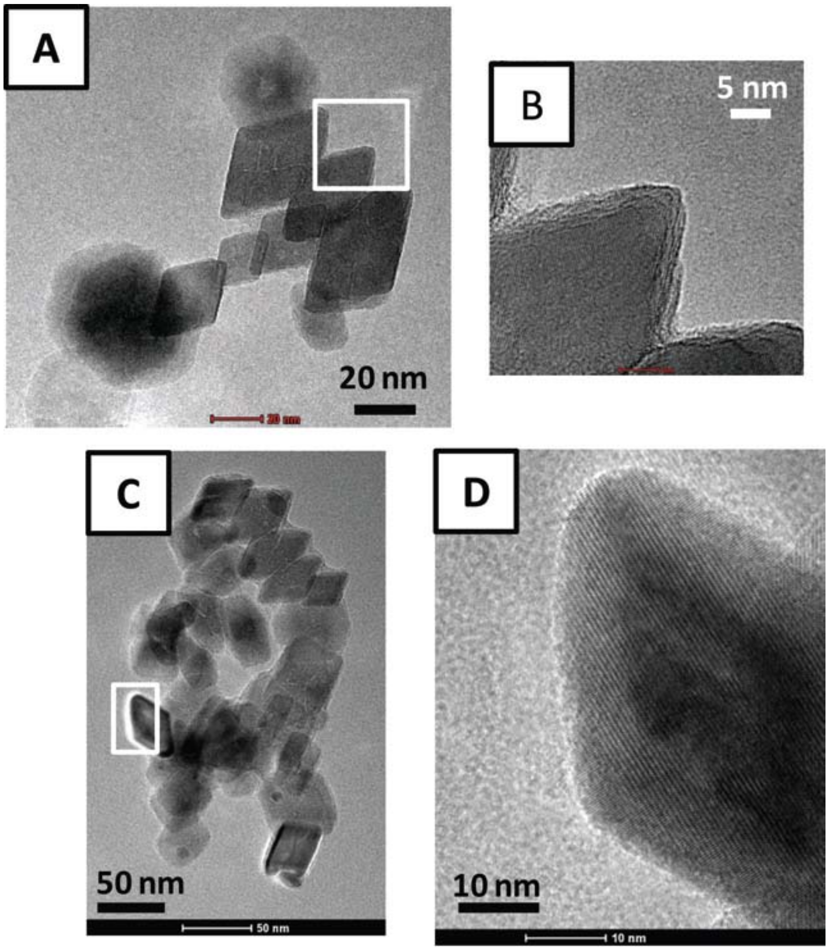

Figure 1. A. 30 nm hematite before dissolution. B. Inset from A, showing rough surfaces of nanoparticles. C. 30 nm hematite after 300 minutes of dissolution. D. Inset from C, showing smooth surfaces after etching.

UNIVERSITY OF WISCONSIN

Department of Physics, Madison WI 53706

Grant: DE-FG02-07ER15899

Mapping of Temporal and Spatial Phase Transitions of $CaCO_3$ in Echinoderm Skeletons: Key Insights into Basic Mechanisms in Biomineralization

PI: Pupa Gilbert; Tel. (608) 358-0164, pupa@physics.wisc.edu

Co-I: Steve Weiner (Weizmann Institute of Science, Rehovot, Israel)

Overall objective: To understand the mechanistic details of the formation process of sea urchin biominerals, including nucleation of single crystals, their propagation through the amorphous calcium carbonate phase and the roles of associated additives, especially magnesium.

Specific objectives:

1. To understand the manner in which the single crystal propagates through the amorphous phase of the larval spicule.
2. To characterize the differences in the phases of the primary formed stereom and the secondary infilling of the adult spine.
3. To characterize the initial, transforming, and mature phases of the adult tooth.

Project Description: In biominerals, the use of transient amorphous precursors that subsequently transform into stable crystalline phases may be a widespread strategy for forming skeletal parts in any desired complex shape. This strategy is employed by echinoids to build single calcite crystals with very intricate morphologies presumably adapted to their function. During the process, a small amount of organic material is incorporated within the mature crystal, endowing it with exceptional mechanical properties. Important mechanistic understanding of the formation process, such as the nucleation of the single crystal, its propagation through the amorphous calcium carbonate phase and the roles of associated additives, will be obtained by mapping the various phases at high resolution. Another enigmatic aspect of sea urchin biomineralization that may well be related to the transient mineral formation process is the incorporation of Mg ions into the calcite crystals in concentrations sometimes exceeding thermodynamically stable Mg-calcite. The different phases, e.g. amorphous calcium carbonate, calcite and high Mg-calcite are differentiated spatially at the micrometer-scale. Thus an analytical technique that can provide spectral information with high-spatial resolution, such as X-ray PhotoElectron Emission spectroMicroscopy (X-PEEM), will be used to unravel the different phases and mechanisms. The acquired insights will have a direct bearing on the design of novel materials with complex controlled shapes inspired by nature.

Results: We analyzed sea urchin spicules **(objective 1)**, spines **(objective 2)**, and teeth **(objective 3)**, and obtained exciting results, leading to seven major publications, including 1 in PNAS and 3 in JACS in FY2010. The research was done in collaboration with Steve Weiner, Lia Addadi, and their group at the Weizmann, where Gilbert spent another month in 2010. Most of the experiments were used spectromicroscopy (X-PEEM), scanning electron microscopy (SEM) and micro-diffraction (µXRD) at the Berkeley Advanced Light Source. In both sea urchin spicules **(1)** and teeth **(3)** the transformation from amorphous-to-crystalline $CaCO_3$ occurs via an intermediate anhydrous amorphous phase. Using spectromicroscopy of transforming spicules and teeth, with pixel sizes down to 20 nm, we observed that the transformation from ACC to calcite occurs via *secondary nucleation*, with crystallinity propagating in connected networks through the amorphous mineral. This mechanism is in contrast with the previous hypothesis by other authors that biominerals nanoparticles aggregate after crystallization, by oriented attachment, thus forming natural mesocrystals. We instead found that each aggregated ACC nanoparticle crystallizes only upon contact with an already crystalline one (Killian et al. JACS 2009). The adult sea urchin spines **(2)** in X-PEEM and XRD behave as an aggregate of crystalline calcite nanoparticles, with high co-orientation, as previously reported and therefore expected. Unprecedentedly, Brunauer-Emmett-Teller (BET) analysis of sea urchin spines revealed that they lack porosity, and subdivision into nano-sized crystals, and in fact fill space as much as a macroscopic single crystals of geologic calcite (Royal Society of Chemistry-Nanoscale, invited article, under review). In collaboration with Alexandra Navrotsky at UC-Davis, we analyzed the enthalpy of crystallization of biogenic ACC in spicules **(1)**, and compared it with that of synthetic hydrated and anhydrous ACC into calcite. From these acid solution micro-calorimetry experiments we conclude that in spicules the most abundant precursor phase is indeed anhydrous ACC (PNAS 2010).

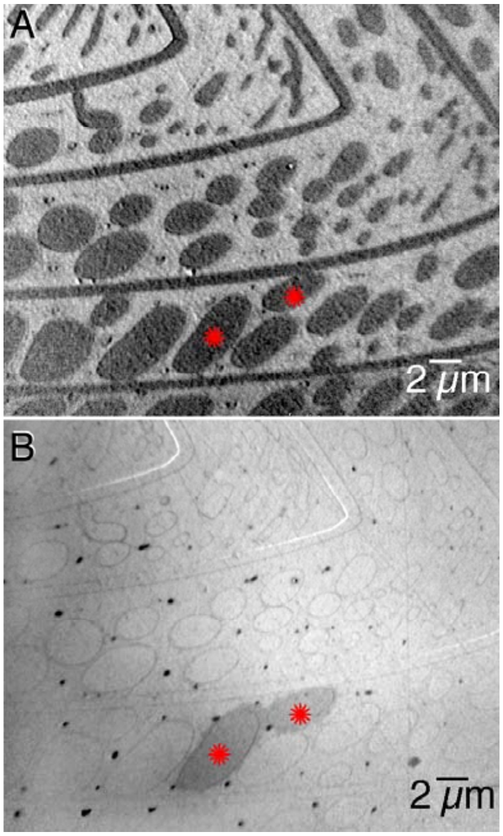

Figure 1: Two stray fibers reveal how co-orientation arises in the sea urchin tooth, one nanoparticle at a time. (A) An X-PEEM Mg distribution map reveals the tooth components: many Mg-poor (dark) elliptical fibers, four elongated plates (also dark), and a myriad calcite 10-nm particles cementing the plates and fibers together. These form the Mg-rich (bright) *polycrystalline matrix* that completely fills the space between plates and fibers. (B) An X-PEEM PIC map from the same region as A, displaying calcite crystal c-axis orientations as gray levels. All tooth components are co-oriented and share the same gray level, except for the two “stray” fibers (red asterisks), which are clearly mis-oriented. Strongly mis-aligned fibers are extremely rare in sea urchin teeth. Typically all fibers are co-oriented with each other and with the polycrystalline matrix. Despite the sharp and smooth edges of the fibers in the Mg map, the PIC map shows that the polycrystalline matrix surrounding and between the two stray fibers is as mis-oriented as the fibers themselves, indicating that the nanoparticles in the polycrystalline matrix get their orientation from the fibers, via secondary nucleation. Data from J. Am. Chem. Soc. 131, 18404-18409 (2009).

UNIVERSITY OF WISCONSIN
Department of Geoscience, Madison WI 53706

Grant: DE-FG02-93ER14389

High Precision Ion Microprobe Analysis of δ^{18}O in Authigenic Quartz

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http://www.geology.wisc.edu/~wiscsims/

Objectives:
1. Improve microanalytical techniques for stable isotope analysis by SIMS.
2. Develop procedures for stable isotope analysis at 1 to 10 micron-scale by ion microprobe.
3. Determine genesis and timing of porosity reducing cements in quartz sandstones that form aquifers, fossil fuel reservoirs, and proposed sites for CO_2 sequestration; and in seal-forming shales.

Project Description: This study focuses on microanalysis of diagenetic quartz cements and secondary silica. New techniques employing ion microprobe analysis permit study of oxygen isotope ratio in ultra-small samples. We have contoured δ^{18}O across individual quartz overgrowths at all scales as small as one micron. Mineral zonation patterns provide new insights into mechanisms and timing of water/rock interaction, and migration of fluids through sandstone aquifers. We are also measuring δ^{30}Si to determine sources of silica, which can be distinct from the water.

We are investigating applications of the new analytical technology to CO_2 sequestration, paleoclimate, fossil fuel reservoirs, and groundwater and hydrothermal systems. We have applied experience gained in the past three year grant by microanalysis of syntaxial quartz overgrowths in the St. Peter sandstone to quartz cements in the Mount Simon sandstone and overlying Eau Claire shales, Wisconsin and Illinois; the Brent group, North Sea; and Carboniferous to Jurassic eolian sandstones of the western U.S.; as well as to opal precipitated in the vadose zone of felsic tuffs.

Results: We have optimized instrumentation and procedures for *in situ* microanalysis of stable isotope ratios at the WiscSIMS laboratory, UW-Madison employing a CAMECA ims-1280, large-radius multicollector ion microprobe/ secondary ion mass spectrometer (Valley and Kita 2009; Kita et al. 2009). Analytical results are excellent. Analyses of 10-micron spots in thin section attain precision of δ^{18}O and δ^{30}Si of 0.1‰ (1 SD) for sample volumes that are 100 times smaller (~ng) than by single collector ion microprobe and 10^6 to 10^9 times smaller than possible by laser fluorination. Procedures have also been developed for use of a sub-micron spot that yields precision of δ^{18}O of 1‰ (Page et al. 2007) and analysis of S and Li isotope ratios (Ushikubo et al. 2008, Richter et al. 2009, Kozdon et al. 2010). Crystal orientation effects have been discovered that degrade accuracy of stable isotope analysis in magnetite and hematite, important as diagenetic cements, and a new analytical protocol was developed to overcome this problem (Kita et al. 2010, Huberty et al. 2010).

Following on our studies of quartz cements in the Ordovician St. Peter sandstone (Kelly et al. 2007), we have completed detailed analysis of δ^{18}O in porosity occluding cements in the underlying Mount Simon sandstone from outcrop in Wisconsin (Trzaskus et al. 2008) and drill core in Illinois (Pollington et al. 2010a,b). In contrast to shallowly buried sandstones in Wisconsin, the new results show that deeply buried sandstone cements have quartz overgrowths that are zoned by up to 8‰/50μm in δ^{18}O recording growth during burial and heating (figure C). These zoned cements are similar to those found by us in the Ness Fm., North Sea and Wilcox Fm, Texas (Harwood et al. 2009). Systematic differences are seen with lower δ^{18}O in latest cements deeper in the Illinois basin, indicating continuous growth of cements with increasing depth and temperature. Analysis of silicon isotope ratios in quartz overgrowths is underway to evaluate the importance of groundwater silcretes during early cementation and if silica is derived from shales in deeper samples.

DOE-sponsored Regional Partnerships, MGSC and MRCSP, have drilled a mega-ton injection well into Mount Simon sandstone at Decatur, Illinois and another is planned in Greenville, Ohio. Parallel monitoring drill holes and sidewall cores are also planned. Our drill core samples from a traverse of the Illinois basin will provide a basis for interpretation of cementation in these new samples. Selected samples of Mt. Simon from the Decatur well are currently in preparation for SIMS analysis.

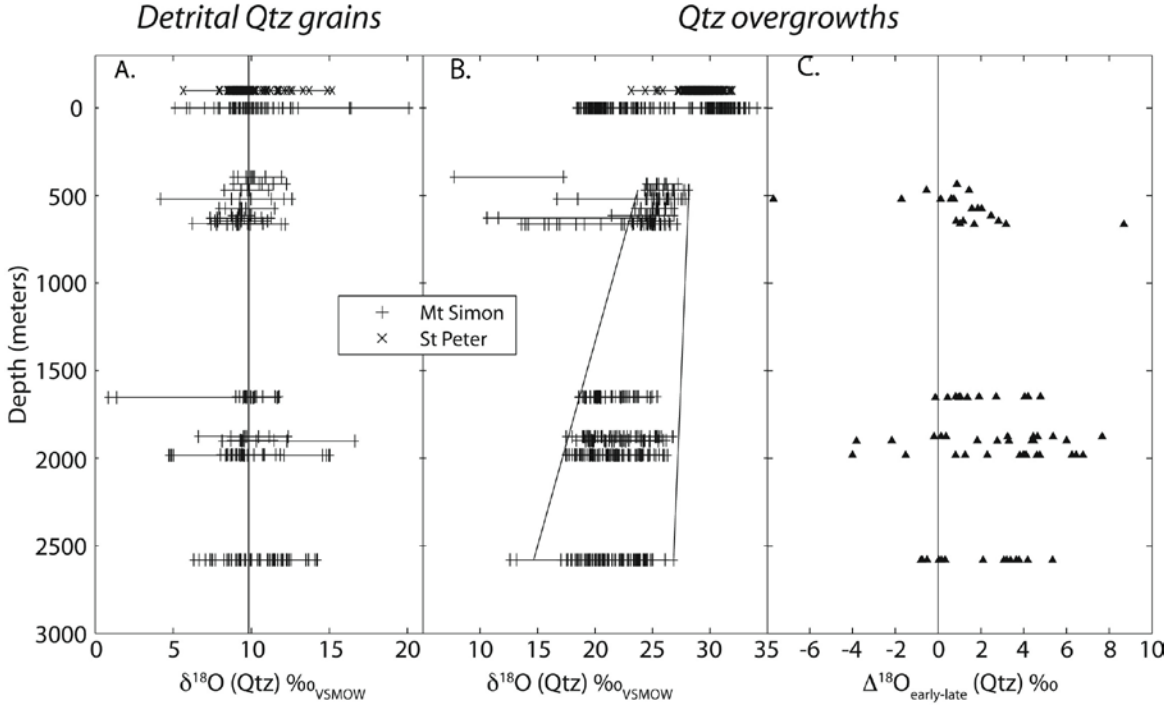

Figure A, B. Oxygen isotope ratios of detrital and overgrowth quartz from Mt. Simon sandstone at depths of 500 to 2500m in the Illinois basin, and in outcrop from Wisconsin. **C.** Gradients in δ^{18}O between earliest and latest cement range up to 8‰ with single quartz overgrowths.

UNIVERSITY OF WISCONSIN
Department of Geoscience, Madison WI 53706

Grant: DE-FG02-09ER16050

Interface Induced Carbonate Mineralization: A Fundamental Geochemical Process Relevant to Carbon Sequestration

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Objectives: To investigate the roles of non-carbonate minerals and solution chemistry in controlling the nucleation of individual carbonate polymorphs and compositions through a synergistic effect of substrate surface electric properties and the epitaxial coordination of the guest-host minerals.

Project Description: In the wake of a strong need to curtail atmospheric CO_2 accumulation, geological carbon sequestration is taking the center stage in the coming decades. With the suggested CO_2 storage in underground geological settings to be one of the leading strategies, however, a shortage in our knowledge basis emerges due to our limited understanding of carbonate mineralization in heterogeneous systems where non-carbonate minerals are often the dominant media. This suggests that efforts need to be made towards understanding how non-carbonate substrates affect carbonate crystallization. The proposed study is to examine the interfacial effect of common rock-forming oxide and silicate minerals on carbonate polymorphic composition during carbonate mineralization. We propose a comprehensive approach by (1) conducting powder and single crystals experiments and (2) using *in situ* (atomic force microscopy) and *ex situ* (high-resolution TEM) microscopic techniques to examine carbonate crystallization on non-carbonate mineral surfaces. We plan to analyze the experimental observations by quantifying the surface energetics and the strain of lattice mismatching. The goal is to construct structural relationship in the framework of surface energy and epitaxy to illustrate their roles in controlling carbonate structures and compositions on different substrate surfaces.

Results: We investigated an ultramafic rock from Isua, West Greenland in order to understand crystallographic relationship between the host silicate mineral anthophyllite and late stage carbonate mineral dolomite. Ultramafic rocks are potential sites for immobilizing carbon dioxide because Mg and Ca in the mafic rocks will react with CO_2 and form Ca-Mg-carbonates during alteration. TEM images indicate that the boundary between the dolomite and amphibole (anthophyllite) is coherent (Figure 1). The angle between (001) of dolomite and (100) of amphibole is about 9 degree. The angle between {110} of [110] of dolomite and [010] of dolomite is also about 9 degree (Figure 1). The surfaces of anthophyllite serve nucleation sites through heterogeneous nucleation.

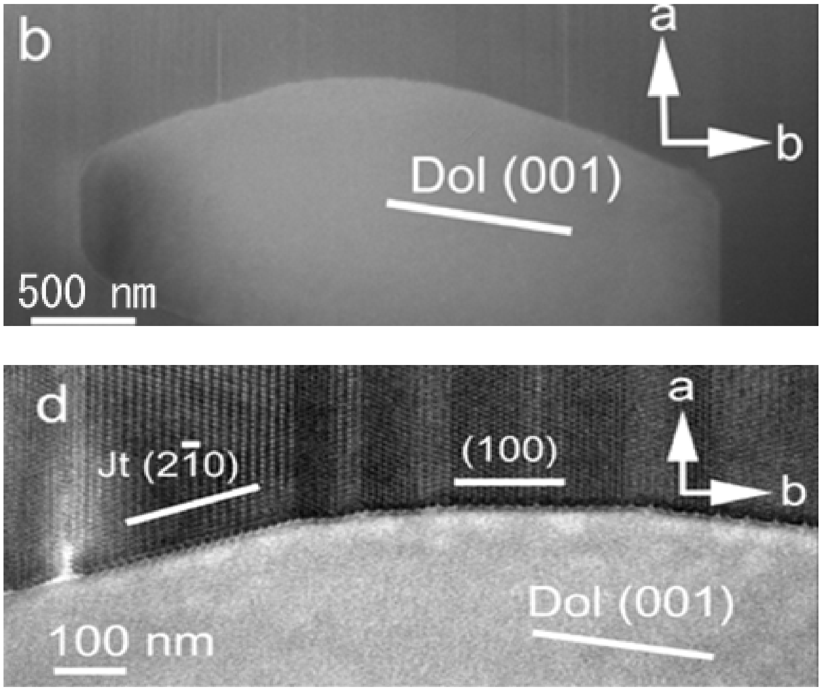

Figure 1: Low-magnification TEM image (upper) and high-resolution TEM image (lower) showing relationship between dolomite and host amphibole (anthophyllite with triple chain domains of jimthompsonite).

We have developed a new calibration curve for correlating composition of (Ca, Mg)CO_3 solid solutions and their unit cell parameters using our synthesized high-Mg calcite and disordered dolomite. The new empirical can be used for calculating composition of synthetic and natural (Ca, Mg)CO_3 based on one d_{104} value from X-ray powder diffraction pattern. This new curve revealed the significant cell parameter changes accompanying the Mg-Ca cation disorder in dolomite, and it can help the characterization of the $MgCO_3$ content of both natural and synthetic magnesian calcite and disordered dolomite, especially for the mineral mixtures which are not suitable for other analysis methods. The pure inorganic method to synthesize high-Mg calcite and disordered dolomite could also shed new light to the "Dolomite Problem" that troubled geologists for decades.

WRIGHT STATE UNIVERSITY

Department of Chemistry, Dayton OH 45435

Grant: DE-FG02-03ER15379

Kinetic Complexity of Mineral-Water Interface Reactions Relevant to CO_2 Sequestration: Atomic-Scale Reactions to Macroscale Processes

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Objectives: We seek to address several problems of critical importance to understanding geochemical processes that occur during the geologic sequestration of CO_2. Specifically, we want to understand the geochemical behavior of the CO_2-aqueous fluid-rock system under the near-equilibrium conditions that will be obtained over the bulk of the lifetime of the sequestration process.

Project Description: We need to understand the morphological relaxation that occurs on a mineral's surface in response to a change in fluid composition as well as how the surface reactivity of a mineral varies as a function of orientation. Geochemical models effectively treat dissolution/growth as an isotropic process, yet we know that this is not the case. Our approach to addressing these questions is to apply a combination of microscopic and macroscopic experimental techniques that permit us to study process details at the specific mineral-fluid interfaces and then to "scale-up" to integrate those processes over all surfaces. Specifically, in-situ experiments using our unique Hydrothermal AFM (HAFM) were conducted on carbonate mineral specimens to characterize the processes of topographic relaxation, crystal face specific dissolution rates and crystal morphology evolution on a nanometer to micrometer distance scale. Corresponding macro-scale experiments were conducted in custom-built Mixed Flow Reactors. The parallel micro/macro investigations are vital for developing and utilizing chemical models in reactive transport simulators that will be employed to assess performance and predict behavior of CO_2 sequestration systems by forward modeling for the thousands to perhaps tens of thousands of years over which CO_2 containment must be evaluated.

Results: Direct measurements of calcite $(10\bar{1}4)$ faces were performed using in situ hydrothermal atomic force microscopy (HAFM) from 50-70 ^{o}C and as a function of solution saturation state. Time-sequential AFM images demonstrated that step velocities at constant temperature increased with increasing undersaturation (**Fig. 1, upper left**). At saturation state $\Omega > 0.02$, a curvilinear boundary was formed at the intersection of two acute steps and the initially rhombohedral etch pit exhibited a nearly triangular shape (**upper right**), suggesting that the $[\bar{4}41]_a$ and $[48\bar{1}]_a$ steps may not belong to the calcite-aqueous solution equilibrium system. To explain the pit shape, we propose that the backward reaction near equilibrium occurs preferentially at the acute-acute kink sites. To address questions raised by our initial investigation above, we further investigated the influence of solute impurity concentration, using magnesium as a proxy. Dissolved Mg^{2+} displayed negligible inhibitory effects on calcite dissolution even at concentrations of 10^{-4} molal. Upon the introduction of 10^{-3} molal Mg^{2+}, the solution saturation state with respect to calcite, $\Omega_{calcite}$, acted as a "switch" (**lower right**) for magnesium inhibition. This non-linear behavior is not captured in current geochemical models used for reactive transport modeling.

Macroscale dissolution: We have conducted pseudo-macroscale dissolution experiments using synthetic calcite crystals in a small column flow-through reactor. Our observations (at 60°C) of dissolution rate reveal that the rate decreases exponentially in time with a relaxation time of 30-40 hours (**lower left**). The long relaxation times are consistent with predictions based on the topographic relaxation model, yet do not match relaxation times predicted from microscale experiments, suggesting that the microscale data does not capture the primary processes governing relaxation. That is, the closer to equilibrium experiments should have had lower step speeds and therefore longer macroscale relaxation times. Instead, nearly the same relaxation times were obtained across a range of solution conditions.

The kinetics of near-equilibrium calcite dissolution presented in this work provide accurate experimental data under likely CO_2 sequestration conditions, and thus are crucial to the development of robust geochemical models that predict the long-term performance of mineral-trapped CO_2. Long-term predictive models based exclusively on macroscale results therefore may have an amplifying effect on short-term inaccuracies.

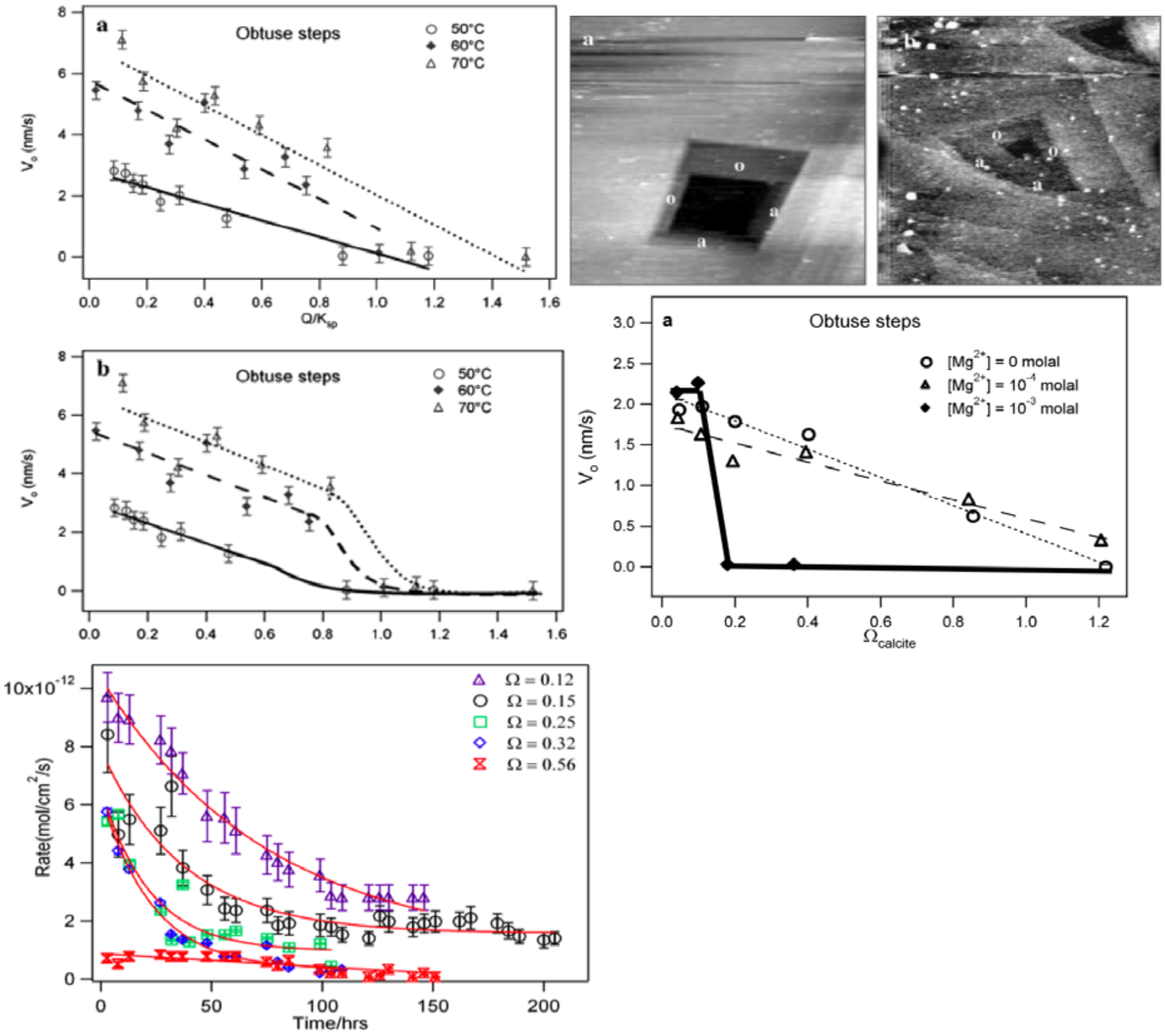

Figure 1. (**Upper left**) Velocity of obtuse steps as a function of W (= Q/Ksp) and T. In (a), lines represent fitting of the data to a linear rate equation at 50, 60, and 70 ^{O}C. Curves in (b) were drawn by hand. (**Upper right**) AFM images of etch pits on the calcite (104) surface during dissolution from (a) de-ionized water at 50 ^{O}C (4 mm x 4 mm), (b) an undersaturated aqueous solution with saturation state $\Omega_{calcite}$ = 0.126 at 50 ^{O}C (3.5 mm x 3.5 mm). (**Lower right**) Speeds of obtuse steps as a function of$\Omega_{calcite}$ at 50 °C. Circles, triangles, and diamonds represent step speeds at calcite-aqueous solution interfaces after adding 0, 10^{-4}, and 10^{-3} molal Mg^{2+}, respectively. Uncertainties are estimated at ± 0.3 nm/s for obtuse step speeds. Dotted and dashed lines represent linear fits of data at 0 and 10^{-4} molal Mg^{2+}. (**Lower left**) Macroscale calcite dissolution rates vs. t and W at 60 ^{o}C (pH= 8.3) from flow-through reactor experiments.

DOE/OBES Geosciences Research: Historical Budget Summary

(Thousands of dollars)

BES GEOSCIENCES BUDGETS	**FY06**	**FY07**	**FY08**	**FY09**	**FY10**
Total, on-site	9,591	10,771	10,509	11,820	13,165
Total, off-site	9,544	9,869	9,605	9,341	10,919
Total, operating	19,135	20,640	20,114	21,161	24,084
Total, equipment					
Total GEOSCIENCES	**19,135**	**20,640**	**20,114**	**21,161**	**24,084**
ON-SITE INSTITUTIONS	**FY06**	**FY07**	**FY08**	**FY09**	**FY10**
Argonne National Laboratory	758	461	506	700	700
Idaho National Laboratory	50	60			60
Los Alamos National Laboratory	963	1,050	415	670	1,025
Lawrence Berkeley National Laboratory	2,939	4,063	4,416	4,880	4,318
Lawrence Livermore National Laboratory	1,141	1,270	1,172	850	1,390
Oak Ridge Institute for Science & Edu.	105	12			
Oak Ridge National Laboratory	1,750	1,750	1,850	1,820	1,920
Pacific Northwest Laboratory	910	975	980	1,935	1,882
Sandia National Laboratory	975	1,130	1,170	965	1,870
Total, on-site	**9,591**	**10,771**	**10,509**	**11,820**	**13,165**
OFF-SITE INSTITUTIONS	**FY06**	**FY07**	**FY08**	**FY09**	**FY10**
Alabama, Univ. of (Dixon)	47	48	48	48	48
Alabama, Univ. of (Dixon)		58	60	63	
Alfred Univ. (Bowers)					83
American Chemical Society (Criscenti)			3		
Arizona State Univ. (Hervig/Williams)	135				
Boston Univ. (Klein)	134		145	152	160
Caltech (Stolper)	167	172	177		
Calif., Univ. of Berkeley (Banfield)	200	200			
Calif., Univ. of Berkeley (Banfield)	123		177		
Calif., Univ. of Berkeley (Helgeson)		100	100		
Calif., Univ. of Berkeley (Wenk)	150	150			117
Calif., Univ. of Davis (Navrotsky)	197	215	221	226	232
Calif., Univ. of Davis (Rustad)	82	85			
Calif., Univ. of Davis (Rustad)	137	68	69	70	
Calif., Univ. of Davis (Casey)		135		170	151
Calif., Univ. of Davis (Rundle)	151		156	163	170
Calif., Univ. of Irvine (Detwiler)				139	119
Calif., Univ. of Los Angeles (Kavner)					149
Calif., Univ. of Santa Barbara (Boles)	95	95	83		97

Calif., Univ. of Santa Barbara (Gibou)			190	190	190
Calif., Univ. of Santa Cruz (Wu)	327				
Calif., Univ. of San Diego (Weare)	269		138		150
Chicago, Univ. of (Sutton/Rivers)	697	718	739	761	784
Chicago, Univ. of (Sutton)				422	348
Chicago, Univ. of (Sutton)	148	139	138	282	205
Chicago, Univ. of (Richter)	143	148	174	180	186
Clark Univ. (Kudrolli)	59	54	55	68	64
Clay Minerals Society (Cygan)		10			
Clay Minerals Society (Ross)			5		
Colorado School of Mines (Gorman)					95
Colorado School of Mines (Tsvankin)		75			
Colorado School of Mines (Snieder)	97	101	106		
Colorado School of Mines (Benson)		79	82	86	
Colorado School of Mines (Scales)				142	149
Colorado, Univ. of (Spetzler)	58	60	62		
Connecticut, Univ. of (Torgersen)	32	34	35	22	
Florida, Univ. of (Ladd)	108	111		194	168
Geochemical Society (Horita)					10
George Washington Univ. (Teng)		48		31	99
George Washington Univ. (IPA Lesmes)	6	5			
Georgia Tech (Stack)		210			
Gordon Res. Conf. (Hirth)	10		10		10
Gordon Res. Conf. (Austin)					6
Harvard Univ. (Martin)	96	99	102		
Hawaii, Univ. of (Jahren)				108	170
Houston, Univ. of (Weglein)		51			
Idaho State Univ. (Magnuson)	88	90	93		
Illinois, Univ. of (Kirkpatrick)	216				
Illinois, Univ. of (Bethke)		135	138	142	135
Illinois, Univ. of (Bass)			151	155	160
Illinois, Univ. of Chicago (Sturchio)	51	53	54	60	61
Indiana, Univ. of (Schimmelman)	141	133	128		
Johns Hopkins Univ. (Garven)	124				
Johns Hopkins Univ. (Veblen)	205	250	250	250	
Johns Hopkins Univ. (Sverjensky)	158	163	176	180	124
Johns Hopkins Univ. (Jahren)	101	105			
Maryland, Univ. of (Zhu)		130		106	106
Mass. Inst. Tech. (Evans)	304	318	328	344	359
Mass. Inst. Tech. (Rothman)	160	168	172	160	182
Mass. Inst. Tech. (Durham)		40	42	43	88
Massachusetts, Univ. of (Boutt)		41			
Michigan State Univ. (Kirkpatrick)			230		185

Mineralogical Society of America (Speer)	35	10	10		
Mineralogical Society of America (Speer)	5		10		
Minnesota, Univ. of (Kohlstedt)	176	185	192	200	369
Missouri, Univ. of (Appold)			107	86	
NAS/NRC (Schiffries/DeSouza)	90	90	90	90	100
New Mexico, Univ. of (Weissmann)			15	15	
NY, City Univ. of CC (Koplik)	107	109	110	94	95
NY, City Univ. of CC (Makse)	85	100	100	100	118
NY, State Univ. of Stony Brook (Schoonen)	87	83	85	91	77
NY, State Univ. of Stony Brook (Wong)	125	128	132		229
NY, State Univ. of Stony Brook (Lindquist)	87	66			
NY, State Univ. of Stony Brook (Reeder)				165	164
North Carolina, Univ. of (Miller)				200	200
North Texas, Univ. of (Bagus)	35	50	50	50	70
Northwestern Univ. (Rudnicki)	113	114	119		
Northwestern Univ. (Geiger)	49	50	52	121	
Northwestern Univ. (Andrade)			304	110	114
Ohio State Univ. (Allen)	44	80	79	83	88
Oregon State Univ. (Egbert)	98	95	104		
Penn State Univ. (Brantley)	176	223	261	274	252
Princeton Univ. (Peters)	160	169			
Purdue Univ. (Pyrak-Nolte)	288		117	163	113
Renesselaer Polytech. Inst. (Watson)	215		199	199	207
Society of Exploration Geophysics (Smith)	5				
South Carolina, Univ. of (Wilson)	54				
Stanford Univ. (Borja)	102	110	110	110	139
Stanford Univ. (Nur)	200	207	221	229	227
Stanford Univ. (Pollard/Aydin)		273	264	272	283
Stanford Univ. (Tchelepi)			208	215	223
Temple Univ. (Strongin)	91	83	87	94	97
Texas A&M Univ. (Morse)	157	149	153		
Texas A&M Univ. (Datta-Gupta)	143	142	145		215
Texas, Univ. of (Katz)	78	75	78	84	86
Texas, Univ. of (Laubach)	197	241	264	246	300
Tufts Univ. (Garvin)		227			114
Utah State Univ. (Evans)					176
Virginia Tech (Dove)	226	250	202	245	253
Virginia Tech (Hochella)	122	127	143	149	589
Virginia Tech (Hochella)			4		
Wisconsin, Univ. of (Goodwin)		73			
Wisconsin, Univ. of (Valley)	217	234	239	248	248
Wisconsin, Univ. of (Gilbert)		325		159	225
Wisconsin, Univ. of (Xu)				74	77

Woods Hole OI (Zhu)	61				
Woods Hole OI (Seewald)	184				
Woods Hole OI (Reddy)	157	164	172	113	
Wright State Univ. (Higgins)	98	110	115	105	111
Wyoming, Univ. of (Eggleston)	154	131	122		
Wyoming, Univ. of (Eggleston)	100	102	105		
Yale Univ. (Wettlaufer)	100	100			
Yale Univ. (Berner)	130				
Yale Univ. (Bolton)		77			
Other	1				
Total, off-site	**9,544**	**9,869**	**9,605**	**9,341**	**10,919**