Summary of FY 2009 Geosciences Research

August 2010

U.S. Department of Energy

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

TABLE OF CONTENTS

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

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CONTRACT: DE-AC02-06CH11357

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

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Website:
http://www.cse.anl.gov/Nuclear_and_Environmental_Processes/Interfacial_Processes.shtml

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 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, primarily in studies of ion adsorption, and also in pursuing advances in interfacial X-ray based analytical techniques.

Measurements (in collaboration with K. L. Nagy, UIC) revealed how fulvic acid (FA) changes the adsorption and distribution of Hg^{2+} at the muscovite-aqueous interface. Hg^{2+} sorbs at the muscovite (001)-aqueous interface distributed in between inner-and outer-sphere adsorption species. The presence of FA leads to a large enhancement in the amounts of bound Hg^{2+} and dissolved organic matter at pH 2 that decreases as pH rises from 3.7 to 12. Variations in the distribution of mercury within the organic films indicate that Hg^{2+}-dissolved organic matter complexes form in solution before sorption. Pre-formed organic films appear to bind Hg^{2+} less effectively, presumably due to different structural arrangement or fractionation of the adsorbed organic molecules, or kinetic effects in the presence of the mineral surface

Ongoing studies have made progress exploring the systematic chemical trends in cation adsorption at the muscovite-aqueous interface, both with and without fulvic acid, and studies have also been made of calcite surface reactivity. Additional studies have explored the ability of X-ray reflection interface microscopy to probe dissolution reactions at orthoclase surfaces.

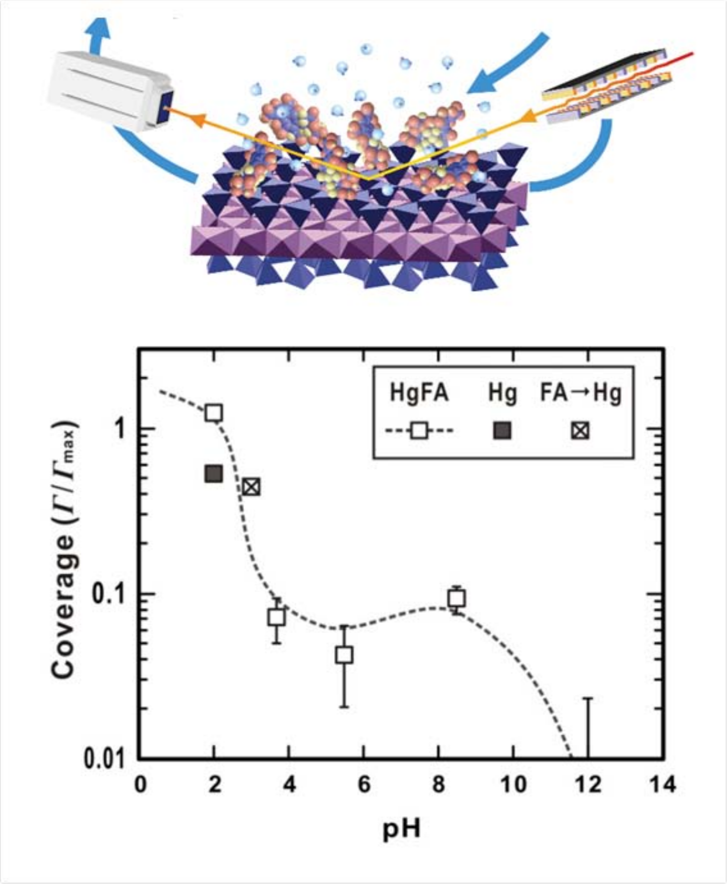

Figure:
Top: Schematic of ion adsorption in the presence of a fulvic acid film as probed by resonant anomalous X-ray reflectivity.
Bottom: Hg coverage variation with pH; HgFA, Hg, and FA→Hg designate uptake from a premixed solution, a solution without FA, and Hg added to muscovite coated with FA.

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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: During FY 2009 the main focus was on theoretical work with the objective of developing methods that will allow us to bridge the gap between first principles atomic/electronic calculations and continuum models for the evolution of crystal morphology under non-equilibrium conditions. An evaluation of the relevant scientific literature and preliminary Monte Carlo simulations indicated that a number of mechanisms could contribute to the formation of growth pyramids on the (001) surface of hematite while dissolution occurs on other surfaces. However, we cannot yet explain why pyramids grow unusually rapidly under the experimental conditions. Theoretical work and Monte Carlo simulations by others indicates that the formation of pyramids during molecular beam epitaxy depends on non-equilibrium slope (orientation) dependent surface currents (the system evolves towards slopes on which the surface current is zero). This has led us in the direction of believing that measuring the orientation dependence of interfacial transport coefficients (atom attachment/detachment kinetic coefficients and surface mobility) and the surface free energy density will enable us to understand the fast growth of pyramids on the (001) surface of hematite. A theoretical moving boundary model, based on this idea (quite similar to the theory of dendritic growth) has been developed. The parameters needed by the macroscopic moving boundary model can be obtained from kinetic Monte Carlo simulations. In FY 2010, this approach will be evaluated by directly comparing the moving boundary approach with efficient large scale Monte Carlo simulations.

The effect of thermodynamic constraints on coupled reaction/dissolution processes in semiconducting crystals was analyzed, and this led to the conclusion that additional experimental work is needed to determine the mechanisms at work during simultaneous growth and dissolution of hematite. Using a linear non-equilibrium thermodynamics approach, we concluded that if simultaneous dissolution and precipitation are coupled by the migration of electrons through hematite, then a free energy lowering solution phase reaction, coupled with the dissolution/precipitation/electron transport process is required to drive electrons through the hematite. However, we are not able to identify a plausible solution phase reaction without additional experimental work.

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Upgrade of the Computational Cluster at LBNL

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Objectives: Provide advanced computational capability in geophysics and geochemistry to address needs in subsurface imaging using seismic and electromagnetic wavefields and complex geochemical modeling. Address critical needs within the DOE mission, including waste legacy issues and energy and environmental security, which are difficult to address with existing computational facilities.

Project Description: Establish a state-of-the-art cluster technology at LBNL that uses advanced message transfer in a parallel fashion between the multi-processor nodes that optimizes load balance between processor speed, memory allocation and data transfer.

Results: In the past year the cluster was utilized at the 92+ percent rate. The cluster is now configured to address two general research areas, Geophysics and Geochemistry. In geochemistry the cluster is supporting 7 different researchers mainly from two different research areas: 1) clay mineral geochemistry and 2) geochemical transport problems (Rate Controls in Chemical Weathering). In geophysics the cluster is supporting electromagnetic imaging research, joint seismic EM inversion, rock physics modeling and seismic imaging. The cluster is proving to be an essential tool in a variety of Earth Science problems including but not limited to: understanding 3-D complex subsurface processes at an unparalleled level of resolution and accuracy, directly impacting BES Geosciences missions in Energy and Environment, and supporting programs in BER, fossil, geothermal energy, nuclear waste disposal and environmental site characterization and clean up.

Center for Nanoscale Control of Geologic CO_2

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

Objectives: The mission of this center is to use new investigative tools, combined with experiments and computational methods, to build a next-generation understanding of molecular-to- pore-scale processes in fluid-rock systems, and to demonstrate the ability to control 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 will be 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 that scale. Multiscale computational models and lab-scale experiments will be used to understand 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, will be 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 will derive from its integrated multidisciplinary approach, and a focus on directing CO_2-rich fluids. The products of the Center will provide the fundamental knowledge necessary to develop a revolutionary level of control and predictive capability for subsurface fluids. It will help facilitate safe long-term storage of CO_2 in subsurface reservoirs to address the threats of global warming, and produce important advances related to fluid manipulation for other types of energy resource development and management**.**

The efforts of the Center investigators are grouped into three Thrust Areas: (1) controlling nucleation and growth, (2) nanopore processes, and (3) emergent processes. The three Thrust Areas, described in more detail below, represent groupings of investigators who use similar experimental approaches and whose work in the Center will be directed at closely allied scientific challenges. However, there are a large number of cross connections within and between these thrust areas. The three thrust or focus 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. All key participants have had BES funding to pursue related studies and continue to be among the most productive and influential Earth scientists in the U.S.

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.

Research Topics:

- Inorganic controls on mineral nucleation, growth, and dissolution
- Alkaline earth oxide or hydroxide nanoparticles as embedded nutrients

- Biomimetic approaches to controlling carbonate mineralization
- Extremophiles for biotic control of carbonate mineralization

Thrust Area 2 – Nanopore Processes: Little is known about the chemical behavior of CO_2-rich aqueous solutions confined in nanopores under sequestration conditions. The overarching goal of research under Thrust Area 2 is to provide a fundamental understanding of these nano-confined fluid CO_2-aqueous solution mixtures using advanced methodologies that probe fluid behavior from molecular to pore scales.

Research Topics:

- Thermophysical properties of nano-confined CO_2-rich fluids
- Structure and dynamics of CO_2-bearing aqueous solutions in nanopores
- Structure and dynamics of CO_2/water interfaces and thin aqueous films

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. This nonlinear response to the coupling of flow, transport, and reaction at multiple scales results in emergent structures and self-organization, an excellent example of which is the reactive infiltration instability. These emergent dynamics must be understood in order to predict how CO_2 will behave in the subsurface.

Research Topics:

- Emergent pore-scale dynamics resulting from coupling of multiphase flow, transport, and reaction multiscale experiments combining X-ray microtomography and pore scale modeling
- Macroscale models from microscale physics and chemistry

Integrated Isotopic Studies of Geochemical Processes

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Objectives: Combine high-precision measurements of isotopic ratios in natural materials with mathematical models and laboratory experiments to understand the nature and time scales of geochemical transport processes from the molecular scale at mineral surfaces to field scale.

Project Description: Geochemical processes are studied using measurements of isotope ratios and trace element concentrations in natural materials and laboratory experiment products. Funding also supports laboratory operations for the Center for Isotope Geochemistry, which includes mass spectrometry labs for the measurement of isotopic ratios 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). Measurements of isotope ratios in natural systems are used to measure the influence of competing chemical and physical processes, and to determine their rates and evolution with time. This information is critical for understanding the workings of geological systems ranging in size from microorganisms, plants, and soils, to groundwater reservoirs, volcanoes, the oceans, and the atmosphere. Experimental studies are used to determine the controls on isotopic fractionation due to phase changes and transport processes, and the effects of nuclear interactions associated with radioactive decay.

Results: (1) *U-Th-He*: We have continued to explore the use of U–Th/^{4}He ages on olivine phenocrysts from late Quaternary basalts. The approach employs abrasion to remove the outer rinds of olivine crystals, which eliminates ^{4}He implantation from U-rich groundmass, and a specially designed extraction system that allows U, Th and He concentrations and isotopic compositions to be measured on the same olivine grains. The method is now being extended to submarine basalts where it may have its greatest value, but where issues with incomplete degassing upon eruption can complicate interpretations. Initial results on submarine Hawaiian basalts have so far been complex; a new round of experiments in now underway to better understand the ^{3}He and ^{4}He observations.

(2) *Ca isotope probe of mineral precipitation*: The mechanisms by which dissolved ions attach to mineral surfaces to allow solid crystals to grow from aqueous solution are poorly characterized. We use Ca isotopes to study calcite and calcium-sulfate precipitation from aqueous solutions. Results indicate that at equilibrium there is no Ca isotopic fractionation during precipitation of calcite; the finite isotopic fractionations observed at low temperatures may be entirely dependent on kinetic processes at the mineral-water interface. It appears that attachment kinetics control isotopic fractionation, but there is competition with solid-fluid exchange, solid phase growth velocity, and aqueous phase diffusion. New precipitation experiments are allowing us to separate the influence of these competing effects. We have also now set up the methods for measuring Mg isotopes and will be using them to get additional information on mineral precipitation processes.

(3) *Theory of isotopic fractionation during mineral precipitation*. Based on available experimental data on Ca isotope fractionation and calcite dissolution we have developed a macroscopic kinetic-thermodynamic model that relates isotopic 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.

(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. In these sediments, even though the biogenic calcite is generally unstable, the δ^{44}Ca of pore fluids is much different from that observed in sections where the sediments are nearly pure biogenic calcite. Isotopic effects mean either that the presence of organic material suppresses calcite dissolution or that the 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 show 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. Results show that surface roughness factors vary with grain size and differ from those estimated with gas adsorption techniques. Comminuted glacial material of zero age has the secular equilibrium characteristics that are expected.

(6) *Field scale Ca isotope effects in hydrothermal systems*: Ca isotopes can provide information on the degassing and precipitation history of hydrothermal fluids. A survey of the Long Valley hydrothermal system was done 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. The degassing and calcite precipitation is further correlated with a 0.5 per mil increase in $\delta^{44}Ca$, consistent with non-equilibrium processes occurring during calcite precipitation. This is the first use of Ca isotopes to study calcite precipitation from hydrothermal fluids. Studies have also been done on epidote from selected fossil hydrothermal systems from mid-ocean ridges, and these also show similar fractionation behavior. It appears that epidote precipitating from hydrothermal solutions at 350-400°C is affected by kinetic Ca isotope fractionation effects that 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) *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.

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

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Objectives: The goal of this project is to impart the latest scientific thinking about the Earth, as reviewed in Origin and Evolution of Earth, in an entertaining and non-technical way for a mass audience, including introductory Earth science students.

Project Description: The National Research Council's new report, *Origin and Evolution of Earth: Research Questions for a Changing Planet*, provides a beautiful, concise, insiders' review of decades of work and accomplishments in the Earth sciences, as well as visions of future breakthroughs. As such, it provides a tremendous foundation for an authoritative, up-to-date television documentary for national and international broadcast and educational distribution on DVD. The documentary will feature film footage of some of the world's most important and spectacular geologic locations and a diverse set of Earth scientists whose vital work not only increases people's knowledge of our planet but helps them live upon it more safely and sustainably.

This project aims to produce a world-class television documentary and DVD designed to have the following impacts on the intended audience:

1. Increase PBS viewers' Science, Technology, Engineering and Mathematics learning and awareness by bringing them up to speed on the most exciting new ways that Earth scientists are tackling difficult and relevant geologic problems.

2. Accelerate and extend the impact of a prestigious NRC report beyond its current audience to a large general audience of laypersons by producing a companion documentary for widespread educational television broadcast and DVD distribution.

3. Increase support for Earth science research and geologic hazard reduction measures by providing the public with a product that communicates positive depictions of the value of this work.

4. Increase the number and diversity of young people who are interested in the Earth sciences as a profession by providing a product that focuses on the popular subject of Earth science and that highlights a diverse set of scientists/characters as influential role models.

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. Latest work on this project has led to the design and demonstration of a new approach for equilibration of multiple samples at different potential energy states of water. This new development will facilitate efficient acquisition of film thickness measurements on variably rough surfaces.

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. A new, multi-sample chamber has been developed to equilibrate solid surfaces with aqueous solutions undergoing radial film flow under subatmospheric pressures. In this new design, samples are cut into discs, inserted into a porous ceramic frame, and contained within a sealed chamber with windows transparent to hard X-rays. Samples are vertically spaced, and hydraulically connected via the porous ceramic to a common reservoir of tracer solution (aqueous RbBr or $MgSeO_4$). 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. Moreover, equilibration of different samples to different matric (capillary) potentials is achieved through their vertical separation. The chamber is placed in front of an X-ray beam (National Synchrotron Light Source beamline X26A) used to determine film thicknesses through X-ray fluorescence of monovalent (Rb^+ and Br^-) and divalent (Mg^{2+} and SeO_4^{2-}) ion tracers in the water films. 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: The new chamber for measuring adsorbed water film thicknesses was successfully tested at NSLS beamline X26A. This test run with 1 M RbBr yielded measurements of films that are in the range predicted by the Langmuir equation, but thicker over most of the tested matric potential range (-90 to -1100 Pa, Figure 1e.). Under these hydraulic conditions, film thicknesses independently determined from Rb and Br X-ray fluorescence yielded very similar values, ranging from 100 down to 60 nm. All measured thicknesses were above the effective thickness resolution limit for this test (about 10 nm), and much greater than the double layer thickness (Debye length) of 0.3 nm. The response times for achieving hydrostatic equilibria were consistent with predictions≈(3 hours). These measurements collectively indicate that the adsorbed films at near-zero matric potentials have characteristics dominated by properties of bulk water. The experimental approach developed here provides a unique capability for measuring water film thicknesses on variably rough mineral surfaces, where reflectivity and ellipsometry become limited. Furthermore, when the primary property of interest is area-averaged film thickness, this fluorescence approach provides a much finer resolution than is achievable by tomography.

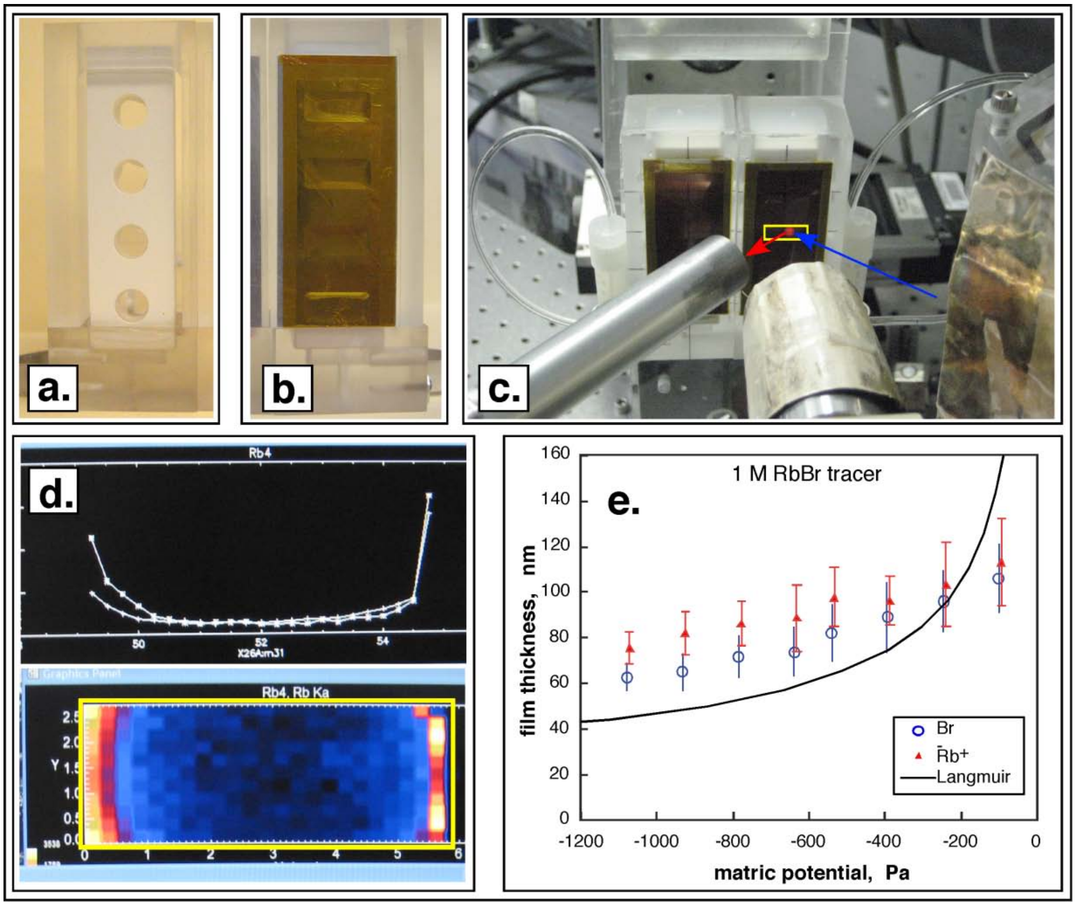

Figure 1. (**a.**) Film cell with windows removed, showing silica sample discs mounted on porous ceramic frame. (**b.**) Film cell sealed with hard X-ray-transparent windows. (**c.**) Pair of film cells mounted on the NSLS X26A stage. Blue and red arrows indicate monochromatic X-ray beam path to sample, and fluorescent X-ray path to detector, respectively. Yellow box indicates mapping area for single sample. (**d.**) Photograph of X26A monitor, displaying raw x-line scan of Br and Rb fluorescence (upper), and x-y map of raw Rb K-alpha fluorescence. (**e.**) Thicknesses of adsorbed water films, determined from X-ray fluorescence of Rb$^+$ and Br$^-$ tracers, compared with predictions of the Langmuir model.

Clay Mineral Surface Geochemistry

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Objectives: The objective of this project is to investigate the geochemical properties of nanoparticulate layer type minerals at molecular scales using computer simulation methods.

Current research focused on the isotopic mass dependence of solute diffusion coefficients in liquid water as the initial phase of an investigation of diffusion in water-filled clay nanopores.

Project Description: In subsurface hydrogeologic systems where molecular diffusion plays an important role, stable isotope distributions are interpreted with models of the mass (m) dependence of solute diffusion coefficients (D) in liquid water. Isotope geochemistry studies routinely assume either negligible mass dependence (as predicted by hydrodynamic models such as the Stokes-Einstein relation) or a kinetic-theory-like inverse square-root relation ($D \propto m^{-0.5}$). We used MD simulations to determine the isotopic mass dependence of D for monatomic solutes in liquid water (alkali metals, alkaline earth metals, halides, and noble gases). Our MD simulations utilized accurate interatomic potential functions to describe one solute atom and 550 water molecules in motion for 8 to 16 ns in a periodically-replicated, *NVE*-ensemble simulation cell at ambient pressure and T = 298 or 348 K. These simulations, performed with the code MOLDY 3.6, required massively-parallel supercomputing resources of the National Energy Research Scientific Computing Center (NERSC).

Results: All simulations yielded solute hydration structures and diffusion coefficients that were consistent with available experimental data. For the solutes investigated, D was shown to have an inverse-power-law mass dependence, $D \propto m^{-\beta}$ ($0 \leq \beta < 0.2$; plotted in log-log transform for the alkali metals and calcium in Fig. 1), with β-values that are consistent with those derived from the isotope dependence of experimental D values. Thus, the mass dependence of D for monatomic solutes in liquid water is actually intermediate between the hydrodynamic ($\beta = 0$) and kinetic-theory model predictions ($\beta = 0.5$) typically adopted *a priori* in isotope geochemistry studies. Molecular-scale analysis of our simulation results suggested that β should be greatest for solutes whose diffusive motions are weakly-coupled to solvent hydrodynamic modes. This interpretation is supported by our finding that β generally increases with the inverse of the residence time τ^S of water molecules in the first hydration shell of the diffusing solute, with larger τ^S indicating stronger hydrodynamic coupling and, therefore, smaller β (Figure 1). These results have far-reaching implications for the interpretation of isotopic studies of paleoclimate, biogeochemical fluxes, and groundwater hydrology, which can be highly sensitive to the mass dependence of D.

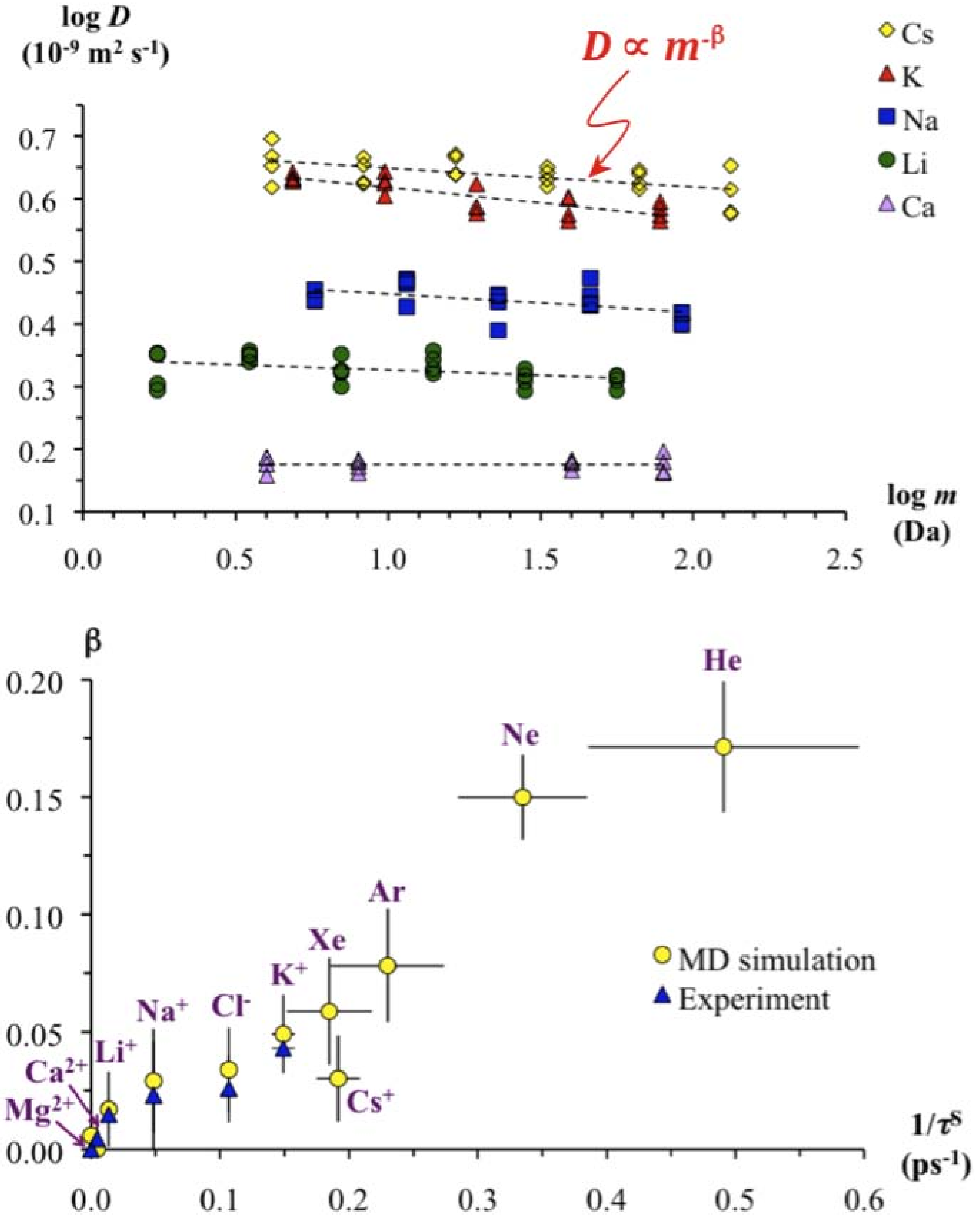

Figure 1. Top: Log-log plot of *D* vs. *m* as predicted by MD simulation for alkali metal cations and calcium. Bottom: Predicted and measured β-values for monatomic solutes plotted against the inverse of the residence time τ^S of water molecules in the first hydration shell as estimated by MD simulation.

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 experimental and modeling components that are intended to complement each other. Preliminary work involved determination of the dissolution and precipitation rate of kaolinite at 22ºC, and this is being followed with coupled illite dissolution and kaolinite precipitation studies to determine the rates of the incongruent reaction. The results are applied to the Santa Cruz chronosequences (Maher et al., 2009; Steefel and Maher, 2009) and to the Shale Hills Critical Zone Network site in Pennsylvania.

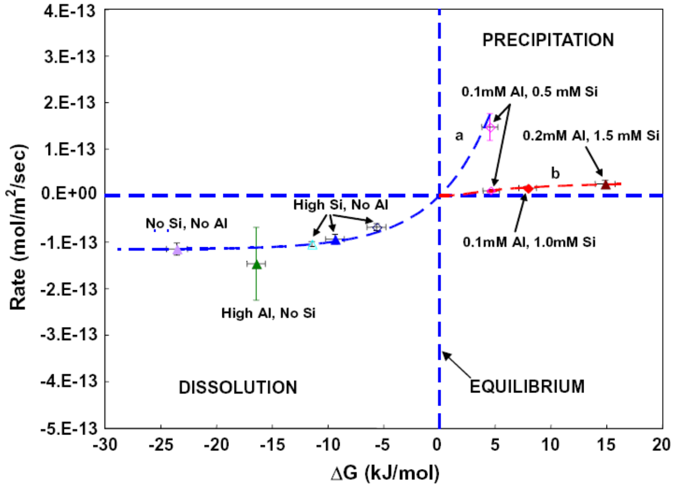

Figure 1: Dependence of the kaolinite dissolution and precipitation rates as a function of Gibbs energy.

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

Reactive transport calculations of chemical weathering at the Santa Cruz Chronosequence indicate that laboratory-determined dissolution rate constants can be used directly when 1) the supersaturation with respect to kaolinite is accounted for, and 2) a nonlinear dissolution rate law for feldspar (Hellmann and Tisserand, 2006) is used. The principal effect of supersaturation with respect to kaolinite (or precipitation of a more soluble clay phase) is to cause the pore water to approach equilibrium with respect to the feldspar, thus slowing rates of dissolution (weathering). This, along with the use of a mechanistic, coupled model for chemical weathering, largely eliminate any "discrepancy" between lab and field rates. Laboratory rates determined in the study by Yang and Steefel (2008) cannot explain the behavior of the Santa Cruz system, which suggests that at circumneutral pH, rates of kaolinite precipitation are either orders of magnitude slower, or 2) a more soluble kaolinitic phase is forming.

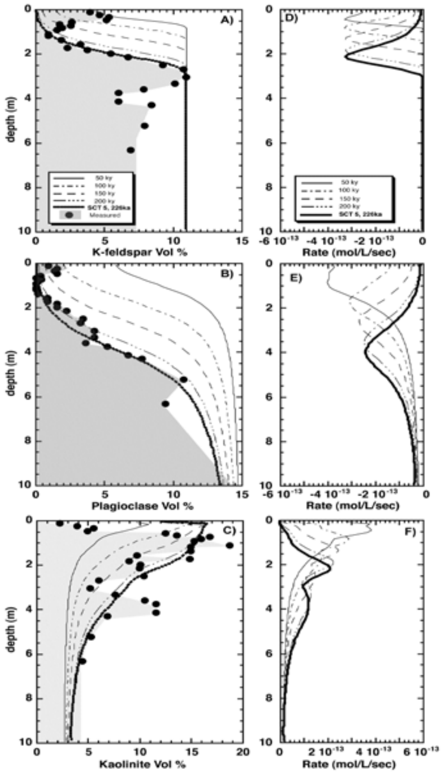

Figure 2: Volume fractions for K-feldspar, plagioclase, and kaolinite after 226,000 years of weathering (left), with corresponding instantaneous rates (right).

The data from the Santa Cruz chronosequence also suggest that the kaolinitic phase that is crystallizing within the profile is changing with time. For example, younger terraces show a greater supersaturation with respect to the reference kaolinite (solubility as determined in Yang and Steefel, 2008), while older terraces show a lower supersaturation. This suggests a gradual aging of the kaolinitic phase, either due to a reconstructive dissolution-reprecipitation reaction, or to crystal growth and consequent solubility lowering (Figure 3).

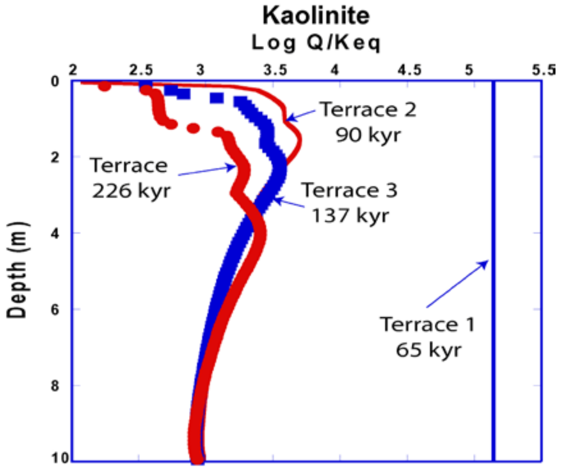

Figure 3: Aging of kaolinite from reactive transport simulations.

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 and to quantify the rates of intrinsic steps. We will focus first on the oxidation of pyrite (FeS_2), a reaction central to acid mine drainage formation and biohydrometallurgy, and the reductive dissolution of iron oxide (Fe_2O_3), a process central to bioremediation of radionuclide-contaminated sites.

Project Descriptions:

Ultrafast X-Ray Studies of Electron Injection into Maghemite Nanoparticles

The reduction of ferric iron bearing minerals is one of the most important chemical changes that occurs in the development of anaerobic soils and sediments. Despite its importance in biogeochemistry, the electron transfer reaction, the evolution of ferrous iron sites created in the mineral, and the iron dissolution steps have been inaccessible to conventional study. We used time-resolved XAS with ~100 ps resolution to monitor the speciation of Fe atoms in maghemite nanoparticles following photo-induced electron transfer from a surface-bound photoactive dye molecule.

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. A major component of this effort will be the preparation of high-quality unreacted surfaces, and we will use pristine sample handling approaches and *in situ* aqueous chemistry control to stabilize the surface against oxidation during measurement. Success in this proposal will enable future studies of *in situ* pyrite oxidation to be performed.

Results:

Ultrafast X-Ray Studies of Electron Injection into Maghemite Nanoparticles

The data in Fig. 1 show that the chemical reduction of an atom at an interface may be (1) initiated by a laser pulse that excites a photoactive molecule; and (2) followed in a pump-pulse experiment by x-ray absorption spectroscopy. These data are the first direct observation of the dynamics of ferrous ion formation and dissolution or subsequent reoxidization in an iron oxide (g-Fe_2O_3). Because we observe the formation of dissolved Fe(II) in continuous illumination experiments, our present hypothesis is that the time-dependent signal represents structural ferrous iron and that the data reveal the kinetics of electron transport within the nanoparticle followed by dissolution.

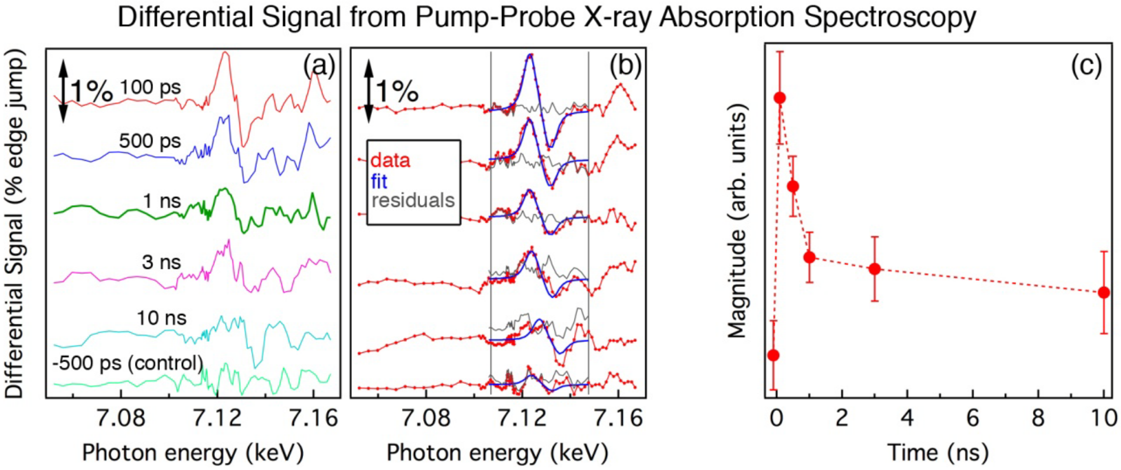

Figure 1. Differential signals obtained by taking the difference between XANES signals acquired before and after a known delay (0.1 – 10 ns) from the 2-ps laser pulse. (b) The same traces shown in (a), with fits of a constant-profile empirical function to estimate the magnitude of the differential signal. (c) The time-dependence of the differential signal following electron injection.

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

We devised a multi-stage anaerobic chemical-mechanical polishing (CMP) procedure that cleans and polishes the surface of natural pyrite crystals. We acquired CTR data as a function of polishing time, and show a steady increase in surface scattering strength. The acquisition of a set of data along 5 crystallographic directions is anticipated to permit a preliminary surface model to be developed.

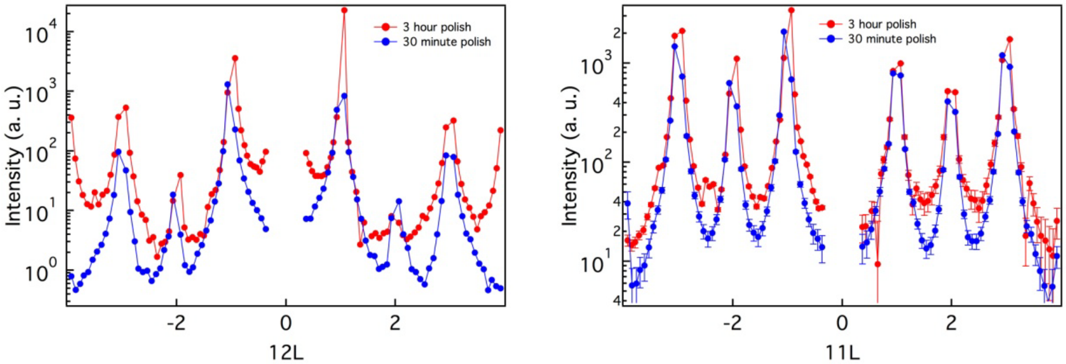

Figure 2. Crystal truncation rod patterns acquired from pyrite (001) surface polished under anaerobic conditions for varying times.

The Center for Nanogeoscience

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The LBNL Center for Nanogeoscience seeks fundamental understanding of nanoparticle properties and their interactions within the natural environment in order to manage our environmental resources and to guide environmental policy. Nanoparticles are abundant products of natural processes and are introduced to the environment via manufacturing and industrial activity. High surface area nanomaterials frequently exhibit elevated reactivity relative to bulk mineral phases and thus can play disproportionally large and unexpected roles in natural systems. For example, nanoparticles can control the bioavailability of nutrients such a phosphate, as well as contaminants such as arsenic and uranium, may stabilize or degrade organic contaminants, impact microbial diversity and distribution, and provide new pathways for radionuclide transport in the atmosphere and subsurface. By identifying the key steps in the interactions of nanomaterials within biogeochemical processes and studying these interactions with a combination of experimental and molecular modeling methods, we will obtain insight into the formation and impacts of natural nanomaterials in the environment. The development of models of nanoparticle surface chemistry is complemented and informed by studies of the structure and chemistry of well-characterized bulk mineral surfaces.

Nanoparticulate Iron Oxyhydroxide Controls on Aqueous Redox Chemistry and Microbial Species Distribution and Activity in Nature

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Objectives: We propose to follow the growth of nanoparticles in neutralized metal-contaminated acid mine drainage (AMD) solutions to describe, at the atomic level, the processes by which nanoparticles form, and determine how interacting and competing processes determine the fate of contaminants.

Project Description: Nanoparticles are important components of natural systems, arising as the result of physical, chemical, and biological processes. A typical example is the formation and transportation of iron oxyhydroxide and oxide nanoparticles formed in neutralization of acidic acid-mine drainage (AMD) solutions. AMD solutions are chemically complex, containing many anions and cations such as zinc and copper in additional to iron. Thus, in the nucleation and crystal growth of iron oxyhydroxide nanoparticles, these impurities can be incorporated into the nanocrystals, impacting the heavy metal cycling in the environment. It is essential to understand how the iron molecular clusters are formed in the neutralization process, how the clusters form the nuclei, how the nanocrystals grow, and how the impurity cations behavior in these processes. To address these questions, we employ a comprehensive approach that combines synchrotron experiments with molecular simulations and modeling. We used molecular dynamics (MD) simulations to predict and understand fundamental steps in AMD neutralization and used synchrotron x-ray adsorption spectroscopy (XAS) to study sulfate anion adsorption on AMD precipitates upon neutralization.

Results: In the first year of this project, MD simulations were used to study iron-hydroxyl molecular cluster formation in an iron chloride solution upon addition of sodium hydroxide, aiming to provide a molecular-level insight of the early nucleation stage of the neutralization process. Results (Figure 1) show that without addition of the neutralization agent, ferric ions are coordinated by six H_2O molecules and/or Cl^- ions (left), forming a octahedral coordination environment. Upon neutralization by NaOH, iron-hydroxyl molecular clusters form (Figure 1) in several hundred pico-seconds. The iron clusters are mainly interconnected via OH^- bridging.

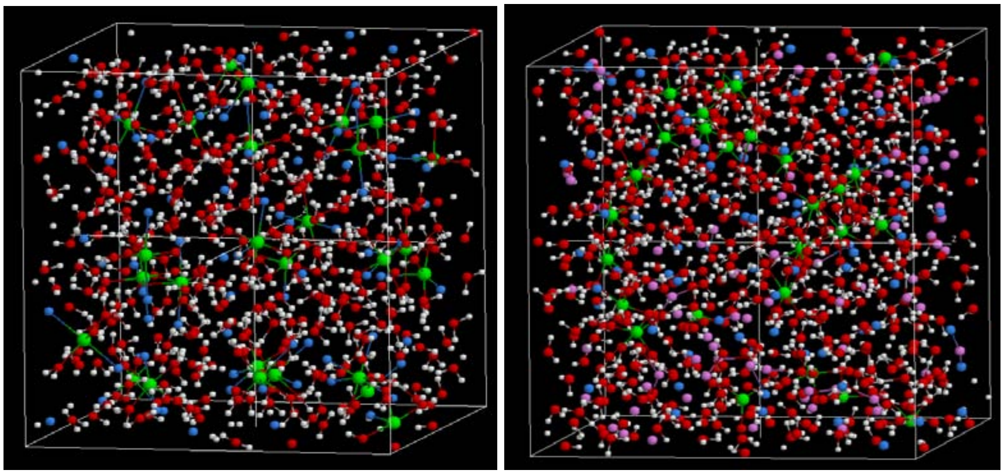
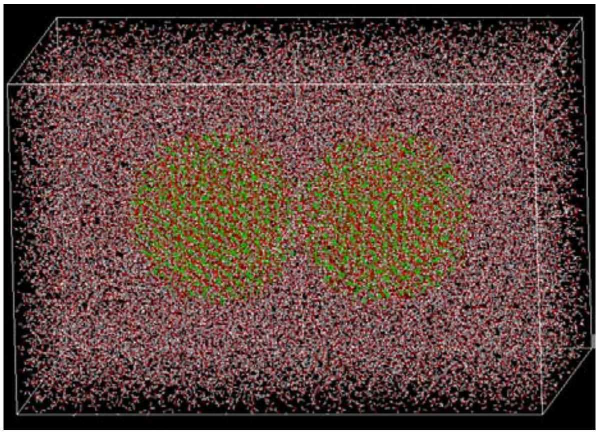


Figure 1. Snapshots of the MD systems, left: a $FeCl_3$ aqueous solution, and right: the solution upon neutralization by NaOH. O: red, H: white, Fe: green, Na: pink, and Cl: blue.

The average Fe-O distance in Fe-H_2O is 2.03 Å and the average Fe-Fe distance in Fe-OH-Fe is 2.92 Å, in good agreement with reported experimental values of 2.01 Å and 3.01 Å, respectively. Subsequent formation of iron oxyhydroxide precipitates is expected as a result of aggregation of the clusters.

We also used MD simulations to study the thermodynamics of oriented attachment (OA) of goethite nanoparticles in water (Figure 2 left), a crystal growth mechanism adopted by nanocrystals under some conditions. The MD results (Figure 2) predict that goethite nanoparticles preferentially attach on the (110) and (111) faces. This may be related to the charge density and/or crystal polarity in the normal directions of the two faces.



OA face	dE(kJ/mol Fe)
100	0.39
010	-0.01
001	0.81
111	-0.61
110	-1.47
101	0.17

Figure 2. Left, snapshot of two oriented 4 nm goethite nanoparticles attached on (100) in water. Right, energy change of OA for two 4 nm goethite nanoparticles in water as a function of the attachment surface.

Our most recent experimental work includes S-K edge XANES / EXAFS measurements of iron oxyhydroxide products formed from neutralization of iron sulfate solutions by sodium hydroxide at different concentrations and solution pH.

Coupled Diffusion and Sorption Processes within Nanoporous Aggregates

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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 of 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 under aqueous chemical conditions typically found in groundwater and surface waters. We are studying the morphology of ferrihydrite aggregates formed through analogs of natural processes including drying and freezing, using small-angle x-ray scattering (SAXS) to derive three-dimensional models of these nanoporous materials. This permits us to study and interpret the rate and extent of heavy metal adsorption and release by aggregates that vary in density and aggregate geometry. Metal ion adsorption geometries are investigated using EXAFS spectroscopy.

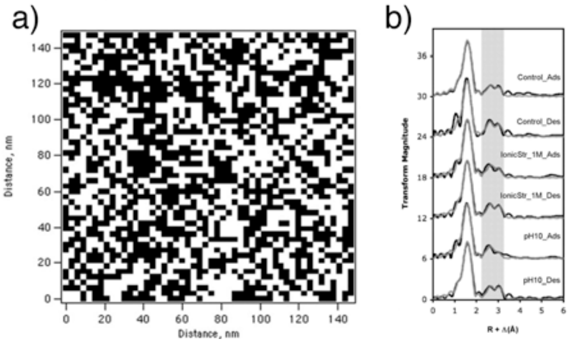

Figure 1 a) Cross-section through model of ferrihydrite aggregate obtained from SAXS data. Black = nanoparticle; white = pore space. **b)** EXAFS study of Cu(II) adsorption geometries following adsorption or desorption. Shaded band highlights differences in next-nearest-neighbor coordination.

Results: When aqueous ions diffuse into aggregates and adsorb to sites on the internal aggregate surfaces, the net uptake is diminished for materials with lower porosity and smaller pore dimensions, indicating that physical loss of accessible surface area is the dominant factor that alters uptake capacity. The transition from low-aggregation states (control) to intermediate and higher aggregation states correlates with both declining degrees of total Cu(II) uptake, lower amounts of Cu(II) desorption (i.e., greater retention). For more aggregated nanoparticles we find increasing proportions of Cu(II) ions in more stable binding geometries, evidenced by an increase in next-nearest-neighbor coordination number. This indicates that ferrihydrite aggregates may be highly effective for contaminant sequestration, retaining adsorbates at particle-particle interfaces or incorporating them structurally. We find, however, that simple geometric parameters (surface area; porosity; pore dimensions) are not sufficient to quantitatively explain the effects of aggregation on uptake and release. Simulations of the mobility of aqueous ions within the pore network are underway.

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

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A. Davis (USGS, Menlo Park, CA)*

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 types of available attachment sites and surface functional groups, the geometry of surface 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 (sum frequency vibrational spectroscopy or SFVS) whereby we can probe the infrared vibrational spectrum of water molecules and hydroxyl groups 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 goethite, diaspore and corundum surfaces. Goethite and diaspore have the same crystal structure, but with Fe^{3+} and Al^{3+} major cations, respectively. For both samples we have analyzed the surface and interface structure via crystal truncation rod (CTR) surface x-ray diffraction, and in the case of diaspore we are now conducting nonlinear optical studies probing the interface hydroxyl and water binding. The goethite surface is terminated by two types of hydroxyl functional groups that bind to two layers of ordered water. Diaspore is expected to have a similar termination, but the slightly smaller interatomic distances in the underlying structure may perturb the nature of the interface water. Goethite nonlinear optical studies are problematical due to small crystal size and IR absorption, but diaspore analysis allow, for the first time, cross referencing of a well-defined ordered water layer using both knowledge of the oxygen positions from CTR analysis, and orientational analysis of the hydroxyls from the SFVS analysis. This approach allows determination of the proton positions at active interfaces under water as a function of pH or other solution parameters. Related to this work are ongoing studies of the hydroxyl orientations on the A, R, C and M planes of corundum using both regular and phase-sensitive SFVS, which we will compare with new CTR data on these planes.

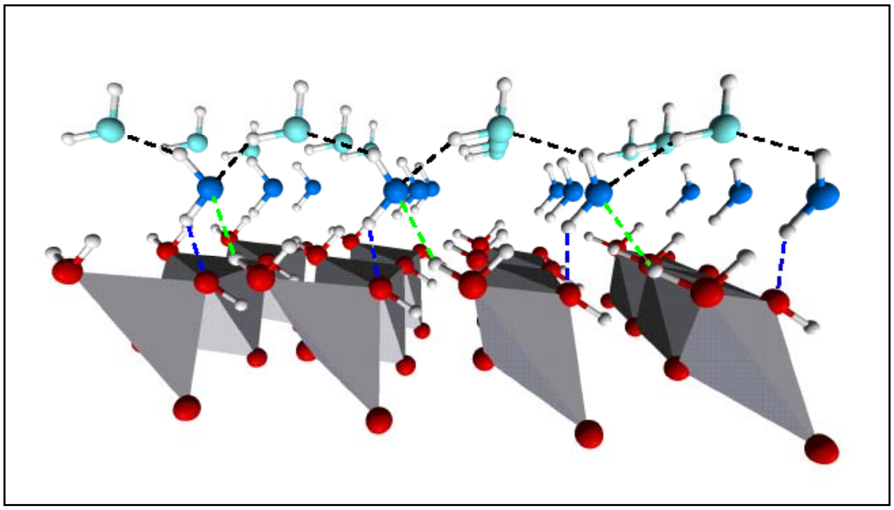

Figure 1. CTR-determined model for the (100) Goethite surface with two layers of ordered water and two surface hydroxyl sites. Dashed lines indicate the positions of hydrogen bonds. The water layer closest to the surface is bound by the –OH acceptor site (blue), and by the –OH_2 donor site (green).
The second water layer is bound by hydrogen bonds to the first water layer.

Development of Isotope Techniques for Reservoir and Aquifer Characterization

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Objectives: This project develops geochemical and isotope techniques for reservoir and aquifer characterization in support of CO_2 geologic sequestration studies and measurement of groundwater ages. Two projects constitute the main focus of our research: (1) the development of isotope tracers to study and quantify water-CO_2 interaction along a flow path during deep CO_2 sequestration, and (2) assisting in the evaluation, verification, and application of new isotopic techniques for placing time constraints on groundwater flow.

Project Description: *Isotope Tracers and CO_2-Injection:*
The primary sites being considered for underground sequestration of anthropogenic CO_2 are active or depleted oil and gas reservoirs, deep aquifers, and underground coal beds. An important issue for gas transport in water-saturated zones is the amount of interstitial pore water, the extent of gas-water interaction and the chemical impact on the reservoir due to CO_2 injection. Modeling predicts that precisely measured details of a chromatographic separation profile for a suite of gases with different solubility would provide important information regarding the extent

of gas-water interaction and provide an integrated gas/H_2O volume ratio. During the Frio Formation (Gulf coast South Liberty Field, Texas) we observed a significant difference in the peak arrival times for injected Kr and SF_6 tracers, leading to an inferred integrated aqueous phase saturation of ~32-45% and a characteristic length scale for exchange in the CO_2-water system of ~10-100 cm, consistent with finger flow.

Results: *Isotope Tracers and CO_2-Injection:*
The Frio pilot test demonstrated the utility of phase-partitioning tracers, such as noble gases, in defining reservoir environments and processes relevant to geologic sequestration of CO_2. However, at present the quantitative analysis of the tracer return data is limited by a lack of data regarding the solubility of the tracers in water-CO_2 systems at the relevant P, T and x_i conditions. The solubility of the noble gases and SF_6 in water are known under ambient conditions. However, there is no data on the solubility distribution of noble gases and SF_6 (or other tracers) between water and supercritical CO_2. In collaboration with Barry Freifield and Kevin Knauss (Earth Science Division, LBNL), water-CO_2 solubility experiments for noble gases and SF_6 are being conducted under the appropriate P, T and x_i conditions encountered in deep aquifer CO_2 sequestration. Flexible gold reactor bags (Dickson bombs) which can be run up to temperatures of 450°C and 200 MPa will be used to equilibrate tracer free CO_2 with tracer saturated water at pre-selected T and P conditions. Aliquots of each phase can be extracted separately at experimental P and T conditions for analysis and direct measurement of the CO_2-water distribution coefficients for the various tracers of interest. Preliminary results run under P, T conditions similar to Frio (~60°C, 10 MPa) indicate that, in the presence of super-critical CO_2, noble gases may be more soluble in water, by as much as a factor of ~10, relative to their solubility with respect to air at similar conditions. The results are considered preliminary while we continue to work out some difficulties related to sample withdrawal from the reactor bags and subsequent processing. These are minor issues and should be remedied with little difficulty.

Project Description: *Groundwater Ages:*
Placing time constraints on recharge and flow of groundwater is an extremely important and difficult problem that affects a wide variety of geologic processes that are relevant to environmental issues, such as water resource management, CO_2 sequestration, waste management, and paleoclimate studies and subsurface water-rock reaction and transport rates. To address these and similar issues, reliable techniques for determining aquifer recharge rates and water residence ages are required.

Results: *Groundwater ages:*
In collaboration with Neil Sturchio, University of Illinois, Chicago and Dr. Zheng-Tian Lu, Physics Division, Argonne National Laboratory, radio-chlorine (^{36}Cl), radio-krypton (^{81}Kr) and radiogenic noble gases (^4He and ^{40}Ar) are measured to assess the residence time of old groundwater. Presently, we are focusing our investigation on old groundwater from aquifers of the mid-continental United States and an initial suite of samples along flow lines of the Western Interior Plains Aquifer in eastern Kansas and western Missouri have been collected. Prior studies of saline groundwater emerging from this vast aquifer suggest meteoric recharge ~1000 km to the west in the Rocky Mountains. There are strong hydrologic, chemical and isotopic arguments in support of the long flow path, but there are no constraints on flow rate. Samples have been analyzed for noble gases and found to be highly enriched in ^4He with concentrations

of 2-4 orders of magnitude greater than that in air saturated groundwater. Analysis of ^{81}Kr in the samples is in progress.

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 silicate melts and in water, and to use the results to better understand transport phenomena in natural systems.

Project Description: Our experiments are designed to measure the isotopic fractionation of Ca Mg, Fe, Li and K by diffusion and other kinetic processes in liquids, including silicate melts and water. The experimental results are used to validate molecular dynamics calculations for the relative mobility and isotopic fractionation of Ca, Mg, K and Li by diffusion in water. For a more complete overview of the project and discussion of results for diffusion in silicate melts see Richter et al. in this volume. Recently our attention has focused on the kinetics of evaporation and its effect on chemical and isotopic fractionation of relatively volatile elements. Higher volatility is correlated with increasing evaporation rates, which in turn leads to the possibility of a diffusion limitation for evaporation. In that case, the rate of diffusion of an element to the evaporating surface limits the rate of evaporation of that element. Evaporation and diffusion of the relatively volatile elements of magmas is important when considering explosive volcanism, gases from volcanically driven geothermal systems, and the thermal histories of volcanic glasses. This has motivated us to investigate experimental systems involving evaporation. Our previous work on K diffusion in water (Bourg et al. 2009, submitted to GCA) has demonstrated that K displays the largest isotopic fractionation among the alkalis, and much greater isotopic fractionation than the divalent cations (e.g., Ca, Mg). This experimental result was then reproduced by molecular dynamic calculations that indicate the underlying factors for this behavior. Carrying on the focus on K isotopic fractionation, we are conducting a series of evaporation experiments on silicate glasses where K is the most volatile element to quantify the isotopic effect. The initial composition for the evaporation experiments is a chondrule-like glass, analogous to a high Mg andesite (by weight ~ 58% SiO_2, 23% MgO, 5% FeO, 4% Al_2O_3, 2% CaO, 3.5% Na_2O, 3.5% K_2O). Beads of this composition were evaporated at 1470°C for various lengths of time into a vacuum ($P=10^{-6}$ Torr) acting as a sink. The residual glasses were dissolved, analyzed for their elemental composition by Q-ICPMS, and aliquots passed through ion exchange chromatography to separate K for isotopic analysis. The K isotopic composition was measured by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) in reference to the K separated from the starting material representing the initial K isotopic composition for the experiments.

Results: Our experimental results regarding the isotopic fractionation of K during evaporation from a silicate melt are presented in Fig. 1. The experiments mapped a large range of isotopic fractionation (up to a δ^{41}K of 62.8 ‰). The data are consistent with Rayleigh fractionation (R/R_o

$= F^{(\alpha-1)}$, where in this case R = $^{41}K/^{39}K$, R_o = initial $^{41}K/^{39}K$, and F = fraction ^{39}K remaining, described by an isotopic fractionation factor (α) for $^{41}K/^{39}K$ of 0.9787±0.0015. The mass dependency of the fractionation factor (α) is given by the equation $\alpha = (m_b/m_a)^{\beta}$, where in this case m_b = mass of ^{39}K, and m_a = mass of ^{41}K. Our value for α indicates a mass-dependent exponent (β) for K of 0.43±0.03 (95% confid.), resolvable from the theoretical limiting value of 0.5. This value for β_K is similar to that for Mg evaporation (β_{Mg} = 0.4-0.25 in the temperature range of 1900-1500˚C, Richter et al. 2007).

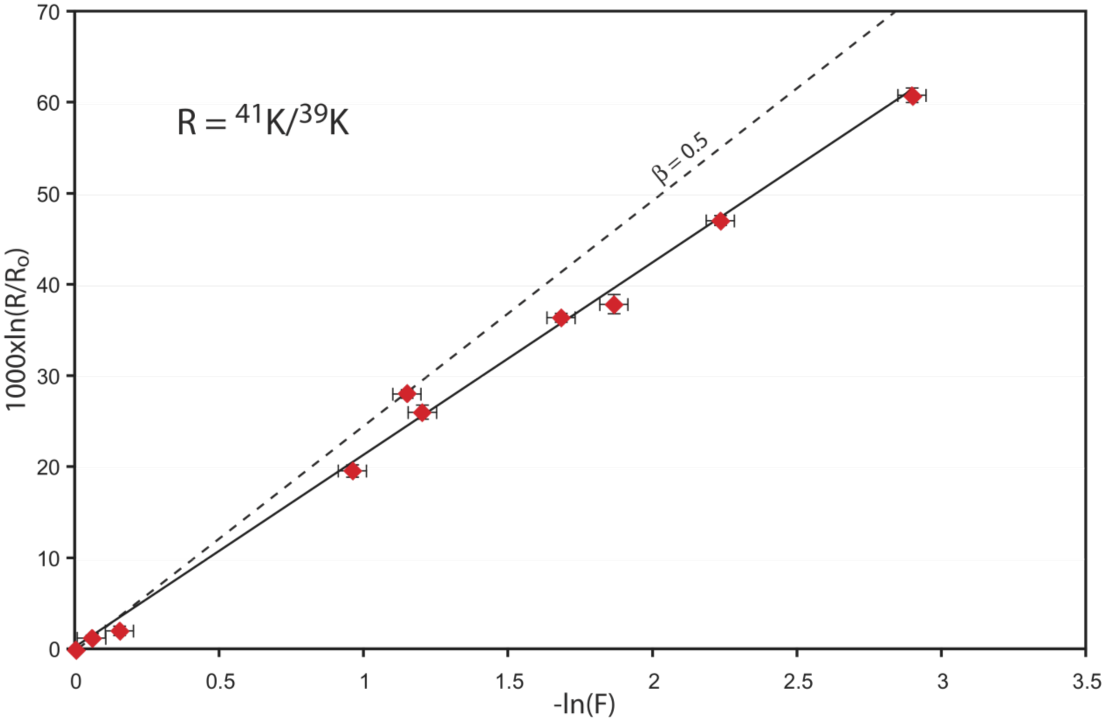

Fig. 1. Plot of 1000xln(R/Ro) against –ln(F), where R/Ro is the ratio between the measured residue and initial $^{41}K/^{39}K$ ratios, and where F is the fraction of ^{39}K remaining in the residue, for experiments regarding the evaporation of K^+. Results for experiments run out to F = ~0.06 indicate an isotopic fractionation factor (α) of 0.9787±0.0015, which in turn suggests a β of 0.43±0.03 (95% confid.), where $\alpha = (m_{39K}/m_{42K})^{\beta}$. The dashed line represents β = 0.5, the theoretical limiting value.

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

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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: From seismic velocity data collected in the laboratory, we determined the five elastic constants of transversely isotropic media (silica sand, glass beads, and halite packs were used) as a function of compaction stress and time. An interesting result was that the off-diagonal components of the elasticity matrix remain more or less unchanged. Also, for most of the samples, S-wave anisotropy was the strongest at the beginning of the compaction in contrast to the P-wave anisotropy. Because these experiments were conducted mostly at water-saturated condition, we developed explicit formulae for extracting dry moduli of the granular packs directly from the “wet” moduli, based upon the anisotropic Gassmann’s relationship. Previously, a relationship that provides wet moduli from dry, anisotropic moduli was known, but the reverse relationship was not. We submitted this result to the Journal of the Acoustical Society of America.

For examining micro-scale grain contact geometry, we performed initial studies of grain contact imaging using synchrotron x-ray microtomography, utilizing image enhancing technique with K-edge contrast agent (potassium iodide [KI]). So far, we have had limited success for this effort because of difficulties in reducing the pendulum fluid accumulated at grain contacts, without precipitating the salt. A new procedure for reducing the fluid, using a mixture of ethanol and aqueous KI solution, has been developed and is currently being tested. Another pore-scale imaging effort is the pore casting of halite grain packs after compaction. We have successfully produced 1-inch cube samples of the pore cast (grain or pore size ~300 microns. A model that relates the electrical conductivity of the pore cast to the average contact patch size has been developed.

Originally, we planned to use halite as a proxy for studying diagenetic cementation of sand grains and the resulting seismic properties. However, after initial studies, we decided to use slower precipitation of calcite from a supersaturated aqueous solution. A laboratory system for continuously producing the supersaturated solution has been built and the precipitation of calcite crystals has been confirmed (Figure 1). This system can be used for simulating calcite cementation within sand packs and fractures in the laboratory.

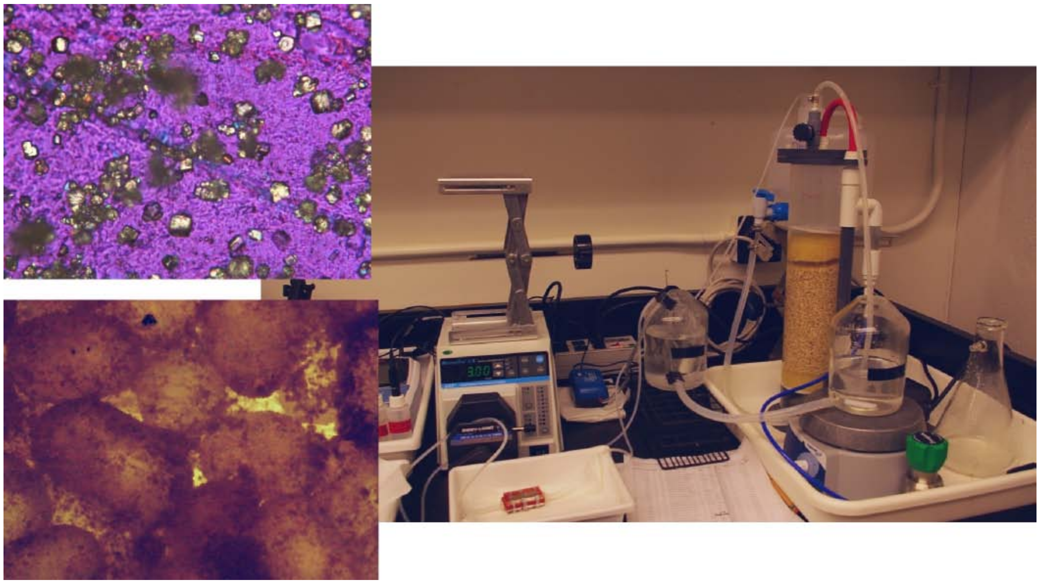

Figure 1. Continuous calcite precipitation system for grain/fracture cementation study. The top left shows calcite crystals (~30 microns) precipitated from a super-saturated aqueous solution. Bottom left shows sand grains (~1mm) containing precipitated calcite crystals.

Propagation of Elastic Waves in Complex Media

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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: The primary task this year was preparing for publication papers that described the research accomplished in the previous two years. A paper on a new model for earthquakes is completed and entering the review process. This new model is rather different from the standard model of an earthquake that has been used in seismology since the 1960's. It treats an earthquake as the breaking of asperities in a manner similar to modern studies of sliding friction. A fairly complete mathematical treatment of this new model is now available that includes elliptical asperities, oblique tectonic slip, dynamic failure of an asperity, dynamic interaction during the failure of multiple asperities, and a probability estimate of the likelihood of this interaction. The advantages of this model include agreement with the observed scaling of repeat time versus seismic moment for repeating earthquakes, a natural explanation of the heterogeneity observed in the fault slip of most earthquakes, the radiation of the high frequencies commonly observed in strong motion data, and a simple relationship between the fractal dimension of asperities and the b parameter of the Gutenberg-Richter scaling equation.

Good progress was also achieved on another paper that solves the boundary value problem for scattering of elastic waves by a spheroidal inclusion. All of the mathematical results for this paper are finished and all that remains are a few details on the numerical implementation of the theory.

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

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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: Establishing the precise relationship between electrical conductivity, seismic wave velocities and mass density and their interrelationships to fluid properties in 3D heterogeneous media (saturation, porosity and permeability) is of fundamental interest in subsurface science. Knowledge of such relationships could lead to a much better understanding of subsurface fluid, flow and transport, with critical implications for environmental site characterization and remediation, exploration for oil and gas and reservoir monitoring for safe sequestration of CO_2. Correlations between electrical, seismic and density properties are increasingly observed at different scales in collocated experiments. For example, relevant data from multidimensional dc resistivity and seismic refraction investigations of the near surface have conventionally been inverted separately leading sometimes to equivocal models. Joint inversion of such data is a better approach.

Results: Joint inversion of reservoir parameters (fluid saturation, permeability and rock fracture density and porosity) is of more interest than the geophysical attributes (velocity, electrical conductivity and density). A rock physics model can sometimes provide the linkage between attributes and reservoir parameters, but in many cases no clear relationship can be defined. Most insight from the joint analysis of different geophysical attributes can be gained in complex geological systems, where rock physics models break down. In such cases, an alternative approach is to seek common structural relationships in the attributes, which can provide indirect information on the underlying geological processes. This approach leads to a purely geophysical type inversion without reservoir parameter estimation. To force structural similarity a cross gradient is being employed during the joint imaging process. This constraint has the desirable characteristic that it can map common geological structure that is not dependent upon changes in magnitude of the various geophysical attributes, and can also admit structure that is only constrained by one data type and not others.

A significant problem in developing joint imaging technology is the resolution at which the different geophysical measurements (seismic, EM and gravity) sense the subsurface. The resolution of seismic imaging is an order of magnitude finer in scale than what can be imaged using electromagnetic fields. However, to produce a consistent joint image of the subsurface geophysical attributes (velocity and electrical conductivity) requires the different geophysical data types to be consistent in their resolution of the subsurface. The superior resolution that is possible for properly-sampled seismic data results from the fact that the energy propagates as a wave, while propagation of EM energy is diffusive and attenuates with distance. On the other hand, the complexity of the seismic wavefield can be a significant problem due to high reflectivity of the subsurface and the generation of multiple scattering events. While seismic wavefields have been very useful in imaging the subsurface too much scattering and too many reflections can lead to difficulties in imaging seismic data.

Low pass filtering the seismic trace (via Laplace transformation) can be effective approach for obtaining seismic data that has similar spatial resolution to EM and gravity data. The effect of this transformation on the filtered trace changes the modeling of the seismic wave field from wave propagation to diffusion. With diffusive type problems the skin depth is a useful parameter that characterizes the depth of penetration of energy into the subsurface and the resolution that can be anticipated from an imaging experiment. For the transformed acoustic wave field it is given by $\delta=v/s$, where v is the velocity of the medium and s is the Laplace transform argument. For inductive EM the skin depth is given by $\delta=503\rho f$, where ρ is the resistivity and f the harmonic frequency. Notice the similarity in the roles of s and f in specifying the skin depth. At three skin depths 95% of the energy has been attenuated and there is very little sensitivity to subsurface below this depth. The smallest features that one can expect to resolve are a fraction of the skin depth, typically $\delta/3$. To produce seismic wave fields consistent for joint imaging we are now developing 3D simulators for wave field simulation and imaging in the Laplace domain for acoustic media using finite difference approximations with iterative based solver methods. We have already established that velocity images can be obtained at resolution and scale consistent with electrical data. The simulator solves for several discrete values of the Laplace transform variable, s, which we have previously indicated is analogous to frequency, f, used to describe harmonic wave field simulation.

Both gradient decent and sequential quadratic programming (SQP) approaches are being tested to enforce the cross-gradient constraint within the joint inversion process. The SQP method builds a linear model about the current iterant, and solves for the model update subject to the constraint using Newton’s method and Lagrange multipliers. Gradient decent adopts a penalty method for implementing the common structure similar to the way regularization is implemented in unconstrained optimization. A new tradeoff parameter is introduced in the problem to insure that the constraint will be satisfied to within a desired tolerance.

Upon completing the coupling of the geophysical simulators within the joint imaging framework, our intention is to investigate the coupled conductivity-velocity-density images for fluid property interrelationships on synthetic and experimental data.

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: Since 2008, the focus of the work has shifted specifically to the seismic properties (velocity and attenuation) of unconsolidated grain packs. Experimentally, there is observed to be more attenuation in grain packs than can be explained using existing models such as those due to Biot (viscous flow between the peaks and troughs of a compressional wave) or those developed earlier in the present study due to mesoscopic-scale fluctuations in the frame properties. We have focused on rattler grains to explain the missing amount of attenuation. Rattlers are grains that have not been jammed into immobile contact with the surrounding grains. They typically occupy 10 to 15% of the grain pack at low confining stress, and become jammed as the stress levels on the pack are increased. When the grain pack is shook by a passing seismic wave, a rattler will experience relative motion between itself and the surrounding jammed grains. This will create an enhanced amount of shearing in the viscous fluid of the pores that will attenuate more energy than either flow at the macroscopic or mesoscopic patch scale. This mechanism has been analytically modeled in different manners over the past year and can explain the attenuation data.

Another part of our work has been to model how the elastic moduli of a random grain pack increases with increasing confining pressure. It is well known that the classic Hertzian pressure dependence $P^{1/3}$ of the elastic moduli does not correspond well to the experimental measurements which are closer to or even greater than a $P^{1/2}$ dependence. To explain the difference, we appeal to the creation of new grain contacts as the material is compressed, or more specifically, to the disappearance of the rattler grains. We propose that the rattlers will either rotate or linearly displace as the jammed grains that surround them are strained to occupy a smaller volume until there is no more wiggle room and the rattler becomes jammed and begins to bear stress. This mechanism has been analytically modeled over the past year in a number of different ways and is able to explain the experimental data.

In the laboratory, we are measuring the mesoscale fluctuation elastic properties on 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. A new apparatus has recently been built that is much stiffer than our old apparatus. Results using the new machine show the apparatus to be working. Experiments on a range of rock types are ongoing.

We also looked into mechanisms of attenuation and induced potential in grain packs in which bacteria have been responsible for an enhanced level of metal precipitation. The lab data show there to be a significant change in both measurements as the metals precipitate. A model was developed that explains how the biomediated precipitation changes both attenuation and induced potential.

Last, over the past year, we extended our finite-difference modeling of wave propagation in porous media to include the full-range of frequencies in which viscous boundary layers develop in the pores of the rock at high-enough frequencies. The effect of the onset of viscous boundary layers is to transform Darcy's law into a convolution integral equation over time and we propose efficient methods for including the convolution into an explicit time-stepping finite-difference code.

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

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Objectives: I am investigating the fundamental relationships between changes in time-lapse geophysical attributes and subsurface 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 subsurface 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: During the past year I explored three topics: (1) The development of a trajectory-based technique for modeling the propagation of a broadband disturbance in a poroelastic medium. (2) Modeling the flow of a fluid with density-dependent properties. (3) Imaging the aperture change in a fracture/fault due to the injection of carbon dioxide.

A trajectory-based technique for modeling the propagation of a broadband disturbance in a poroelastic medium.

An asymptotic method, valid in the presence of smoothly-varying heterogeneity, is used to derive a semi-analytic solution to the equations for fluid and solid displacements in a poroelastic medium. The solution is defined along trajectories through the porous medium model, in the manner of ray theory. The lowest order expression in the asymptotic expansion provides an eikonal equation for the phase. There are three modes of propagation, two modes of longitudinal displacement and a single mode of transverse displacement. The two longitudinal modes define the Biot fast and slow waves which have very different propagation characteristics. In the limit of low frequency, the Biot slow wave propagates as a diffusive disturbance, in essence a transient pressure pulse. Conversely, at low frequencies the Biot fast wave and the transverse mode are modified elastic waves. At intermediate frequencies the wave characteristics of the longitudinal modes are mixed. A comparison of the asymptotic solution with analytic and numerical solutions shows reasonably good agreement for both homogeneous and heterogeneous Earth models.

Modeling the flow of a fluid with density-dependent properties.

In the derivation of the linear diffusion equation governing fluid flow, aspects of the dependence of the fluid density upon the pressure, particularly the spatial gradient of density, are often neglected. In this task I investigate the modeling of fluid flow while retaining the full pressure dependence of the density. Using a transformation, first proposed by Hopf and Cole, one can convert the resulting nonlinear pressure equation into a quasi-linear diffusion equation. For a consolidated medium, in which the porosity does not vary significantly with pressure, the transformed equation is fully linear. Using an asymptotic approach, I derive a solution to this equation for a heterogeneous medium with smoothly-varying properties. It is found that the importance of the nonlinearity depends upon the ratio of porosity to conductivity as well as upon the ratio of the compressibility of the porous medium to the compressibility of the fluid multiplied by the conductivity. For pore fluids consisting of both pure water and of supercritical carbon dioxide, the solution to the linear diffusion equation agrees quite well with the solution to the complete nonlinear equation.

Imaging the aperture change in a fracture/fault due to the injection of carbon dioxide. Interferometric Synthetic Aperture Radar (InSAR), gathered over the In Salah CO_2 storage project in Algeria, provides an early indication that satellite-based geodetic methods can be effective in monitoring the geological storage of carbon dioxide. An injected volume of 2.5 million tons of carbon dioxide, from one of the first large-scale carbon sequestration efforts, produces a measurable surface displacement of approximately 5 mm/year. Using geophysical inverse techniques I am able to infer flow within the reservoir layer and within a hypothesized fracture/fault zone intersecting the reservoir. I find that, if we use the best available elastic Earth model, the fluid flow need only occur in the vicinity of the reservoir layer. However, flow associated with the injection of the carbon dioxide does appear to extend several kilometers laterally within the reservoir, following the suspected fracture/fault zone.

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

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Objectives: This project seeks to (1) isolate noble gas components and carrier phases in sediments to address the fundamental processes that lead to the observed enrichment/depletion patterns of noble gases in sedimentary rocks and fluids, (2) examine the processes by which such noble gas patterns are acquired and the mechanisms by which such patterns are trapped, and (3) thereby improve the application of noble gas isotope studies to multiphase fluid processes in the Earth's 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. Although abundance patterns suggest an adsorption hypothesis, three observations argue against adsorption as the only mechanism: (1) The difference between Xe and Ar adsorption coefficients (Xe ~30× Ar) is too small to account for the observed large relative Xe enrichments; (2) heating experiments suggests the enriched component is tightly bound, counterintuitive to a simple adsorption history; (3) many sedimentary rocks (~half) and some oil field gases contain excess Ne in conjunction with excess Xe.

Results: We are concentrating on noble gas abundances in a variety of silica samples. In samples of inorganic silica, (except for a hydrothermal sinter), noble gas abundances are consistent with occlusion of air-saturated water (ASW) in trapped fluid inclusions and lack requisite enrichment/depletion factors needed to explain the noble gas inventory in oil field fluids. On the other hand, replicate analyses of noble gases extracted from silica spicules from live sponges (Calyxnicaeensis) show significantly enriched Ar, Kr, and Xe concentrations ($[^{i}\mathrm{Ng}]_{sample}/[^{i}\mathrm{Ng}]_{asw} > 1$), very little if any mass dependence in the acquisition and trapping of Ar, Kr and Xe, and essentially no Ne. To our knowledge, this is the first evidence that noble gases are either directly or indirectly processed and enriched during the formation/secretion of biominerals. Noble gases in silica samples from the (diatomaceous) Monterey Formation (Elk Hills oil field, CA) and an Atlantic box core are somewhat depleted with respect to the sponge spicule, are fractionated, favoring the heavy noble gases, and approach the compositions observed in bulk deep sea sediments. Unlike the sponge spicule, these samples appear to be strongly enriched in Ne, an observation currently being confirmed with additional analyses. We believe 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 are currently being processed to address these questions. In collaboration with Ben Gilbert (Earth Sciences Division, LBNL), we have also measured noble gases in laboratory-synthesized nanoparticle agglomerates. Absolute noble gas abundances in samples of goethite (alpha-FeOOH) clusters agglomerated under different pH conditions (pH = 2, 7, and 12) show a strong dependence (up to a factor of ~1000x) on pH. The most enriched sample (pH = 7) has noble gas concentrations similar to that observed in the biogenic silica samples. However, despite the large range in absolute concentrations, the samples indicate little or no mass dependent fraction, other that the complete exclusion of He and Ne. As the sites, mechanisms and materials in which noble gas enrichments are created, trapped and released is explored in greater depth, the results could have far reaching implications regarding trapping, storage and release of gases from nano-structured materials.

In a parallel effort, it is known that source rock noble gas enrichment is diluted during transport by interactions with groundwater and the groundwater noble gas composition is significantly influence by the local accumulation of the crustal degassing flux in helium. We have evaluated the observed measures of the ^{4}He degassing flux from continents in terms of its mean as well as their spatial and temporal variability. The time-and-area weighted arithmetic mean (standard deviation) of n=33 ^{4}He degassing fluxes is found to be $3.32(\pm 0.45) \times 10^{10}$ ^{4}He atoms m^{-2} s^{-1}. The log normal mean of measurements (n=33) of the crustal degassing flux is 4.18×10^{10} ^{4}He atoms m^{-2} s^{-1} with a best estimate one sigma log normal error of */45x based on an assumption of symmetric error bars. The log normal mean continental heat flow is 62.2 mW m^{-2} with a log normal variance of 1.8x. (for comparison, the best estimate mean of 65±1.6 Wm^{-2}, Polach et al., 1993). A simplistic interpretation would suggest that the variance in ^{4}He flux as a result of transport and release is 25x greater than the variance in the heat flux as a result of reduced heat flow and thermal conductivity.

Seismic Wave Propagation in Earth Systems with Fluids and Fractures

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Objectives: The main objective of this continuing project has been to understand the physics of seismic wave propagation in earth systems, especially those containing fluids (oil, gas, water, CO_2) in rock pores and fractured reservoirs. Seismic waves provide the tool used to image the earth, and thereby locate potential deposits of resources or contaminants, depending on the focus of each investigation. In some cases, the waves can also be used to characterize the nature and state of the 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 reservoirs in recent work.

Project Description: Recent 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). Anisotropy has been analyzed using both approximate and rigorous analytical methods, as well as computational methods when appropriate. Very flat fluid-filled or only partially saturated cracks, and/or dry cracks all might result in strong effects on the seismic wave propagation speed, and also in losses via wave attenuation. Recent and important results for reservoirs containing arrays of vertical fractures containing fluids have implications for estimating fluid permeability, as well as pore-fluid type and its spatial distribution. One of our recent successes has been to show how to analyze large amounts of such data and reduce the information contained therein to a few pertinent constants that can then be used to analyze and/or study other characteristics of fractured reservoirs. In all cases we take special care to incorporate as much rigorous information (such as mathematical bounds and results from modern effective medium theories) and such known-to-be-correct physical theories such as Biot-Gassmann for the mechanics of systems having fluids saturating pores.

Results: Fractures (filled with either gas or liquid) have been the major focus of recent work, although some other work on granular media has also been published this year. Some of this research has appeared in Geophysics, and further extensions of the work were more recently published in Geophysical Prospecting (GP). Results are expected to help explain various discrepancies that have been noted in well-logging, laboratory, and field data by many workers. Thomsen’s weak anisotropy approximation in seismology has been found to have a serious weakness when applied to vertically polarized shear waves. A way of correcting this deficiency has been found and is the main focus of the paper in GP. We are also trying to popularize a parametric method of Sayers and Kachanov (1991) for mechanical and seismic behavior of fractured systems. The method has been used relatively little, but has a natural generalization that permits rigorous analysis of fluid effects in fractured systems. The resulting exact formulas differ significantly from the usual ad hoc approach taken by most workers in the field. This new method (with included fluids) shows explicitly and easily how liquids influence both compressional- and shear-wave speeds in fractured media. Recent advances in understanding of waves in fluid-saturated granular media were also submitted for publication this year.

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

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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: 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. Video recordings of time-dependent patterns of pH change were enhanced through post-processing (Fig. 1). From the visual recordings, quantitative characteristics of the DDC process were deduced, such as number and wavelength of convective fingers, rates of finger advancement and growth, and increase of dissolved inventory with time. Numerical simulations of our system showed good agreement with the experiments for onset time of convection and advancement of convective fingers. Rapid onset of cell-scale convection occurs in the laboratory tests, however this does not occur in the numerical simulations. This has been attributed to a slight thermal convection induced by the cell illumination.

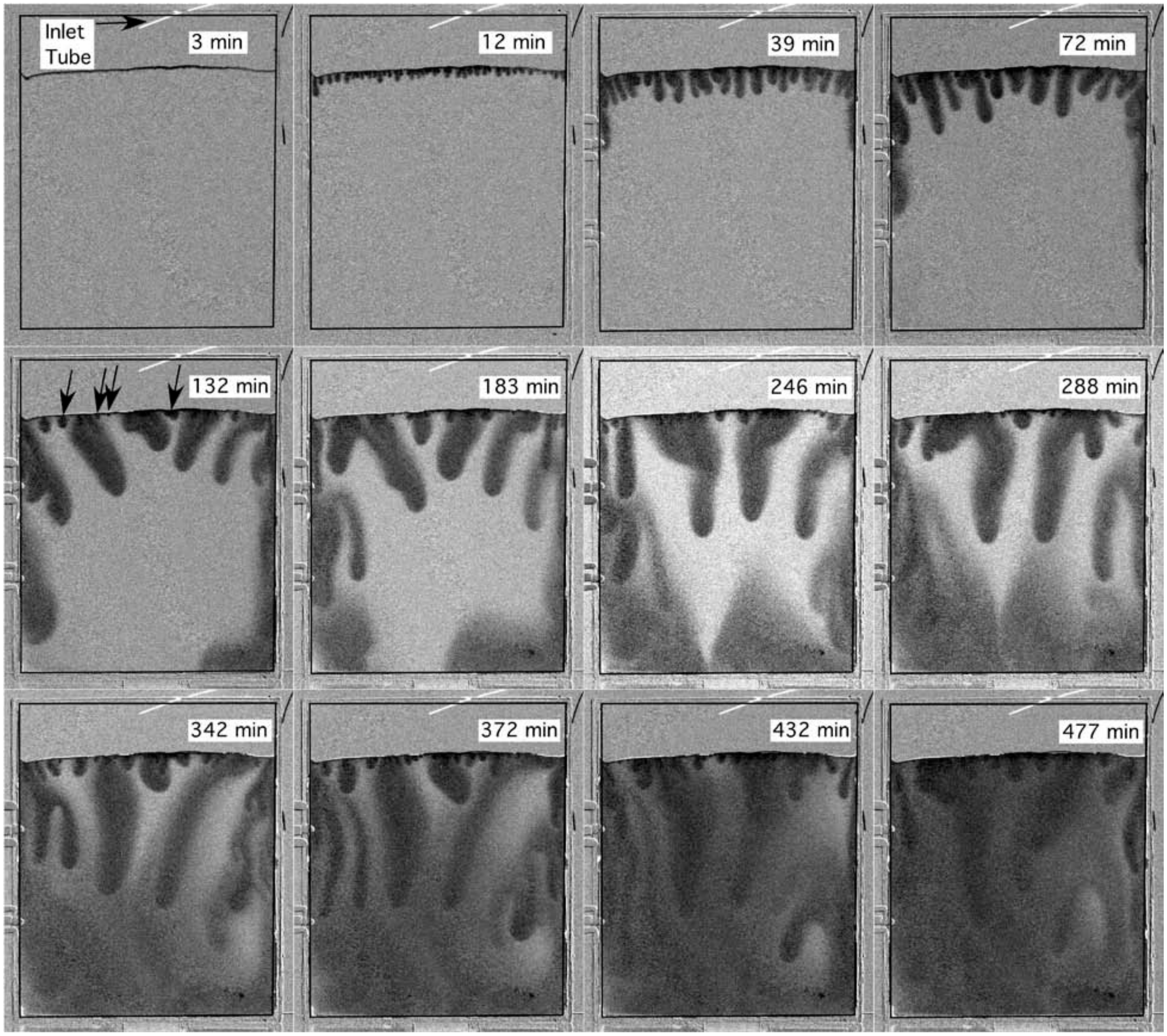

Figure 1. Laboratory visualization of CO_2 dissolution and convection.

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/ECO2N 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, it does not affect the rate of plume advancement. 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.

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 calcite. 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 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.

Results (selected) for FY09: Over the last year, we have prepared a number of new publications that reveal fundamental differences between the growth of biomineral phases of low solubility, like calcite, and the behavior expected from long-accepted theories of crystal growth. We have extended our AFM resolution to the molecular level and, for the first time, directly investigated peptide-step interactions. That advance led to new insights into the consequences of peptide-step interactions for mineral growth dynamics. Following on our Lee et al. (*JACS*, 2007) study, we have further investigated the key factors that lead to templated nucleation of calcite on organothiol self-assembled monolayers (SAM). The results provide a clear picture of SAM evolution during the templating process. To our knowledge, these studies with carbonate nucleation and growth are novel to the literature.

Rethinking classical crystal growth models through molecular scale insights: Consequences of kink-limited kinetics. *(Crys. Groth. Des., pending minor revision).* 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 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.

Sub-nm AFM imaging reveals source of acceleration and hysteresis during peptide-directed crystallization. (*PNAS, In review*). *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. By imaging the growth of a biomineral phase with positively and negatively charged faces under the influence of aspartic-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. Interactions with the positively charged face 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 including growth hysteresis characterized 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 suggest strategies for directing the timing and rate of crystallization.

The importance of structural flexibility in templated nucleation of calcite on carboxylic self-assembled monolayers *(In prep).* A preponderance of structural evidence from marine organisms shows that formation of calcium carbonate biomineral structures often occurs through directed growth of a mineral phase from an amorphous precursor on an organic matrix that controls crystal orientation. Organothiol self-assembled monolayers (SAMs) have been successfully used as an in vitro model for this process, giving a high degree of control over ordering of the mineral phase. However, realization that the pathway to the final crystalline state, even in this in vitro system, first passes through a transient phase comprised of amorphous nanoparticles and that, in at least one case, the SAM completely disorders during this transient stage suggests an active role for the SAM. Here we use (NEXAFS), photoemission spectroscopy (PES), X-ray diffraction (XRD) and scanning electron microscopy (SEM) to investigate the key factors that lead to templating. We apply these methods to $CaCO_3$ formation on a SAM specially designed with a long alkyl chain to achieve a high degree of SAM order, a phenyl ring to provide orientation dependent X-ray absorption, and a carboxylic headgroup that can be varied in position and number around the phenyl ring. Our results reveal the critical role that SAM flexibility and reorganization plays in template-directed nucleation. When the headgroup structure allow the SAM monomers to reorganize, templating occurs with a high degree of control over crystal orientation. However, even when the headgroup chemistry is the same, an inability of the SAM to reorganize leads to random crystal orientation.

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: 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 Wright State University (Dr. Steven R. Higgins, Grant: DE-FG02-03ER15379), the project emphasis at LBL is high temperature macro-scale experiment development, HAFM capability development and VSI measurements. During this first year of the project, a considerable effort was required to renovate a lab at LBL, and then to move and reinstall equipment from Livermore to Berkeley. A commercial AFM (DI MultiMode w/ Nanoscope IV controller), the home-made Hydrothermal AFM and all its accessories, and 6 hydrothermal experimental systems (plus pressure vessels, pumps, etc.) were moved and made operational at LBL.

The macroscale dissolution results obtained at WSU (Fig. 1a) clearly suggest that sample history can impact reactivity, especially at short time. The initially high dissolution rate and the relaxation time required to achieve solution composition controlled dissolution rate can both result from an initial surface morphology created under different solution composition conditions. We used VSI to characterize the "as prepared" synthetic calcite crystals and observed some large etch pits (Fig. 1b) apparently created by the very brief washing they received when removed from the growth media.

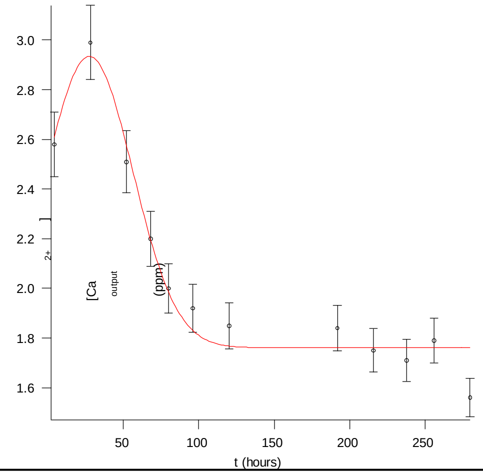

Fig 1a Ca^{2+} output concentration (related to dissolution rate) vs. time from pseudo-macroscale reactor experiments using synthetic calcite crystals

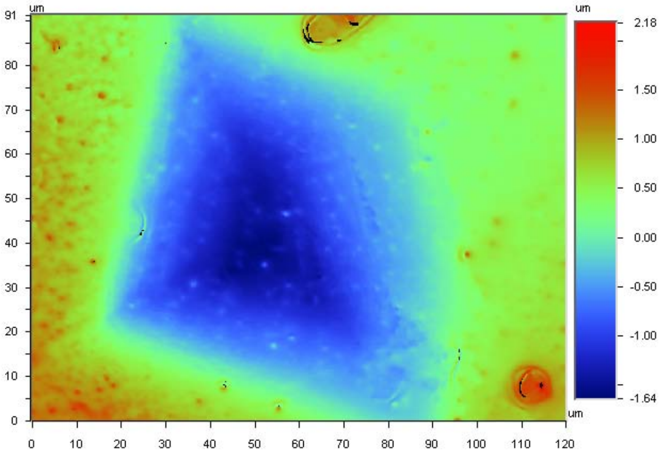

Fig. 1b VSI image of synthetic calcite

The step density within the etch pit is significantly higher than the step density achieved at steady state under near equilibrium solution composition. This could account for the initially high dissolution rate observed. We also performed geochemical modeling calculations to aid WSU in designing their experimental solution compositions and in interpreting their results.

Following installation of the HAFM at LBL, we completed the last of the tests of the custom etched foil heater. This involved measuring optical head surface temperatures at a variety of flow cell temperatures. We are presently evaluating the efficiency of optical head cooling achieved with our new water-cooled Cu base plate.

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Aqueous Geochemistry at High Pressures and Temperatures

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Objectives: The goal of this study is to understand 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 (~ 15 km 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: One of the major technical difficulties that has limited spectroscopic measurements on fluids under high pressure and temperature conditions was the lack of instrumentation that could generate the required pressures and temperatures and remain stable over long periods of time. The LLNL group has focused on the design, and production of a new generation of high temperature diamond anvil cells for use in Brillouin scattering measurements with a ~50° scattering geometry. The cells were tested and Brillouin spectra were collected at UIUC jointly by both groups. LLNL has taken the lead in the experimental infrastructure and training of UIUC staff and graduate students and has profited from the experience of the UIUC group in Brillouin experiments. Together, both groups have made significant progress in furthering Brillouin spectroscopic techniques at high pressures and temperatures. To date, we have collected high pressure and high temperature Brillouin data on liquid CO_2 and several solid CO_2 phases (I, II, III, IV). For the first time, data was collected on the dynamics of CO_2-IV up to P=18 GPa and T=450°C. We performed Brillouin experiments on supercritical water up to 500°C at 2 GPa, well above the temperatures of previous high-pressure measurements. We have made our first measurements of the sound velocities of H_2O-NaCl solutions, obtaining high-quality data to 7 GPa and 500°C. These are the highest P-T velocity measurements performed to date on aqueous solutions. Furthermore, in FY09 we began construction of a new high temperature DAC for Brillioun spectroscopy in a 90° scattering geometry. The design uses custom built conical diamonds in a Boehler-Almax style seat arrangement. Modifications to the Brillouin system are being made to accommodate the newer DAC design for 90° scattering, which will be advantageous for all future measurements.

Quantification of Mineral Precipitation Kinetics Using Solution Chemistry and NMR Spectroscopy

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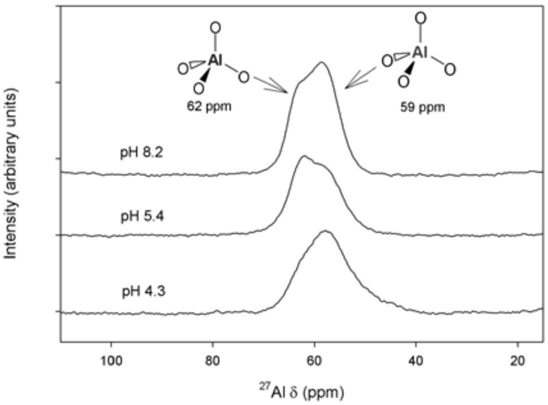
Objectives: This project investigates aluminum geochemistry in the presence of silicate phases combining water chemistry with NMR to determine the reaction mechanism responsible for the observed effect of dissolved aluminum on silicate reaction rates.

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 in FY09 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^{o}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.

Kinetic Isotope Fractionation

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Objectives: The primary objective of the proposed research is to explore and quantify major element isotopic fractionations (i.e., "isotopic fingerprints") associated with mass transport processes within and between phases, one of which is in most cases a liquid – either water or a silicate melt.

Project Description: The Lawrence Livermore National Laboratory part of this project involves measuring the isotope fractionation of chemically diffusing species using the GV IsoProbe and the Nu Instruments multi-collector ICP-MS and the Cameca NanoSIMS. In FY08 we proposed to make new basalt-rhyolite diffusion couples similar to those used in Richter et al. (2003) to measure the kinetic isotope fractionation of Mg and Fe associated with the chemical diffusion of these elements between molten basalt and rhyolite. We also propose to expand studies of isotopic fractionation driven by thermal gradients (i.e., Soret diffusion), focusing in particular on the heavy elements, Pb and U.

Results: The LLNL activities in FY09 focused on (1) characterization of Pb and U isotopic and elemental fractionations during thermal diffusion experiments, and (2) investigation of K and Na elemental fractionation during evaporation experiments. The thermal diffusion experiments were performed on a homogeneous silicate glass that had been doped with U (natural isotopic composition) to ~200 ppm. Because Pb is easily lost during the preparation of the experiment starting glass, Pb was added to the starting glass at a lower temperature, immediately prior to the initiation of the thermal diffusion experiment, for a Pb concentration in the experiment of ~300 ppm. Upon completion of the experiment, the charge was cut into seven pieces perpendicular to the thermal gradient, each of which was analyzed as a bulk sample. Concentrations of U and Pb in the glasses were measured by ICP-MS. Although U and Pb concentrations vary across the thermal gradient of the experimental charge, they do not show the systematic variability of major element gradients observed in earlier experiments. Uranium isotopic compositions vary slightly across the thermal gradient, but the overall variation is much smaller than the percent-level variations observed in light elements (Mg, Ca). Lead isotopic analyses are underway, as are additional experiments to verify these results and expand the range of thermal conditions for investigation.

A series of experiments were completed to investigate the elemental and isotopic fractionation of Na and K during evaporation of chondrule-like liquids in a vacuum. Concentrations of Na and K were measured by ICP-MS in residues remaining after evaporation for variable amounts of time. Our results validated concentration measurements that had been measured on the same samples by electron microprobe. These results were used to calculate evaporation coefficients for Na (γ_{Na}

= 0.09) and K (γ_K = 0.06). These new values indicate that the evaporation rates of these two elements from a chondrule-like melt are lower than expected based solely on their vapor pressures.

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:

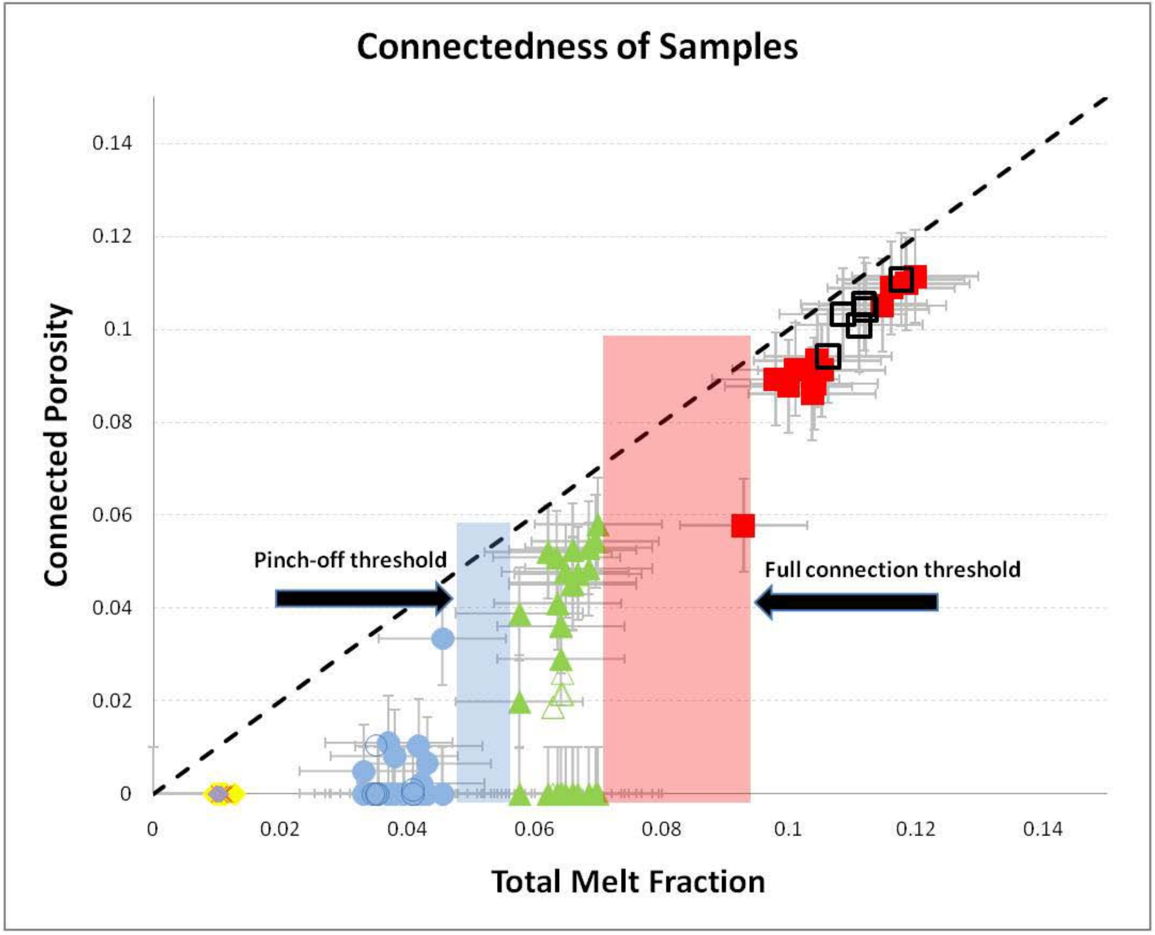
1. Synthesis and characterization of compositionally relevant silicate-sulfide partial-melts.
2. Perform x-ray microtomography on recovered samples and relate the 3D melt structure to transport properties.
3. Perform electrical conductivity measurements on the partial-melts at controlled conditions.
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: In FY09 several significant results were achieved, including two conference abstracts, successful proposals for tomography beamtime at ALS and APS. A key achievement was the completion of two full series of X-ray tomography measurements on the partial melt samples before and after the electrical conductivity experiments. We have also completed a complete series of lattice Boltzmann calculations of permeability on up to twelve sub-volumes of each sample, and quantified the full connection threshold and the pinch-off threshold of the samples

(Figure 1). This amounts to almost an order of magnitude increase in the number of measurements done previously. We have also calculated a reasonable upper bound for permeability of sulfide melts in an olivine matrix, and migration velocity at conditions appropriate to planetesimal differentiation.

Further development of measurement, imaging and analysis techniques has resulted in higher quality data in all aspects of the project. X-ray micro-tomography was performed at the Advanced Light Source beamline 8.3.2. at a routine spatial resolution of 1.8 microns Similar micro-tomographic measurements (in-situ) on sulfide bearing olivine samples undergoing deformation at high pressures and temperatures were performed at the Advanced Photon source (GSE-CARS beamline). These promising new results and techniques will expand the scope of geological and physical problems that can be addressed with the current methodology.



Geochemical Imaging with the NanoSIMS

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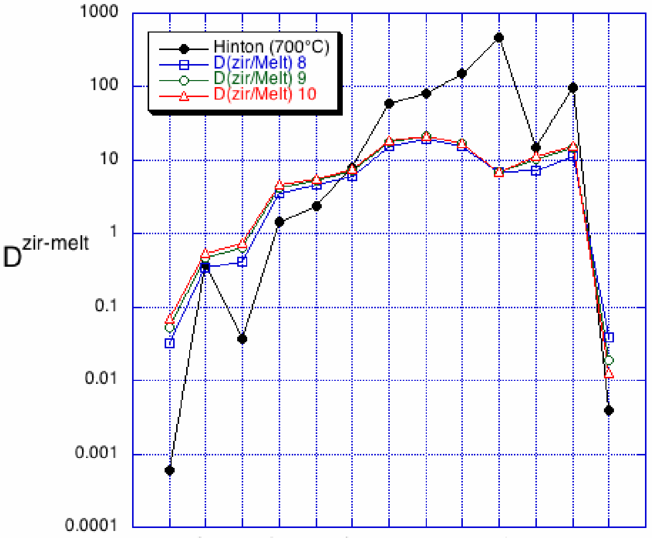
Objectives: The objective of the project is to develop the operating procedures and fundamental parameters required for the routine application of the NanoSIMS, the latest development in elemental and isotopic microanalysis, to geochemical problems, by addressing problems that cannot be solved without this capability. We will determine the relative sensitivity factors required for quantification, investigate the use of energy filtering and quantify parameters such as the M^+/MO^+ relative ion yields for a variety of geochemically important trace elements and matrices. We will couple the chemical imaging capabilities of the NanoSIMS with the synthesis capabilities of the laser-heated diamond anvil cell to determine the partitioning of trace elements among phases characterizing the earth's lower mantle. We are also investigating the partitioning of trace elements between zircon and melt to support studies of zircon provenance. Finally we will develop the combined use of conventional SIMS and NanoSIMS profiling to obtain average lattice and grain boundary diffusion coefficients and to sample diffusive anisotropy at the individual grain level.

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 must, however, be verified and 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. The applications include: (1) experimental determination of trace element partitioning between zircon and melt, and chemical imaging of natural zircons to assess chemical changes induced by radiation damage, (2) an experimental investigation of the partitioning of transition metals in lower mantle phases, applying the NanoSIMS to materials synthesized in the diamond anvil cell (DAC) and determining the effects of pressure induced spin-state transitions on mineral composition, and (3) the development of methods to determine diffusion profiles in single micron-size grains in a polycrystalline matrix, enabling the investigation of the effects of composition on diffusive transport in minerals.

Results: Along with preservation of isotopic signatures, the trace element chemistry of detrital zircons can also serves as indicators of provenance. This, however, is dependent upon the relationship of zircon chemistry to that of source magma and requires experimental determination of the partitioning of minor and trace elements between zircon and, *sensu lato*, granitic melts. Surprising, given its ubiquity, there are very few measurements of zircon-melt partitioning. Watson [1980] obtained partitioning data for two REEs between zircon and a peralkaline granite, determining the relative slope of the



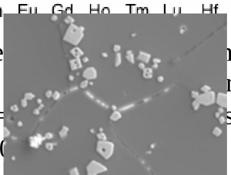


Figure 1. Zircon-me nts at 1100°C for
and andesitic melt red to those of
Hinton (estimated T= s zircons in glass
matrix (scale bar is 1(

REE partitioning trend. Thomas *et al.* [2002] measured zircon-melt partition coefficients using a novel method in which natural melt inclusion were rehomogenized in the lab. In addition, zircon-melt data have been obtained from a natural phenocryst matrix pair (data from Hinton, presented in Blundy and Wood, *Rev. Mineral. Geochem* 52 [2003]). (Figure 1). Here we are utilizing the high spatial resolution imaging capabilities of the NanoSIMS to determine zircon-melt partitioning for a range of "granitic" ranging from tonalite to dacite compositions.

Results from our experiments reveal two particular challenges: (1) the complexity of the secondary ion mass spectrum and (2) the difficulty in growing zircons of sufficient size even for NanoSIMS analysis. To circumvent the first problem, we now dope our experiments with a trace element solution comprising mono-isotopic REEs and isotopically-enriched REEs obtained from Oak Ridge National Laboratory**.** The REE tracer utilized in these experiments La, ^{140}Ce (>99.5%), Pr, ^{152}Sm (>98%), ^{152}Eu (>92%), ^{158}Gd (>95%), Ho, Tm and Lu. Barium has been eliminated from the trace element budget due to barium oxide interferences of the REEs. As the Ba, like Pb, is expected to be extremely incompatible in zircon, little is lost by this omission. Other elements of interest such as Hf, Nb, Ta, Th and U have been retained, and glass standards matching the compositions of the melts in Table 1 have been synthesized for calibration.

The partition coefficients obtained for an andesitic composition AA 1100°C are in reasonable agreement with those from Hinton although LREE/HREE fractionation is "flatter" and Lu/Hf partitioning much less pronounced. Both features could be explained by beam overlap and we are attempting to grow larger crystals in "seeded" runs to minimize these effects.

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Nonlinear Elasticity in Rocks

Paul Johnson, 505-667-8936, paj@lanl.gov; Bill Carey, Pierre-Yves LeBas; Robert Guyer, Tim Darling (University (University of Nevada, Reno); Cedric Payan (Universite du Meditereanée, Aix-en-Provence, France)

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. Included in chemistry is separating the role of the material from the influence of water. 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.

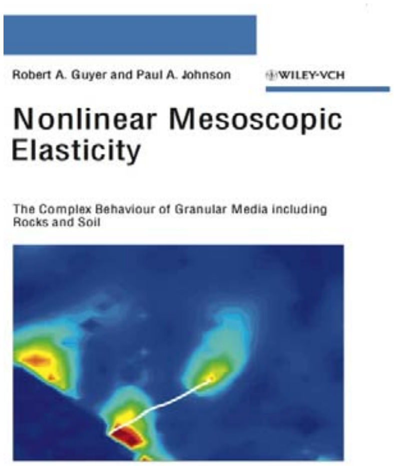
Results: We have a number of topics and results to present from this year's efforts. Work includes basic research exploring pressure, temperature, humidity, and the effects of supercritical CO_2 on carbonate rich rock.

(1) We recently published a book on the topic of nonlinear elasticity (Publication date August 19, 2009; Fig. 1). Much of the actual work in writing the book was supported by OBES, and

many of the experimental and theoretical results described in the book were supported by OBES in years past.

(2) We developed a method based on coda wave interferometry to determine acousto-elastically-derived, third order nonlinear coefficients. Much of the development took place using samples of concrete, an example of a material that exhibits strong multiple scattering as well as significant elastic nonlinear response. We show that intense scattering in Earth and some industrial materials can be employed to robustly determine velocity changes at progressively increasing applied stress using coda wave interferometry. We can thereby extract nonlinear coefficients, the so-called Murnaghan coefficients, and the combination of these coefficients, β, known as the first order nonlinear parameter. This work, published this year in *Applied Physics, Letters* was conducted in collaboration with the University of the Mediterranean (Aix-en-Provence, France).

(3) 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 know that fluids have an enormous influence on nonlinear response from past work. Our goal is eliminate fluids under temperature and hard vacuum. We have taken samples to 800 degrees C in air in order to test the vessel. We will attempt to conduct the acoustical tests in the next run, under hard vacuum. This will eliminate all fluids, including monolayer fluids. The apparatus, which took 8 months to assemble, has a mass spectrometer that will used to determine when the sample is perfectly dry. This work is being conducted in collaboration with the University of Nevada, Reno.
We developed a second pressure vessel measurement system in order to subject rock samples to supercritical CO_2 while applying nonlinear diagnostics. In preliminary experiments completed one year ago, 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. The observation indicates that there is a redistribution of the carbonate phase (including some mass loss) that results in a distinct change in mechanical properties related, we believe, to healing. This past year we added an automatic nonlinear acoustic experimental and data collection apparatus. The development took about 5 months but is now operating. We tested the new system exposing carbonate rich sandstones to CO_2 only (no water). Tentatively we see changes in the nonlinear elastic behavior while the linear modulus and density appear unchanged. 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.


Robert A. Guyer and Paul A. Johnson

WILEY-VCH

Nonlinear Mesoscopic Elasticity

The Complex Behaviour of Granular Media including Rocks and Soil

Figure 1. Cover of book written by R. Guyer and P. Johnson on the topic of elastic nonlinearity in materials with emphasis on geomaterials, published in August 2009 by Wiley VCH.

Elastic Wave Effects on Colloid Interactions and Their Influence on Porous Fluid Transport

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Objectives: The geophysical and physicochemical processes coupling stress waves to porous mass transport behavior are being investigated experimentally. The major goals are to: 1) quantify the physical and chemical conditions under which stress waves influence porous fluid flow and sub-pore size (colloidal) particle transport, and 2) obtain improved experimental data that will be used to validate and quantify detailed understanding of physical mechanisms.

Project Description: This project is investigating how elastic waves can alter the transport of solid particles and immiscible liquids in geologic porous media. Understanding this phenomenon will allow it to be harnessed for valuable applications, such as enhanced oil recovery and groundwater remediation. Of particular interest, the mechanism of elastic waves coupling to sub-micron particle (colloid) interactions has been observed over a wide range of frequencies (roughly 10 Hz to 10 MHz). This mechanism can induce pore-scale colloid attachment and/or detachment at solid surfaces at frequencies within the range listed above, and the resulting induced redistribution of colloids in a porous matrix causes profound changes in permeability. Thus, this is an important mechanism influencing porous transport at larger geologic scales (cm to km). Understanding the physical, chemical, and dynamic-stress parameters that control colloid interactions with themselves (aggregation) and with solid surfaces (attachment and detachment) is also important to this research project, using advanced conceptual understanding, unique facilities and capabilities. The scale dependence of these interactions being investigated involves microscopic colloid visualization and core-scale fluid and colloid transport.

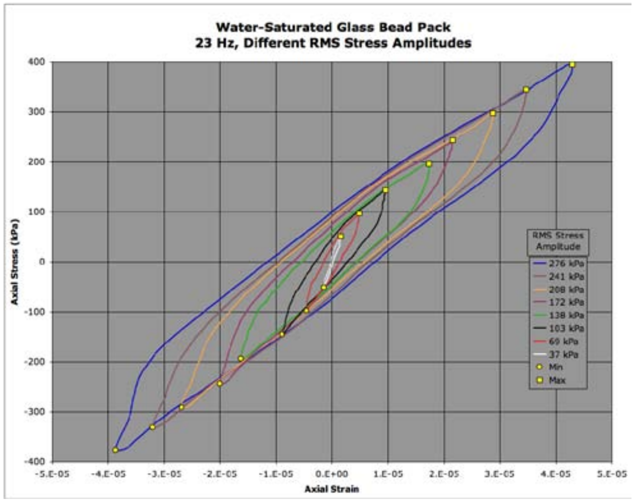

Figure 1. Stress/strain loops at constant frequency and at different RMS stress amplitudes for saturated bead pack.

Results: We demonstrated previously that low-frequency dynamic stress mobilizes colloids trapped in a synthetic porous medium composed of 1-mm-diameter glass beads and causes cyclic variations in the colloid release rate. The cyclic release behavior only occurred above a certain threshold for applied dynamic stress amplitude. Dynamic, axial stress/strain measurements were used to characterize Young's modulus and energy dissipation for the bead pack over a frequency range of 10 to 30 Hz before the microsphere mobilization experiments were performed. The data indicate a possible link between the nonlinear elastic response of the porous medium and the amplitude-dependent variations in colloid release behavior. Axial stress oscillations were applied to the sample over a range of RMS stress amplitudes from 37 to 275 kPa. Dynamic stress/strain was measured before and after the core was saturated with deionized water. The resulting RMS strain amplitudes ranged from 1.1e-06 to 2.8e-05. The slope and area of the hysteresis loops were used to estimate Young's modulus and energy dissipation as a function of frequency and amplitude for both the dry and wet sample. The modulus and dissipation were observed to increase after the dry sample was saturated. For both dry and wet samples, the modulus decreased and the dissipation increased with increasing dynamic RMS stress amplitude at a constant frequency of 23 Hz. Figure 1 shows the 23-Hz stress/strain loops at different amplitudes for the saturated sample. Notice how the slope between loop extrema (min and max) decreases rapidly and the loop width increases rapidly at lower amplitudes up to about 200 kPa. At constant RMS stress amplitude, the modulus increased strongly with increasing frequency for the wet sample but remained relatively constant for the dry sample. The dissipation showed no frequency dependence in either case. The observed amplitude dependence of Young's modulus (Fig. 2) and energy dissipation (Fig. 3) for the wet sample show a change in behavior at roughly 150-200 kPa RMS stress amplitude and 1e-05 to 1.4e-05 RMS strain that indicates a possible transition from one nonlinear mechanism to another. This transition amplitude is similar to that observed in the microsphere release experiments, where the cyclic release behavior appears at stress amplitudes above 208 kPa. We hypothesize that bead-to-bead strain, rearrangement, and/or rotation are possible causes of this transition. Microscopic visualization of bead behavior under similar conditions supports these possibilities and indicates that bead grinding may also be the cause of the change in release kinetics. Although strain amplitude is the variable that quantifies bulk mechanical deformation of a porous medium, the force distribution in a granular material due to an applied stress is inherently non-uniform. Stress concentrations can produce locally higher grain-to-grain strains relative to the bulk. Thus, quantifying the applied stress and modeling the resulting force distribution are required for testing our hypothesis.

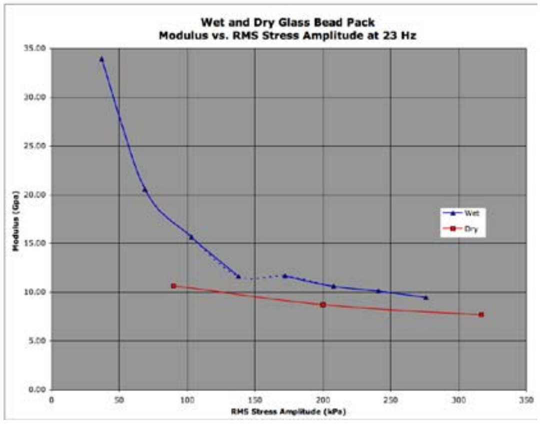

Figure 2. Modulus vs. RMS stress amplitude at constant frequency for dry and saturated bead pack.

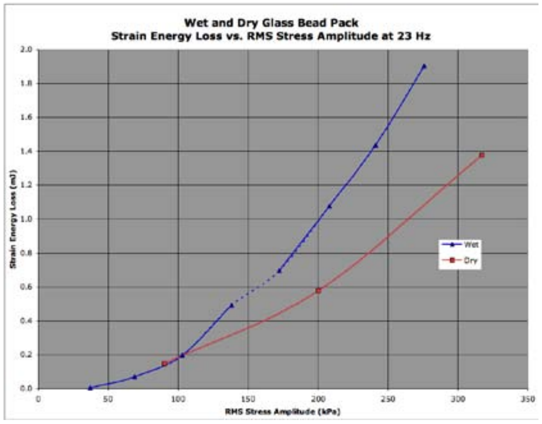

Figure 3. Energy loss vs. RMS stress amplitude at constant frequency for dry and saturated bead pack.

Summer of Applied Geophysical Experience (SAGE)

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Objective: Objectives of SAGE 2009 included: (1) providing hands-on training and research experiences in basic and applied geophysics for 25-30 students and other participants, (2) conducting innovative research with students on a variety of important problems, and (3) introducing students to a range of career options in geophysics. Research results are expected to make significant contributions in a number of national security areas such as development of new energy sources, nuclear and non-nuclear waste disposal, environmental remediation, groundwater resources, and carbon sequestration. In addition, results will also impact basic research related to the structure and tectonics of continental tectonics.

Project description: SAGE 2009 conducted research on three related topics. In the Santo Domingo basin of the Rio Grande rift, SAGE conducted several concurrent surveys to examine basin depth and the role of connected faults in accommodating deformation. This study furthers understanding about how individual faults link into deformation zones that form a major continental extension boundary (Fig. 1). A second project was undertaken to identify and characterize man-made structures at an archaeological site, which was interesting *per se* and also served as a proxy for a small-scale environmental-restoration or waste-disposal site. A third project, added this year, undertook to characterize a small, CO_2-driven cold-water geyser, which is under investigation by the Los Alamos National Laboratory as part of the CO_2-sequestration project.

The geophysical techniques and tools used included: seismic reflection and refraction, gravity, time-domain electromagnetics and controlled-source magnetotellurics, ground penetrating radar, and integration with existing aeromagnetics and geology. SAGE full- and part time faculty from LANL, several universities, U.S. Geological Survey, and companies, each expert in different techniques, instructed and supervised the students.

Results: Twenty seven undergraduate- and graduate students and a senior faculty member from 16 institutions attended SAGE 2009. Data quality and quantity for this year were excellent, thanks in part to industry participation. A major find at the archaeological site was a buried kiva, a 6-m diameter ceremonial structure originally constructed partially below ground level. This discovery will enable a better understanding of social organization of San Marcos in pre-Spanish times. SAGE 2009 repeated last year's unsatisfactory seismic reflection/refraction survey across the Budagher's fault, this time with excellent results (Fig. 1). The structural role played by the Budagher's fault, which links major rift-parallel faults, has never been clear but now seems to break a dipping relay ramp at the margin of the continental Rio Grande rift. Also, gravity data obtained this year filled gaps in our extensive data base, allowing us to extrapolate structural information into areas where detailed geophysical surveys have not been conducted. Finally, our pilot studies at the site of the cold water CO_2-driven geyser focused on a preliminary assessment of the site and on evaluating the feasibility of further surveys. SAGE conducted gravity, TEM, and controlled source MT surveys to search for faults and characterize electrical resistivity.

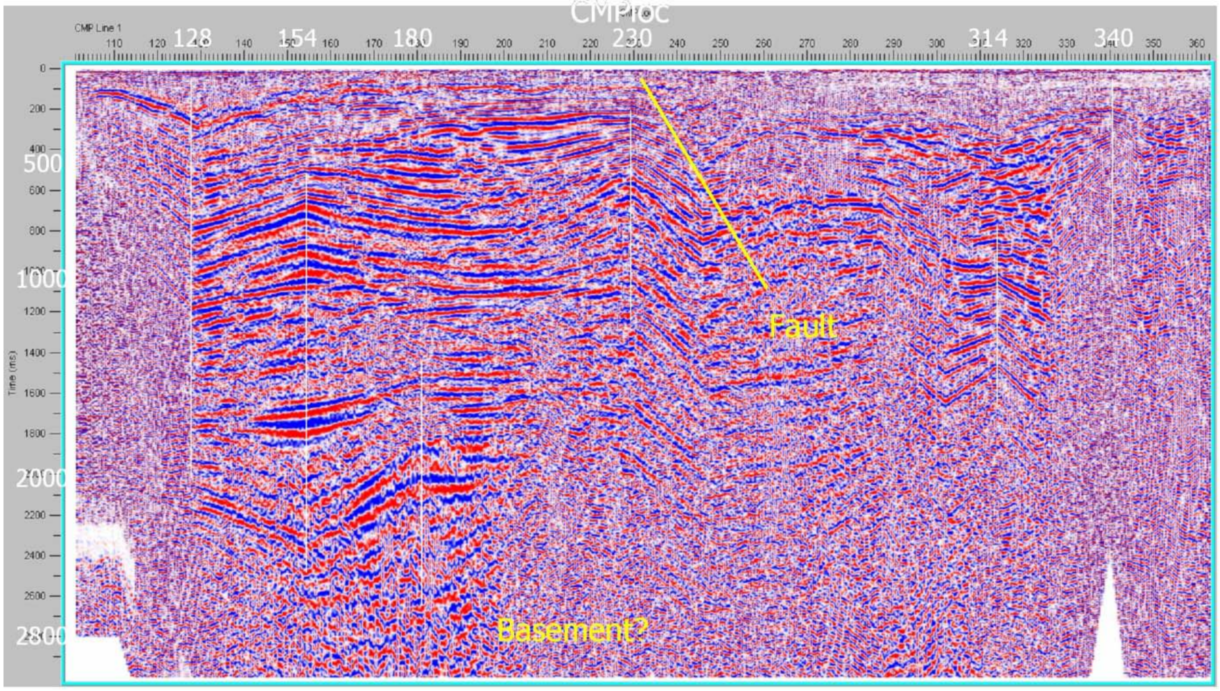

Figure 1. Seismic reflection time and depth section across the Budagher's fault, Rio Grande rift, acquired during SAGE 2009. Source was $30x10^3$ kg vibroseis truck provided by Ion Geophysical Company.

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

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

Results: We have measured U-Th concentrations and isotopic compositions from 5 glass and 2 powdered naturally sourced reference materials from the USGS and the Max Planck Institute. Data were obtained using TIMS and MC-ICPMS instruments. A comparison of powdered source materials with the resulting glass standards found a few occasions of significant difference, suggesting that the values determined in the powdered standards should not be assumed for the glass versions. While not affecting the utility of the result, we were surprised to see that one of the older samples was substantially out of secular equilibrium. These are the first reported U-series results for these solid standards, and the data will benefit the greater earth science community by enabling more accurate and precise reporting for a broad range of U-series work. These new [Th]/[U] and activity ratios can be used for microanalytical studies as well as for bulk sampling in U-series dating and other applications. A manuscript is in preparation for submission to *Geostandards and Geoanalytical Research*. These results will contribute to our project goal of *in-situ* measurements of contaminant transport, fracture flow, and the stability of natural analogs for the long-term storage of high level radioactive waste.

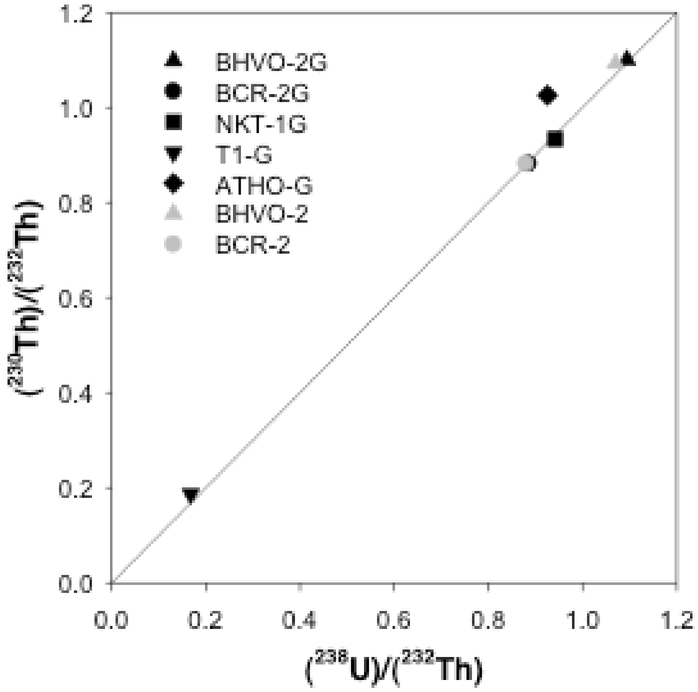

Figure 1. U-Th activity data for all measured SRMs. Glass SRMs are in black, powdered SRMs are in gray. The range in [Th]/[U] is apparent. Sample T1-G despite its age of ~30 Ma is more that 10% out of secular equilibrium. The data point symbols are larger than the 2 sigma error bars.

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Nanoscale Complexity at the Oxide/Water Interface

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Objectives: We seek a complete understanding of the complex, nanoscale domain where crystalline minerals (oxides, silicates) interface with aqueous solutions, over wide ranges of temperature and solution composition. Our goal is to quantitatively link atomic-scale structure and dynamics of interfaces with their macroscopic manifestations, including surface charging, ion adsorption, heterogeneous reaction 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 oxide-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 and electrophoretic mobility; and macroscopic models of the of 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). These properties of the substrate are hypothesized to exert a fundamental influence on the nature of ion adsorption and interfacial structure and dynamics.

Results: Studies were completed of the charging of cassiterite powder suspensions in NaCl and RbCl brines from 10-50°C via pH titratrions as a function of temperature and ionic strength. These were coupled with electrophoretic mobility studies of the same powder to 260°C using a high temperature zetameter. The isoelectric pH's determined from the electrophoretic mobility studies are consistent with the pH of zero net proton charge determined from the titrations. Both sets of results were found to be consistent with predictions of the point of zero charge of cassiterite from the MUSIC model, with surface bond lengths taken from *ab initio* DFT calculations, and hydrogen bonding to surface oxygens obtained from classical MD simulations of the cassiterite (110) surface. The pH of zero charge is determined by the distribution of species associated with two specific surface sites, bridging $\equiv Sn_2OH$ and terminal $\equiv SnOH_2$ sites. On isostructural rutile, the equivalent bridging site is more acidic than the terminal site, whereas on cassiterite, the terminal site is more acidic than the bridging site. This is entirely consistent with our previous DFT studies of these surfaces which indicate that water that chemisorbs at the terminal site is much more likely to dissociate to form bridging and terminal hydroxyl groups on cassiterite surfaces, whereas the rutile surface is largely decorated by bare bridging oxygens and terminal water molecules. These differences appear to arise largely from the much higher polarizability of the electron cloud around Ti atoms than around Sn atoms, which also manifests itself in a large difference in the bulk dielectric constants of the two phases (~121 for rutile, vs ~ 11.3 for cassiterite, as compared to bulk water, which at room temperature has a bulk dielectric constant of 78.5). The modified MUSIC model predictions are also consistent with the lower pH of zero net proton charge on cassiterite (4.3) than on rutile (5.4). In addition to a large difference in the bulk dielectric constants of rutile vs cassiterite, both the pH titrations and MD simulations demonstrate significant differences in the sorption of cations on the two minerals. Na^+ binding on rutile is much stronger than on cassiterite, whereas Rb^+ binding is nearly the same on the two phases. This arises from the observation that on both mineral surfaces, Rb^+ sorbs predominantly at a tetradentate site involving two bridging and two terminal surface sites. Na^+, on the other hand, binds almost entirely at bidentate sites between two terminal oxygens and between a bridging and terminal oxygen on cassiterite, whereas on rutile, the tetradentate site is also important. The result is that sodium ion is able to approach the rutile surface more closely on rutile than on cassiterite, giving rise to enhances surface charge density for a given pH, temperature and ionic strength. This difference in ion adsorption appears to be mainly controlled by the larger unit cell parameters of cassiterite versus rutile, such that the small sodium ion is not able to form a stable tetradentate complex.

During this period, analysis was also completed of quasielastic (QENS) and inelastic (INS) studies of rutile and cassiterite nanopowders with the (110) crystal face predominant. The QENS studies were conducted using the High Flux Backscatter Spectrometer at the National Institute of Standards and Technology. The rutile nanopowders were prepared at three hydration levels: a.) fully hydrated, containing the three structural water layers (L_1+L_2+L_3) that were identified in our MD simulations and which form spontaneously on rutile powders exposed to laboratory air with about 75% relative humidity; b.) partially dehydrated, with L_1+L_2+0.3L_3 coverage; and c.) dehydrated, with just L_1+0.5L_2 present. The QENS results, combined with MD simulations, reveal a translational diffusive motion of L_2 water molecules on the nanosecond time scale that exhibits Arrhenius behavior at temperatures below about 220K and a strong-fragile transition to much faster dynamics at higher temperatures. Interestingly, the diffusive motions of L_2 become faster with decreasing total coverage, with the dynamic transition shifting to higher temperature for the intermediate water coverage, and disappearing altogether at the lowest water coverage. Our MD simulations were able to capture the essential features of the dynamics and show that the essentially temperature-independent and fast diffusion at the lowest coverage, observed from 195 to 340K, can be attributed to competing effects of collective motions of rows of L_2 water molecules and the much faster motions of individual water molecules that escape from the ends of such a row and move quickly around the surface before reconnecting to an adjacent row. This behavior is significant for two reasons: a.) It is the L_2 water that hydrogen bonds to surface oxygens, greatly influencing the protonation constants of these surface oxygens and thus the charging and ion adsorption characteristics of the minerals; and b.) we have documented fast water diffusivities at temperatures well below the freezing point of bulk water, which has important implications for geochemical reactions under low temperature conditions (e.g., permafrost, cosmic dust, the surface of the Moon, etc.).

We have completed and published the first in a series of papers from our *ab initio* molecular dynamics simulations of rutile and cassiterite (110) surface at $L_1+L_2+L_3$ coverage (and lower coverages), using ORNL's Cray XT3 (Jaguar) supercomputer. The results are entirely consistent with our classical MD and static DFT calculations, and also with inelastic neutron scattering studies conducted at Argonne's Intense Pulsed Neutron Source. Our results show much more dissociation of water on cassiterite than on rutile, and a 10-fold increase in proton transfers between terminal and bridging sites on cassiterite, facilitated by the presence of strongly-hydrogen-bonded L_2 water molecules. The AIMD simulations nearly perfectly reproduced the vibrational density of states obtained in the INS experiments.

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

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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: Water and aqueous solutions are undoubtedly the most widespread, important fluids in natural environments, including deep-earth conditions (*e.g.*, geothermal-hydrothermal systems, volcanoes, subduction zone), where temperature and pressure may exceed 1000ºC and 10 GPa, respectively. To understand the thermophysical and transport properties of water and aqueous fluids under deep-earth conditions, we have investigated the evolution of the tetrahedral character of the hydrogen-bond network in water, perhaps the most important structural characteristics of liquid water, to high temperatures and pressures conditions (*e.g.*, T>500ºC and P>5 GPa) by means of isothermal isobaric molecular dynamics simulation of our advanced water model, Gaussian Charge Polarizable model (GCP). The main target was to: (a) address explicitly the role played by the polarizing environment on the water coordination resulting from the induced charge asymmetry on the water's hydrogen sites, (b) discuss its significance as well as implications for understanding the hydrogen-bond structure in light of the recent controversial interpretation of X-ray absorption spectroscopic data, and (c) characterize the dramatic change of water coordination from the open tetrahedral network to the closed-packed twelve-coordination under extreme, but geologically relevant aqueous environments. Our important discoveries include a strong and direct link between water's induced dipole moment (molecular polarization in the local and condensed environment relative to isolated water molecule) and the strength of the tetrahedral character of the hydrogen-bond network (characterized by the so-called 'tetrahedral parameter'). It was found that with increasing temperature and particularly pressure, water transformed from the well-documented, open four hydrogen-bonded network to a compact, twelve coordinated molecular system of the Lennard-Jones type. A recent high-pressure (5 GPa) neutron diffraction study of water supports our finding of closed-pack coordination of water.

The high-pressure behavior and isotopic properties of brucite and calcite were investigated by means of high-pressure neutron diffraction and thermophysical modeling. The observed systematic differences in unit-cell volumes between $Mg(OH)_2$ and $Mg(OD)_2$ under high pressures confirmed for the first time that the reduced partition function ratio (β-factor) of brucite increases by 370 ‰ with pressure to 10 GPa, which is consistent with our previous calculations and a recent Density Function Theory study to 1 GPa. This result has a direct implication for the distribution of hydrogen isotopes in hydrous minerals in the deep-earth. Brucite preferentially incorporates deuterium over hydrogen with increasing pressure. This pattern of deuterium enrichment in brucite continues at least to 10 GPa, suggesting that D/H fractionation between hydrous minerals and water under mantle conditions differ significantly from near-surface environments. We have also constructed a unified model for calcite to elevated temperature and pressure. This improved vibrational density-of-state based model predicts very accurately thermophysical properties (*e.g.*, heat capacity), equation of state, and isotopic properties of C, O, and Ca up to 1500 K and 2 GPa. The effect of pressure and other anharmonic effects with increasing temperatures and pressures were explicitly treated, using Grüneisen and intrinsic anharmonic parameters. Results from our calcite model are largely consistent with experimental results for thermophysical properties and isotopic fractionation under elevated temperatures and pressures.

Rates and Mechanisms of Mineral-Fluid Interactions at the Nanoscale

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Objectives: The purpose of this effort is to advance our fundamental understanding of rates and nanoscale-level mechanisms of mineral-fluid reactions both near and far from equilibrium, over the full range of temperatures and compositions encountered in near-surface shallow crustal environments.

Project Description: Determination of the rates of dissolution-precipitation and isotopic exchange at variable departures from equilibrium will be coupled with a mechanistic description of the initiation of reactions at reactive surface sites. Detailed investigation of the formation of, and chemical communication across, leached layers and reaction zones, and the structure and dynamics of fluid species present in porous reacted solids will contribute to a more complete understanding of equilibrium/disequilibrium processes preserved in the mineralogical record resulting from water-rock interaction. We will measure the rates of dissolution and precipitation near- and very-near equilibrium that utilizes our unique, high temperature, *in situ* pH measurement facilities. We will also interrogate the nature of porosity generation and its role in fluid transport and confinement in mineral reaction zones using advanced chemical and isotopic imaging approaches (e.g., secondary ion mass spectrometry, Fourier infrared spectroscopy, neutron scattering, and others) coupled with modeling and simulation.

Results: This project involves a multi-disciplinary-multi-institutional team focusing on various aspects of fluid-matrix interactions from ambient conditions to elevated temperatures and pressures.

Detailed analysis of quartz dissolution and precipitation rates, determined at 125-200°C in 0.1m NaCl at pH 8-10 using a unique, high-temperature pH perturbation and monitoring technique, indicates two distinct reaction mechanisms controlling dissolution rates near, and very near equilibrium. The faster rate is suggested to be associated with etch pit opening, and does not influence dissolution until a sufficient degree of undersaturation is achieved in order to overcome the activation energy for this process. The slower rate, which applies at all degrees of undersaturation, is interpreted to be associated with step edge retreat. The two reaction rates are additive, and at far-from-equilibrium conditions extrapolate within experimental error to published far-from-equilibrium rates obtained by several researchers using conventional flow-through techniques. Both reaction mechanisms are described by transition state theory, suggesting a single rate-limiting fundamental reaction. Also, our limited precipitation results indicate that both rates apply even very close to equilibrium for the equivalent precipitation processes, step edge advance and growth hillock formation, described by the same TST equations.

We have completed a detailed investigation of the solubility of hematite in near-neutral NaCl solutions at 200°C in order to: a.) resolve the hydrolysis speciation of Fe^{3+} in aqueous systems; and b.) to aid in the interpretation of our magnetite-hematite transformation rate studies. The dissolution of hematite to the neutral $Fe(OH)_3^o$ species in circumneutral solutions follows behavior previously predicted by this group in past publications, giving us confidence in our interpretation of the behavior of solutions in contact with magnetite-hematite mixtures over a range of pH and temperature conditions. The transformation of magnetite to hematite under highly reducing conditions as a result of acid-leaching of Fe^{2+} out of the magnetite lattice appears to be limited at temperatures of 100°C or less by the stability of maghemite (γ-Fe_2O_3), which is isostructural with magnetite (α-Fe_3O_4), and at temperatures of 200°C and higher by the redox-equilibrium dissolution and precipitation of magnetite. At intermediate temperatures, hematite precipitates and only very slowly transforms to magnetite under reducing conditions due to the slow kinetics of reduction of Fe^{3+} to Fe^{2+} in the aqueous phase.

Relying heavily on FTIR and SIMS isotope-tracer methods, we have interrogated the speciation and transport of hydrogen-bearing species in a number of solid-fluid systems: synthetic glass and natural obsidian, alkali feldspars, olivine and uraninite. Our studies of the interaction of water vapor (used to avoid dissolution) with obsidian, silica glass and albite glass below their glass transition temperatures (T_g) have revealed new insights into the mechanisms and rates of water uptake into glass. For example, SIMS profiles of D and H in glasses reacted with water vapor from 30 to 150°C exhibit a complex s-shape indicative of concentration- and time-dependent, non-Fickian diffusion influenced by the build-up and relaxation of self-stress caused by influx of diffusing water species. Complex-s-shaped and stepped H and O profiles have also been documented in alkali feldspars altered by cation exchange at elevated temperature (600°C) and pressure (200MPa). In this case there is a structurally complex reaction front formed by replacement of adularia or sanidine by albite. Sanidine exhibited an equilibrated replacement rim, whereas adularia showed a continuous change in composition with depth. We also observed that O and D diffused into the unreacted crystal beyond the chemical reaction front. FTIR results indicate that the dominant H and O transport species in reacted adularia was H_2O but OH^- was also present in modest quantities.

We used a combination of TEM and SANS- and ultra small angle neutron scattering (USANS) 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. SANS and USANS data from bulk samples provide quantitative insight into pore geometry, pore orientation, pore surface area and the fractal nature of pore wall surfaces. 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. Data were also obtained from samples collected along two transects in the metamorphosed Hueco limestone at the Marble Canyon, Texas, contact aureole. Significant changes are observed in the surface and mass fractal dimensions as well as the correlation lengths (pore and grain sizes), surface area to volume ratio and surface Gibbs free energy as a function of distance, including regions of the aureole outside the range of classic reaction petrology.

We used SANS to study the sorption properties of sub- and supercritical fluids inside mesoporous (~60Å pores) silica. The Adsorbed Phase Model (APM) developed at ORNL allows, for the first time, a means to quantify the physical properties of the adsorbed phase formed by fluids inside porous media in terms of the mean density and volume of the sorption phase. Knowledge of these quantities permits the model-free calculation of the absolute adsorption, a property relevant to application of adsorption equations and molecular modeling. The APM model has been applied to the SANS data obtained for sorption of CO_2 and d-propane in silica aerogel at supercritical conditions. Our results show clear evidence for fluid depletion for conditions above the critical density of the bulk fluid. The density and volume of the sorption phase change in a sensible, complex fashion as a function of pressure and temperature. We have also used quasielastic neutron scattering (QENS) to investigate the dynamical behavior of water in aqueous solutions (LiCl, $CaCl_2$) confined in silica pores ranging in diameter from 13.5 to 40Å. We found that the effect of dissolved ions on the translational dynamics of the water molecules in solution was amplified by confinement by at least an order of magnitude compared to the bulk aqueous solutions, whereas rotational dynamics slows down much less, usually by a factor of two or less. The greatest suppression of water mobility was observed in the $CaCl_2$ solutions (more than order of magnitude slower H_2O diffusivity compared to pure H_2O), which suggests that cation charge and perhaps the cation hydration environment have a profound influence on the dynamics of the water molecules. Our recent MD simulations of 1 molal LiCl in 13.5 Å silica pores indicate that solvated ions tend to concentrate near the center of the pore at ambient conditions (30^{o}C), whereas at elevated temperature, 500^{o}C, the Li and Cl ions more readily compete with water molecules for surface sites on the pore wall.

Center for Nanoscale Control of Geologic CO_2

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Objectives: The overarching goals of the LBNL-led 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 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 will use 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 will be synergistically link 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.

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

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Objectives: This Small Group Research project funded through Pacific Northwest National Laboratory 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 ORNL-led portion of the project concerns the study of the pristine and reacted minerals (e.g. olivine, muscovite) and the properties of sorption phase formed at the mineral grain surfaces. Neutron scattering experiments (SANS) carried out at the neutron sources in Oak Ridge and NIST Gaithersburg will measure the surface area and fractality of different minerals found in caprock formations (i.e., phyllosilicates and orthosilicates) in pristine and reacted states. The pristine and reacted minerals will be provided from our collaborators at PNNL. The second subtask studies the sorption from mixtures of CO_2 and water (D_2O) to pristine and reacted mineral surfaces.

Results: The goal of this SANS study is to measure the density and composition as well as the volume (thickness) of the sorption phase for different conditions of temperature and fluid mixture composition. The combined analysis of neutron scattering and sorption analysis 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.

PACIFIC NORTHWEST NATIONAL LABORATORY

CONTRACT: RL01830

PERSON IN CHARGE: A. Felmy

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

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Objectives: Research is evaluating the mechanisms by which ferrous iron [Fe(II)] induces the recrystallization and reductive transformations of ferrihydrite (FH) and lepidocrocite (L). These two structurally dissimilar mineral phases are the most common and reactive Fe(III) oxides found in soil, sediment, and subsurface environments that experience redox cycling. We speculate that the mechanisms and rate of Fe(II) delivery to oxide-water interface, and the generation of localized domains of Fe(II) surface site saturation, are of primary importance in determining the nature of mineralization products. Our specific objectives are to explore 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), 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 have focused on the $Fe(II)_{aq}$-, AH_2DS-, and FMNH- FH/L systems as we work out details for the more complex experiments with cytochromes of different heme contents. The cytochrome experiments require a physiologic reductant to maintain heme groups in the reduced state. The physiologic reductant must not react with the mineral phase; duriquinol and NADH have been evaluated with NADH exhibiting the best properties. We have observed surprising differences in reactivity between FMNH, and $Fe(II)_{aq}$ and AH_2DS; the latter two behaving in like manner. Some have suggested that FMNH, or other flavins of like composition, are secreted by metal reducing bacteria and function as exogenous Fe(III) oxide reductants. Our new experiments reveal that while FMNH undergoes electron transfer with both ferrihydrite and lepidocrocite, no crystalline products result. In contrast, and under identical conditions of redox state, $Fe(II)_{aq}$ and AH_2DS induce rapid re-mineralization to goethite or magnetite depending on reductant to Fe(III) oxide ratios. These results are clearly shown in Figure 1 where pristine lepidocrocite (a.) remains unchanged after 30 days of reaction with FMNH (b.), but recrystalizes completely to the Fe(II)/Fe(III) oxide magnetite (c.) after 30 days reaction with Fe(II). The end states of both of these reaction systems contain equal concentrations of Fe(II), the presumed catalyst for mineral transformation. The absence of mineral transformation for FMNH was unexpected given the hypothesized importance of flavins to Fe(III) oxide reduction and mineralization in suspensions with metal reducing bacteria. It appears that oxidized FMNH adsorbs to the mineral phase, and surface localization of this redox produce may inhibit subsequent dissolution/reprecipitation involved in reductive mineral transformation.

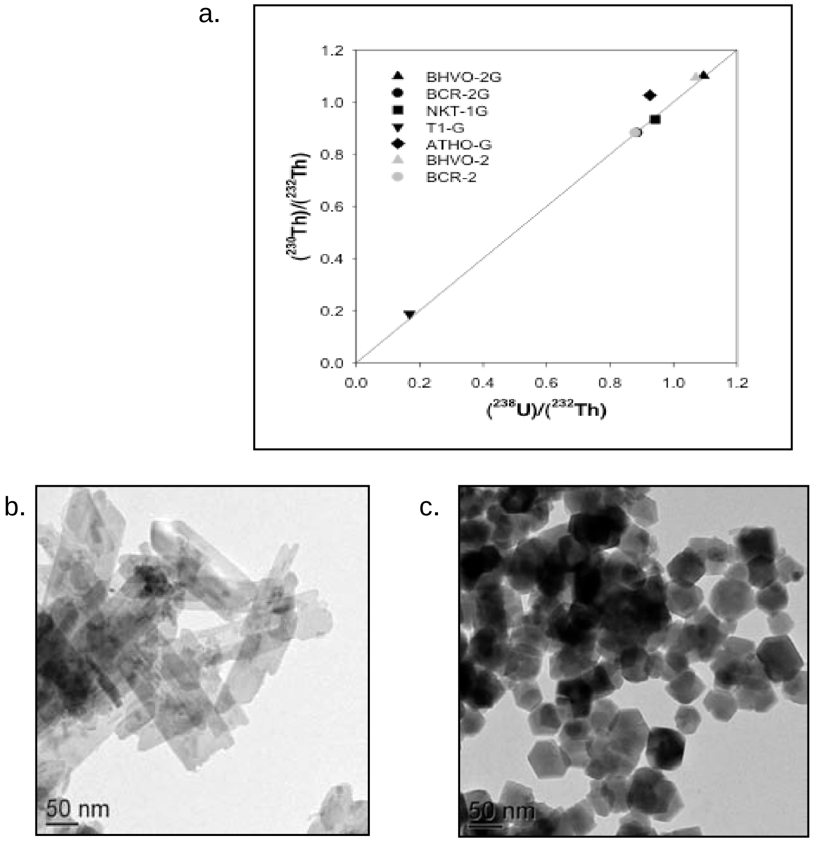

Figure 1. A variety of Fe(II)-producing biogeochemical reductants are being investigated for their mineralization promoting behavior. Lepidocrocite (a) is partially reduced by FMNH, but Fe(II) dissolves rather than recrystallizing (b). Reaction with ferrous iron $[Fe(II)_{aq}]$ alone, leads to magnetite formation (c).

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

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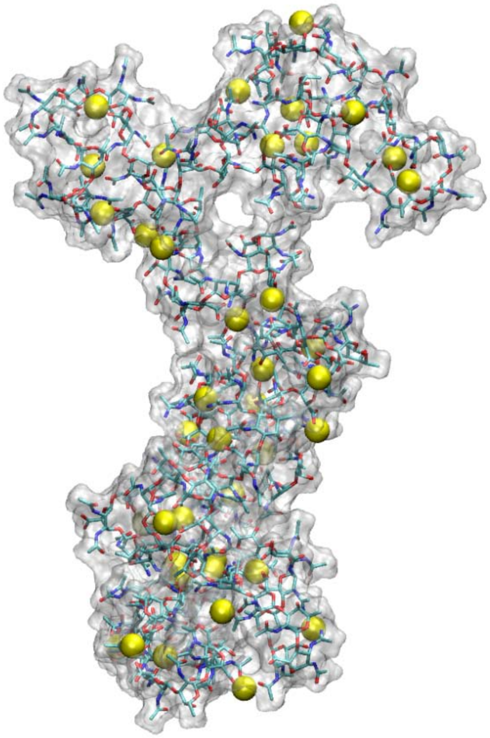
Objectives: The goal is to develop a molecular level description of the interactions of microbial membranes and membrane constituents with subsurface mineral materials. We are developing a molecular level view of microbial metal binding, microbial attachment to mineral surfaces, and, eventually, oxidation/reduction 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 the ubiquitous environmental bacterium *Pseudomonas aeruginosa* with minerals and with solvated ions in the environment. It is a combined computational and experimental project 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: The outer membranes of Gram-negative microbes such *Pseudomonas aeruginosa* are highly non-symmetric and exhibit a significant electrostatic potential gradient across the membrane. This gradient has a significant effect on the uptake and transport of charged and dipolar compounds. To study the effectiveness of microbial systems for environmental remediation that depend on the uptake of targeted contaminants by a particular cell walls, we use our previously developed model for the lipopolisaccharide (LPS) membrane of *Pseudomonas aeruginosa*, to determine the thermodynamics of metal ion uptake (including sodium, calcium, chloride, uranyl) by the bacterial LPS membrane.

This work has been expanded into study of the interactions involving the extracellular so-called B-band polysaccharide, which has significant flexibility, and does not interact with the sugar units from the LPS core surface residues. Our molecular dynamics simulations of the rough LPS membrane suggest that the presence of the B-band promotes membrane expansion. In addition, this O-antigen chain dramatically alters the electrostatic potential and surface charge of the LPS membrane. This is illustrated by the resulting electrostatic surface potential. Comparison with the same property in rough LPS aids to explain the increased ability of B-band expressing microorganisms to adhere to surfaces. Simulations of large B-band structures in aqueous environment reveal the formation through folding of the saccharide chain of specific ion binding conformations. A representative snapshot is shown in the following figure.



A set of simulations has also been initiated to determine the effect of the number of alkyl chains in the LPS on the exposure and mobility of the polysaccharide exposed to mineral surfaces. Phenotypical variations in the lipid region of the LPS of *P aeruginosa* have been observed according to the microbe lifestyle and environment. In addition to the penta-acylated form used in our studies, hexa-acyl LPS is also commonly found in the endotoxic form of the bacteria. Structural and dynamical analyses reveal clear differences between the penta- and hexa-acylated LPS. The presence of an extra alkyl chain in the hexa-acyl form results in a slightly higher area per LPS. As a consequence, it leads to a spatial rearrangement of the two NAc-glucosamine units (inner-core moiety) with respect to each other that is propagated throughout the outer core resulting in an increased flexibility and solvation of the sugar chains.

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 FY09, to complement ongoing microscopic observations and surface potentiometry measurements, we worked on the development of computational molecular models for pH-dependent single crystal surface charge with post-doctoral fellow Dr. Piotr Zarzycki at PNNL. Replica kinetic Monte Carlo simulations were used to study the characteristic time scales of potentiometric titration of model metal oxides and (oxy)hydroxide surfaces. The effects of surface heterogeneity and surface transformation on the titration kinetics were also examined. Two characteristic relaxation times are often observed experimentally, with the trailing slower part attributed to surface nonuniformity, porosity, polymerization, amorphization, and other dynamic surface processes induced by unbalanced surface charge. However, our simulations show that these two characteristic relaxation times are intrinsic to the proton-binding reaction for energetically homogeneous surfaces, and therefore surface heterogeneity or transformation does not necessarily need to be invoked. However, all such second-order surface processes are found to intensify the separation and distinction of the two kinetic regimes. The effect of surface energetic-topographic nonuniformity, as well dynamic surface transformation and interface roughening/smoothing, were described in a statistical fashion. Furthermore, our simulations show that a shift in the point-of-zero charge is expected from increased titration speed, and the pH-dependence of the titration measurement error is in excellent agreement with experimental studies. In addition to these atomistic simulations, we also performed a computational modeling analysis of surface potential nonlinearity at metal oxide/electrolyte interfaces. By using Grand Canonical Monte Carlo simulations of a simple lattice model of an interface, we showed that a correlation exists between ionic strength as well as surface site densities and the non-Nernstian response of a metal oxide electrode. We proposed two approaches to deal with the nonlinearity: one based on perturbative expansion of the Gibbs free energy and another based on assumption of the pH-dependence of surface potential slope. The theoretical analysis based on our new potential form gives excellent performance at extreme pH regions, where classical formulae for the surface potential fail. The new formula is general and independent of any underlying assumptions. For this reason, it can be directly applied to experimental surface potential measurements, including those for individual surface of single crystals. These computational molecular models provide a foundation for construction of coupled surface complexation and electron transfer models to describe electron exchange driving forces at specific surfaces of metal oxide and oxyhydroxide crystals under a range of pH and ionic strength conditions, and subsequently the role of bulk conduction of charge on redox transformation.

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

Eugene S. Ilton, Eugene.Ilton@pnl.gov, Paul S. Bagus (UNT)

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

Project Description: This project concerns reactions between minerals and toxic metal-bearing aqueous fluids. Specifically, we are exploring the mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals. Key techniques used are electron microscopy, x-ray photoemission spectroscopy (XPS), and x-ray adsorption near edge structure (XANES). The project includes major theoretical efforts on the interpretation and prediction of XPS and XANES; the *ab initio* theoretical work is coupled to the experimental efforts.

Results: A major experimental effort during the present grant period concerned the interaction of U^{VI}aq with nano-particulate magnetite. A combination of high resolution cryogenic and non-cryogenic XPS, XANES, and EXAFS indicated that U^{IV} did not form; instead, U^{V} formed and was a long-lived intermediate in the system. This was the first application of cryo-XPS to hydrated samples containing U. The results were significant because they demonstrated that U^{V} is not an artifact of dehydration and UHV conditions. EXAFS indicated that an appreciable portion of sorbed U was present in the uranate structure with strong short to intermediate range coordination by Fe, whereas in other samples TEM indicated the presence of uranium rich precipitates. Thus, the stability of U^{V} might be related to incorporation into an Fe (hydr)oxide and/or uranium phase. The percent uranate (EXAFS) was correlated to percent U^{V} (XPS) which suggests that U^{V} had the uranate coordination structure. Coupled to the fact that thermodynamic calculations indicated that U^{IV} should have been stable in this system, we conclude that the initial coordination environment of the U^{V} that forms could exert a strong effect on conversion of U^{V} to U^{IV}. In related work, and in collaboration with the Cahill group at George Washington University, we synthesized $[U^{V}(H_2O)_2(U^{VI}O_2)_2O_4(OH)](H_2O)_4$, a mixed-valence U^{V}/U^{VI} oxide material, under mild hydrothermal conditions; ~120°C. The results are particularly notable because most previous synthetic routes to U^{V} compounds involved either solid state methods or coordinating organic ligands. The only other published hydrothermal route required very high temperatures (600°C) and silicate coordination. The overall topology is very similar to the mineral ianthinite. This phase was essential for developing an XPS standard for U^{V}. Further, it provides a conceptual model of possible coordination sites for U^{V} in uranyl phases as well as insight into the magnetite results: for example, it is possible that U^V was stabilized in the magnetite experiments by incorporation into rapidly forming uranyl precipitates. Advances in simulating XPS spectra for heavy element compounds are described in the Summary of the Co-PI, Paul S. Bagus (UNT).

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

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Objectives: The goal is to understand at the molecular level the interactions of aqueous carbonate species with oxyhydroxide and silicate surfaces. The interaction of carbonate, bicarbonate, and CO_2 with these materials is highly relevant to the development of processes to sequester CO_2 in the subsurface in order to mitigate its impact on the environment.

Project Description: The experimental component of this research effort was designed to provide insight into the mechanisms through which aqueous carbonate ions are incorporated to the bulk of iron oxyhydroxide and silicate mineral surfaces. The iron oxide particles were synthesized by exposing aqueous solutions of ferric iron to various levels of PCO_2, pH and temperatures. The silicate minerals were obtained as pure mineral specimens or synthesized in high temperature melts.

Results: In FY09 the project shifted from an emphasis on the interaction of CO_2 with iron oxide surfaces to an emphasis on examining the possible interactions of CO_2 with other mineral surfaces, specifically a complete range of divalent orthosilicates. The orthosilicates of interest included Mg_2SiO_4, Ca_2SiO_4, Fe_2SiO_4, Mn_2SiO_4, Ni_2SiO_4, Co_2SiO_4, and Be_2SiO_4. The overall objective was to define the impact of the changing divalent metal cation on the mineral reaction rate and mechanism in supercritical CO_2 containing systems and contrast this rate with previous work done on acidic aqueous solutions. Our initial emphasis was on obtaining high quality mineral samples. In this regard we obtained high quality specimens of forsterite (Mg_2SiO_4), fayalite (Fe_2SiO_4) and phenakite (Be_2SiO_4). We were also successful in synthesizing Co-olivine (Co_2SiO_4) and Ca-olivine (Ca_2SiO_4) from high temperature melts. Studies of the forsterite and Co-olivine surface have also been initiated using *in situ* FTIR (Fourier Transform Infrared) to quantify the amount of adsorbed water and characterize its average molecular structure and NMR spectroscopy to probe the hydration/dehydration mechanisms of the mineral surfaces. The FTIR studies require deuteration of the water or surface hydroxyls to avoid CO_2 rendering the hydroxyl spectral region opaque. The NMR studies involve high pressure *in situ* ^2H and ^1H MAS NMR including high pressure static ^2H NMR spectroscopy using a high pressure *in situ* NMR probe in the EMSL. Electronic structure calculations are also being used to help interpret the FTIR and NMR spectra to identify the specific coordination environments responsible for supercritical CO_2 reactivity. The water content in the supercritical CO_2 is being systematically varied during these studies.

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

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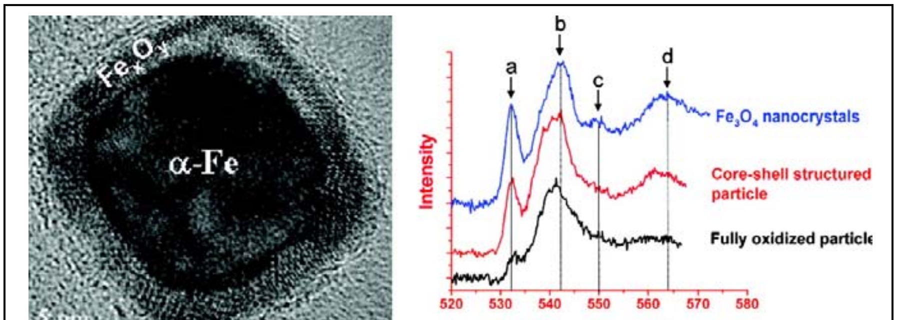
Objectives: The objective of this project is to obtain fundamental information about the physical and chemical transformations that occur on and within mineral oxide nanoparticulates due to electron transfer reactions and other interactions with their local environment. Although geochemically induced changes occur for bulk materials, the nature and rate for the changes can be more dramatic for nano-sized mineral phases.

Project Description: This project will focus on obtaining information about these geochemically mediated transformations and how they alter particle reactivity, electron availability and particle mobility. Natural particles and specially grown model particles will be used to study particle transformations, interfacial reaction products and particulate reactivity. The work is organized into 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 objectives.

Results: A combination of x-ray and electron microscopy and spectroscopy were used to obtain detailed information about the surfaces and coating on nanoparticulate iron particles. Electron energy loss spectroscopy measurements made with a transmission electron microscope demonstrates that the oxide shell on iron nanoparticles is highly defective in comparison to bulk version of these oxides. The high quantity of defects alters the chemical and physical properties the particles and contributes to their altered reactivity. We have also conducted a set of measurements characterizing the sorption of organic molecules, including natural organic material, and measuring the impact on particle reactivity and aging. As a continuation of efforts to understanding the role of contaminants and dopants on nanoparticle shell aging and reaction properties, particles with varying concentrations of sulfur have been produced and their reaction and aging properties are being examined in detail.



A combination of model experimental and theoretical studies were undertaken to assist fundamental understanding of reaction pathways. The interaction of Fe^0 atoms and clusters with multilayers of CCl_4, D_2O, C_2Cl_6 and C_2Cl_4 supported on an FeO(111) substrate was investigated using a novel "atom dropping" method at 30 K. A novel reaction mechanism is observed where Fe atoms insert directly into a C-Cl or D-O bond even at 30 K. This reaction mechanism is supported by complementary density functional theory calculations.

First Principles Simulation of the Temperature, Composition and Pressure Dependence of Natural Fluids

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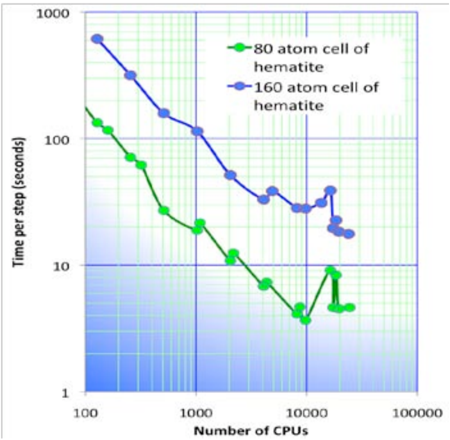
Objectives: To address the problems associated with future energy strategies a much more quantitative, parameter-free interpretation of elementary geochemical processes will be required. In this program, new 1^{st} principles simulations methods are being developed and applied to the study of the chemical 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 1^{st} 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 1^{st} 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 as 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, and 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: See UCSD report (PI John Weare)

Methods Developments Results: It is well known that local density functional theory even with the inclusion of generalized gradient corrections will not correctly describe weakly bound anionic states, localized charge states such as polarons, excitons and solitons, and the prediction of proton transfer barriers. These problems are particularly severe in applications to highly correlated systems (e.g., Fe_2O_3, TiO_2). Approaches in which the exchange correlation functionals in local density approaches are augmented with small a amount of exact exchange (hybrid-DFT, e.g., B3LYP and PBE0) have been shown to provide at least semi-quantitative descriptions for these problems. Examples of interest to DOE include charge localization in transition elements with tightly bound *d* electrons in oxide materials (see Figure 1), the underestimation of reaction barriers and band gaps in solids, and accurate predictions of spin structure of solids and nanoparticles.

The drawback of hybrid-DFT is that it adds a significant amount of expense to an already expensive AIMD simulation. Until recently, it was infeasible to contemplate such



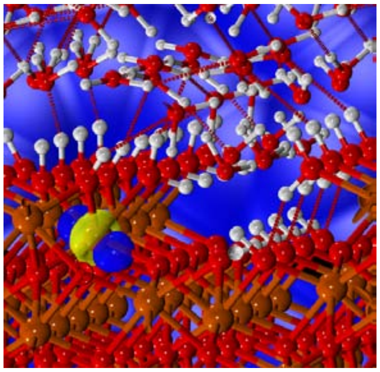


Figure 1: (top) Timings for exact exchange calculations for 80 and 160 atom supercells of Hematite. (below) Localized excess electron calculated at the hybrid DFT level with full surface hydration. The charge is localized at an Fe^{3+} center as a result of exact exchange.

computations. However, as we approach the Petaflop milestone, we can think about coping with the high computational costs through vastly increased parallelism. In the last year a parallel algorithm for computing exact exchange was developed for use in AIMD algorithms. This algorithm makes use of a two-dimensional processor geometry proposed by Gygi *et al.* for use in AIMD algorithm and employs an incomplete butterfly to overcome the communication bottleneck associated with exact exchange term, and it makes judicious use of data replication. Initial testing has shown that this algorithm can scale to over 20,000 CPUs even for a modest size simulation. **Key Result:** This overcomes the inefficiencies associated with exact exchange and provides a much needed improvement in the level of solution to the electronic structure problem for large systems so that dynamics is possible. In Figure 1 the overall and major constituent timings for hybrid-DFT calculations of 80 and 160 atom supercells of hematite (Fe_2O_3) are shown.

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

Andrew R. Felmy, 509-371-6356 ; ar.felmy@pnl.gov; David Dixon (The University of Alabama), Jianzhi Hu (PNNL), Eugene Ilton (PNNL), Pete McGrail (PNNL), Kevin Rosso (PNNL), Gernot Rother (ORNL), James Rustad (UC Davis), and Zheming Wang (PNNL)

Objectives: The goal of this project is to unravel the molecular mechanisms governing the reactivity of mineral phases important in the geologic sequestration of CO_2 with variably wet $scCO_2$ as a function of T, P, mineral structure/composition and solution phase composition. A key aspect of the research program is the integration of molecular level theory and experiment to provide unique insight into the molecular level phenomena that occur and establish a basis for how such molecular level processes can be represented at the macroscopic level.

Project Description: Two classes of mineral phases will be emphasized: orthosilicates (e.g., forsterite, Mg_2SiO_4) and hydrous phyllosilicates (e.g., montmorillonite, hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$). Orthosilicates have been well studied with respect to their structure and aqueous dissolution behavior. This provides an information base to compare with their behavior in neat and hydrous $scCO_2$. Orthosilicates also represent important reactive phases with respect to carbonation in many reservoir environments (especially basalts), and our previous studies have shown the critical importance of small amounts of water in determining the reactivity of these phases in CO_2 dominated fluids. Phyllosilicates can be the majority phase in low permeability cap-rocks. Their reactivity towards CO_2, and wetting and hydration/dehydration behavior directly affect one of the most important issues in subsurface CO_2 sequestration, namely the long term sealing capability of shale dominated caprocks. By studying these two important mineral classes we will be able to develop important molecular level insight into the reactivity of water and CO_2 on mineral surfaces with different interface/interlayer water structures as well as provide insight into appropriate models for mineral reactivity and thermodynamics.

The amount of adsorbed water and its average molecular structure along with the mechanisms of mineral hydration/dehydration will be determined by using a combination of experimental probes including *in situ* FTIR (Fourier Transform Infrared), high pressure *in situ* ^{2}H and ^{1}H MAS NMR, and small angle neutron scattering (SANS). Longer term macroscopic mineral reactivity and transformation mechanisms will also be studied using high pressure cells capable of measurement in both batch and flow-through mode and can be conducted at pressures ranging up to 200 bars and temperatures up to 475 K. *Ex situ* solid phase analysis both before and after reaction will be conducted using electron microscopy (FIB/SEM and TEM) scanning probe microscopy (AFM), x-ray photoelectron spectroscopy (XPS), and time-of-flight SIMS chemical mapping analyses.

Our experimental effort will be closely integrated with a computational effort. Our overall computational approach will integrate molecular dynamics simulations with highly accurate electronic structure calculations and advanced chemimetric techniques.

Results: This project was selected for funding at the end of FY09. Preparation of the divalent metal silicate and phyllosilicate phases for study was initiated.

SANDIA NATIONAL LABORATORY/ALBUQUERQUE

CONTRACT: AL85000

PERSON IN CHARGE: J. Merson

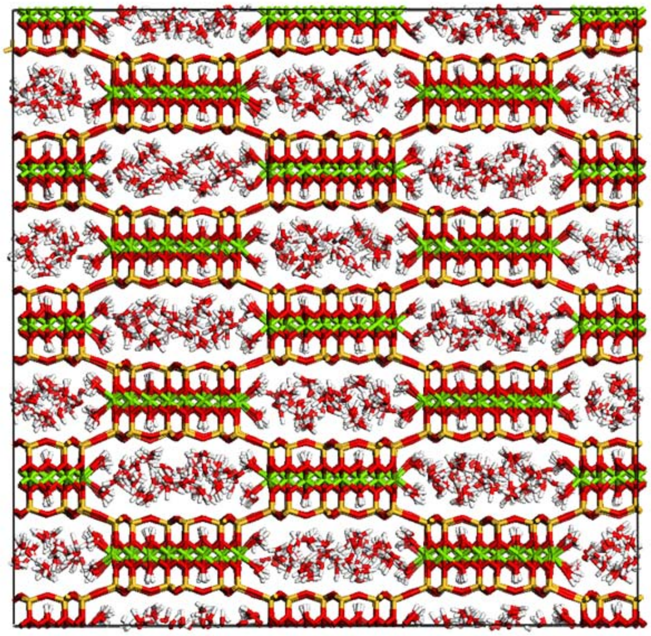
The Nature of the Mineral-Water Interface: A Molecular Simulation and Spectroscopic Investigation

Randall T. Cygan, 505-844-7216, rtcygan@sandia.gov; Jeffrey A. Greathouse, 505-284-4895, jagreat@sandia.gov

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 modern analytical and spectroscopic methods, we are expanding our efforts in molecular simulation to address the atomistic behavior of the mineral-water interface. Specifically, we are investigating 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 the addition of polarization effects in our force field will help understand the nature of the adsorption process. We are also examining the disposition of water in talc and pyrophyllite and in other phyllosilicates that have channels, and combining simulation and spectroscopy of the heterovalent manganese oxide mineral birnessite that plays a significant role in controlling heavy metals in the environment.

Results: The structural and vibrational properties of various clay minerals and the behavior of nanoconfined water were investigated using quantum and classical molecular dynamics simulations. The classical MD simulations using our updated CLAYFF force field reproduce the crystal structures with relatively simple analytical functions that include primarily non-bonded interactions. Results from simulations using density functional theory are particularly useful for determining layer hydroxyl structure and dynamics as these properties are difficult to obtain experimentally. From our analysis of water in two important fibrous minerals, we found that distortions of silicate tetrahedra in the small pores of palygorskite exhibit a limited number of hydrogen bonds with relatively short bond lengths. However, without the distorted silicate tetrahedra, an increased number of hydrogen bonds are observed in the larger pores of sepiolite with corresponding longer bond distances. Because there is more hydrogen bonding at the pore interface in sepiolite than in palygorskite, we expect librational modes to have higher overall frequencies (i.e., more restricted rotational motions); experimental neutron scattering data obtained at the Los Alamos LANSCE facility clearly illustrate this shift in spectroscopic signatures associated with the water molecules residing in different-sized channels. It follows that distortions of the silicate tetrahedra in these minerals effectively disrupts hydrogen bonding patterns at the silicate-water interface, and this has a greater impact on the dynamical behavior of nanoconfined water than the actual size of the pore or the presence of coordinatively-unsaturated magnesium edge sites.



Structure of water molecules in the nano-sized channels of sepiolite as obtained from molecular dynamics simulation using the CLAYFF force field.

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, infra-red, 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 year, the SNL team completed surface potential of mean force (PMF) calculations for the adsorption of alkaline earth metal cations to the gibbsite (001) surface, using classical force field methods. The free energy profiles for metal adsorption each exhibit two local minima that correspond to inner-sphere and outer-sphere complexation. Although the alkaline earth metal cations are generally observed to adsorb as outer-sphere complexes at 25°C, the calculations suggest that both Ca^{2+} and Sr^{2+} achieve lower energy states as inner-sphere complexes. This suggests that the activation energy barriers associated with the removal of hydration water from Ca^{2+} and Sr^{2+} inhibit the formation of inner-sphere complexes for these cations (see Figure). Only Mg^{2+} exhibits a strong preference to adsorb as an outer-sphere complex. Consistent with these calculations, simulations at higher temperatures resulted in the formation of inner-sphere alkaline-earth metal complexes. Adsorption data collected at UT-Austin as a function of temperature and ionic strength are qualitatively consistent with the molecular modeling results. Surface maps of calculated alkaline earth-metal and chloride adsorption are now under study to determine changes in surface site binding and ion-pairing at the surface as a function of concentration. Potential of mean force calculations using *ab initio* molecular dynamics (Leung, SNL) were also performed to investigate the two pKa's measured on silica surfaces. These simulations show that the acidic silica surface sites can be attributed to locally strained regions with sparse silanol coverage, and rule out previously proposed hypotheses related to chemical connectivity or inter-silanol hydrogen bonds.

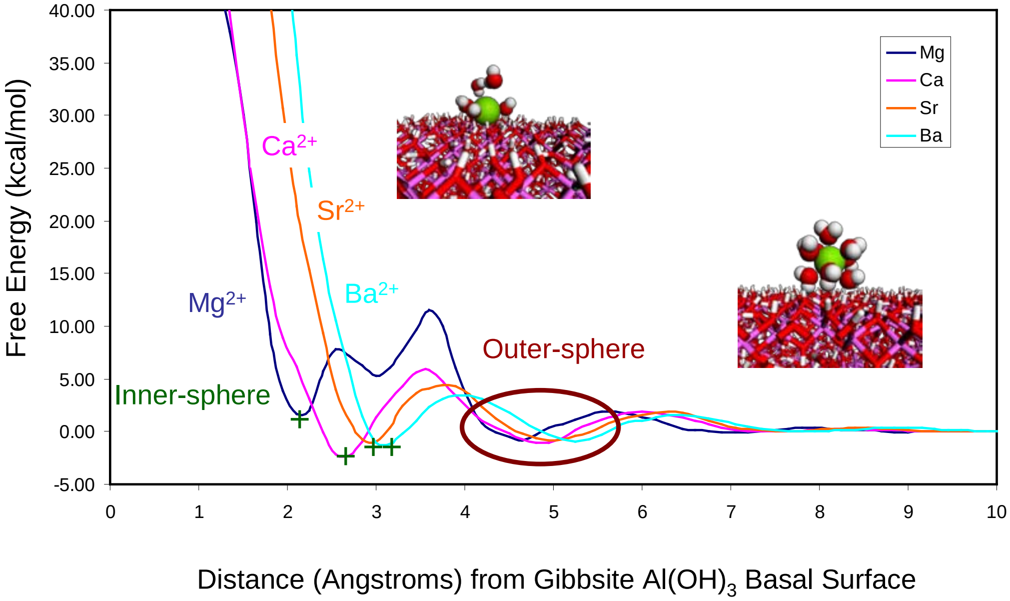

Figure. Potential of mean force profiles for M^{2+} adsorption on gibbsite surface. Two free energy minima are present for inner-sphere Mg^{2+}. These minima correspond to two different configurations. Close to the gibbsite surface (2 Å) Mg^{2+} is coordinated by 3 H_2O molecules and 3 –OH surface groups. Further away (3 Å), Mg^{2+} is coordinated to one –OH group and 5 H_2O molecules.

Pore Network Evolution and Chemo-Mechanical Coupling in Shales and Mudrocks

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Objectives: This project investigates coupled mechanical and chemical dynamics of mudrocks. 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?

Project Description: This research involves 5 specific tasks – these are (1) Measure influence of fluid chemistry on shale pore network evolution via permeability and electro-osmotic (semi-permeable membrane properties) effects; (2) Acoustic measurements of changes in shale 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 shale permeability and membrane efficiency; (4): Quantitative three-dimensional imaging of organic distribution and pore networks in mudrocks; and (5): Modeling shale 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/FIB imaging of pore structures, and pore scale modeling.

Results: In *Task 1*, we have assembled/purchased microscope loading/heating/cooling stage and associated pumps, high pressure pore lines, valves, fittings etc. This includes 5 ISCO 50 ml high pressure pumps, thermal chamber, and a dedicated pressure vessel, to be brought online in October of 2009. For *Task 2*, we have brought a 24 channel high speed acoustic emissions system online and written software for control and analysis, which enables 50-100 waveform events per second from a 15 sensor array. For *Task 3*, we have begun building a microscopic flow-through and axial loading system built around a 2000-lb miniature loading frame and sapphire pressure vessel for use with LSCM, and will be brought on line in December 2009. In *Task 4*, we have undertaken imaging of shale pore networks and organic matter distribution for 4 shale samples from the US Gulf Coast and Colorado Plateau, at sub-micron resolution using Laser Scanning Confocal Microscopy. We have also undertaken imaging and digital pore reconstruction of nanometer-sized shale pores using Dual SEM/Focused Ion Beam milling and SEM imaging. For *Task 5*, we have initiated pore scale (computational fluid dynamics) modeling using COMSOL Multiphysics Software using portions of SEM/FIB-rendered 3D pore networks.

Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media

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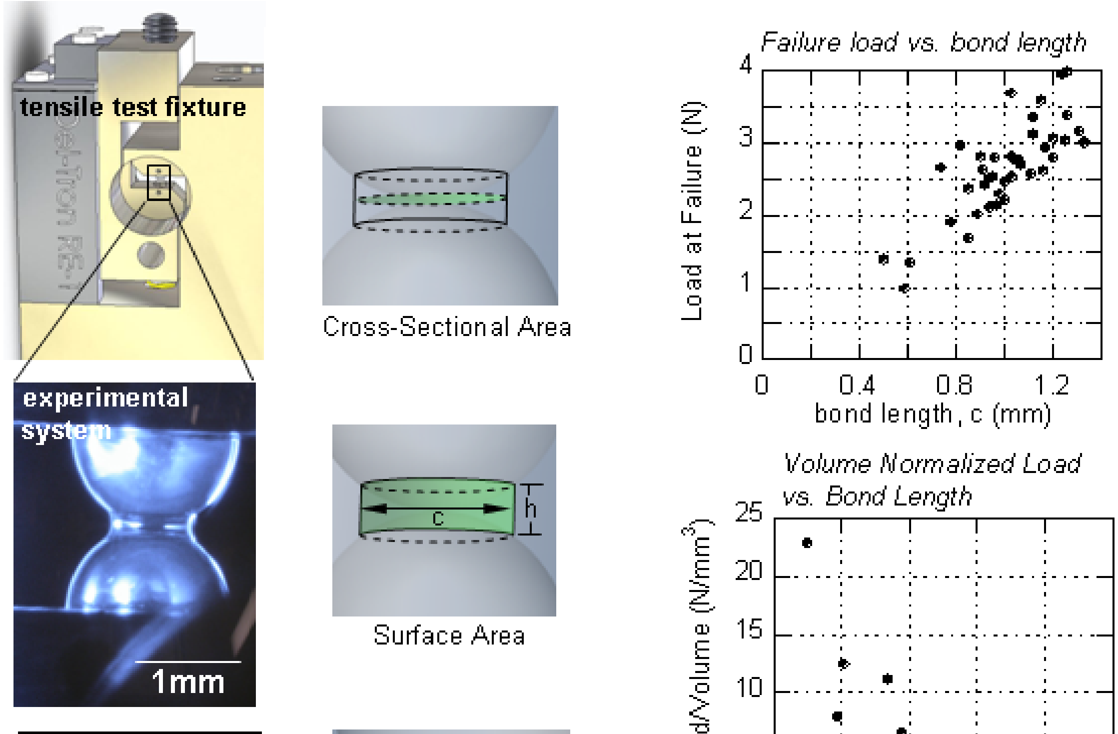
Objectives: (1) To quantify grain-scale physical effects of variable cement quantity and distribution on the elastic and inelastic deformation of granular porous media. (2) To use the resulting understanding of the fundamental micromechanical processes that govern macroscopic deformation to accurately capture meaningful grain-grain interactions in Discrete Element Model (DEM) simulations.

Project Description: The project scope encompasses development of appropriately small-scale experimental deformation and structural characterization of granular porous media to address the two objectives. A key component of this project is the use of simulation tools to identify the geometric microstructure parameters which govern the response of cemented granular materials, which, in turn, guide development of the experiments. Over the course of the project, both *natural* and *synthetic* grain-cement systems were investigated using novel approaches that provide insight into grain-scale mechanics. The Sandia Laboratories portion of the project concluded by developing and successfully demonstrating a method for fabricating and testing the mechanical properties of synthetic cemented 2 grain assemblages.

Results: As representative granular porous media, natural sandstones have grain-cement-pore geometries that are largely dictated by grain and cement mineralogy. Quartz cement, for example, is typically precipitated as overgrowths on quartz grains with a geometry that is crystallographically controlled. Current understanding of the impact of cement on the mechanical response of granular porous media is largely based on a conceptual model of narrow cement bridges bonding circular grains. Although idealized, this conceptual model has not been experimentally exercised in a fashion to isolate specific microscale parameters that govern the macroscopic response of a granular porous system. To address this specific problem, we developed and successfully demonstrated an experimental method to mechanically test a cemented two-grain system representative of two grains within granular porous media using ice as an analog cement. Figure 1(a) illustrates the experimental method and the proposed direct coupling between the experimental tests and a simulation that could be used to better inform cement-bond stiffness necessary for DEM models.

Successful demonstration of the test method resulted in a dataset containing failure loads and cement bond geometry, defined by cross-sectional area, surface area, grain-cement contact area, as illustrated in Figure 1(b), from 40 experiments. These results have been analyzed in several different ways to reveal trends in cement geometry and volume as functions of load and stress related parameters. Three examples are given in Figure 1(c). The first example shows a plot of failure load vs. cement bond length, c- defined in Figure 1(b). The plot suggests a *linear* trend of increasing failure load with increasing cement bond length. When load is normalized, either by a cement area defined in Figure 1(b), or by cement volume, the influence of the constraint imposed by the grains on the cement becomes apparent. The plot of 'volume normalized load' vs. bond length illustrates this by showing that as the cement bond length decreases the apparent strength of the cement, as defined by a 'volume normalize load', increases as a function of 1/c. Finally, the results were analyzed with statistical models, as is demonstrated by the comparison with a Weibull distribution in the cumulative distribution plot also given in Figure 1(c).



The Importance of Flow-Enhanced Precipitation and Pulsatile Dispersion in Geochemical Systems

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Objectives: This study was designed to determine how complexities of real systems – intentionally suppressed in most experiments, but ubiquitous in nature – could enhance mixing, reaction, and precipitation in nature.

Project Description: The first part of the study, dealing with mixing in pulsatile systems, was published as two articles in the journal *Biomechanical Engineering*. The second part of the study deals with the possible enhancement of growth by flow; specifically, the tendency to fill space quickly with minimal solids, when growth is dendritic or fingered. Such growth would quickly shut down flow; this result might be beneficial if one were concerned about precipitates from nuclear waste dissolution, or undesirable if one were concerned about sequestration of CO_2, by precipitation of carbonate minerals in fractured rock. The approach uses lattice Boltzmann (LB) models that incorporated flow, dispersion, and solid precipitation/dissolution, and investigates the tions that give rise t gered and sparse growth, versus compact growth. Most prec on models deal wit gle crystals, and inherently depend on surface tension

(a) (b) (c)

inhomogeneity to spur growth of dendrites; but this study is concerned with aggregates of multiple crystals, more than a few microns in size, and the role of surface tension must be negligible or very indirect. Numerical experiments are designed that mimic experimental conditions achievable in the laboratory (e.g., in growth of gypsum in mm-wide Hele-Shaw cells).
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Results: The models have shown that dendritic growth can occur in the Hele-Shaw cell, quickly filling space. However, such growth requires very high flow- or diffusion-based Damköhler (Da) numbers. More normal conditions (as might be expected for growth of gypsum, or less soluble minerals) cause a bias of growth into the direction of flow, but do not result in fingers or dendrites. A review of the literature (e.g., precipitation of barite in chimneys near hydrothermal vents), suggests that many dendrites do not grow by direct chemical precipitation, but rather by agglomeration of pre-existing particles under flow. This type of growth allows an apparent very high Da, as the particles have very low effective Einstein-Stokes diffusion coefficients; in addition, the mass of material that may be added to the exiting aggregate in one step is large (several microns in diameter), giving an apparent very high "reaction rate".

In addition, it was found that there is a subtle grid dependence in the LB model, which becomes apparent only when there is fluid flow at relatively high Da. This dependence is due to compression of the reactive boundary layer to a width less than the separation of nodes on plane perpendicular to flow. In absence of flow, precipitates grow uniformly outward. Any calculation that "fills" grid blocks– including many of the early diffusion-limited aggregation models – is subject to this bias, which effectively acts like a slight inhomogeneity in a non-existent surface tension. A method was devised to virtually eliminate this bias, but this method breaks down at the highest Da. To model this very high "apparent" Da realm, one must develop a mixed LB-particle tracking mode that is truly grid-independent.

Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport

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Objectives: The objective of this project is to characterize the influence that naturally complex geologic media has on anomalous dispersion and to determine if the nature of dispersion can be estimated from the underlying heterogeneous media.

Project Description: This project combines outcrop-scale heterogeneity characterization, laboratory experiments, and numerical simulations. The study is designed to test whether established dispersion theory accurately predicts the behavior of solute transport through heterogeneous media and to investigate the relationship between heterogeneity and the parameters that populate these models. The dispersion theory tested by this work is based upon the fractional advection-dispersion equation (fADE) model. Unlike most dispersion studies that develop a solute transport model by fitting the solute transport breakthrough curve, this project will explore the nature of the heterogeneous media to better understand the connection between the model parameters and the aquifer heterogeneity.

Results: In the third year of this project, we continue exploring causal factors of non-Fickian dispersion using both numerical studies and laboratory-scale experiments. In the numerical study, we use natural aquifer analogs developed through lidar imagery to track the importance of connectivity on dispersion characteristics. The use of two-point (SISIM) and multipoint (Snesim and Filtersim) stochastic simulation methods are then compared based on their ability to replicate dispersion characteristics using the aquifer analog (Figure 1A). Detailed particle tracking simulations are used to explore the streamline-based connectivity that is preserved using each method (Figure 1B). We found that while solute transport through the simulated and lidar-based heterogeneity sample from very similar distributions of continuous sand and gravel travel path lengths, the dispersion characteristics and velocity profiles differ. This discrepancy is a function of differences in the way continuous travel paths are organized in space based on the various simulation techniques. Multipoint methods are designed to preserve local heterogeneous features of the training image. Filtersim, in particular, extracts actual sections of spatial patterns from the training image. We conclude that the simulation technique used in Filtersim leads to better replication of streamline-based connectivity and resulting dispersion characteristics. Connectivity analysis details the importance of preserving the percent travel distance in gravel on replicating dispersion characteristics.

Laboratory-scale experiments were conducted using sand packs to test the lidar/segmentation process, as well as visualize the complex process of solute transport through structured sand packs based on natural heterogeneous media. The sand pack experiment uses heterogeneity structures based on one of the segmented lidar fields as a guide for laboratory-scale heterogeneity (Figure 1C). Throughout the solute transport experiments, X-ray visualization and ion specific probe measurements are taken to record the spatial distribution and concentration of the potassium iodine solute. Results from the experiment will be processed at a later date and will be used to compare streamline-based simulations to the experimental results. This experiment will provide controlled physical experiment data to verify numerical simulation results based on lidar analog outcrop images.

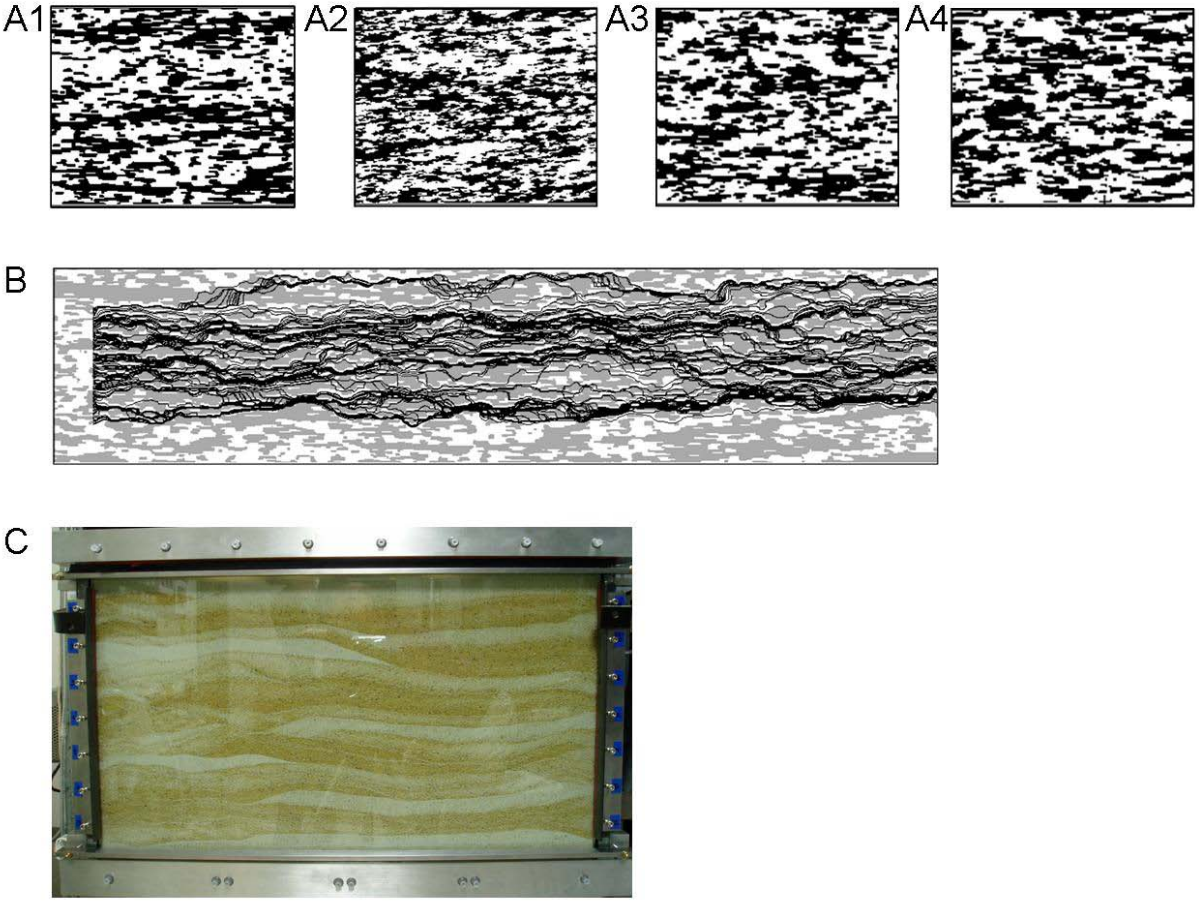

Figure 1. A) A 60 cm by 50 cm subset of A1) the SL field, A2) an example SISIM realization, A3) an example Snesim realization, and A4) an example Filtersim realization (black = sand, white = gravel). B) Binary segmented lidar field (221.8 by 50.0 cm) gray = sand, white = gravel) with particle tracking simulation overlay used in the connectivity analysis. C) Heterogeneous sand pack containing high, medium, and low permeability units created using different mixes of 12/20 (yellow) and 50/70 (white) sand.

PART II: OFF-SITE

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Grant: DE-FG02-06ER15764

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

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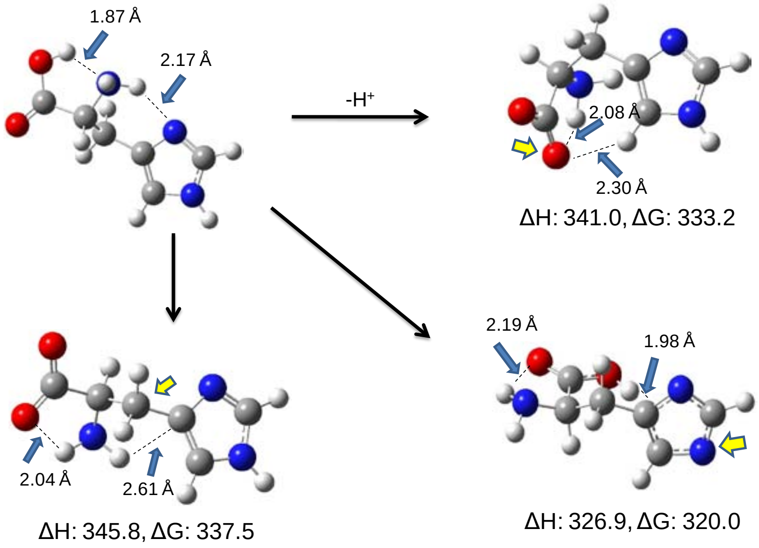
Objectives: The goal is to develop a molecular level description of the interactions of microbial membranes with subsurface materials. We are developing a molecular level view of microbial metal binding, microbial attachment to mineral surfaces, and, eventually, oxidation/reduction reactions (electron 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 previous work on the acidities of glycine, glutamic acid and aspartic acid to the remaining 17 amino acids, where the gas phase acidity is the free energy ΔG_{acid} for the reaction $AH \rightarrow A^- + H^+$. The acidities have been predicted using high level electronic structure theory at the composite G3(MP2) level. A broad range of neutral structures were studied to determine the lowest energy conformer with the strongest hydrogen bonding. Anions were created by removing protons at different sites including the important –CO_2H and NH_2 groups. Excellent agreement is found with the available experimental gas phase deprotonation enthalpies and the calculated values are all within the experimental error bars. Our results confirm the amino acid as phase acidity scale and can be used to substantially reduce the error bars on the values. The proton is lost from the –CO_2H acid group to form the –CO_2^- anionic group, in all cases but histidine. Removal of a proton from the –CO_2H group results in GA values between 330 and 334 kcal/mol showing that substituent effects are not very large except for serine where a strong hydrogen bond can form from the side chain OH group. For histidine, the loss of the proton from the ring NH is the most acidic site (GA = 320.0 kcal/mol), 13 kcal/mol more acidic than removal of the proton from the -CO_2H group. For about half of the amino acids, the calculated pK_a's are in reasonable agreement with experiment within ~ 2 pK units ($\Delta\Delta G < 3.0$ kcal/mol at 298 K). For others the difference can be larger, perhaps due to the zwitterionic nature of the amino acids in solution as the zwitterionic structure is more stable in aqueous solution than the non-zwitterionic structure. An important result is that the anionic structure corresponding to the lowest gas phase acidity may not be that for the lowest pK_a in aqueous solution. The heats of formation of the neutral compounds were calculated from atomization energies and isodesmic reactions to provide the first reliable set of thermodynamic properties of the amino acids in the gas phase.



Histidine Acidity (kcal/mol)

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Grant: DE-FG02-07ER15840

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

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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: We have continued to develop computational approaches to the prediction of critical geochemical quantities. The equilibrium constant α_{34} for the isotope exchange reaction $^{10}B(OH)_3(aq) + {}^{11}B(OH)_4^-(aq) = {}^{11}B(OH)_3(aq) + {}^{10}B(OH)_4^-(aq)$ is the basis for a method commonly used to infer the pH of the ancient oceans and, hence, the PCO_2 of the ancient atmosphere. The equilibrium constant for this reaction, α_{34}, is difficult to measure directly. Most estimates of ocean pH were based on a value obtained using an empirical valence force field to calculate the vibrational partition function, giving $\alpha_{34} = 1.019$. Subsequent theoretical work used frequencies obtained from electronic structure calculations and predicted significantly larger values (1.025-1.035). A series of DFT and MP2 calculations on hydrated boric acid and borate clusters, $B(OH)_3.nH_2O$ clusters (n=0, 6, 32), and $B(OH)_4^-.nH_2O$ (n=0, 8, 11, 32) yields an extrapolated value of the equilibrium constant α_{34} for the isotope exchange reaction $^{10}B(OH)_3(aq) + {}^{11}B(OH)_4^-(aq) = {}^{11}B(OH)_3(aq) + {}^{10}B(OH)_4^-(aq)$. The predicted value of α_{34} = 1.024 -1.028 is expected to be close to the MP2 complete basis set limit. The range of uncertainty arises from contributions from a $B(OH)_3 \cdot 32H_2O$ Lewis acid-base complex and from the effects of solvation beyond n = 8 for borate ion.

At the pH values commonly encountered in low-temperature aqueous systems, Fe^{2+}(aq) coexists with Fe(III) oxide/oxyhydroxide mineral phases at the mineral-water interface. Due to the low solubilities of the ferric oxide phases, Fe^{2+}(aq) is the principal mobile iron species. However, because of the interplay of sorption, hydrolysis, electron transfer, and re-dissolution, the Fe(II) aqueous-ferric oxide/oxyhydroxide interface is a surprisingly dynamic environment with facile exchange of iron between the mineral and the solution. The rapid shuffling of iron among aqueous species, surface complexes, and oxide phases suggests that equilibrium between the iron isotopes might be readily established in interfacial environments, despite the insolubility of the Fe(III) oxides. The distribution of iron isotopes between aqueous complexes and minerals is an important aid in reconstructing the iron cycle in the early Earth and has important geobiological implications. Density functional theory electronic structure calculations have been used to compute equilibrium constants for iron-isotope exchange among Fe^{2+}(aq), Fe^{3+}(aq), and hematite (□-Fe_2O_3) in both bulk and surface environments. The iron-isotope fractionation between Fe^{2+}(aq) and Fe^{3+}(aq), determined using a range of exchange-correlation functionals and basis sets, is in good agreement with experimental measurements. The calculated reduced partition function ratio for bulk hematite is very close to previous estimates based on Mössbauer and inelastic nuclear resonance X-ray spectroscopy. However, the calculated fractionation between hematite bulk and the aqueous species Fe^{3+}(aq) and Fe^{2+}(aq) differs from experimental measurements carried out at the aqueous-hematite interface. We find a heavy iron enrichment trend in the order Fe^{2+}(aq) < hematite bulk ≈ hematite surface < Fe^{3+}(aq). In contrast to experimental studies, we find a significant positive fractionation (heavy enrichment) for Fe^{3+}(aq) relative to hematite, regardless of whether the hematite is represented by a bulk or a surface model. Our calculations indicate that it is unlikely that the aqueous interfacial structure of hematite is a simple termination of the bulk structure. Coupled with theoretical calculations, experimental measurements of isotopic composition of iron oxide surfaces provide more valuable information concerning their surface structures than previously thought.

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Grant: DE-FG02-95ER14498

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 involve 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: We have investigated two specific areas. The first is the kinetics of the phase transitions associated with catastrophic failure in materials. Specifically we studied the way a system brought into an unstable state evolves when there is a spatial symmetry change. We discovered two new effects; First, in systems with long range elastic forces, we found that there is an initial nonlinear evolution prior to the usual linear evolution one sees in systems with long range elastic forces. The second effect occurs if the symmetry of both the initial unstable phase and the final stable phase are non-uniform. In this case a linear growth regime occurs after the initial nonlinear growth discussed above. However, the linear growth modes are no longer Fourier modes but eigen-vectors of an evolution matrix generated by the interaction of the symmetries of the two phases. These results are relevant to understanding the catastrophic failure mode in many systems including metals, plastics and rocks. Two papers have been published reporting the results of these investigations. R. Dominguez, K. Barros and W. Klein "Early Time Kinetics of Systems with Spatial Symmetry Breaking" Phys. Rev. E 79, 041121 (2009) and K. Barros, R. Dominguez and W. Klein, "Beyond Cahn-Hilliard-Cook: Early Time Behavior of Symmetry Breaking Phase Transition Kinetics" Phys. Rev. E. 79, 042104 (2009).

The second area we investigated is the legitimacy of using equilibrium methods to describe systems with damage. To investigate this issue we have proposed a new model of damage based on a model introduced to study earthquakes. The model consists of a lattice which has stress σ_j associated with each vertex as well as a failure threshold σ^F and a residual stress σ^R. In the evolution of the original model if the stress on the sight is less than σ^F then we choose another site. If however σ_j exceeds the failure threshold then the stress on the sight is reduced to the residual stress. A fraction $\alpha(\sigma_j - \sigma^R)$ is dissipated and $(1-\alpha)(\sigma_j - \sigma^R)$ is distributed to the neighboring sites. This process continues until all sites have σ_j, σ^F At this point the system is "loaded". The loading can be done in several ways. In the original model the site with the largest stress is brought to failure by adding enough stress to the site, and every other site, so that the jth site has σ^F stress. Then the process repeats. We could also continuously add a fixed small amount of stress until we generate a failure. Another, equivalent method would be to decrease the failure thresholds slowly until there is a failure. This method of "loading" is similar to what is found in a model of damage. We will refer to this class of models as earthquake models.

The modification of the model is to deem as died, or inactive, all sites that have failed (in the sense described above) at least N times. These sites do not hold stress so that when a live site fails it only transmits the stress to other live sites in its neighborhood. If we set $\alpha = 0$, $N = 1$ and make the stress transfer neighborhood the entire lattice we have the equal load sharing fiber bundle model. We can vary the stress transfer neighborhood, N and α to obtain a model of different kinds of damage. Our investigation of this class of models has yielded several results including: 1) Using a metric to detect ergodicity we showed that even though the undamaged earthquake models are ergodic and in equilibrium, the appearance of damage breaks the ergodicity. Hence damaged models cannot be treated with equilibrium methods no matter how slowly the damage is introduced. 2) Introduction of any degree of damage and then stopping the damage and running in earthquake mode still results in non-ergodic systems. 3) The introduction of damage changes the Gutenburg-Richter scaling as well as decreasing the scaling region. However, if the number of events of size s for all of the levels of damage is plotted together we obtain an excellent Gutenburg- Richter scaling with a slope corresponding to a *b* value of 1. A manuscript resulting from these investigations has been submitted to Physical Review E for publication

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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_{H_2O}) in basaltic, andesitic, and rhyolitic melts in order to understand its compositional dependence, especially water content. Profiles of water concentration in hydration and diffusion couple experiments have been analyzed by Fourier transform infrared spectroscopy (FTIR) using a computer-automated stage on the microscope attached to the FTIR spectrometer. D_{H_2O} values were determined from FTIR 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 phosphorus 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 have generated similar P, Al, and Cr zoning in olivines grown experimentally at 1 atm with cooling rates of 15-30°C/hr in a synthetic Hawaiian basalt. We have also begun measuring Al and P chemical diffusivities in olivine.

Results: *Part 1:* This year we have concentrated on understanding the dependence of water diffusivity (D_{H2O}) on water concentration (C_{H2O}) from experiments with small water concentration gradients. These are hydration and couple experiments with the extremes of the water concentrations varying by less than ~1 wt. %. They allow us to build up the D_{H2O} - C_{H2O} relationship through a series of experiments with different water contents, using Boltzmann-Matano analysis. We are comparing our results to relationships in which D_{H2O} is proportional to C_{H2O}, D_{H2O} is an exponential function of C_{H2O}, and a speciation model in which $D_{H2Omolecules}$ is constant and hydroxyl groups are immobile. Results from our experiments for water contents 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 functions diverge at very low and high C_{H2O}. Therefore we are now focusing efforts on the very low water content region because of the importance of understanding these conditions in order to address such issues as water in the moon and fire fountaining in Hawaii. Initial experiments for Fe-free basalt and andesite indicate that D_{H2O} at very low C_{H2O} becomes very low, which is consistent with either a proportional relationship or the speciation model but not the commonly used exponential relationship. 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 water contents, the vast majority of the water dissolved in a silicate melt is present as OH and not as molecular water (as is the case when total water contents reach weight percent levels) and thus diffusion coefficients (D) should be much lower than at high total water contents since $D_{OH} << D_{H2O}$. Our experimental approach is quite simple: we have made up 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 1340°C (~10°C above the liquidus temperature of our composition) and IW+1, the P_{H2O} of the gas is ~0.3 atm. Based on water-solubility models, this should lead to ~300 ppm water dissolved in the melt. Our preliminary experiments support this and we are presently conducting time series runs to determine how long it takes to reach steady-state water contents in the glass. 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_{H2O} from ~0.3 to near zero atmospheres. For an equilibrated melt bead with ~300 ppm water, changing the gas mixture to CO-CO_2 will cause water to diffuse out of the melt and into the furnace atmosphere. By quenching changes after various times we can measure the water loss profiles in the glasses and constrain the bulk water D. Also by varying either the fO_2 or by adding an inert gas (Ar or N_2) to the H_2-CO_2 mix we can lower the initial water contents in the melts and explore how D varies with decreasing total water content.

Part 2: We are currently working on placing quantitative constraints on the diffusion coefficients of P, Cr, and Al in olivine using both experiments and natural samples. Given the importance of crystallographic continuity across a diffusion couple (in this case a low P, Cr, and Al olivine and a relatively high P, Cr, and Al olivine) we have spent a fair amount of time developing a recipe whereby a polished spherical grain of San Carlos olivine within a melt bead suspended from a FePt wire loop in a 1-atm gas mixing furnace develops (isothermally) an overgrowth of olivine (enriched in P, Cr, and Al) from the melt. We have succeeded in doing this, thus providing a starting point for our diffusion experiments. Our approach is similar in concept to that used by Vielzeuf et al. (2007, CMP 154, 153-170) to measure Ca diffusion in garnet. We expect to have the actual diffusion experiment completed in the next several months. We are continuing to collect X-ray maps of olivines from the Kilauea Iki lava lake, having increased the dwell time on each spot so as to decrease the detection limit for Al. In our earlier maps of olivines from a depth of 246 ft (near the thermal maximum of the lava lake), coupled P and Cr oscillatory zoning bands were visible; however Al zoning was not observed. We have re-mapped these grains, and now, in addition to P and Cr, coupled Al zoning is also observed. Coupled fine-scale P, Cr, and Al zoning is also observed in olivines from a depth of 246 ft. In addition, we have collected X-ray maps from olivines at depths of 149, 198, 209, and 285 ft, and all grains show fine-scale P zoning. Somewhat surprisingly, none of these grains show coupled Cr or Al zoning. We are presently looking at descriptions of the core to see whether our samples at 246 and 268 ft could represent foundered crust. Finally, in an effort to provide some experimental context for the P, Cr, and Al maps that we have collected on Gorgona komatiitic olivines, we are proceeding with 1-atm cooling rate experiments on a CaO-MgO-Al_2O_3-SiO_2 + P_2O_5 + Sc_2O_3 analogue composition. We are following the approach of Faure et al. (2006, J Pet 47, 1591-1610) of producing spinifex textures at relative slow cooling rates in a thermal gradient, since our cooling rate experiments on Hawaiian compositions have produced olivine morphologies and P, Cr, and Al zoning that is unlike those observed in spinifex olivine.

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Grant: DE-FG02-01ER15218

Nanoparticulate Iron Oxyhydroxide Controls on Aqueous Redox Chemistry and Microbial Species Distribution and Activity in Nature

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Objectives: We propose to follow the growth of nanoparticles in neutralized metal-contaminated acid mine drainage (AMD) solutions to describe, at the atomic level, the processes by which nanoparticles form, and determine how interacting and competing processes determine the fate of contaminants.

Project Description: Nanoparticles are important components of natural systems, arising as the result of physical, chemical, and biological processes. A typical example is the formation and transportation of iron oxyhydroxide and oxide nanoparticles formed in neutralization of acidic acid-mine drainage (AMD) solutions. AMD solutions are chemically complex, containing many anions and cations such as zinc and copper in additional to iron. Thus, in the nucleation and crystal growth of iron oxyhydroxide nanoparticles, these impurities can be incorporated into the nanocrystals, impacting the heavy metal cycling in the environment. It is essential to understand how the iron molecular clusters are formed in the neutralization process, how the clusters form the nuclei, how the nanocrystals grow, and how the impurity cations behavior in these processes. To address these questions, we employ a comprehensive approach that combines synchrotron experiments with molecular simulations and modeling. We used molecular dynamics (MD) simulations to predict and understand fundamental steps in AMD neutralization and used synchrotron x-ray adsorption spectroscopy (XAS) to study sulfate anion adsorption on AMD precipitates upon neutralization.

Results: In the first year of this project, MD simulations were used to study iron-hydroxyl molecular cluster formation in an iron chloride solution upon addition of sodium hydroxide, aiming to provide a molecular-level insight of the early nucleation stage of the neutralization process. Results (Figure 1) show that without addition of the neutralization agent, ferric ions are coordinated by six H_2O molecules and/or Cl^- ions (left), forming a octahedral coordination environment. Upon neutralization by NaOH, iron-hydroxyl molecular clusters form (Figure 1) in several hundred pico-seconds. The iron clusters are mainly interconnected via OH^- bridging. The average Fe-O distance in Fe-H_2O is 2.03 Å and the average Fe-Fe distance in Fe-OH-Fe is 2.92 Å, in good agreement with reported experimental values of 2.01 Å and 3.01 Å, respectively. Subsequent formation of iron oxyhydroxide precipitates is expected as a result of aggregation of the clusters.

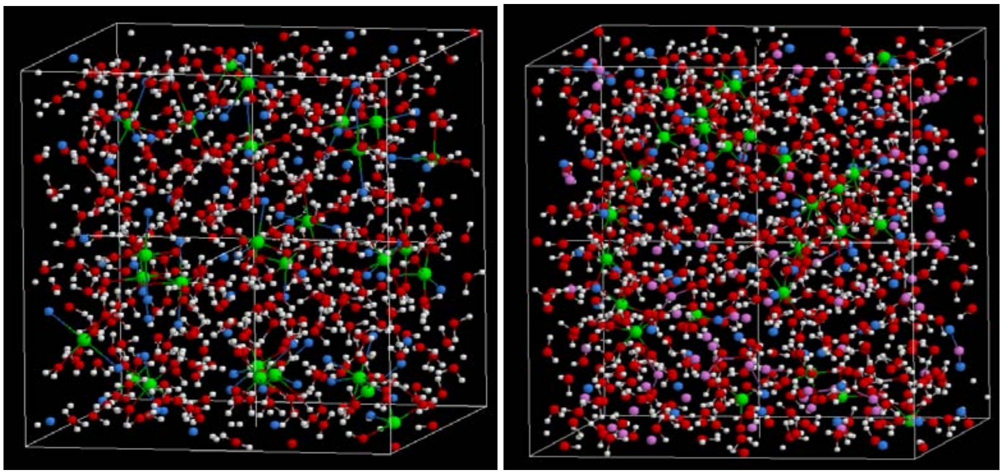
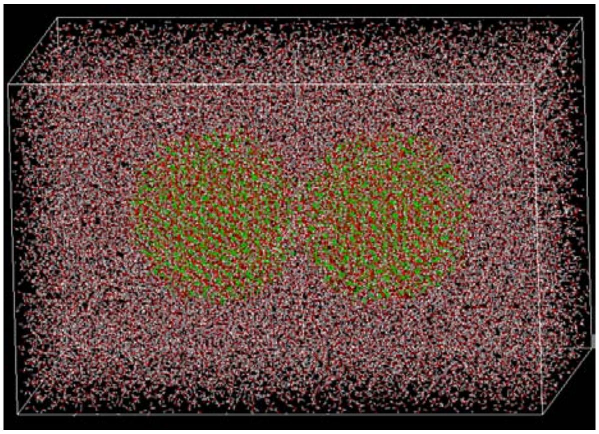


Figure 1. Snapshots of the MD systems, left: a $FeCl_3$ aqueous solution, and right: the solution upon neutralization by NaOH. O: red, H: white, Fe: green, Na: pink, and Cl: blue.

We also used MD simulations to study the thermodynamics of oriented attachment (OA) of goethite nanoparticles in water (Figure 2 left), a crystal growth mechanism adopted by nanocrystals under some conditions. The MD results (Figure 2) predict that goethite nanoparticles preferentially attach on the (110) and (111) faces. This may be related to the charge density and/or crystal polarity in the normal directions of the two faces.



OA face	dE(kJ/mol Fe)
100	0.39
010	-0.01
001	0.81
111	-0.61
110	-1.47
101	0.17

Figure 2. Left, snapshot of two oriented 4 nm goethite nanoparticles attached on (100) in water. Right, energy change of OA for two 4 nm goethite nanoparticles in water as a function of the attachment surface.

Our most recent experimental work includes S-K edge XANES / EXAFS measurements of iron oxyhydroxide products formed from neutralization of iron sulfate solutions by sodium hydroxide at different concentrations and solution pH.

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Grant: DE-FG02-08ER15992

Nanoparticulate Iron Oxyhydroxide Controls on Aqueous Redox Chemistry and Microbial Species Distribution and Activity in Natural Environments

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Objectives: The objective of this project is to investigate how nanomineral structure and properties, geochemistry, and fine scale variation in bacterial genotype are interconnected. We will test the hypothesis that microbial strain variants are selected for based on their ability to utilize iron oxyhydroxide nanomaterials of different phase, morphology and particle size and will determine if proliferation of specific strain variants can shape subsurface mineralogy.

Project Description: Under anaerobic conditions that occur in soils and sediments, some microorganisms such as species of *Shewanella* and *Geobacter* pass electrons from respiration of organic carbon to iron oxyhydroxide minerals, causing the minerals to dissolve. Microbial iron reduction occurs within natural multi-species consortia, which alter their membership and biochemistry as the result of changes in their physical and chemical surroundings. The mineral electron acceptors are often poorly defined surface coatings and colloidal aggregates composed largely of nanoscale particles. We will investigate how differences in the nanomineralogy of the subsurface drive changes in the strain makeup of the microbial consortia responsible for iron reduction.

Natural microbial communities are likely to include organism types with the range of genomic potential needed to profit from the expected suite of electron accepting minerals encountered in their habitats. As we predict that redox potential is likely to be a mineral characteristic key to strain selection, we will experimentally adjust the redox potential of electrodes coated with iron oxyhydroxide nanoparticles and test for reproducible patterns of organism response. We hypothesize that we can drive selection for the strain with cytochromes best optimized for electron transfer to the available mineral substrate. The biochemical basis for selection will be investigated through identification of protein variants involved in energy metabolism and protein-nanomaterial interactions. The redox characteristics of relevant nanomaterials will be measured so as to calibrate the results of the manipulation experiments for application to natural systems.

Results: The first objective of this research has been to obtain isolates and mixed consortia that can be used in the microbial fuel cell and other experiments. Six enrichments of Rifle, CO, sediment were set up under anaerobic conditions and incubated at 30°C using 10 mM acetate as the carbon source and e- donor, and with varying electron acceptors. The forms of available Fe used are 50mM Fe-gel, 20 mM Fumarate, 10 mM FeNTA, 50 mM akaganite, 50 mM goethite and 200 mM Fe-phosphate. Of these 6 enrichments, the Fumarate and FeNTA yielded the fastest growing bacteria, and have each been sub-cultured multiple times prior to isolation. The 16S rRNA gene-based identifications are underway. To date, plates of FeNTA are not exibiting growth. The Fe-gel cultures have been sub-cultured multiple times and isolation experiments are ongoing. The akaganite and goethite cultures are also moving toward isolation. To date, Fe-phosphate does not appear to be available to the bacteria, as it is not being reduced, as shown by a ferrozine assay. Progress has been made isolating Geobacter-like organisms in shake flask Fe(III)-NTA media. Initial results indicate specific types of microorganisms are enriched based on the type of electron acceptors available, as hypothesized. We will continue to characterize these iron-reducing microorganisms by isolating pure strains and comparing their genetic potentials for electron transfer proteins.

Geobacter sulfurreducens, a representative iron-reducing bacterium of which key electron transfer proteins has been established on the surfaces of graphite electrodes in a standard and newly designed microbial fuel cell (Figure 1a, b). The electrode will be poised at potentials representing those of iron oxyhydroxide nanoparticles and the variations, if present, in the electron transfer proteins will be examined. *G. sulfurreducens* are also being grown with different iron oxyhydroxide particles for directed evolution of electron transport proteins.

Figure 1: Microbial fuel cells established with Fe-reducing bacteria: left, standard cells and right, newly designed cell optimized for the current research.

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Grant: DE-FG02-05ER15637

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

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Objectives: Many sedimentary rocks are complex in composition and microstructure, particularly shales. A quantification of structural and textural characteristics is essential in the context of hydrocarbon reservoirs and carbon sequestration. Diffraction 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 are 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, to understand formation processes (sedimentation, compaction, diagenesis, deformation) and to establish models that link the internal structure to macroscopic physical properties. The focus is on shales, which comprise over 75% of rocks in sedimentary basins. Natural samples are compared with experimental analogs. Also, 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: A method to use hard synchrotron X-rays to obtain diffraction images of fine-grained multiphase rocks is becoming a routine at beamline BESSRC of APS. Also, methods of data analysis with the Rietveld method have been refined, with improvements for stacking disorder and corrections for monoclinic crystal symmetry. We obtain quantitative information on phase proportions, preferred orientation and grain size for shales with up to 10 components. Figure 1a shows a (001) pole figure of kaolinite for the diagenetic Qusaiba shale.

We have started to investigate 3D microstructures with X-ray microtomography (at SLS), obtaining resolutions of <1µm. Figure 1b shows the pore distribution in Qusaiba shale.

An interpretation of macroscopic anisotropy from microstructures has to rely on information about single crystal elastic properties of clay minerals. Since they can not be determined experimentally, we have begun systematic first principles calculations (in collaboration with Burkard Militzer and Lars Stixrude). Results indicate that elastic properties of disordered clays are much softer than ideal mica.

With 1μm microbeam X-rays (at ALS) it has been established that considerable lattice strain is preserved in deformed quartz. The histogram of equivalent strain (Figure 2) illustrates that 1000 microstrains (corresponding to 50 MPa stress) is present in metamorphic quartz, and over 3000 microstrains (150MPa) in shocked quartz. These studies will be applied to investigate residual strain in the vicinity of faults.

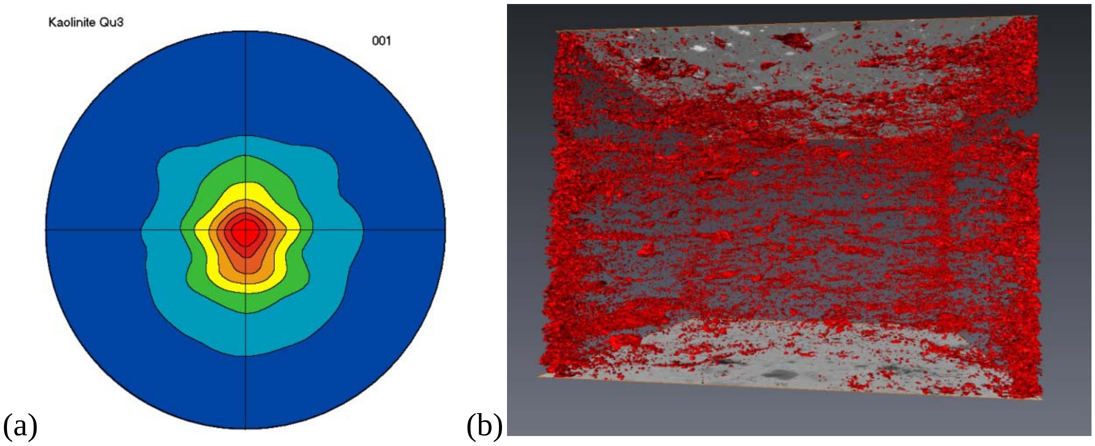

Fig. 1. Qusaiba shale. (a) (001) pole figure of kaolinite. (b) 3D porosity map measured with synchrotron X-rays at SLS.

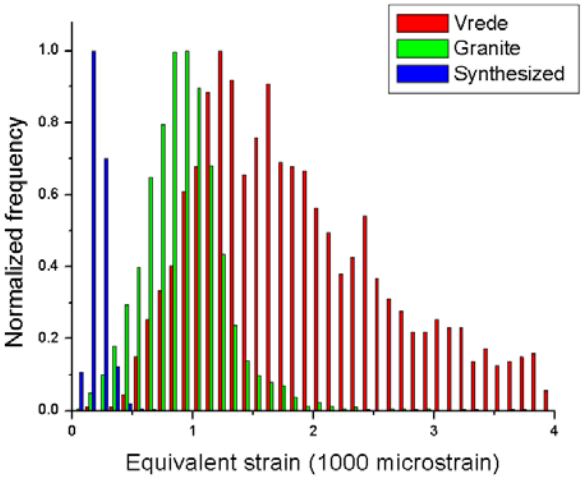

Fig. 2. Histograms of equivalent lattice strain mapped in ideal synthetic quartz (blue), undulatory quartz in moderately deformed granite (green) and Vredefort quartzite subjected to meteorite impact (red).

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Grant: DE-FG02-97ER14749

Thermodynamics of Minerals Stable Near the Earth's Surface

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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 essentially completed work on iron oxides and oxyhydroxides with ferric iron and confirmed the very close balance of energetics of many polymorphs at the nanoscale. A summary of our results and some other work has been published as an invited review in Science. Figure 1 illustrates the major effect of size on dehydration equilibria in iron oxide systems. Because of the smaller surface energy of oxyhydroxides compared to anhydrous oxides, the former are favored at the nanoscale and their dehydration may be shifted upward by as much as 100 degrees in temperature as a thermodynamic, rather than kinetic, effect.

We are starting work with Chris Drouet in Toulouse, France on energetics of apatites and the role of their evolving thermodynamic state in biomineralization. We are continuing work on hydrotalcites and are revisiting some manganese oxide phases to separate the effects of polymorphism and surface energies. We are collaborating with Peter Burns and Jeremy Fein at Notre Dame on the thermodynamics of uranium minerals. We are obtaining Fe_3O_4 nanoparticles for study of surface energy. Because of large differences in surface energies of spinels and rocks at oxides, and of metals and oxides, we are finding that redox equilibria are quite sensitive to particle size.

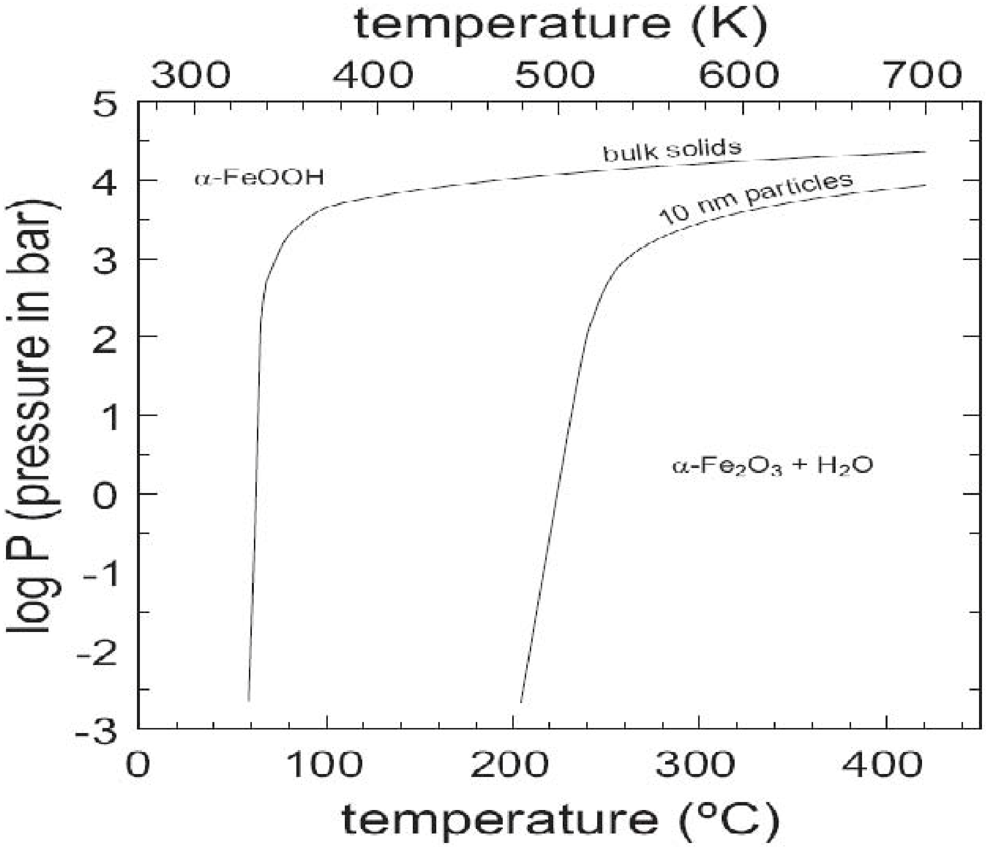

Figure 1. Effect of particle size on the dehydration curve of goethite to hematite plus water

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Grant: DE-FG02-04ER15498

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

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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: Identification of the types of the hydroxide functional groups present on the surfaces of oxide soil minerals has been a long-standing problem in interfacial geochemistry. Over the last three decades, infrared (IR) spectroscopy has been used to attempt to identify these groups. If the various kinds of surface functional groups η-OH, $\eta-OH_2$ (terminal hydroxide and water groups bound to a single iron atom), μ-OH (doubly bridging OH, bound to two iron atoms), μ_3-OH (triply bridging OH, bound to three iron atoms) have distinct OH stretching vibrations, a sufficiently high-resolution measurement of the infrared vibrational spectrum would reveal some of the details of the molecular level surface structure. Thus far, however, there have been no unequivocal assignments of the surface vibrational bands on iron oxide minerals.

We have carried out density functional calculations of vibrational frequencies of OH groups on an idealized goethite (110) surface, represented by a large embedded cluster model. The calculations show that isolated surface groups bound to one, two, and three metal ions can have nearly identical O-H stretching frequencies. This finding provides a strong constraint on interpretations of infrared spectra of oxide surfaces, and resolves the long-standing problem in OH vibrational assignments on goethite surfaces, where, in general, too few peaks have been observed relative to the expected heterogeneity of surface functional groups. These calculations serve as a baseline for the interpretation of IR spectra of carbonate bearing goethite.

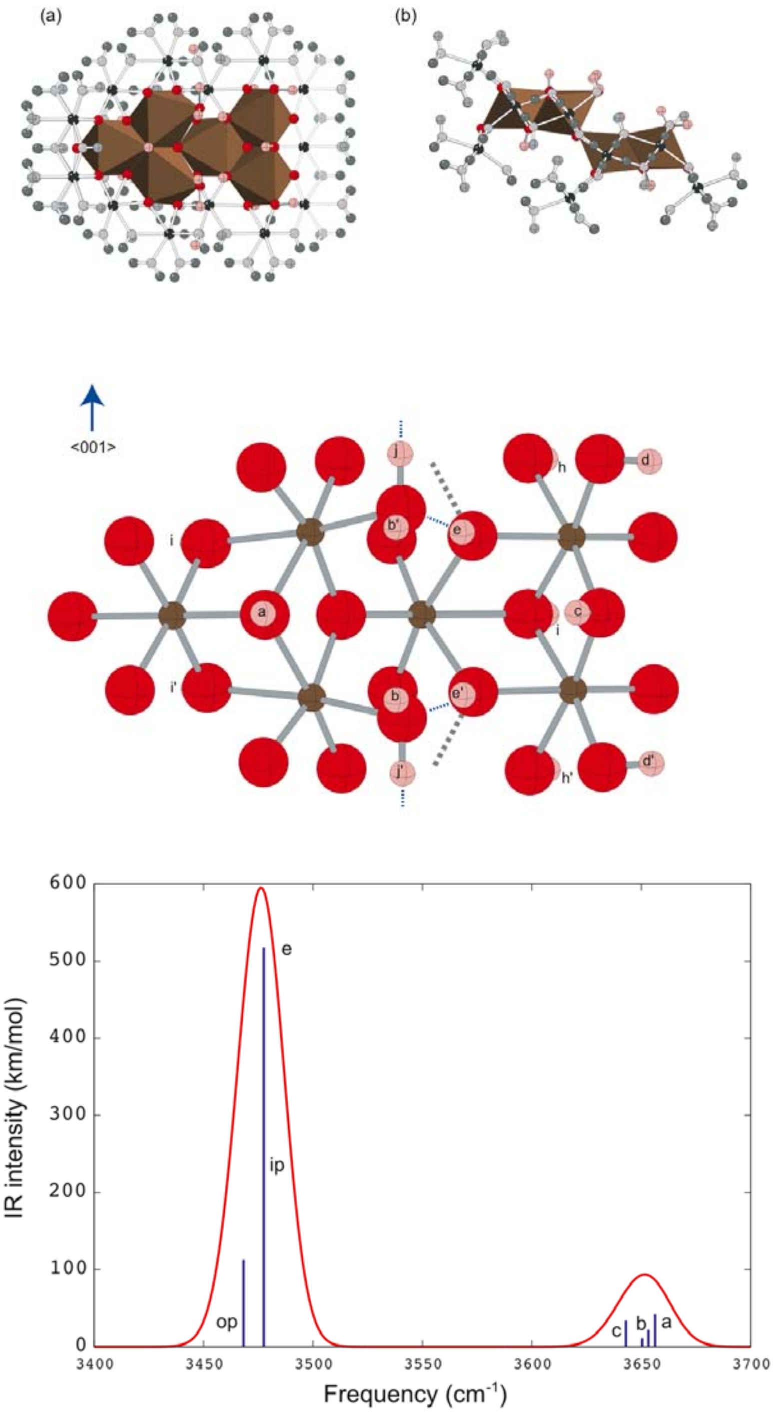

Figure: Model goethite cluster (top) and predicted B3LYP/6-31G* vibrational spectrum showing contributions from each functional group

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Grant: DE-FG-02-05ER15693

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

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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 Description: Geochemically important reactions often involve a bonded atom or functional group that is replaced with another. We probe these reactions at the molecular scale in order to establish reliable methods for predicting rates that cannot be experimentally studied. We rely on nanometer-size oxide ions as models because we know these solution structures with complete confidence, including the protonation states.

Results: The results divide broadly into two classes: **(i)** rates of exchange of waters bound to trivalent metals on nanometer-size clusters, such as the enormous 2.5 nm Keplerate shown in **Figure 1**; and **(ii)** rates of isotopic exchange of structural oxygens in nanometer-size ions of Group 5b metals. Experimentally, we measure rates of oxygen-isotope-exchange reactions between sites in nanometer-size aqueous molecules and solutions at the *elementary* or near *elementary* scale. The research requires that we synthesize the molecules with ^{17}O, an NMR-sensitive nucleus, or ^{18}O in various structural positions and follow the loss of signal as a function of time and solution composition using either mass spectrometry or NMR or both. Such clusters are the best molecular models for geochemical materials because we determine the reaction rates at individual structural sites, we understand the structure with confidence, and the molecules are sufficiently small to treat at a comprehensive level via computation.

In the last year we synthesized several new clusters and measured the rates of oxygen isotopic exchange into the various structural sites; the results were identified by *Science* as one of their '*Editor's Choices* (June, 6, 2008)' of important results. We simultaneously followed the dissociation pathways and products of a nanometer-size oxide ion using electrospray ionization mass spectrometry (ESI-MS). We showed that, at the nanometer-size scale, reactivities are not identifiable from the ground-state structures. Oxygen-isotope exchange rates do not suggest themselves from bond lengths, partial charges or from easily calculated parameters such as Pauling bond strengths. The rates span a range of ~10^4 and aren't predictable from the simple structural features of the stable molecule. Furthermore we showed that the oxygens in the structure react in concert. At low pH, a single protonation increases rates of isotopic substitution throughout the molecule and, as pH rises and the molecule begins to slowly dissociate, the entire cluster responds to increased [OH^-] concentrations. The results indicate that dynamic simulations are needed on model clusters that are structurally faithful to the actual molecule or the results will miss the essential chemistry.

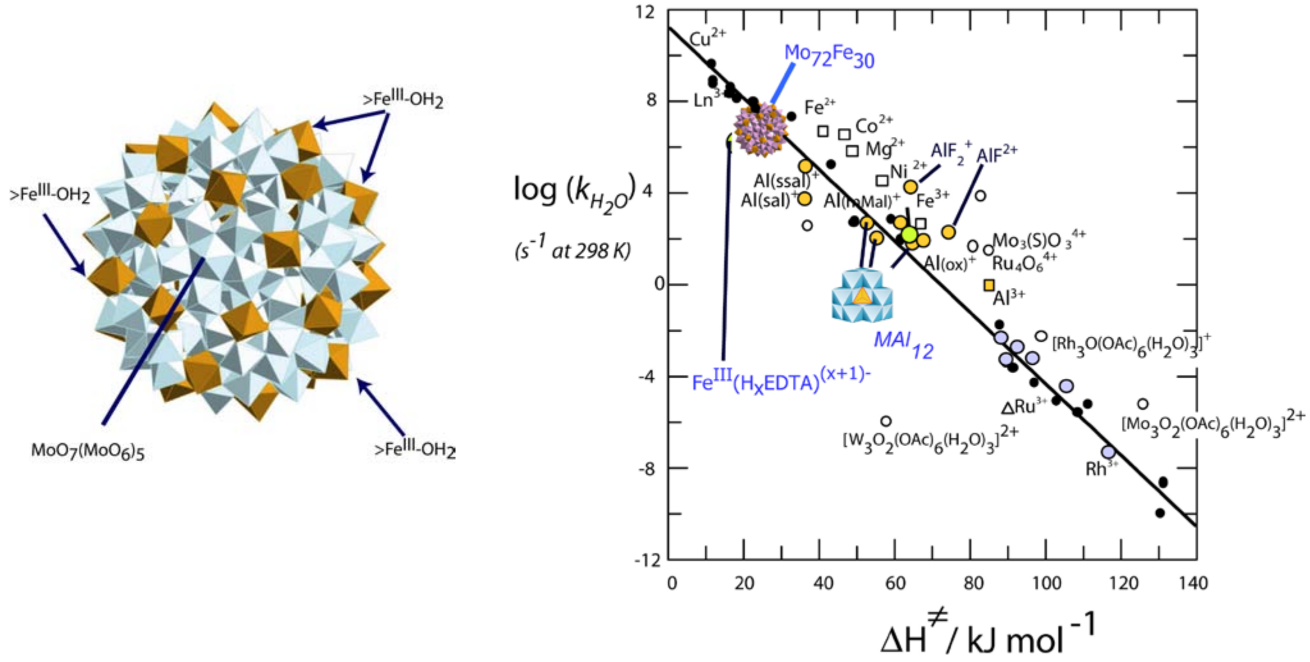

Figure 1: Real molecules can advance geochemistry in ways that are impossible using either bulk solids or simulation. (**left**) A 2.5 nm size oxide ion, a Keplerate, with 30 >Fe^{III}-OH_2 that can be studied spectroscopically to understand ligand-exchange reactions on natural materials like iron (hydr)oxide sols. When the rate parameters for such large molecules are compared to smaller ions **(right)** they indicate complete consistency--for these reactions there is nothing inherently mysterious about the size of the cluster. The ordinate, k_{H_2O}, is the rate of exchange of bound with bulk waters and $\Delta H^{\neq}$ is the activation enthalpy. Rates vary by over a factor of 10^{20} but in a consistent way across size scales.

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Grant: DE-FG02-04ER15568

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.

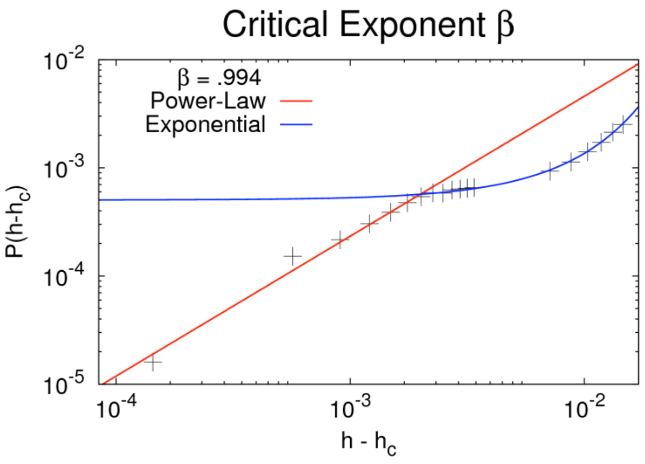
Project Description: Storage of nuclear waste, oil recovery and earthquakes are examples of how the structure and failure of rock masses affect processes of interest to the DOE. Each of these processes involves the multi-scale physics of geological materials at shallow depths. Observations of rock masses 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.

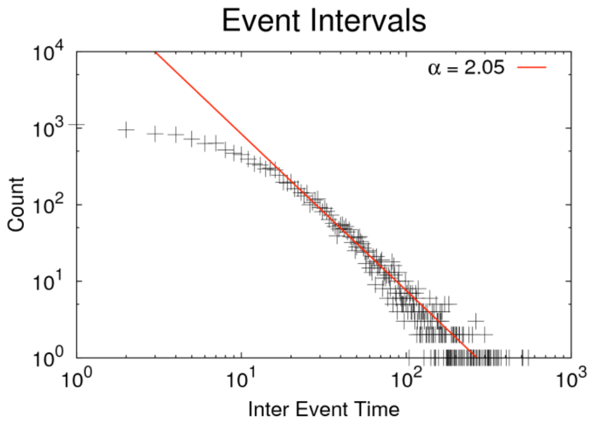
Results: In this year’s research, we have studied the physics of progressive material damage under load using models that incorporate both failure thresholds and load sharing. Models of this class include both slider block models and fiber bundle models. In both models, external loads are applied to a load plate to which each of the blocks or fibers is attached. Fully interacting fields of defects and damage are generally not included in most current models for material deformation. Instead, defect density and damage fields are assumed to be non-interacting or dilute, implying a strictly mean field approach. This year we are studying several models, one of which is an interacting block-slider system with transient damage and healing, and another of which is a blockslider with progressively degrading strength under load. In both models we have found that large nucleation events are observed, and can be characterized by an order parameter much like large spanning clusters in percolation theory, or the magnetized phase in an Ising model, both of which possess associated order parameters.

Summarizing our results, we have found that, using simulations of a model for damage and failure with healing in materials, we are led to a family of scaling exponents that can be measured in simulations. We find that for a mean field model, the exponents are those that also characterize mean field percolation clusters. Furthermore, we note that these exponents have also been seen to characterize fracture and failure in laboratory experiments. As a result, we conclude that failure in materials may be dominated by the mean field nature of the interactions, a result that has been seen in other studies of related models.

In our simulations, we find that as the weakening parameter h increases ($h > 0$), a value is eventually reached at which large spanning clusters, or nucleation events, begin to appear. This result was noted in previous work by other authors, which demonstrated that it is possible to tune such a model so that intermittency in the appearance of spanning clusters is observed. Thus large spanning clusters should be associated with an order parameter in the same way as in percolation systems. We then defined the order parameter $P(h)$ as the fraction of observed avalanche events that are spanning clusters, or alternatively, as the probability that a large spanning cluster ("characteristic earthquake") will appear as the next cluster. In general, we find that for $h = 0$, $P(0) = 0$ in any finite time interval, but that for some value $h > h_c$, $P(h) > 0$, a nucleation event appears with significant probability. This is essentially equal to the failure probability for the system as a whole.

Our simulations are carried out on L × L square lattices ranging in size from L=175 to L=500. As boundary conditions, we use both open boundary conditions, meaning that some stress is dissipated off the edge of the lattice, as well as compensated open boundary conditions, meaning that the interactions are adjusted near the lattice boundaries such that no stress is lost from the sides of the lattice. Below we show the probability of grid-size events vs. the weakening parameter adjusted by the critical weakening value. The plot is on a logarithmic scale emphasizing the power-law dependence of $P(h-h_c)$ with a scaling exponent $\beta = 1$. The second region of increasing $P(h-h_c)$ is fit to an exponential curve. The value $\beta = 1$ is characteristic of mean field percolation on a Bethe lattice. Other interesting data are shown in the next figure, which plots the "time interval" (as measured in very small events) between moderate to large events. The exponent $\alpha = 2$ has been observed in the laboratory in the fracture and failure of stress fiberboard experiments.


Critical Exponent β
β = .994
Power-Law
Exponential
10^{-2}
10^{-3}
10^{-4}
10^{-5}
P(h-h_c)
10^{-4}
10^{-3}
10^{-2}
h - h_c


Event Intervals
α = 2.05
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
Count
10^{0}
10^{1}
10^{2}
10^{3}
Inter Event Time

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Grant: DE-FG02-09ER16003

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 when 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 a recently developed 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 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: During the first half-year of this project, we carried out a series of reactive flow experiments in partially saturated fractures. The 9.4 x 14.5-cm analog fractures were fabricated by mating a rough glass surface with a soluble, smooth, transparent surface (single KH_2PO_4 crystal). We conducted several experiments in which a reactive fluid (under-saturated water) flowed through a fracture occupied by an entrapped, residual non-wetting phase (air). By rotating the fracture plane to a different orientation for each experiment, we changed the influence of gravity, and thus the initial distribution of the residual phase. Because each experiment used the same textured glass plate, the initial fracture aperture fields were identical. Changes in fracture aperture caused by dissolution resulted in alterations of local capillary forces and eventual mobilization of the entrapped phase. In the absence of buoyant forces, bubbles migrated counter to the prevailing pressure gradient and tended to block incipient dissolution channels. The result was the formation of a single, narrow dissolution channel through the center of the fracture (a). The addition of buoyant forces led to the eventual upward mobilization of bubbles until they eventually left the fracture. This resulted in broader dissolution channels within the fracture and did not inhibit the formation and growth of secondary channels (b). In a previous experiment in a saturated fracture at a similar flow rate with similar reaction kinetics (c), a doubling of the mean fracture aperture led to a 3.5-fold increase in fracture transmissivity. By contrast, in the partially saturated experiments, a doubling of the mean fracture aperture caused up to a 20-fold increase in transmissivity above the initial transmissivity in the saturated fracture. These results suggest that the presence of a persistent residual phase (such as CO_2 or oil) in fractures undergoing chemical alterations may significantly impact the magnitude of permeability alterations.

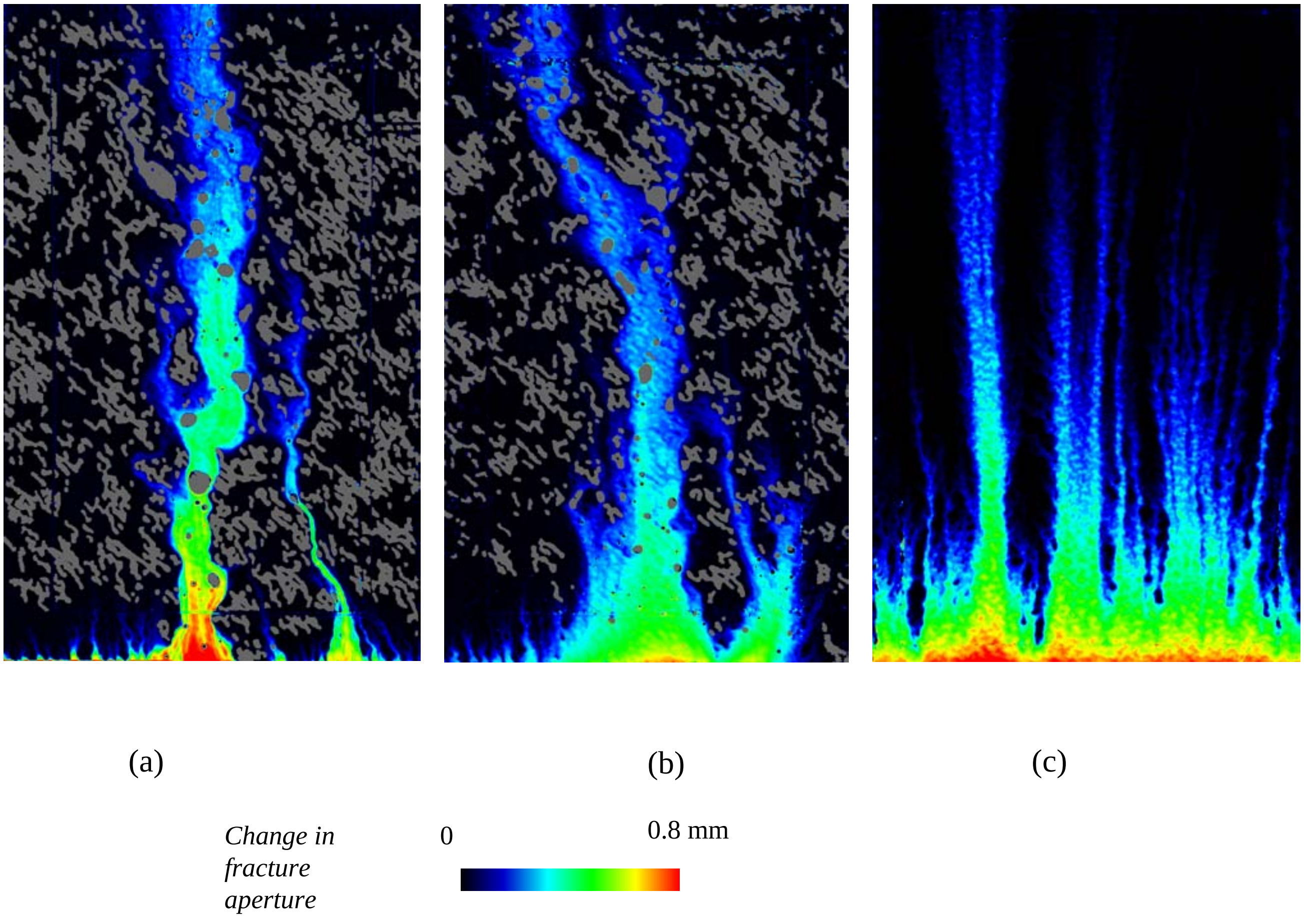
(a) (b) (c)

Figure. Measurements of change in fracture aperture caused by mineral dissolution during reactive fluid flow experiments. Each frame shows a different experiment when at the time when the mean fracture aperture had increased by a factor of two. The first frame shows a horizontal fracture with an entrapped residual phase (gray regions); the second frame shows the same fracture oriented 35° from horizontal; and the third frame shows results from a similar experiment

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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 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 latest studies of the South Ellwood fault in the Santa Barbara basin 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). We have recently been able to chemically document local seawater influx into the reservoir in terms of oxygen and deuterium isotopes and elevated magnesium and sulphate compositions. 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-Inglewood 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 a 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.

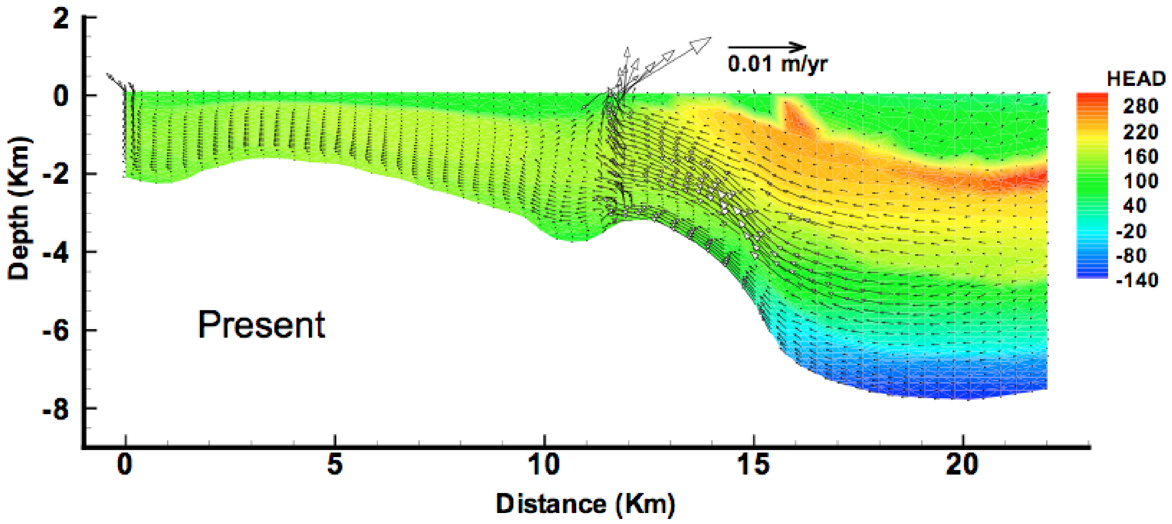

Figure 1. Large-scale SW-NE profile FEM model of the LA basin, showing flow patterns.

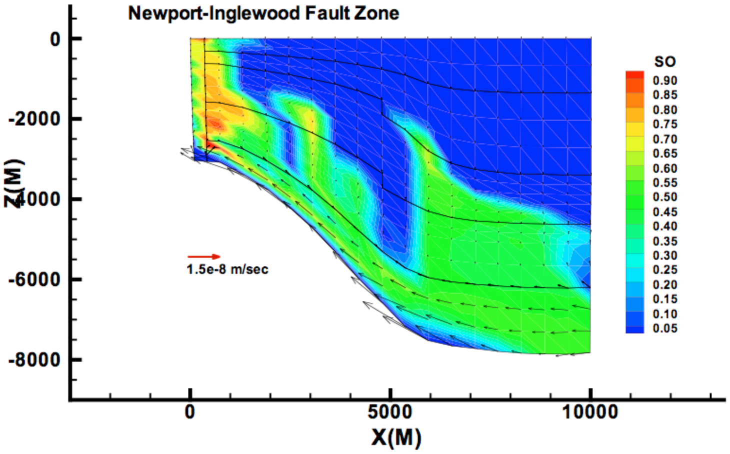

Figure 2. Zoomed view of petroleum saturations and flow patterns near area of discharge.

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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: This project began in Sept. 2008. 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 level set method on adaptive mesh refinement to keep track of the interface between two phases. This method automatically refines near the interface between phases and allow for the accurate computation of interface curvatures. The loss of mass inherent to level-set methods is negligible thanks to refinement and robust reinitialization schemes.

- We have developed a numerical method to compute the contribution of singular source terms on a surface, as for example the contribution of surface tension forces. 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 are developing and implementing two approaches for inclusion of complex solid boundary shapes. One relies on the Immersed Boundary Method, the other on the novel approach to the discretization of Dirac delta functions on Octree. The advantage of the novel approach is that a sharp boundary can be considered instead of relying on a smearing of the variables near the rocks boundaries. Analysis of those approaches will identify the best treatment of solid boundaries.

- We are developing 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. We expect that this solver, along with the saving in computational resources from the Octree data structure, will produce a method capable of simulating large three dimensional two-phase flows.

- We are developing and implementing a numerical method for treating the contact line at the solid/fluid interface. Here, the main challenge lies in dealing with the well-known force singularity that arises in the context of applying the standard no-slip boundary condition along solid walls. We are currently testing and validating numerical implementations of a Navier-slip condition in a fashion that yields numerical convergence and accounts for essential contact line hysteresis effects.

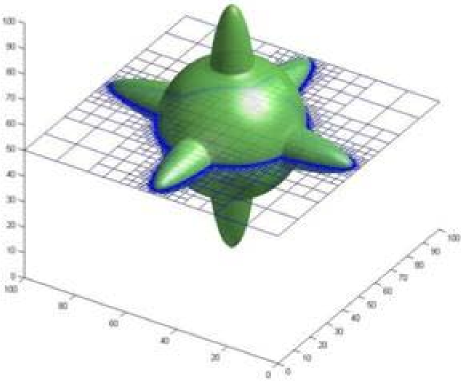

Figure 1: Cross-section of our automatic adaptive mesh refinement scheme. The geometry of arbitrary objects is implicitly captured by the level-set function and robust and efficient solvers are developed on such grids.

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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°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°K of $CaCl_2$ in 64 waters are shown. The results are in qualitative agreement with the EW mechanism. For this 650°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°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.

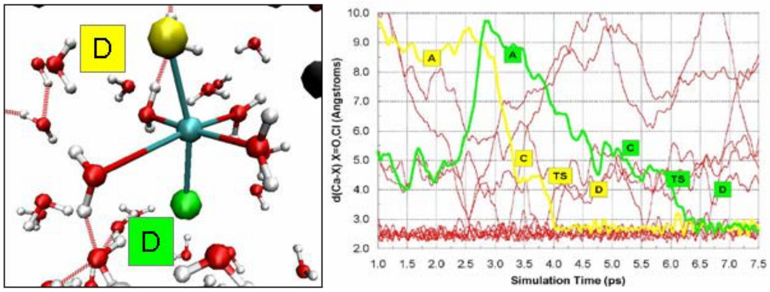

Figure 1. Diffusion-controlled high PT ion pair formation.

Methods Developments Results: (please see PNNL Report)

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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 and microtomography; (3) powder, microcrystal and surface diffraction; (4) high-pressure crystallography with diamond anvil cells and multi-anvil presses, and (5) 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 sixty seven (269) beam time proposals were received, 319 unique users conducted experiments, and 65 papers were published. Published results included the following (lead collaborators and affiliations in parentheses). (1) Uranium and copper contaminants in vadose zone and aquifer sediments from the Hanford site were found to exist as fine-textured grain coatings of chlorite, hydrous-silicate, hydrous-phosphate and x-ray amorphous phases (D. M. Singer and G. E. Brown, Jr., Stanford University). (2) Degradation of organic matter within shallow sediments of the Mekong Delta drives reductive dissolution of Fe (hydr)oxides and reduces As(V) to As(III), releasing As to porewater (B. D. Kocar and S. Fendorf, Stanford University). (3) Predominant antimony sinks from weathering of metals in Swiss shooting ranges were found to be amorphous and crystalline iron oxides (S. Ackermann, Albert-Ludwigs-Universität-Germany). (4) After exposing the α-Fe_2O_3 (0001) surface to aqueous Fe(II), the surface structures of the two, chemically-distinct, co-existing structural domains were modified, resulting in six-coordinated adsorbed Fe at the surface with bond-length evidence for the oxidation of Fe(II) to Fe(III) upon adsorption (K. S. Tanwar and T. Trainor, University of Alaska - Fairbanks). (5) Copper K-edge X-ray absorption spectra recorded from natural polyphase brine fluid inclusions in miarolitic quartz from the Omsukchan Granite, Russia, indicated that $[CuCl_2]^-$ is stable in the Cu-poor inclusions at magmatic hydrothermal temperatures (~700 °C), extending the known range of this complex by 200 °C and providing an example of how inclusions can be used as sample cells for the spectroscopic study of fluids at extreme conditions (A. J. Berry, Imperial College London, and A. Harris, University of Tasmania). (6) A grazing incidence x-ray fluorescence technique was developed to nondestructively differentiate terrestrial surface contamination from the low concentration implanted solar wind in Genesis collectors, demonstrating an approach for quantifying low concentration surface chemical species in solids (K. Kitts, Northern Illinois University).

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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 and bioaccessibility of toxic metals and metalloids in contaminated sediments and particulates, efficiencies of contaminant remediation strategies, studies of how bioaccumulation processes affect the distribution of trace toxic metal species in soils, using iron oxidation states determined by XANES to infer the oxygen fugacity conditions of magmatic systems, and mineral surface controls on metal partitioning.

Results: Fifty-six (56) unique users conducted experiments within the past year and 15 papers were published. Research included the following (lead collaborators and affiliations in parentheses): (1) Binding of molybdenum to natural organic matter helps prevent leaching of molybdenum, and is thus a critical step in securing new nitrogen in terrestrial ecosystems (T. Wichard and S. Myneni, Princeton University). (2) the mineralogical and chemical makeup of the bentonite from a geosynthetic clay liner used as a reactive barrier allowed *in-situ* distinction of accessory crystalline phases present in the “starting material” bentonite from those formed as a result of interaction with metal-bearing leachates, thus, providing crucial insight into the development of metal-attenuating crystalline phases that have a significant long-term impact on metal mobility (K. Lange and H. Jamieson, Queens University). (3) Mineralogy of As in weathered tailings (Nova Scotia) is highly variable, with aggregates of more than one As-bearing phase common, and major differences in As mineralogy in the tailings are mainly controlled by factors that influence the weathering history (e.g., presence or absence of mill concentrates, degree of water saturation, and abundance of relict carbonate minerals) (S. Walker and H. Jamieson, Queens University). (4) Magmatic $Fe^{3+}/\Sigma Fe$ ratios increase toward subduction zones and correlate linearly with H_2O content and element tracers of slab-derived fluids, demonstrating a direct link between mass transfer from the subducted plate and oxidation of the mantle wedge (K. Kelley, University of Rhode Island, and E. Cottrell, Smithsonian Institution). (5) Cadmium selenide quantum dot nanoparticles fed to planktonic crustaceans (*Daphnia magna)* were confined to the gut, and there was evidence of neither further assimilation into the organism nor dissolution of the nanoparticles, suggesting limited toxicity (B. Jackson, Dartmouth College).

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Grant: DE-FG02-09ER16092

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 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: Because initial funds were received at the end of this fiscal year, this report focuses on the upgrade plans. The upgrade involves addition of a second undulator, replacement of the magnetic array in the existing undulator, modification of an existing experimental enclosure and addition and modification of beamline components. The two undulators will be installed in a canted geometry to provide two independent x-ray sources. The existing 13-ID-C enclosure will be partitioned into two enclosures by adding a dividing wall, door, and pass-through shielded beam pipe. X-rays will be provided to this new enclosure (13-ID-E) by installing the second undulator, two horizontal deflecting mirrors, a monochromator and two shutters. The new configuration will provide x-radiation from the new medium-energy undulator (2.3 to 23 keV) to the x-ray microprobe, which will also be able to perform non-laser heated diamond anvil cell (DAC) spectroscopy and diffraction experiments. The downstream undulator will supply both double-focused monochromatic x-radiation from 5.6-80 keV and white beam to the surface diffractometer, the laser-heated DAC, and the 1000-ton multi-anvil press. These three instruments will each receive an increase in beam time of ~33% and the microprobe will operate continuously, doubling the total beam time available on the undulator beamline. The work plan involves an aggressive construction timeline which will allow this upgrade to be achieved with minimal impact and interruption to the existing user program.

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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 silicate melts and in water, and use the results to better understand transport phenomena in natural systems.

Project Description: Experiments designed to measure the isotopic fractionation of calcium, magnesium, iron, lithium, and most recently potassium by chemical diffusion in natural silicate melts using diffusion couples with starting materials made from Mid-Ocean Ridge Basalt juxtaposed with a natural rhyolite glass or natural materials from coeval mafic and silicic magmatic systems. Given that the laboratory experiment document kinetic isotope fractionations that are large compared to modern precision a natural progression of our work involves finding natural examples of such isotopic fractionations that can them be interpreted in terms of particular transport mechanisms. A separate set of piston cylinder samples were made entirely of basalt and intentionally displaced from the hot spot of the heater assembly in order to maintain a temperature difference of about 150°C for up to 100 hours across the sample while molten. The goal was to document and quantify thermal isotope fractionations of all the major element of basalt except for aluminum that is mono-isotopic in nature. The project also involves determining the magnitude of isotope fractionation of dissolved species by diffusion in water and using these to validate molecular dynamics calculation for the relative mobility and isotopic fractionation of Ca, Mg, K and Li.

Results:
Laboratory experiments: We have now completed our study of the isotopic fractionations of all the major elements (Si, O, Mg, Ca, and Fe) except for Al of molten basalt due to thermal diffusion (also referred to as Soret diffusion in the geochemical literature). A temperature difference of 100°C maintained for a few tens of hours across 10 cm of molten basalt results in easily measured isotopic fractionations of all the major elements (e.g., 4‰ per atomic mass unit per 100°C for Mg). The relevance of such thermal fractionations for natural systems will often be limited by the fact that in most settings temperature differences will dissipate much more quickly than the time it would take for significant chemical and isotopic fractionations to evolve. This has led us to now focus our thermal fractionation experiments on potassium and we are finding that when we counter diffuse potassium and iron, the timescale for thermal fractionations of these elements to reach a steady state is a few minutes rather than a few tens of hours as in our earlier experiments.

Potassium is proving to be a very interesting element in terms of several other types of kinetic isotope fractionation. Our recent experiments on isotopic fractionation by diffusion of dissolved salts in water show that potassium is the most fractionated of the alkalis, and much more fractionated than divalent cations. The experimental results have been reproduced by molecular dynamics calculations, which give special insight as to what controls the relative isotopic fractionation of different elements as they diffuse in water. We have also completed a series of evaporation experiments where potassium is the most volatile element and find a very large isotopic fractionation between the evaporation flux and the condensed source.

(II) Applications to Natural Systems: We recently completed and published a review of our work on high-temperature kinetic and equilibrium fractionations in molten silicate and metal alloys. The equilibrium fractionations involved isotopic measurements of Fe, Mg and Li olivine that crystallized from Kilauea Iki lake (Hawaii). The important result is that there is measurable isotopic fractionation of iron (but not Li or Mg) even at the high temperatures of partially molten basalt. Together with a graduate student we have completed a study of magnesium isotope fractionation between a mafic melt that intruded partially molten silicic rocks form the Vinal Cove complex of the Vinalhaven Intrusive Complex in Maine. Piston cylinder diffusion couples were made by juxtaposing natural silicic and mafic rock powders from Vinal Cove. The diffusion couples produce magnesium isotopic fractionations of about 2 per mil per atomic mass unit. The magnesium isotopic compositions of closely spaced samples from across the exposed contact between the mafic and more silicic in Vinal Cove are virtually identical to those of the laboratory diffusion couples. This leads to the conclusion that the transport mechanism in the natural system was by molecular diffusion, not mechanical mixing, and that at the contact the system was partially molten for not much more than a few hours.

(III) Analytical developments: Isotopic analyses by multi-collector inductively coupled plasma mass spectrometry (LA-ICPMS) are becoming increasingly used because of their ability to measure small spots and because they don’t require tedious chemical purification of the elements to be measured. But laser ablation has potential problems with isotopic artifacts due to matrix effects. We have been making a special effort to determine the magnitude of such matrix effects by comparing isotopic measurements by (LA-ICPMS) to those made on purified solutions. We have so far focused mainly on Si and Mg in silicate samples ranging from rhyolite to basalt and on highly isotopically fractionated evaporation residues. The results show that there are significant matrix effects regardless of whether the ICPMS is a Neptune or an ISOPROBE. The laser being used for our study is a 193 nm excimer laser, which is commonly used for LA-ICPMS isotopic measurements. 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.

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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. Our investigations suggest that the focusing of groundwater at the channel head selects a regular shape. We seek to better understand how this form is selected and to specify the conditions under which it is stable. 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.

In all cases, our investigations involve physical reasoning, mathematical modeling, laboratory experimentation, and observations of kilometer-scale channels. Our laboratory investigations focus on a table-top experiment that simulates the growth and bifurcations of a single channel. Our field investigations, performed at the Apalachicola Bluffs and Ravines Preserve, near Bristol, Florida, emphasize quantitative tests of our theoretical predictions.

Results: In FY2009 we studied the focusing of groundwater at channel heads and the resulting channel growth. Figure 1 shows our theoretical predictions for water table height and the resulting water flux to the network. Comparison between predicted and measured fluxes in the streams shows excellent agreement. Theoretical analysis of our experimental setup indicates a linear relationship between water flux and erosion rate. By combining these field and laboratory observations into a simple theoretical model, we are then able to predict the typical "amphitheater" planform shape of the valley heads.

As valley heads grow forward, sediment on valley walls moves to streams by a diffusive process. We evaluate the diffusion coefficient from a high-resolution topographic map of the field site. Notably, the diffusion coefficient shows sensitivity to the exposure to sunlight. Once sediment is removed from the valley walls, it is transported away from the head by the stream. This process couples the elevation profile of an individual stream to the water table. Comparison of the predicted power-law profile to real streams shows strong agreement.

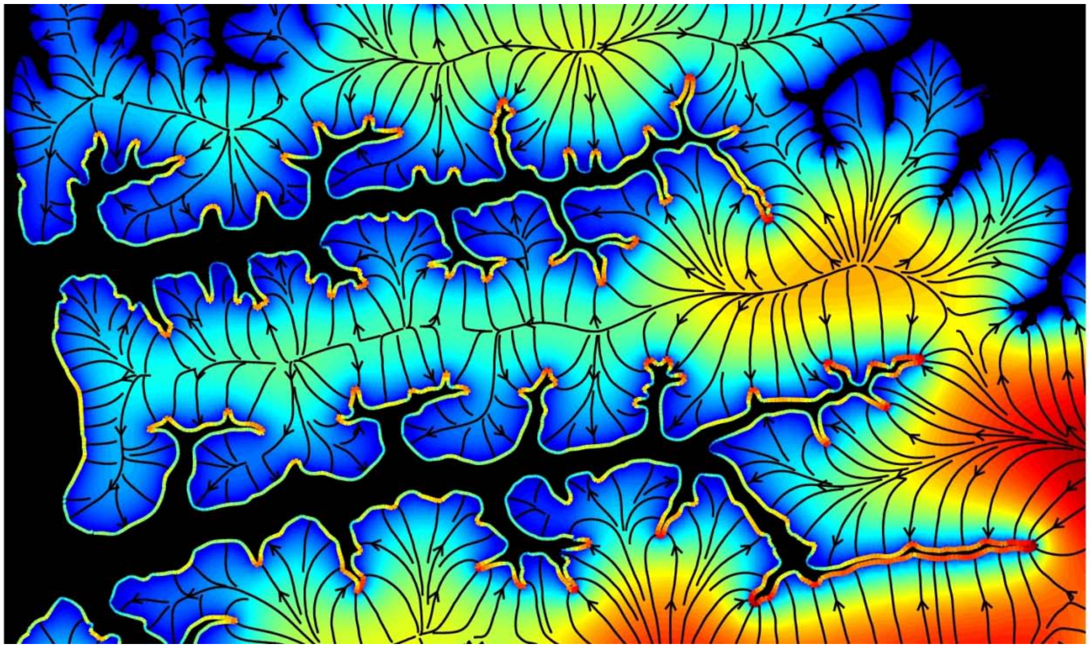

Figure 1: Network of "steephead ravines" (black) draining into the Apalachicola River (left), near Bristol, Florida. Changes in the water table elevation focus groundwater to different sections of the network. The parts of the network that receive more water grow faster. Warm colors between ravines indicate a high water table. Warm colors on the network boundaries indicate a high flux. Groundwater flows along the black lines. The horizontal dimension is roughly 4 km.

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Monitoring the Subsurface with Quasi-Static Deformation

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Objectives: To investigate the use of measured changes in the tidal tilt as a diagnostic for the infiltration of fluids in the subsurface.

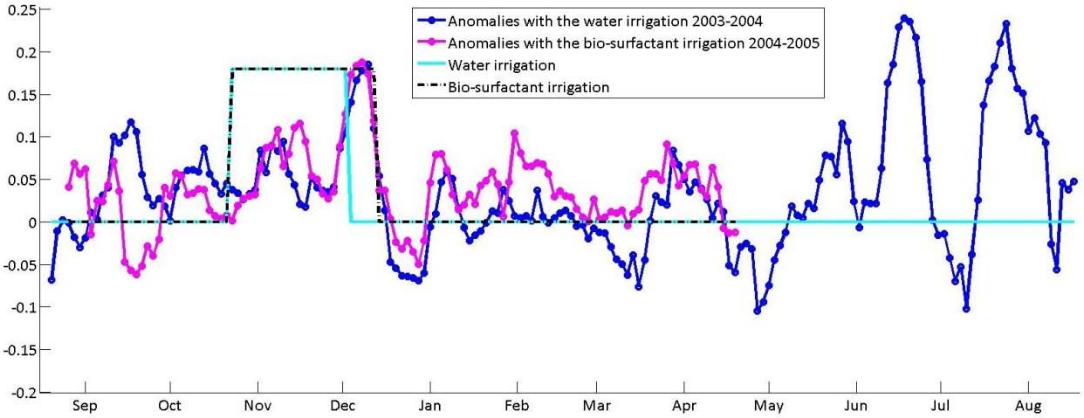
Project Description: Nature is performing a deformation test on a daily basis by the stress associated with earth tides. Although the associated deformation is small, it results in changes in the tilt (about 100 nano-radians) that are detectible with modern tilt meters (that have an accuracy of a few nano-radians). We use recorded tilt measurements at a field test where the soil is irrigated, once with clean water, and once with water mixed with a bio-surfactant. Previous laboratory measurements carried out by co-PI Hartmut Spetzler indicate that for low frequencies, changes in the water content in soil can lead to changes in the elastic moduli that are of the order of 40%. The earth tides have a dominant period of about 12 hours, and are essentially quasi-static. They thus constitute an appropriate loading to diagnose the low-frequency changes in elastic moduli measured in the laboratory under field conditions.

A three year field study at the Maricopa Agricultural Center of the University of Arizona involved two six-week irrigation periods of a 50m by 50m area. The first irrigation was with water only and the second with water containing a bio-surfactant. We analyzed measurements from three tiltmeters, which are installed at a depth of 13 m along an East-West line at distances of 3 m, 13 m and 23 m from the edge of the irrigation area. We compare theoretical tidal tilts with the tilts measured at the three tiltmeters.

We have used first-order perturbation theory to account for the change in the tidal response due to changes in the mechanical properties of the irrigation area. In this perturbation treatment we used the response of an elastic homogeneous half-space as a reference state. This model makes it possible to relate observed changes in the tidal tilt to the changes in the shear modulus of the irrigation area.

Results: Tidal tilts have maximum amplitudes of about 100 nano-radians. The accuracy of the tiltmeters is about 1 nano-radian, but complicating physical phenomena such as the response to distant loading (e.g., irrigation), earthquakes, and electrical noise, required significant pre-processing of the data to extract the tidal response.

The measured change in the amplitude of the tidal tilt is shown in the figure below, where the vertical axis is the ratio of the change in the amplitude of the tidal tilt to the tidal tilt predicted by tilt for a laterally homogeneous earth model. The observed changes in the tidal tilt are about 20 nano-radians. Although the tilt anomalies are fairly noisy, there are consistent changes in the tilt at the end of the irrigation periods in the two years near the end of December.



Observed changes in the tidal tilt versus time in the borehole closest to the irrigation area measured in 2003-2003 (blue line) and 2004-2005 (purple line). The period of irrigation in both years took place from late October through early December, as indicated by the rectangle.

The theory used to quantify changes in tilt is relatively crude and the noise in the tilt anomalies is fairly large. For this reason it is not possible to carry out an inversion for the change in the mechanical properties caused by the irrigation. Numerical modeling shows that a change in the shear modulus of about -40% in the irrigation area can explain the observed change in the tidal tilt. When the water spreads beyond the immediate surface area where the soil is irrigated, one can explain the observed changes in tidal tilt with weaker changes in the shear modulus. A change in shear modulus of -40% may appear to be large, but it is comparable to the change in this modulus measured in laboratory experiments.

The field experiment was not designed for carrying out the measurements reported here, and the location of the wells with the tiltmeters was not optimized for the purpose of this study. We are currently investigating where tiltmeters should be placed to have the largest sensitivity to changes in the tidal tilt. We are doing this for shallow perturbations, as in the field experiment reported here, as well as for deeper targets such as hydrocarbon reservoirs.

This technology has potential applications to monitoring changes in (1) leakage at buried waste sites, (2) contaminant remediation, and (3) flooding during enhanced petroleum recovery.

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Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport

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Objectives: The objective of this project is to characterize the influence that naturally complex geologic media has on anomalous dispersion and to determine if the nature of dispersion can be estimated from the underlying heterogeneous media.

Project Description: This project combines outcrop-scale heterogeneity characterization, laboratory experiments, and numerical simulations. The study is designed to test whether established dispersion theory accurately predicts the behavior of solute transport through heterogeneous media and to investigate the relationship between heterogeneity and the parameters that populate these models. The dispersion theory tested by this work is based upon the fractional advection-dispersion equation (fADE) model. Unlike most dispersion studies that develop a solute transport model by fitting the solute transport breakthrough curve, this project will explore the nature of the heterogeneous media to better understand the connection between the model parameters and the aquifer heterogeneity.

Results: Our work this year was focused on the following questions: 1) Can the multi-rate mobile/immobile continuum equations that describe late breakthrough tailing be recast in terms of single-particle dynamics, allowing a simple random walk formulation, and 2) Does high heterogeneity lead to unmixed plumes and reduced reaction rates?

1) Multi-Rate Mobile/Immobile (Mass Transfer) Physics: We developed the one-to-one relationship between single particle dynamics and the upscaled continuum multi-rate mass transfer equations. This was done in such a way that the numerical implantation is extremely efficient and accurate (Benson and Meerschaert, *Adv. Wat. Res.*, 2009). The method can be incorporated in any existing particle tracking model (and already has appeared in the popular code RWHet). Our findings also show that the effects of an immobile phase can be added to a mobile-only solution by subordinating to the inverse of the immobile waiting time distribution (related directly to the multiple rates). The subordination integral is similar to a convolution. The agreement between analytical and particle tracking solutions for several immobilization types is quite good and user-specified through the particle number.

2) Mixing-Limited Reactions: It is a logical extension to think that highly heterogeneous material will lead to unmixed plumes. Therefore, reactive solutes will be sequestered in undermixed domains, and classical Eulerian codes that assume perfect mixing in any "block" will vastly overestimate reaction rates. We started from basic physics and formulated a reaction code for particle-tracking routines that explicitly determines the probability of mixing along with the thermodynamic probability of reaction upon meeting (Benson and Meerschaert, *Water Resour. Res.* 1998). Our code calculates reactions without ever using concentrations, yet perfectly reproduces the transition from thermodynamic to diffusion-limited reaction rates first predicted in the theoretical physics literature (Figure 1). Here we simulate a precipitation reaction $A+B \rightarrow 0$. A fascinating aspect to this is the self-organization of reactants into "islands" of separate reactants (Figure 1a inset). This would explain samples far from equilibrium in a "globally" equilibrated system.

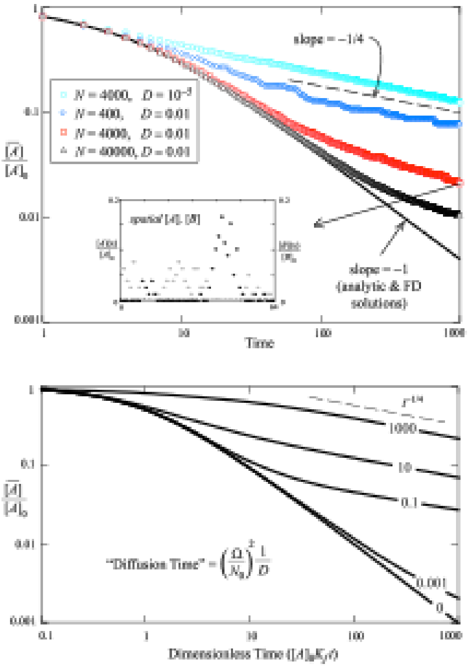

Figure 1. Top: Concentration change simulated by particle models (symbols) and analytic solution to continuum, rate-limited, equations (solid curve). Changes of a single numerical parameter are denoted on the plot. Deviations from the rate-limited solution are due to diffusion-limited reaction. Inset: Spatial concentration segregation of [*A*] and [*B*] in 4000 particle, D=0.01 simulation at t=1000. The −1/4 slope and reactant segregation are asymptotically predicted by Toussaint and Wilczec [1983] and Kang and Redner [1985]. Bottom: Dimensionless concentration versus dimensionless time curves, labeled by various values of a characteristic "diffusion time" (Domain size/# of particles)^2 D^{-1}.

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

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Objectives: The project will combine millimeter-scale measurements of acoustical and electromagnetic properties of rocks to develop a comprehensive picture of the interrelation of these fundamental properties and thereby reduce the ambiguity in geophysical interpretation.

Project Description: The first phase of this work consists of characterization and spatial mapping of a rock suite using a millimeter wave vector network analyzer and laser vibrometer to determine the correlation between electrical and mechanical anisotropy in rocks. The effect of water wet versus oil wet pore spaces will be characterized via the established set of dielectric and acoustic measurements, with the goal of determining how the chemical, mechanical and electrical properties of selected host rocks change due to different fluid mixtures. A series of micro-hardness versus water content experiments will be conducted for both indenture and acoustic microscope measurements to explore the mechanisms behind the observed shear modulus softening resulting from water adsorption.

Results: Using novel quasi-optical millimeter wave EM techniques we have developed an EM analog of near-field optical scanning. With this we can measure the complex permittivity or rocks at a resolution of better than 100 microns. On the other hand, for many years we have used scanning laser vibrometery to measure time-resolved high-spatial-resolution ultrasonic wavefields produced in rocks by pulsed-IR laser excitation. We are currently extending the latter system to a kind of near-field ultrasonic probe that will give us mechanical information at the same or higher resolution than we currently achieve via millimeter waves. At the same time, we are pursuing theoretical analysis of the relation between electrical and elastic properties in granular media at the mesoscale.

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Grant: DE-FG02-95ER14528

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

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Objective: This project seeks to (1) isolate noble gas components and carrier phases in sediments to address the fundamental processes that lead to the observed enrichment/depletion patterns of noble gases in sedimentary rocks and fluids, (2) examine the processes by which such noble gas patterns are acquired and the mechanisms by which such patterns are trapped, and (3) thereby improve the application of noble gas isotope studies to multiphase fluid processes in the Earth's 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. Although abundance patterns suggest an adsorption hypothesis, three observations argue against adsorption as the only mechanism: (1) The difference between Xe and Ar adsorption coefficients (Xe ~30x Ar) is too small to account for the observed large relative Xe enrichments; (2) heating experiments suggests the enriched component is tightly bound, counterintuitive to a simple adsorption history; and (3) many sedimentary rocks (~half) and some oil field gases contain excess Ne in conjunction with excess Xe.

Results: We are concentrating on noble gas abundances in a variety of silica samples. In samples of inorganic silica, (except for a hydrothermal sinter), noble gas abundances are consistent with occlusion of air-saturated water (ASW) in trapped fluid inclusions and lack requisite enrichment/depletion factors needed to explain the noble gas inventory in oil field fluids. On the other hand, replicate analyses of noble gases extracted from silica spicules from live sponges (*Calyxnicaeensis*) show significantly enriched Ar, Kr, and Xe concentrations ($[^{i}\mathrm{Ng}]_{\mathrm{sample}}/[^{i}\mathrm{Ng}]_{\mathrm{asw}} > 1$), very little if any mass dependence in the acquisition and trapping of Ar, Kr and Xe, and essentially no Ne. To our knowledge, this is the first evidence that noble gases are processed and enriched either directly or indirectly during the formation/secretion of biominerals. Noble gases in silica samples from the (diatomaceous) Monterey Formation (Elk Hills oil field, CA) and an Atlantic box core are somewhat depleted with respect to the sponge spicule, are fractionated, favoring the heavy noble gases, and approach the compositions observed in bulk deep sea sediments. Unlike the sponge spicule, these samples appear to be strongly enriched in Ne, an observation currently being confirmed with additional analyses. We believe 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 are currently being processed to address these questions. In collaboration with Ben Gilbert (Earth Sciences Division, LBNL), we have also measured noble gases in laboratory-synthesized nanoparticle agglomerates. Absolute noble gas abundances in samples of goethite (alpha-FeOOH) clusters agglomerated under different pH conditions (pH = 2, 7, and 12) show a strong dependence (up to a factor of ~1000x) on pH. The most enriched sample (pH = 7) has noble gas concentrations similar to that observed in the biogenic silica samples. However, despite the large range in absolute concentrations, the samples indicate little or no mass dependent fraction, other that the complete exclusion of He and Ne. As the sites, mechanisms and materials in which noble gas enrichments are created, trapped and released is explored in greater depth, the results could have far reaching implications regarding trapping, storage and release of gases from nano-structured materials.

In a parallel effort, it is known that source rock noble gas enrichment is diluted during transport by interactions with groundwater and the groundwater noble gas composition is significantly influence by the local accumulation of the crustal degassing flux in helium. We have evaluated the observed measures of the ^{4}He degassing flux from continents in terms of its mean as well as their spatial and temporal variability. The time-and-area weighted arithmetic mean (standard deviation) of n=33 ^{4}He degassing fluxes is found to be 3.32(±0.45) x 10^{10} ^{4}He atoms m^{-2} s^{-1}. The log normal mean of measurements (n=33) of the crustal degassing flux is 4.18 x 10^{10} ^{4}He atoms m^{-2} s^{-1} with a best estimate one sigma log normal error of */45x based on an assumption of symmetric error bars. The log normal mean continental heat flow is 62.2 mW m^{-2} with a log normal variance of 1.8x. (for comparison, the best estimate mean of 65±1.6 Wm^{-2}, Polach et al., 1993). A simplistic interpretation would suggest that the variance in ^{4}He flux as a result of transport and release is 25x greater than the variance in the heat flux as a result of reduced heat flow and thermal conductivity.

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Grant: DE-FG02-98ER14853

Pore-Scale Simulations of Dissolution Breakthrough in Rough Fractures

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Objectives: To develop numerical models for dissolution in rough fractures, by coupling detailed models of fluid flow, chemical transport, and surface kinetics. These detailed microscopic models form the basis for the development of network models of long-time dissolution processes, which can be used to extend the space and time scales that can be modeled.

Project Description: The processes leading to dissolution of a fractured rock by a reactive fluid depend on a subtle interplay between chemical reactions at mineral surfaces and fluid motion in the pores. The complex geometry of a typical fracture makes both numerical and theoretical calculations very demanding. Existing models of fracture dissolution are rarely constructed on a microscopic (pore-scale) level. Instead, various approximations are usually resorted to in order to make the analysis more tractable at the cost of accuracy. For example, it has been shown that the Reynolds equation may significantly overestimate the flow, especially for fractures of high roughness and small apertures. The complicated topography of the fracture is also the reason why the transport of the dissolved material from the walls into the bulk of the fluid is usually accounted for in a simplified way, with the effects of convection assumed to be adequately expressed by a Sherwood number for transport in ducts.

Results: We have now completed a major upgrade of our computational methods and software. This includes a new parallel LB fluid solver, a new finite-difference solver for the reactant concentration field, a new implementation of the reactive boundary condition and a new method for describing the geometry of the fracture surfaces. A manuscript is being prepared for submission to the Journal of Computational Physics. We also completed a large scale study of the dissolution of model fracture systems, using the previous generation of codes. Numerical simulations were used to study conditions under which long conduits (wormholes) form in an initially rough but spatially homogeneous fracture. The effects of flow rate, mineral dissolution rate and geometrical properties of the fracture were investigated, and the optimal conditions for wormhole formation determined. This work has been recently published in the Journal of Geophysical Research (P. Szymczak and A. J. C. Ladd. *Wormhole formation in dissolving fractures.* J. Geophys. Res. 114:B06203, 2009).

We are currently using a simplified two-dimensional code to investigate dissolution on large length scales. This is the beginning of new work on multi-scale modeling of fracture dissolution.

The first objectives are a direct comparison of results from two and three-dimensional simulations of dissolution. There are very few three-dimensional simulations of a sufficient scale for a comparison, but we are now in the position to make an assessment of the validity of the two-dimensional models.

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Grant: DE-FG02-02ER15366

Crystal Defects, Etch Pits, and Rough Surfaces: A More Complete Picture of Mineral-Water Interactions during Dissolution and Growth

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Objectives: To examine brucite carbonation by (1) identifying the mineralogical species in the carbonated product and (2) gaining a better understanding of the reaction kinetics and mechanism through examining the extent of carbonation over time.

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. Compared to other sequestration strategies, this method could eliminate the need for capturing, compressing, and transporting CO_2, currently a significant cost factor. The intent of this study is to examine brucite carbonation in hope to establish a baseline reference for our contingent investigation in enhancing the carbonation process.

Results: Experimental study of brucite carbonation is carried out in H_2O and diluted HCl at room temperature and moderate pCO_2 to explore the products' mineralogy and reaction kinetics. Results show nesquehonite is by far the dominant carbonate species formed despite its poorer thermodynamic stability relative to magnesite and possibly hydromagnesite. Time-dependent measurements reveal carbonate formation within 30 minutes regardless the original acidity of the slurry (see Fig. below). However, while the fraction of reacted brucite in H_2O increases gradually over time and approaches unity (~98%) at 2.5 hours, it rises rapidly in HCl within the first hour and levels off thereafter, leaving a significant amount of brucite unreacted. Such behavior suggests that the quantity of initial Mg^{2+} affects the reaction kinetics. Fitting a pseudo first-order rate law to the data yields a higher rate constant for the HCl experiments. These observations may imply that the carbonation does not proceed through heterogeneous reaction between gaseous CO_2 and solid brucite. Solution chemistry analysis indicates that the level of HCO_3^- in HCl drops below that in H_2O after about 2 hours, implying the observed inferior carbonation extent in HCl may result from a lower concentration of CO_3^{2-}.

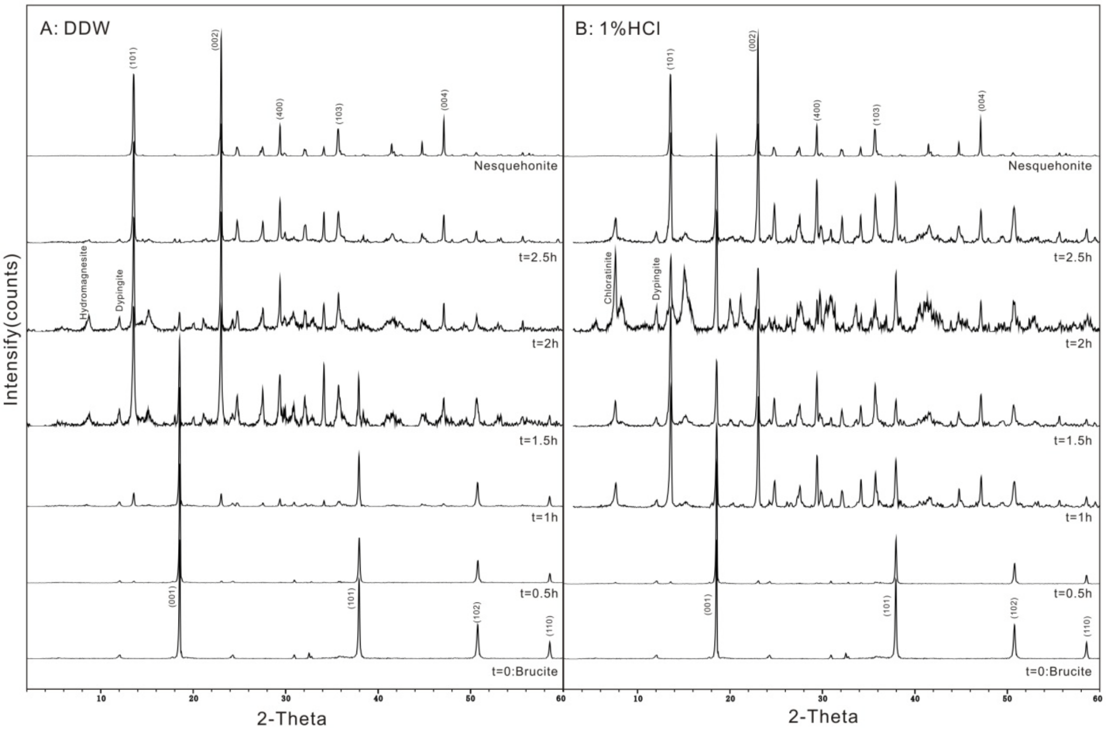

Figure: Time-dependent XRD analyses of carbonation products in DDW (A) and 1% HCl (B). Notice the initial development of nesquehonite (ref. top spectra) marked by the appearance of the (101) and (002) faces after 0.5 h reaction. Compared to DDW, carbonation is stronger in HCl in the first hour as indicated by the high XRD signal intensity. However, there remains more unreacted brucite in HCl than in DDW after 2.5 h reaction as shown by the still strong (001), (101), and (102) brucite peaks in (B).

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Reaction Mechanisms for Growth and Dissolution on Barite

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Objectives: The main objective of this research is to test proposed reaction mechanisms for barite dissolution and growth by directly comparing rates of step movement measured experimentally to reactions simulated using atomistic computational methods.

Project Description: The desire to understand and control barite growth and dissolution is motivated by the mineral's occurrence in oceans, use as a biomineral, and precipitation as scale in oil pipelines and reservoirs. At intermediate saturations, the rate of growth or dissolution of a crystal surface is limited by the rate of movement of monomolecular steps whose net velocity is controlled in part by two reactions: kink site formation and propagation. Many growth modification agents such as biomineralization proteins are thought to act by inhibiting these reactions. In this project, rates of step movement will be measured during growth and dissolution as a function of saturation and temperature using the atomic force microscope (AFM). Step velocities will be used to estimate the formation and activation energies of kink sites. The rates of these reactions will be compared to estimates made using molecular dynamics (MD) simulations after validation of the model.

Results: In FY2009, the experimental portion of the work has been conducted. Firstly, rigorous velocity measurements for the steps parallel to the [120] direction on the {001} barite surface have been made. We have developed a crystal growth theory that allows us to directly estimation of rate constants of attachment and detachment of individual barium and sulfate ions from experimental measurements. We are currently expanding the model to consider both growth and dissolution, parameterizing it using the above step velocities and comparing the results to the kink site formation energies we previously estimated computationally.

Additionally, we are examining the effect of reactive moieties commonly found on amino acids and in biological membranes on barite crystallization. To mimic a biological membrane, gold {111} surfaces are coated in self-assembled monolayers of alkanethiols terminated with amine, hydroxyl, carboxyl, and methyl groups. It is found that the identity of the functional group strongly affects the morphology and nucleation density of barite crystals. The goal is to understand, at a molecular level, how these various moieties influence and even direct crystallization of barite. Thus, nucleation densities are being correlated to the behavior of [120] steps in the presence of soluble compounds with similar functional groups.

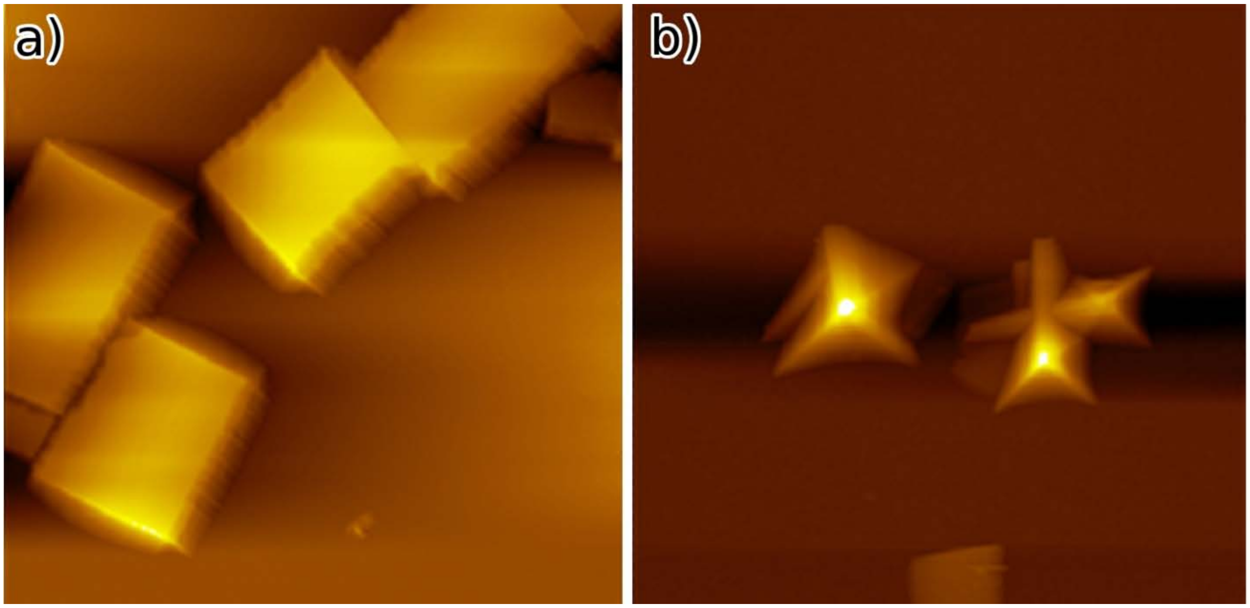

Figure 1: 10 × 10 μm atomic force microscope images showing barite crystallites grown on self-assembled monolayers (SAM) as a model of a biological membrane. a) SAM terminated with a carboxyl (-COOH) group and b) a methyl (-CH_3) group. There is an obvious preference in growth morphology for nucleation of barite on the two different materials with a) showing dominantly {001} surfaces and with b) showing a preference for a kinetically or thermodynamically unstable surface.

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Grant: DE-FG02-03ER15384

Growth and Dissolution of Iron and Manganese Oxide Films

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Objectives: The first objective is to understand the growth and dissolution of Fe and Mn oxide films on mineral surfaces, especially as influenced by the adsorption of other ions. The second objective is to establish how adsorption affects surface charge distribution and how, in turn, surface charge affects the growth of the Fe and Mn oxide nanostructures that make up the film.

Project Description: Nanostructure iron oxide films are grown on $FeCO_3$ (siderite) substrate through the *in situ* oxidation of $Fe(II)_{(aq)}$ ion by the heavy metal ion Cr(VI) under anoxic conditions. Control experiments were also conducted in deionized water under anoxic conditions for comparison. The dissolution of siderite and subsequent formation of iron oxide nanostructures are characterized using an *in situ* flow-through reactor equipped with atomic force microscopy (AFM). Microscopic dissolution and precipitation kinetics is examined by monitoring the morphology and height of surface changes, including dissolution pits, edge retrieving, and precipitation hillocks. Macroscopic dissolution behavior is evaluated by monitoring the pH and total metal concentrations in the effluent. Oxidation states and structures of the oxide nanostructures are characterized using X-ray photoelectron spectroscopy (XPS).

Results: Over the past year, we have characterized the dissolution behavior of $FeCO_3$ (siderite) substrate in the presence of heavy metal ion Cr(VI) and the subsequent formation of iron oxide nanostructures on the surface. Macroscopic analysis of total Fe in the reaction effluent shows reduced dissolution rate in Cr solution below pH 4 as comparing to that in anoxic DI water. Total Fe concentration is very low (below detection limit) at pH range 4–9. Both suggest the formation of low solubility reaction products at pH below 9. Unusually high dissolution rate is observed at pH > 9, possibly due to the role of $Fe(III)_{(aq)}$ as electron shuttle for promoted dissolution. *In situ* AFM images provide microscopic evidence of simultaneous dissolution and precipitation. Under acidic conditions, widespread surface etching, edge step retrieving, as well as isolated dissolution pits were observed. Simultaneous precipitation also occurs (Figure 1). At intermediate to alkaline pH range, dissolution pattern is dominated by isolated pits, with precipitation observed at both edges and terraces. The formation of surface precipitates under anoxic condition is likely due to the oxidation of $Fe(II)_{(aq)}$ by Cr(VI) and subsequent precipitation of Fe(III)-(hydr)oxides or Cr(III)-containing Fe(III)-(hydr)oxides with limited solubility.

The information obtained in this study can help understanding the effect of heavy metal ions on the formation of iron oxide nanostructures, and the subsequent role of these oxide nanostructures in controlling heavy metal contaminant speciation and transport in the natural environment.

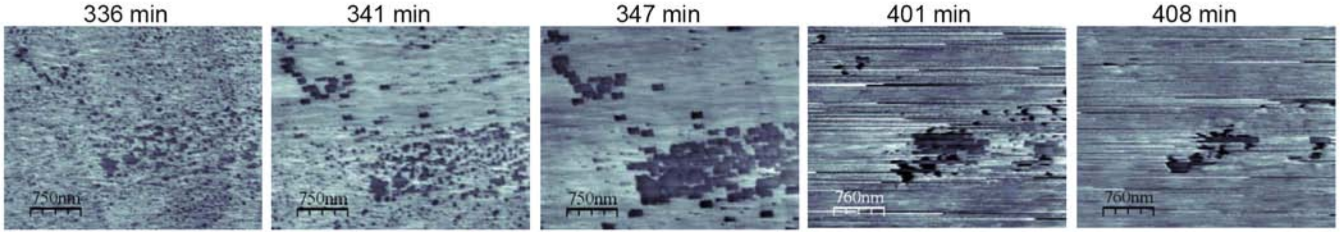

Figure 1. AFM images of $FeCO_3$ surface under 1 mM anoxic chromate solution at pH 3. Flow rate is 0.6 mL min^{-1}. All images are in height mode.

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Grant: DE-FG02-06ER15831

Development of New Biomarkers for Surficial Earth Processes

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Objectives: To quantify the carbon isotopic fractionation between plant tissue and the atmosphere at pCO_2 levels up to 1791 ppm (~6x), which encompasses the entire range of projections for the Cenozoic, in order to test the use of plant tissue to determine $\delta^{13}CO_2$ across the highly fertilizing environment of the last ~65 million years.

Project Description: The $\delta^{13}C$ value of fossil terrestrial plant tissue is increasingly used as a biomarker of paleoenvironment. In 2000, we proposed that $\delta^{13}CO_2$ can be calculated from the $\delta^{13}C$ of terrestrial land plants ($\delta^{13}C_p$) based on the strong linear correlation between $\delta^{13}CO_2$ 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 pCO_2 levels (i.e., levels similar to those seen through the last 65 million years) in order to evaluate the relationship between $\delta^{13}CO_2$ and $\delta^{13}C_p$ values under enhanced growth. We grew *Raphanus sativus* L. (common radish) under pCO_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 $\delta^{13}CO_2$ value of each experimental chamber was monitored.

Results: The carbon isotope composition of chamber CO_2 ranged across ~25 ‰, caused by the addition of ^{13}C-depleted CO_2 in order to increase pCO_2. The $\delta^{13}C_p$ value of above-ground and below-ground biomass ranged across the same magnitude: from -58.7 to -34.0 ‰ and from -56.7 to -32.2 ‰, respectively. We observed a striking and consistent correlation between $\delta^{13}C_a$ and $\delta^{13}C_p$ across the total range of pCO_2 (Figure 1). Above-ground $\delta^{13}C_p$ was equal to ($\delta^{13}C_a$ – 24.7 ‰)(R^2=0.99); below-ground $\delta^{13}C_p$ was equal to ($\delta^{13}C_a$ – 22.6 ‰)(R^2=0.98). These mean offsets were within 0.7 ‰ of the isotopic offsets we reported for above- and below-ground tissue in *R. sativus* grown at lower pCO_2 levels (-25.4 and -23.2 ‰ respectively). Although we observed biomass fertilization upon increase in RCO_2 consistent with the extensive literature on ecological experiments growing plants at 2× today's pCO_2 concentration, we did not see any change in the isotopic fractionation of carbon across these dramatic changes in both environment and tissue production. The persistence of correlation between $\delta^{13}CO_2$ and $\delta^{13}C_p$ through and beyond pCO_2 levels that span the evolution of all major Angiosperm families, suggests the possibility of a carbon-isotope "setpoint" for photosynthetic isotope fractionation in terrestrial ecosystems through time.

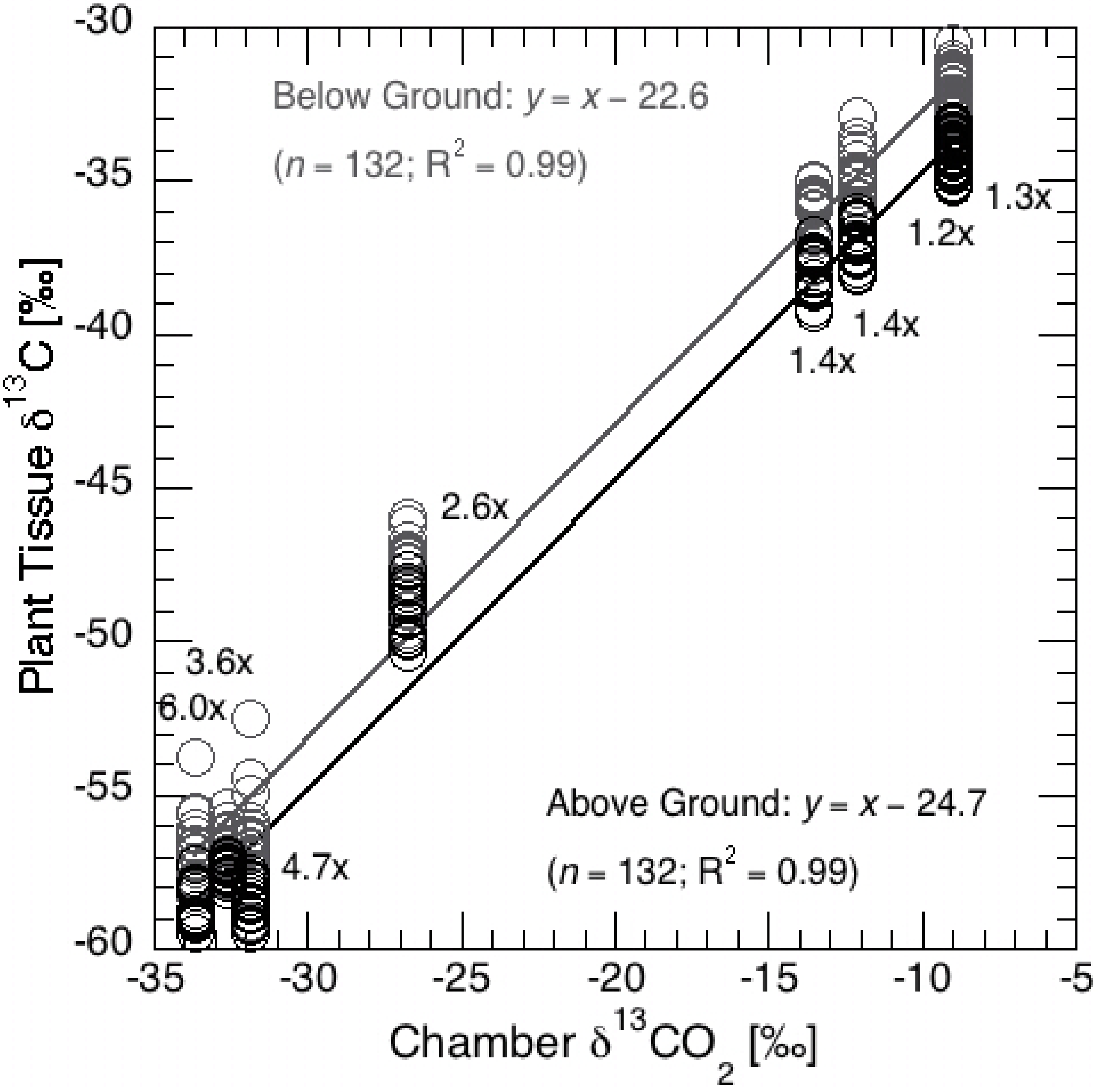

Figure 1: The carbon isotope dependency of above- and below-ground plant tissue upon atmospheric CO_2 for *R. sativus* grown at elevated CO_2 (RCO_2 1-6×).

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Grant: DE-FG02-05ER15697

Seismic Imaging Beneath an Unknown Overburden: Method Development and Evaluation on Synthetic and Real Data

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Objectives: We identify two main branches of research necessary to develop and extend existing inverse scattering series algorithms to more completely accommodate measured seismic reflection data measured over a complex subsurface structure. First, we must carry out the basic research into the formalism itself, to extract and compute terms that locate and invert for structure at depth in situations of rapidly-varying media and corrugated/rugose boundaries. Second, and equally important, we must develop and refine forward modeling methods such that the very wave field complexity required by the inverse scattering series can be provided synthetically, and under controlled circumstances, as a tool to validate and test our derived algorithms.

Project Description: The inverse scattering series (ISS) is a comprehensive theory for processing primaries and multiples without the traditional need for a subsurface velocity. Several task-specific subseries of the ISS corresponding to classical objectives of seismic data processing have been identified: subseries for (1) free-surface multiple elimination, (2) internal multiple attenuation and elimination, (3) imaging reflectors at depth, and (4) determining the parameter changes at reflectors. In addressing the first branch of our research objectives, in this project our team has specifically developed and refined algorithms which address task (3) above, that is, imaging reflectors at depth. The deliverables in this case are formulas for determining the location of reflectors in 2D from measurements of reflected primary data.

Results: In the imaging branch of our research, progress has been achieved (subsequent to our last report) on several fronts. In the last report we mentioned that the imaging capability within the 2D inverse scattering series had been identified and collected that address multi-dimensional imaging objectives that have a 1D analog. We also mentioned that a term within the series that addresses imaging challenges that occurs exclusively in a multi-dimensional earth (e.g., imaging issues due to rapid lateral variations above the target, or diffractions, which only exist in a multi-dimensional earth). The initial tests on that single term proved to be a computational challenge. Those tests with the more inclusive and complete code version of that new imaging term could impact outstanding challenges for all current imaging methods in subsalt plays in deep water Gulf of Mexico.

The recent report by the US Department of the Interior, Mineral Management Service, points to the deep water GOM 25% drilling success rate in 2000 and 8% success rate in 2007. Collecting wide azimuth data and developing faster computers, while useful, will by themselves not address the fundamental imaging problems due to innate imaging algorithm assumption failure. Our algorithms avoid the assumptions made by all conventional leading edge capability. Specifically they avoid the need for overburden information above the target in order to locate the target. This past year we have initiated the identification of good candidate deep water GOM field data sets to test our new imaging capability in cooperation with our petroleum sponsors.

In this past year (FY-09), we continued developing the math-physics behind the imaging at depth algorithm that accommodated an earth where both the velocity and density could vary and where the velocity and density configurations are unknown and remain completely unknown, before, during and after the imaging. The configurations in velocity and density are assumed to allow rapid variations (that generate reflections), when either one or the other or both parameters experience rapid change.

All seismic exploration imaging algorithms today require an adequate velocity model. With all current imaging algorithms the velocity model combines with the data’s phase (or arrival time), it directly outputs the spatial location of the reflector. When the adequate velocity model is not available/achievable, then the depth can be directly determined from the inverse scattering series by combining times and amplitudes of different events. Events that derive from reflections that only have rapid changes in density need to be excluded from the data ‘conversations’ within the inverse scattering series that allows direct depth imaging without knowing or determining the velocity or density. Tests are underway that are progressing the algorithm’s development towards the first in a series of field data tests. The first field data tests are expected within the next year.

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Grant: DE-FG02-06ER15824

Redox Interaction of Cytochromes and Bacteria with Oxide Surfaces: Probing Redox-Linked Conformation Change

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Objectives: The objective of this research is to better understand the role of conformation change in electron transfer from cytochromes to minerals, a process that underpins respiratory metal reduction by bacteria in nature and in bioremediation strategies, including reductive immobilization of radioactive contaminants.

Project Description: The biochemistry of bacterial proteins involved in redox transformations of metals and minerals is, without dispute, an important area of research. Nevertheless, most studies on bacterial metal transformation have focused not on biochemistry but on genetics and genomics. Our DOE-funded work is specifically focused on answering long-standing questions about the biochemical behavior of these very interesting proteins, and our findings in FY09 have continued to support our basic idea of conformational gating and control of electron transfer to mineral and other electrochemically active surfaces.

Results: Progress Highlights in FY 09 include:

1. ***Examination of redox protein complexes that reside in membrane vesicles and the extracellular biofilm matrix.*** We have moved from studies of single proteins to examination of redox protein complexes. Experimental evidence suggests that *Acidiphilium cryptum* (one of our model organisms) forms outer membrane vesicles when grown under biofilm-forming conditions. These vesicles are known to contain c-type cytochromes, and represent a viable means of extracellular electron transport to mineral surfaces (Figure 1).

2. ***Structural determination of ApcA and ApcB, two periplasmic cytochromes that play roles in both Fe(III) and Cr(VI) reduction.*** We have continued our collaboration with Dr. John Cort of the Pacific Northwest National Laboratory on NMR structure determination of the periplasmic cytochromes ApcA and ApcB from A. cryptum. The structures of ApcA in both oxidized and reduced states have been solved, and experiments are underway to obtain NMR spectral data for ApcB.

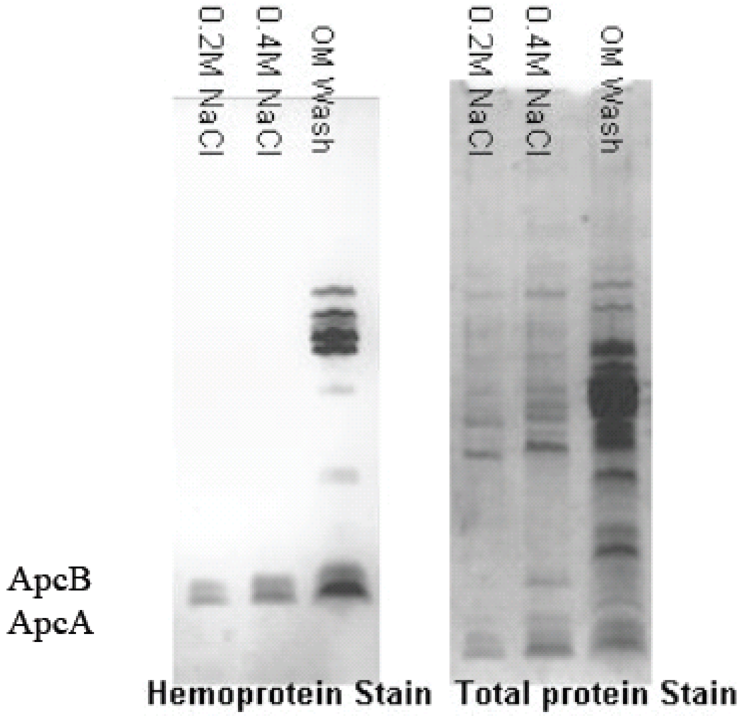

Figure 1. SDS-PAGE analysis of A. *cryptum* biofilm-associated proteins. Lanes 1 and 2 are 0.2M and 0.4M NaCl washes of biofilm material while Lane 3 shows a detergent extract of whole A. *cryptum* cells that liberates the outer-membrane (OM) and periplasm proteins. Left panel is a hemoprotein stain and right panel shows the same gel after total protein staining. Notice the exclusiveness of the NaCl washes compared to the detergent extract. This indicates that the NaCl wash is selective for loosely associated proteins on the exterior of the cell or extracellular polymeric substance (EPS). The two small-mass cytCs released with NaCl wash are ApcA and ApcB.

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Grant: DE-FG02-02ER15317

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? 3) What kinetic and thermodynamic factors in the subsurface control the rate of microbial activity? 4) How do the methods available to sample and observe the microbial community affect our knowledge of its nature? 5) 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 bench-top 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: Our comparative analysis of actively growing microbial communities in wells completed in the Mahomet aquifer indicated a relationship to the sulfate concentration. In contrast, we found no relationship of ferrous iron concentration to community composition in the aquifer, even where iron reducers seem predominant. Examining 16S rDNA clones, we found actively growing bacteria associated with iron reduction on the sediment samplers we used, regardless of sulfate concentration or any other primary geochemical parameter. Analyses of sulfide concentration and gas composition in the same region of the aquifer suggest multiple metabolisms are active within geochemical zones hosting groundwater spanning a broad range of chemical composition. The results may indicate that the microbes detected possess versatile metabolisms, but we believe otherwise; that fundamental thermodynamics and microbial ecological principles drive development of community composition and activity.

We have developed numerical models to test this hypothesis; that thermodynamic, microbial kinetic and ecological parameters provide a predictive modeling approach for demonstrating coexistence and exclusion among different metabolisms. This contrasts with the widely accepted paradigm that thermodynamics in the form of the electron tower (i.e., the larger negative $\Delta G°'$ of competing electron accepting reactions wins) drives competitive zonation in aquifers. We developed a model that shows neither thermodynamic nor simple kinetic interpretations explain the mechanism by which a microbial population excludes others from a zone (Figure 1). 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. From an ecological perspective, the model predicts areas dominated by mixtures of microbial metabolism. Sulfate reducers, for example, likely provide mutualistic benefit to iron-reducing bacteria by precipitating ferrous iron, a thermodynamic and kinetic inhibitor of biotic iron reduction, as sulfide minerals.

In the laboratory we have focused on quantifying the rates of reactions in the aquifer and the dynamics of the microbial community in response to geochemical variation. To accomplish these goals we are incorporating molecular biology tools that focus on RNA content, which correlates directly to rates of activity. We are using anaerobic microcosms to investigate sulfate reduction rate variation in response under nearly *in-situ* conditions and used column studies to investigate how Mahomet aquifer communities shift in response to changing the groundwater input from high sulfate to low sulfate and vice-versa. Integrating the microbial activity metrics with the geochemical and community dynamics will provide further support to our reactive transport modeling efforts.

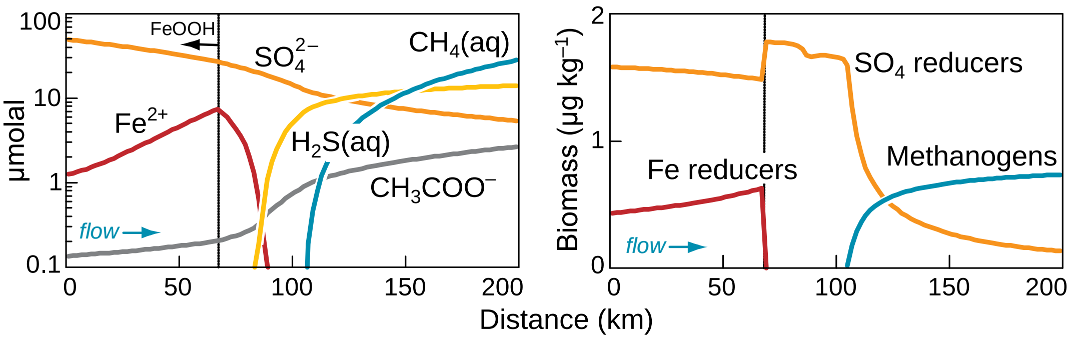

Figure 1. Ecological model shows groundwater chemistry and the distribution of microbial activity in an anaerobic confined aquifer. The community composition results from solving ecologic equations posed on the basis of thermodynamics and the concept of metabolically usable free energy ΔG_U. ΔG_U is the energy in excess of that stored internally in microorganisms as ATP. Where ΔG_U <0, no energy is available for metabolism. Resulting zonation illustrates both coexistence (e.g., iron reducing and sulfate reducing bacteria living together, and sulfate reducing bacteria with methanogens) and ecologic exclusion (e.g., absence of methanogens in upstream portion of aquifer).

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Grant: DE-FG02-08ER15961

Aqueous Geochemistry at High Pressures and Temperatures

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Objective: 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 (~ 15 km 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: One of the major technical difficulties that has limited spectroscopic measurements on fluids under high pressure and temperature conditions was the lack of instrumentation that could generate the required pressures and temperatures and remain stable over long periods of time. The UIUC group has modified the Brillouin spectrometer to accomodate a new type of membrane diamond anvil cell (DAC) which was designed and fabricated by the LLNL group for use in Brillouin scattering measurements in a ~50° scattering geometry. The cells were tested and Brillouin spectra were collected jointly by the UIUC and LLNL groups. High pressure and high temperature Brillouin data were collected on liquid CO_2 and several solid CO_2 phases (I, II, III, IV). For the first time, data were collected on the dynamics of CO_2-IV up to P=18 Gpa and T=450°C. We performed Brillouin experiments on supercritical water to 500°C at P=2 GPa, well above the temperatures of previous high-pressure measurements. We have made our first sound velocity measurements on H_2O-NaCl solutions, obtaining high-quality data to 7 Gpa and 500°C. These are the highest P-T velocity measurements performed to date on aqueous solutions. Modifacations to the Brillouin system are being made for a newer DAC design that will allow for 90° scattering, offering significant advantages for all future measurements.

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Grant: DE-FG02-03ER15381

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 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 has been focused on resolving mineral-water interface structure and reactivity with Å-scale resolution, primarily in studies of ion adsorption and dissolution-reprecipitation reactions. During the past year, we initiated a series of experiments using *in situ* X-ray reflectivity techniques to examine the structure of calcite (104)-water interface and its dissolution behavior under conditions of elevated temperature and CO_2 pressure, leading to a test of a new carbonate surface complexation model for CaMg carbonates. Changes in interfacial speciation of water or carbonate molecules, compared with that observed under ambient conditions (25°C, atmospheric CO_2 pressure), are readily detectable by X-ray reflectivity, but no measureable difference in interfacial structure or reaction rate was observed at $T = 84°C$ and $pCO_2 = 1$ atm. Increasing ionic strength to 1 M NaCl did not effect substantial change in interfacial structure. In addition, further experiments were performed on dissolution kinetics and alkali ion exchange at the orthoclase (001)-water interface, showing linear increase in dissolution rate with ionic strength. Observations of the orthoclase surface as a function of reaction time using X-ray reflection interface microscopy showed inhomogeneous spatial distribution of dissolution-induced roughening that was roughly correlated with step density.

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Grant: DE-FG02-00ER15032

Significance of Isotopically Labile Organic Hydrogen in the Thermal Maturation of Source Rocks

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Objectives: Explore geochemical conditions and mechanisms that contribute to changes in hydrogen and nitrogen stable isotope ratios in sedimentary organic matter during thermal maturation. Evaluate the diagenetic and/or paleoenvironmental significance of D/H ratios (i.e., $^2H/^1H$, expressed as customary δD values) in different types of kerogen, specific materals and isolates, oils, fractions of oil, and gas.

Project Description: Isotopically labile organic hydrogen in fossil fuels occupies chemical positions that participate in isotopic exchange and in chemical reactions during thermal maturation from kerogen to bitumen, oil and gas. Carbon-bound organic hydrogen is isotopically far less exchangeable than hydrogen bound to nitrogen, oxygen, or sulfur. We explore why organic hydrogen isotope ratios express a relationship with organic nitrogen isotope ratios in kerogen at low to moderate maturity. We develop and apply new techniques to utilize organic D/H ratios in organic matter fractions and on a molecular level as tools for exploration for fossil fuels and for paleoenvironmental research. The scope of our samples includes naturally and artificially matured substrates, such as coal, shale, oil and gas.

Results: (1) Our study on the thermal maturation of organic nitrogen demonstrates that nitrogen isotopic exchange between pools of organic and inorganic nitrogen is common and proceeds fast when formation fluids carrying dissolved nitrogen species interact with sedimentary organic matter, even at temperatures well below 100°C. Nitrogen isotopic exchange also affects the hydrogen isotopic exchangeability (i.e., the fraction of exchangeable hydrogen in total organic hydrogen) because some exchangeable hydrogen is linked to $–NH_2$ etc. functional groups (paper published in *Geochimica et Cosmochimica Acta*, and one paper in press in *Organic Geochemistry*).

(2) Our ongoing study of D/H ratios in natural gases in the Illinois Basin is expanding from Pennsylvanian coalbed gases to shale gases that are present in the Devonian New Albany Shale and in the Ordovician Maquoketa Shale Formation (manuscript submitted to *AAPG Bulletin*).

(3) Our results demonstrate that paleoenvironmentally relevant D/H ratios of non-exchangeable hydrogen in kerogens across Permian-Triassic (P-Tr) boundaries aid in the detection of environmental changes leading to the P-Tr mass extinction (manuscript submitted to *Earth and Planetary Science Letters*).

(4) We are empirically developing criteria for the interpretation of compound-specific δD patterns of homologous series of *n*-alkanes in crude oils. Various types of patterns have been found in natural crude oils, but in the absence of satisfactory explanations for their causes it has been difficult to exploit this geochemical information in exploration. On the compound-specific molecular level, we are documenting the changes in D/H ratios of individual *n*-alkanes that result from artificial maturation (hydrous pyrolysis, 330°C for 72 hours) of different source rocks in isotopically defined waters. Selected preliminary data are shown in Figure 1 where δD values of C_{14}–C_{29} *n*-alkanes express diagnostic patterns distinguishing between four different parent source rocks containing kerogen types I, II, IIS, and III. Other data sets compare the effects of varying temperature, time, and δD values of the waters used in hydrous pyrolysis.

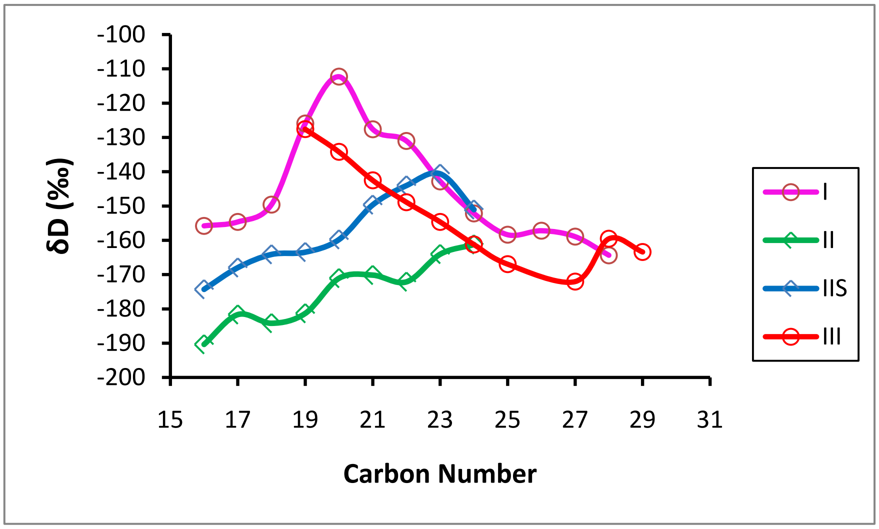

Figure 1: Compound-specific δD values of homologous series of *n*-alkanes from oils that were generated artificially using hydrous pyrolysis. Four different parent source rocks provided kerogen types I (Green River Shale), II (New Albany Shale), IIS (Ghareb Formation), and III (lignite from Wilcox Group, Texas).

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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: During this third year of the project cycle, 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. To date, samples appear amorphous to electron diffraction. More complete characterization of the structure and chemistry of this material will include synchrotron-based x-ray microprobe, microXRD and microXAFS investigations scheduled for late this year.

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 countings 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 (NSLS, Brookhaven) 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.

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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 analyzing 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 focused on describing the attachment of organic acid anions to mineral surfaces and began work on describing the simultaneous adsorption of anions and cations. Both organic anion species and metallic cations typically adsorb in multiple ways, with different preferences for site densities. As a broad generalization, metallic cations prefer a larger site density than organic anions which appear to be more specialized in the sites they prefer. As a consequence, modeling the simultaneous adsorption of both anions and cations requires separate sites. Nevertheless, it may be possible to adopt the approach of separately modeling the two and then combining the results.

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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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Objectives: 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.

Project Description: 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.

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

It is known that microstuctural damage induced dilatancy precedes macroscopic failure of a rock. However, the quantitative relationship between microcrack damage and fault development is not clearly understood. To better understand the process of fault growth, a detailed microstructural study was conducted on porous sandstones deformed to various post-failure stages. We used a new loading configuration, called lateral relaxation compression 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. Progressive microstructural damage was investigated. Quantitative characterization of crack damage indices, crack density, grain size distribution, and porosity reduction provides characteristic failure patterns.

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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 the interrelationships among permeability, mechanical properties, and the pore structure of rocks under hydrothermal conditions, with and without metamorphic reactions. We are collaborating with Prof. W.-L. Zhu, Univ. Maryland, College Park, MD.

Project Description: To understand some effects of reservoir depletion on rock permeability, we collaborated with Prof. M. Li of the Southwest Petroleum University, Chengdu, China to investigate the effective pressure law for permeability in tight sandstones. In a second component of the project, we investigated the deformation of carbonate in the semi-brittle regime. Finally, we completed some model calculations for a single pair of asperities pressed together in the presence of a fluid.

Results: In tight sandstones from the E-bei gas reservoir, China, permeability was strongly sensitive to fluid and confining pressures, decreasing quite strongly with increasing confining pressures. Significant hysteresis was observed, suggesting the presence of inelastic processes.

For our investigation of carbonate deformation, within a narrow window of P_c and T, the deformation of Solnhofen limestone (average grain size of 5 μm and initial porosity of 3-5%) involves transitions from brittle fracture to compactive flow, and then from dilatant flow to plastic pore collapse. Water enhances compaction and/or suppresses dilatancy. At elevated temperatures when water is present, both yield strength and the stress required for the inception of dilatancy and localization decrease considerably. The coupling of deformation and permeability was also indicated in a suite of triaxial deformation experiments on aggregates of quartz and calcite at 300-800 K, confining pressures up to 300 MPa and various pore pressures (argon gas). Axial and volumetric strains were measured during purely isostatic loading and during conventional triaxial loading; permeability was measured concurrently using the oscillating pore pressure method. Under isostatic loading, the permeability reduction rate co-varies with compaction rate and increases with increasing of P_{eff}. Counter to intuition, the percolation threshold for the triaxially deformed material is lower than that during isostatic compaction. The bulk and shear viscosity of the creeping aggregates are functions of both mean and deviatoric stresses.

The numerical analysis for a single pair of asperities pressed together in the presence of a fluid was intended to investigate a process called pressure solution, thought to be important during compaction of sediments. The analysis differed from earlier work in that it incorporated a more realistic stress distribution between two elastic bodies; and the “dissolution” step for material moving from the solid grain “into” the grain boundary was explicitly coupled to the boundary solute diffusion at every point.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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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.

Project Description: Our studies of channel shape concentrate on the growth and form of elevation contours. Our investigations suggest that the focusing of groundwater at the channel head selects a regular shape. We seek to better understand how this form is selected and to specify the conditions under which it is stable. 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.

In all cases, our investigations involve physical reasoning, mathematical modeling, laboratory experimentation, and observations of kilometer-scale channels. Our laboratory investigations focus on a table-top experiment that simulates the growth and bifurcations of a single channel. Our field investigations, performed at the Apalachicola Bluffs and Ravines Preserve, near Bristol, Florida, emphasize quantitative tests of our theoretical predictions.

Results: In FY2009 we studied the focusing of groundwater at channel heads and the resulting channel growth. Figure 1 shows our theoretical predictions for water table height and the resulting water flux to the network. Comparison between predicted and measured fluxes in the streams shows excellent agreement. Theoretical analysis of our experimental setup indicates a linear relationship between water flux and erosion rate. By combining these field and laboratory observations into a simple theoretical model, we are then able to predict the typical "amphitheater" planform shape of the valley heads.

As valley heads grow forward, sediment on valley walls moves to streams by a diffusive process. We evaluate the diffusion coefficient from a high-resolution topographic map of the field site. Notably, the diffusion coefficient shows sensitivity to the exposure to sunlight. Once sediment is removed from the valley walls, it is transported away from the head by the stream. This process couples the elevation profile of an individual stream to the water table. Comparison of the predicted power-law profile to real streams shows strong agreement.

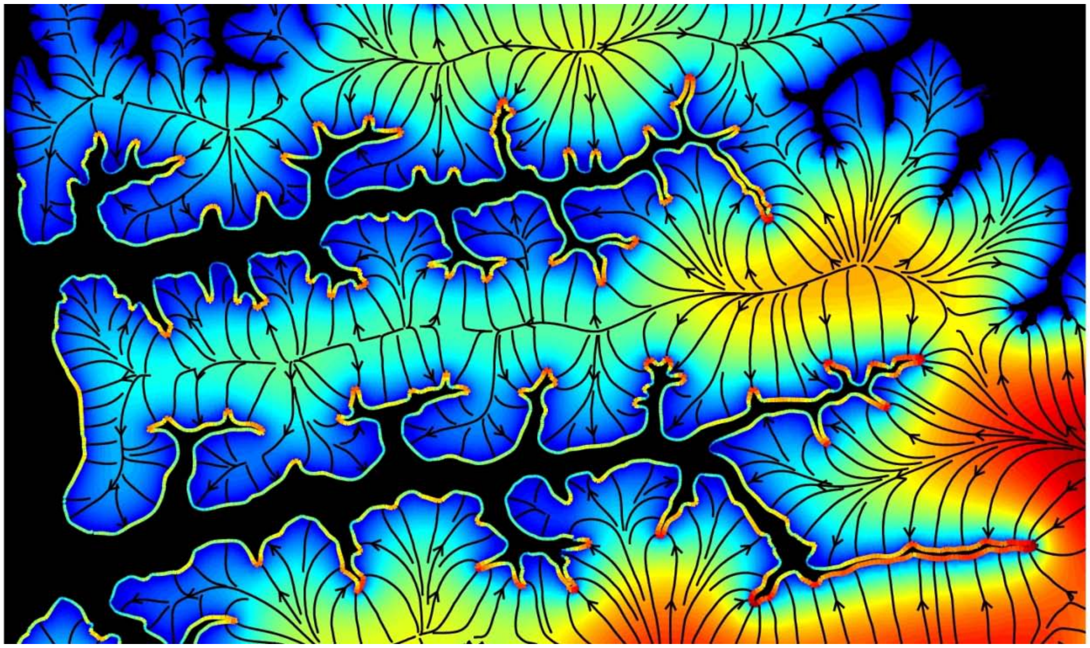

Figure 1: Network of “steephead ravines” (black) draining into the Apalachicola River (left), near Bristol, Florida. Changes in the water table elevation focus groundwater to different sections of the network. The parts of the network that receive more water grow faster. Warm colors between ravines indicate a high water table. Warm colors on the network boundaries indicate a high flux. Groundwater flows along the black lines. The horizontal dimension is roughly 4 km.

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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 objective of this work is to measure the flow properties of olivine-bearing rocks under lithospheric conditions, which have been heretofore unachievable in deformation experiments, and to understand deformation processes sufficiently to extrapolate measurements to the geologic setting.

Project Description: Experiments are carried out in a Deformation-DIA (D-DIA) at temperatures in the range 673 to 1273 K and pressures from 4 to 9 GPa. We focus on quantifying low-temperature plasticity of olivine under anhydrous conditions. Second, we are extending this research to hydrous conditions. Our primary goal is to produce low-temperature flow laws (i.e., to quantify the dependence of creep rate (viscosity) on differential stress, pressure, temperature, and water fugacity) for olivine-rich rocks. The results of this study then provide the basis for modeling geodynamic processes occurring in the mantle. We work in close collaboration with David L. Kohlstedt and Shenghua Mei at the University of Minnesota.

Results: We have completed a set of experiments sufficient to characterize the rheological behavior of polycrystalline olivine at high stress and low lithospheric mantle temperatures, under strictly water-free conditions, where it is presumably stronger than under wet conditions. We made our measurements of stress and plastic strain by x-ray imagery and x-ray diffraction, and we carried out the work primarily at beam line X17B2 at the National Synchrotron Light Source, Brookhaven National Laboratory. At the pressure and temperature conditions given in the previous paragraph, resultant stresses to produce deformation at laboratory rates in the range of 10^{-5} to 10^{-6} s^{-1} were 2 – 3 GPa. This is a high enough value that the intrinsic resistance of the crystalline lattice, the so-called Peierls stress, that at which dislocation motion becomes athermal, must be considered. We were able to fit our data to a flow law in which the Peierls stress has a value of approximately 6 GPa, and in which the activation energy, i.e., the sensitivity to temperature, decreases sharply with increasing stress. This is the expected mode of deformation in the mantle portion of Earth’s lithosphere.

Compared with published results for low-temperature plasticity as well as high-temperature creep of olivine, our results indicate the following: (1) A transition from low-temperature plasticity to high-temperature creep occurs at ~1300 K for laboratory strain rates. (2) The flow stress in the low-temperature plasticity regime is less temperature sensitive than reported in earlier studies that used micro-indentation and load relaxation techniques; in those tests, samples were deformed in a transient rather than a steady-state regime. (3) A strength envelope for the lithospheric mantle is established using the low-temperature plasticity flow law obtained from this study. It predicts an integrated strength of ~ 3×10^{13} Pa·m. for the lithospheric mantle to a depth of 100 km. The low-temperature, high-stress flow law for olivine from this study provides a solid basis for modeling tectonic processes occurring within Earth's lithosphere.

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Grant: DE-FG02-05ER15740

Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media

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Objectives: (1) To quantify grain- and pore-scale physical effects of variable cementation and compaction and relate these to the elastic, inelastic, and hydrologic behavior of granular porous media.
(2) To use the resulting data to parameterize Discrete Element Model (DEM) simulations to explore meso- and macro-scale poroelastic behavior.

Project Description: The project scope requires us to develop and use small-scale structural characterization and experimental deformation of granular porous media. We chose to work with natural sandstones using novel approaches that provide insight into grain-scale mechanics:

1) Integrating microstructural and experimental analyses to relate changes in grain and pore geometries with progressive diagenesis to changes in its mechanical behavior.

2) Developing quantitative relationships describing the poroelastic response of cemented granular systems to internal and external forcings by incorporating microscale material response into a DEM framework.

Results: Quartz overgrowths are the most common form of authigenic cements in sandstones and are responsible for significant porosity and permeability reduction. The distribution of quartz cements is mineralogically and space controlled. Therefore progressive quartz cementation should modify the grain framework in consistent, predictable ways, thereby impacting both the mechanical and hydrologic behavior of the material. We have quantified these modifications in a series of variably cemented quartz arenite samples, and demonstrated their effect on mechanical and hydrologic properties.

To investigate these relationships, the UW group designed and implemented a strategy to integrate detailed microstructural characterization with analyses of ultrasonic velocities, permeability and mechanical properties to quantitatively characterize and determine the mechanical and hydrologic impact of progressive diagenesis and natural cement morphologies in the St. Peter Sandstone, a quartz-cemented quartz arenite. Samples analyzed have cement abundances that vary from < 1% to 16%, final porosities between 8% and 25%, and original porosities between 20% and 30%. To quantify the geometric changes associated with progressive compaction and cementation, detailed back-scattered electron and cathodoluminescent images were collected. Image analysis indicates that the St. Peter Sandstone exhibits typical quartz overgrowth geometries but that cement morphology changes with progressive cementation. Grains in low-cement (< 5%) samples exhibit thin, encrusting layers of quartz with isolated crystal facets and interconnected pore spaces. In contrast, high-cement (> 10%) samples have an interconnected network of cement with well-defined facets and diminished pore connectivity. Results of image analyses suggest that with progressive compaction and cementation, the number and length of grain contacts increase and the number of pores increases. However, the number of large, well-connected pores decreases, decreasing pore size variability and permeability exponentially, and systematically altering pore shape. Cement precipitation is more efficient than compaction in increasing grain contact length and altering pore shape.

The UMass team has continued to explore the influence of cementation at both the meso- and macroscale. The developed DEM models provide quantitative insight into the effects of changing grain size and cement content on bulk material properties at a multi-grain scale. We are currently investigating the influence of changes in cementation on the mechanical behavior of materials in situations where the deformation is driven by pore fluid volume changes (i.e., pumping or injection of fluids). As shown through observations made by this team at a variety of scales, cement influences the mechanical properties of the porous media. Additionally, change in cement volume has been shown to also significantly modify the intrinsic permeability of the material. To evaluate the competing effects mechanical and hydrologic influences of cementation on large-scale fluid removal and resulting reservoir deformation, the theoretical bulk modulus properties from the DEMs with low (BGR 0.5) and high (BGR 2.25) cement content were input into 2D, axially symmetric, poroelastic continuum models. Permeabilities corresponding to a suite of cemented materials were estimated using available laboratory data on variably cemented St. Peter sandstone. Poroelastic model results suggest that that deformation behavior is strongly controlled by *both* the hydrologic and mechanical influences of cement. The magnitude and location of peak radial deformation around a pumping is strongly affected by the hydrologic influence of cement.

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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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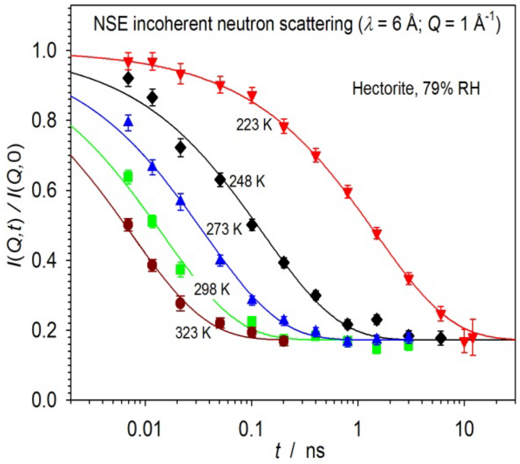
Objectives: Research supported by this grant focuses on development of molecular scale understanding of a range of central issues related to the structure and dynamics of geochemically important fluids, fluid-mineral interfaces, and confined fluids using computational modeling and experimental methods.

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 continued development of advanced computational approaches to address these problems, application of these approaches to important geochemical questions, relevant experimental 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 2009 we completed a comparative molecular dynamics (MD) study of the structural differences between three classical aqueous interfaces: (i) the free liquid water surface, which has no substrate structure or solid barrier, and can be considered hydrophobic; (ii) the talc (001) basal surface, which is also hydrophobic but is structured on the molecular scale; and (iii) the muscovite (001) basal surface, which is structured on the molecular scale, hydrophilic and has strong H-bond interaction with water molecules. Muscovite and talc are classical mineral surfaces, and the behavior of the water-vapor interface is important in many problems in vadose zone hydrogeology and in atmospheric science. The MD simulation results provide an explanation for the so-called depletion layer near solid hydrophobic surfaces, about which there has been considerable uncertainty in the recent literature. The results show a region of reduced water density near the surface but no large open volumes.

Natural organic matter (NOM) is a compositionally and structurally complex and chemically active component of many environments and can play an important role in binding of many metal species. To better quantify the structure and energetics of the metal cation complexation with NOM, in 2009 we focused on accurate calculations of *potentials of mean force* (PMF) for metal-carboxylate interactions in aqueous solutions. The calculated free-energy profiles are used to determine the equilibrium constants of metal-organic complexation.

In 2009 we also continued inelastic and quasi-elastic neutron scattering experiments to probe the dynamics of nano-confined water in layer-structure materials. The temperature dependence of H_2O diffusional dynamics in K-hectorite was investigated using the neutron spin echo (NSE) instrument at NIST. The NSE results allowed us to determine the relaxation time, τ, of H_2O diffusion over the same temperature range studied earlier in our NMR work. In agreement with the NMR results, the relaxation time decreases by more than two orders of magnitude from -50 to 50°C.



Normalized intensity of incoherent neutron scattering illustrating the temperature dependence of the H_2O diffusion in K-exchanged hectorite based on neutron spin echo measurements.

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Grant: DE-FG02-01ER15127

Support of MSA and GS Short Courses and the Companion Reviews Volumes

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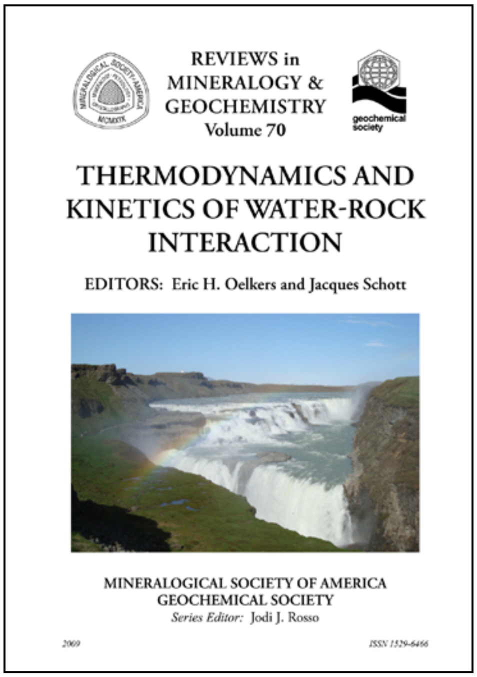
Objectives: The grant was for support of short courses and the companion *Reviews in Mineralogy and Geochemistry* volumes proposed to and accepted by the Mineralogical Society of America (MSA) and Geochemical Society (GS) held in 2004-2009. The support has two purposes: (1) keeping student registration fees affordable; and (2) producing the Reviews volumes. Speaker travel costs have become the most significant MSA and GS short course expense. Student fees were kept low indirectly through support of that speaker travel.

Project Description: The grant was for support of short courses and the companion *Reviews in Mineralogy and Geochemistry* volumes proposed to and accepted by the Mineralogical Society of America (MSA) and Geochemical Society (GS) held in 2004-2008. The support has two purposes: (1) keeping student registration fees affordable; and (2) producing the Reviews volumes. Speaker travel costs have become the most significant MSA and GS short course expense. Student fees were kept low indirectly through support of that speaker travel.

Results: There was one short course during FY2009, with a companion *Reviews in Mineralogy and Geochemistry* volume:

[1] ***Minerals, Inclusions and Volcanic Processes***. December 13-14, 2008. Conveners were Keith Putirka (California State University Fresno) and Frank Tepley (Oregon State University). The course had 207 participants (107 students, 82 professionals, and 18 speakers).

The presentations and the discussions during the course showed that there is much work to be done to better determine volatile saturation conditions and equations of state for complex fluids, as well as crystal kinetic parameters, and the development of mineral textures. The short course also highlighted that many current lines of investigation are highly complementary, and can still be used to great effect in concert. For example, U-series ages appear to indicate the earliest stages of magma generation while diffusion profile ages inform us of the latest phases of transport. Similarly, mineral-melt barometers appear to inform us about the deeper parts of volcanic systems, and volatile-saturated equilibria inform us of the shallower—while fluid inclusions appear to record both, perhaps with higher precision. An alliance of methods can also provide key tests of our assumptions and interpretations. For example, if kinks in CSDs are an indicator of degassing, then melt inclusions from related rocks with non-kinked CSDs should yield higher volatile contents; if melt inclusions are being trapped largely upon upward transport, the times scales of such residence and transport, as might be inferred from diffusion profiles, should be consistent with transport times that might be inferred from a combination of ascent rate estimates from hornblende reaction-rims, and estimates of the depths from which magmas are delivered, as determined from geobarometers. To the extent that such tests yield a coherent picture of a volcanic system, the advances outlined at the short course and within the volume illustrate the promise of petrology and mineralogy for affording fundamental tests of the evolution of magma storage, transport and eruption.



REVIEWS in
MINERALOGY &
GEOCHEMISTRY
Volume 70

THERMODYNAMICS AND KINETICS OF WATER-ROCK INTERACTION

EDITORS: Eric H. Oelkers and Jacques Schott

MINERALOGICAL SOCIETY OF AMERICA
GEOCHEMICAL SOCIETY
Series Editor: Jodi J. Rosso

2009 *ISSN 1529-6466*

Reviews in Mineralogy and Geochemistry volume 69: Minerals, Inclusions And Volcanic Processes, Keith D. Putirka and Frank J. Tepley III, Editors, editor, i-xiv, 674 pp. ISBN 978-0-939950-83-6. ($40 non-members, $30 MSA, GS, & CMS members). Copies were distributed to all short course participants, 546 copies to library subscribers to *American Mineralogist* (who include library subscribers to *Geochemica et Cosmochimica Acta*), book reviewers, and by mail and meeting sales. Volume 69 is also posted on *GeoScienceWorld* (GSW) that, as of March 2009, had 321 subscribers.

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Grant: DE-FG02-08ER15928 – Amendment No. A000

Publication Support: Two 2008 Special Issues by the Magazine *Elements*

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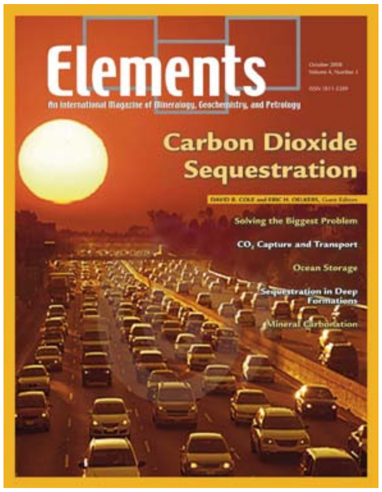
Objectives: *Elements* (ISSN 1811-5209) is a bi-monthly publication of 14 national mineralogical and transnational geochemical societies. It was started with the goal of unifying the different disciplines dealing with earth science materials, showcasing the research activity in the mineral sciences, and demonstrating their importance. Each issue of *Elements* has small number of scientific articles based on a topical theme and guest-edited by scientists who are specialists in the topical research area, but are generalists enough to oversee a group of peer-reviewed invited papers that must be written for a general audience. Themes are interdisciplinary topics that have not previously been adequately or broadly presented by other publication. Topics generally represent established, but progressing fields that would interest a broad cross section of readers and are important current issues in the geosciences.

Project Description: The grant was for partial support of two thematic issues of the magazine on “Sequestration of Carbon Dioxide” and "Deep Earth and Mineral Physics".

Results: There were two publications supported by the grant, one of which appeared in October of 2008:

Elements volume 4 number 5 (October 2008) 31 pages in 5 articles devoted to the topic of *Sequestration of Carbon Dioxide*. **Guest Editors:** David R. Cole and Eric H. Oelkers



This thematic issue of *Elements* on “Sequestration of Carbon Dioxide” is the result, in part, of the DOE Office of Basic Energy Sciences workshop held in February 2007. The workshop was entitled “Basic Research Needs in Geosciences: Facilitating 21st Century Energy Systems”.

Storage of carbon in the subsurface involves introduction of supercritical CO_2 into rock formations beneath the surface of the Earth, typically at depths of 1000 to 4000 meters. Although CO_2 is a relatively benign substance, the volume being considered is large. If developed to its envisaged potential, geologic sequestration will entail the pumping of CO_2 into the ground at roughly the rate we are extracting petroleum today. To have the desired impact on the atmospheric carbon budget, CO_2 must be efficiently retained underground for hundreds of years. Any underground storage system will have to account for the natural characteristics of subsurface formations; some are advantageous for storage while others are not. When foreign materials are emplaced in subsurface rock formations, they change the chemical and physical environment. Understanding and predicting these changes are essential for determining how the subsurface will perform as a storage container. The specific scientific issues that underlie sequestration technology involve the effects of fluid flow combined with chemical, thermal, mechanical, and biological interactions between fluids and surrounding geologic formations. Complex and coupled interactions occur both rapidly as the stored material is emplaced underground, and gradually over hundreds to thousands of years. The long sequestration times needed for effective storage and the intrinsic spatial variability of subsurface formations provide challenges to both geoscientists and engineers. A fundamental understanding of mineralogical and geochemical processes is integral to this success.

- Eric H. Oelkers and David R. Cole, *Carbon Dioxide Sequestration A Solution to a Global Problem*, ELEMENTS 4(5): 305-310.

- Edward S. Rubin, *CO_2 Capture and Transport*, ELEMENTS 4(5): 311-317.

- E. Eric Adams and Ken Caldeira, *Ocean Storage of CO_2*, ELEMENTS 4(5): 319-324.

- Sally M. Benson and David R. Cole, *CO_2 Sequestration in Deep Sedimentary Formations*, ELEMENTS 4(5): 325-331.

- Eric H. Oelkers, Sigurdur R. Gislason, and Juerg Matter, *Mineral Carbonation of CO_2*, ELEMENTS 4(5): 333-337

10,595 copies were distributed to individuals, libraries, and societies. The issues are also available on line, through GeoScienceWorld (http://elements.geoscienceworld.org/) and the *Elements* magazine (www.elementsmagazine.org/) websites.

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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 broad objective of this study is to quantify the rheological behavior of olivine, the primary mineral in Earth's upper mantle, in order to provide the basis for modeling geodynamic processes. The specific goal is to determine experimentally the constitutive equation governing flow under lithospheric conditions.

Project Description: We have carried out a series of creep experiments on fine-grained samples of olivine using the deformation-DIA (D-DIA), a solid-medium deformation apparatus with the capacity of allowing tri-axial deformation experiments at pressures up to12 GPa. Advanced synchrotron x-rays techniques provided *in-situ* measurements of pressure (i.e., mean stress), differential stress, strain, and strain rate.

Experiments were conducted at temperatures ranging from 673 to 1273 K at pressures from 4 to 9 GPa. The results of these measurements provided the basis for establishing the flow behavior of olivine in terms of the dependence of creep rate on deformation conditions at lithospheric values of stress, pressure, and temperature.

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 ($\leq$673 $T \leq 1273$ K), and anhydrous conditions with a D-DIA. Differential stress and sample displacement were monitored *in-situ* using synchrotron x-ray diffraction and radiography, respectively. Experimental results were fit to the low-temperature plasticity flow law,

$$\dot{\square} = \mathrm{A}^{/}_{\mathrm{P}} \frac{\overline{}^{\,11/4}}{T^{1/2}} \exp\left[-\frac{E_{\mathrm{k}}(0)}{\mathrm{R}T}\left(1-\sqrt{\frac{\overline{}}{\overline{}_{\mathrm{P}}}}\right)\right].$$

Based on this analysis, the low-temperature plasticity of olivine deformed under anhydrous conditions is well constrained by our data with a Peierls stress of $\sigma_{\mathrm{P}} = 6.2 \pm 0.2$ GPa, a zero-stress activation energy of $E_{\mathrm{k}}(0) = 290 \pm 60$ kJ mol^{-1}, and a material parameter of $\mathrm{A}^{/}_{\mathrm{P}} = 2.7 \times 10^{-8}$ s^{-1} MPa$^{-11/4}$ K$^{1/2}$.

Compared with published results for low-temperature plasticity as well as high-temperature creep of olivine, our results indicate the following: (1) A transition from low-temperature plasticity to high-temperature creep occurs at ~1300 K for laboratory strain rates (10^{-6}-10^{-5} s^{-1}).

(2) The flow stress in the low-temperature plasticity regime is less temperature sensitive than reported in earlier studies that used micro-indentation and load relaxation techniques; in these tests, samples were deformed in a transient rather than a steady-state regime. (3) A strength envelope for the lithospheric mantle is established using the low-temperature plasticity flow law obtained from this study. It predicts an integrated strength of ~ 3×10^{13} Pa·m. for the lithospheric mantle to a depth of 100 km. The low-temperature, high-stress flow law for olivine from this study provides a solid basis for modeling tectonic processes occurring within Earth's 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 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 mini basin, 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 fluid generation and disequilibrium compaction. The present research consists of developing a numerical model for solitary wave initiation and propagation, based on Eugene Island geology. The first step of the research consists of developing a numerical solution describing fluid flow through a fault and quantifying the conditions that give rise to solitary waves and the flux of fluid that they transmit. The second step consists of coupling the solitary wave solution to a basin-scale model for fluid flow that characterizes solitary wave origin and motion within the context of sedimentary basin evolution.

Results: Work thus far has focused on the behavior of solitary waves in fault zones with elastic rheologies. A numerical finite difference solution to the governing equation for a one-dimensional vertical fault zone is being developed. Results thus far indicate that solitary wave formation requires an environment in which permeability changes more rapidly than porosity with respect to changes in effective stress. Solitary wave formation also requires the existence of very low effective stress within the fault zone such that fluid pressure is nearly equal to the total stress and the fault zone is largely fluidized. Calculated solitary wave velocities are strongly dependent on the density and viscosity of the pore fluid but are generally fast. Based on published physical properties of Eugene Island sediments, solitary wave ascent velocities on the order of 1's to 10's of kilometers per year (km/yr) are possible for water and petroleum pore fluids and 10's to 100's of km/yr are possible for methane. Solitary waves are expected to be dampened by viscous effects, but these have not yet been included in the present models. The project is currently in its second year and is funded through June 14, 2010.

NATIONAL ACADEMY OF SCIENCES
Board on Earth Sciences and Resources
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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 2009, the Board oversaw 14 studies. Examples of studies underway during FY 2009 are New Research Opportunities in the Earth Sciences at the NSF; Assessment of DOE's Methane Hydrate Research and Development Program; Management and Effects of Coalbed Methane Development and Produced Water in the Western United States; Private-Public Sector Collaboration to Enhance Community Disaster Resilience; and National Earthquake Resilience--Research, Implementation, and Outreach. BESR completed one study in FY 2008 and two at the beginning of FY 2009. The results of BESR's studies are published in its peer-reviewed reports. These 2009 studies are *Applications of Social Network Analysis for Building Community Disaster Resilience: A Workshop* and *Mapping the Zone: Improving Flood Map Accuracy*. For the first time, the Board produced a Summary of Technical Findings for one of its studies--*Mapping the Zone*. This report is somewhat unusual in the sense that it contains original research.

During this reporting period, the Board held two meetings. The December 2008 meeting was held at the Beckman Center in Irvine, California. At this meeting, one BESR standing committee, the Geographical Sciences, was reviewed. We were provided with an update of the congressionally mandated DELS study, “America’s Climate Choices.”

The BESR members visited the San Diego Supercomputer Center and participated in a symposium that included talks on the GEON Project and the Southern California Integrated GPS Network. The board convened a roundtable on GeoInformatics, which was introduced and moderated by Keith Clarke of the University of California, Santa Barbara (chair of the Mapping Science Committee).

The May 2009 meeting was held at the Keck Center in Washington, DC. The board convened a roundtable, “Federal Land Use Considerations for U.S. Energy Resources.” The roundtable was introduced and moderated by Murray Hitzman of the Colorado School of Mines (chair of the Committee on Earth Resources). Presentations were made by Tony Ferguson, U.S. Forest Service; Linda Resseguie, Bureau of Land Management; Colin Williams, U.S. Geological Survey; Doug Dahle, DOE National Renewable Energy Laboratory; Jeffrey Eppink, Enegis, LLC; and Frank Burke, Independent Consultant. Robert Detrick, Earth Science Director, NSF, spoke to BESR about GEO and his expectations for the new study, “New Research Opportunities in the Earth Sciences at the NSF.”

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Grant: DE-FG02-08ER15930

Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport

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Objectives: The objective of this project is to characterize the influence that naturally complex geologic media has on anomalous dispersion and to determine if the nature of dispersion can be estimated from the underlying heterogeneous media.

Project Description: This project combines outcrop-scale heterogeneity characterization, laboratory experiments, and numerical simulations. The study is designed to test whether established dispersion theory accurately predicts the behavior of solute transport through heterogeneous media and to investigate the relationship between heterogeneity and the parameters that populate these models. The dispersion theory tested by this work is based upon the fractional advection-dispersion equation (fADE) model. Unlike most dispersion studies that develop a solute transport model by fitting the solute transport breakthrough curve, this project will explore the nature of the heterogeneous media to better understand the connection between the model parameters and the aquifer heterogeneity.

Results: In the third and last year of this project, we continued to evaluate lidar imagery in both two dimensions and three dimensions. We acquired lidar imagery from an approximately 3 x 1.5 meter area of an outcrop previously evaluated by Gaud et al. (2004). This portion of the outcrop contains sediment textures ranging from gravel and cobbles to silty sand to silty clay. We are currently segmenting the data to produce a facies map from the lidar results. Once these results are available, we will use permeability measurements from Gaud et al (2004) to populate a model area for groundwater modeling through the measured heterogeneity. In addition to constructing an additional groundwater model at this resolution, we are working with the data to drape photographs over the lidar imagery. This procedure is necessary for future work at building larger-scale models.

We are also creating a 3D characterization of braided river deposit heterogeneity by successively scraping and scanning an outcrop in approximately 2 cm intervals over an approximately 3 x 2 meter area. After scanning each slice, we use a device to smoothly scrape the outcrop approximately 2 cm. Each successive slice is projected into the same coordinate system, thus a 3D point cloud is obtained for the exposed volume. Since most segmentation approaches have been developed for 2D data, we segment sand from gravel from each 2D slice of the outcrop. Combining these segmented slices we are developing a 3D grid that delineates the regions of sand versus gravel. At present, our segmentation is binary and uses 2D data; however we are currently developing means to interpolate the point clouds into a regular 3D grid and segment facies from this grid.

We face several challenges with this new 3D data set. First, we are creating a point cloud with over 100 million points. Ultimately, the 3D grid at a 2mm x 2mm x 2cm spacing has over 25 million nodes. This size is difficult to process on most computers. Second, the 25 million node grid is much too large for running standard groundwater models. For both of these reasons, we are beginning to work on possible upscaling approaches that account for the facies distributions. This is not a trivial issue since the facies are not in layers and averaging may compromise the detail that we’ve strived to collect. The 3D upscaling and analysis will ultimately become targets for future proposals and studies.

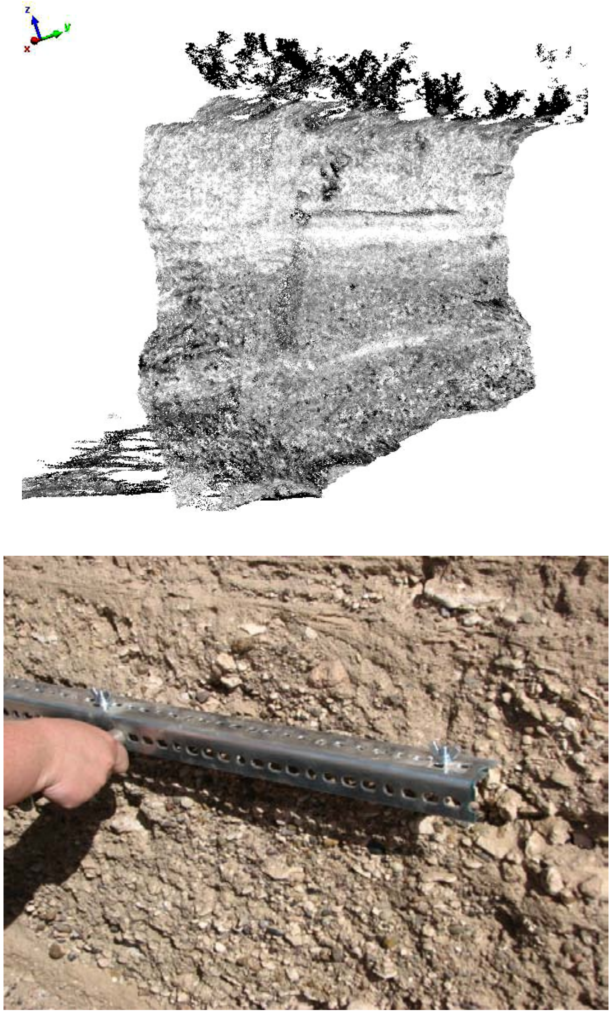

Figure 1: A) A side view of the three-dimensional point cloud of data from the arroyo scan site. B) The scraping of the arroyo outcrop.

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK

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Grant: DE-FG02-06ER15817

Complex Fluids in Self-Affine Fractures

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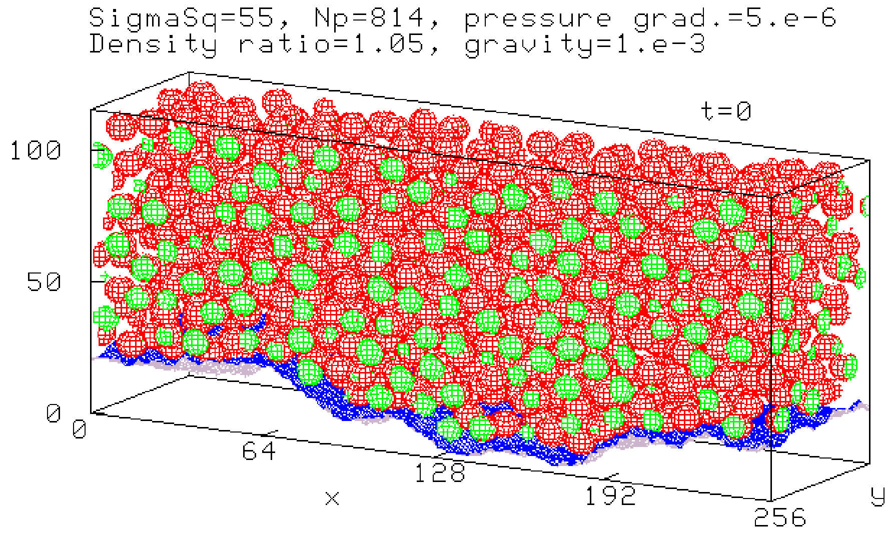
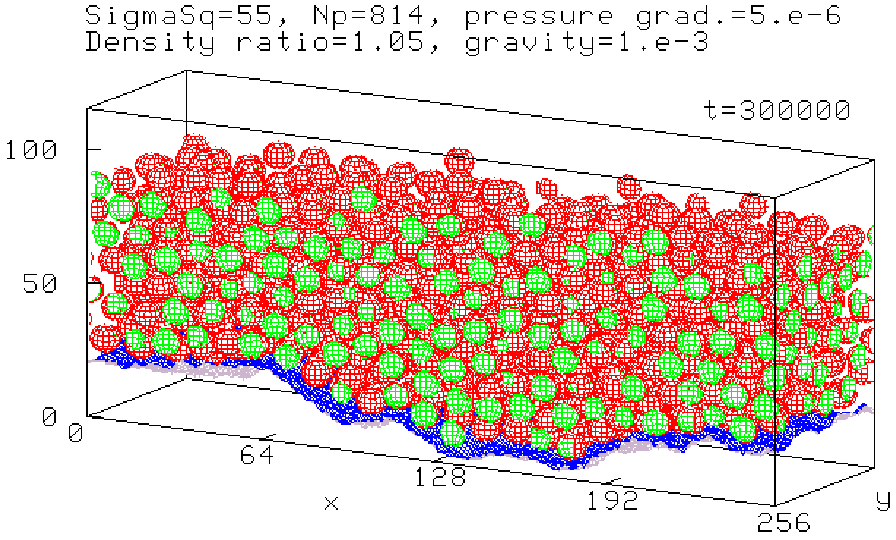
Objectives: To understand the dynamics of non-Newtonian liquids and particulate suspensions in self-affine fractures, and in particular how the correlated surface roughness affects permeability, tracer dispersion and sedimentation.

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 render 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 are in the midst of examining the changes in particle transport and sedimentation resulting from the roughness of fracture walls. We have simulated the flow of suspensions of spherical particles in a Newtonian liquid through fractures with two planar walls in previous published work, and recently we extended these studies to channels with a self-affinely rough bottom and a planar top. Calculations which consider fully self-affine fractures and the effects of lateral displacements and surface consolidation will be carried out next. In addition to determining the properties of the sediment layer, the analysis focuses on flow profiles – variation of particle concentration and fluid and particle velocity across the fracture gap, global transport – the variation of particle and fluid flux with pressure gradient, density ratio and fracture inclination. We are also pursuing detailed questions such as whether the shape of the sediment exhibits any effects of the self-affine bottom surface, and in particular whether the top of the sediment is itself a self-affine, and the effects of flow rate on resuspending.

Snapshots of the initial and final states in a typical simulation is shown in the figure below, which involves a suspension of 814 mono-disperse spheres at a volume fraction of 26%.





The fracture channel has periodic boundaries in both horizontal directions, a planar top and a self-affine bottom surface shown in blue. The particles are the red spheres, green indicates the faces of particles which are cut by the periodic boundary, and the suspending fluid is not shown. The settling of the particles due to gravity is evident.

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Grant: DE-FG02-03ER15458

Study of Damping of Acoustic Modes in Granular Materials

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Objectives: The goal of this project is to combine experimental characterization, continuum and micromechanical modeling and computer simulations to understand the elastic properties and the mechanisms of dissipation of acoustic modes in granular materials.

Project Description: This project is motivated by a desire to understand acoustic propagation and dissipation in earth formations. A distinct feature of granular materials is the ability to dissipate acoustic energy through the network of interparticle contacts or viscous dissipation through the surrounding medium. Indeed, loose grains damp acoustic modes very efficiently and they are routinely used as an effective method to optimize the damping of unwanted structure-borne acoustic signals. Despite its fundamental importance and practical applications, the microscopic origins of the mechanisms of dissipation in jammed granular materials are still unknown. To this end, we pursue the concept of the effective mass of a loose granular aggregate contained within a rigid cavity which is vibrated at different frequencies as well as the flexural modes in a resonance bar with a cavity filled with grains. Apart from the fundamental aspects of this research we are motivated by the practical need to develop an effective method for optimizing the damping of waves in structure borne sound.

Results: We have performed a series of experiments, simulations and theoretical studies done in parallel at Schlumberger and CCNY. We report a theoretical and experimental investigation into the fundamental physics of why loose granular media are effective dampeners of acoustic modes. We demonstrate that a measurement of the effective mass of the granular medium is a sensitive and direct way to answer the question: What is the specific mechanism whereby acoustic energy is transformed into heat? Specifically, we apply this understanding to the case of the flexural resonances of a rectangular bar with a grain-filled cavity within it. The pore space in the granular medium is air of varying humidity. The dominant features of the effective mass are a sharp resonance and a broad background, which we analyze within the context of simple models. We find that: a) On a fundamental level, dampening of acoustic modes is dominated by adsorbed films of water at grain-grain contacts, not by global viscous dampening or by attenuation within the grains. b) These systems may be understood, qualitatively, in terms of a height-dependent and diameter-dependent effective sound speed (100-300$ m/s) and an effective viscosity (50,000 Poise). c) There is a monotonically increasing effect of humidity on the dampening of the fundamental resonance within the granular medium which translates to a non-monotonic, but predictable, variation of dampening within the grain-loaded bar.

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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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Objectives: 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 (DSF) 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 DSF. 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 ferrihydrite conducted in Strongin's research group is complemented by geochemical modeling to understand the changes in solution composition and mineralogy as the reaction proceeds. Of particular interest are changes in pH and saturation index for siderite. Figure 1 shows that reaction of 7 millimol of ferrihydrite will result in saturation with siderite, which represents about 25% of the total ferrihydrite in the system. We are also using geochemical models to evaluate the interaction between $scCO_2$ containing H_2S/H_2SO_3 with iron minerals in sediments. Of particular interest is the fate of sulfur in these systems and whether siderite is formed.

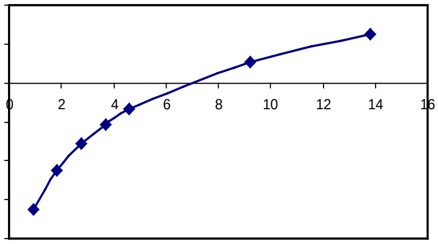

Figure 1: Saturation index with respect to siderite in simulation of ferrihydrite experiments in Strongin group. Note that after reaction of about 7 millimol, or 25% of total amount of ferrihydrite in system, saturation with siderite is achieved. System equilibrated with 82 bar CO_2 and T= 70°C

The focus of Schoonen's effort this last year has been, however, on building our capability to conduct experiments to evaluate the interaction of $scCO_2$ containing H_2S or H_2SO_3 with iron-bearing sediments. The goal of our experimental work is to be able to advect $scCO_2$ containing H_2S or H_2SO_3 over packed, loose sedimentary material and, eventually, through intact sediment cores. After significant delays in the delivery of several key components, we now have the necessary components to build a system that allows us to conduct the experiments.

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Grant: DE-FG02-99ER14996

Microscale Processes and Macroscopic Behavior of Porous Geomaterials

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Objectives: This project aims to provide a fundamental understanding of microscale basis for the macroscopic deformation and transport properties of porous geomaterials, using an integrated approach consisting of experimental rock mechanics testing, quantitative microscopy and statistical microgeometric characterization, and theoretical and numerical analyses.

Project Description: The microstructure of natural earth materials is extremely heterogeneous and complex. The underlying microscale characteristics that control deformation and transport processes are not understood quantitatively for natural earth materials such as siliciclastic and carbonate rocks. Increased fundamental understanding of the microscale basis for the macroscopic response such as deformation behavior (and stability) under changing loading conditions (such as may be experienced in a subsurface geologic reservoir during CO_2 sequestration, or during production of hydrocarbons) is necessary. Likewise, an increased understanding of how the pore structure and its evolution with deformation affect fluid transport processes (during underground injection of greenhouses gases to mitigate climate change, or during primary and enhanced oil recovery) is required. Systematic experimental investigation provides a detailed understanding of the microstructure of porous earth materials and how those microscale characteristics affect the deformation and fluid transport properties at the macroscale. The laboratory data together with quantitative microscopy are used to formulate and evaluate theoretical and numerical models of rock deformation and fluid flow.

Results: Major accomplishments in this funding period are primarily related to failure mode and compaction of porous carbonate rocks. Previous studies reveal that while compact carbonate rocks display exclusively dilatancy under compressive deformation, compaction may be observed in their more porous counterparts. In their compactive behavior the porous carbonate rocks are phenomenologically akin to sandstone. Whereas the micromechanics of brittle faulting and cataclastic flow for sandstone has been studied extensively, little is known about these processes in a porous limestone.

(1) We deformed samples of Tavel limestone with ~12% porosity to various stages of deformation, at confining pressures corresponding to brittle faulting and cataclastic flow, and investigated the damage evolution in this micritic limestone. Cataclasis is the dominant mechanism of deformation in both failure modes. The microcracks initiate as pore-emanated and while all pores contribute to microcrack initiation, it is the large pores that drive crack propagation and coalescence leading to failure. In brittle faulting, dilatancy arises from microcracks growing parallel to maximum principal stress, with their coalescence leading to shear localization. In cataclastic flow the microcracking is relatively isotropic, and the interplay

between pore collapse and microcracking determines the compactive versus dilatant character of inelastic failure.

(2) A parallel study was conducted on Indiana and Majella limestones. While the micromechanics of failure is qualitatively similar, our observations also underscore the complexity of damage evolution and pore collapse in these two more porous allochemical limestones, which is possibly related to the mechanical contrast between allochems and cements.

(3) Our microstructural observations indicate that pore collapse in a limestone initiates at the larger pores, and microcracking dominates the deformation in the periphery of a collapsed pore. These two features are in discrepancy with a conventional plastic pore collapse model. To capture these micromechanical processes, we developed a cataclastic pore collapse model treating the limestone as a dual porosity medium, with the total porosity partitioned between macroporosity and microporosity. The representative volume element is made up of a large pore which is surrounded by an effective medium containing the microporosity. Cataclastic yielding of this effective medium obeys the Mohr-Coulomb or Drucker-Prager criterion, with failure parameters dependent on porosity and pore size. An analytic approximation was derived for the unconfined compressive strength associated with failure due to the propagation and coalescence of pore-emanated cracks. For hydrostatic loading, identical theoretical results for the pore collapse pressure were obtained using the Mohr-Coulomb or Drucker-Prager criterion. For nonhydrostatic loading, the stress state at the onset of shear-enhanced compaction was predicted to fall on a linear cap according to the Mohr-Coulomb criterion. In contrast, nonlinear caps in qualitative agreement with laboratory data were predicted using the Drucker-Prager criterion.

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Grant: DE-FG02-05ER15635

Up-Scaling Geochemical Reaction Rates for CO_2 in Deep Saline Aquifers

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Objective: The goal of this project is to use a combination of experiment and numerical simulation to bridge the gap between our knowledge of small-scale geochemical reaction rates and rates meaningful for modeling reactive transport at core scales. The focus is on CO_2-water-rock interactions in the context of geological sequestration of carbon dioxide – specifically acid-driven mineral dissolution and precipitation.

Project Description: The work combines (i) spectroscopic imaging and innovative image processing to characterize sedimentary rocks, (ii) development of new pore-scale network models of reactive transport in porous media, and (iii) simulations to examine reaction rate upscaling. Rock specimens came from the Viking formation in the Alberta Sedimentary Basin, provided by the Alberta Geological Survey. Imaging methods include X-ray computed microtomography, backscatter electron microscopy (BSE) and energy dispersive X-ray (EDX) spectroscopy. The dual goals of the analysis of the imaging are to capture the 3D void space network as well as reactive mineral patterns to determine pore contact with individual minerals thereby quantifying meaningful surface areas for use in reactive transport models. Reaction rates computed from network models, which account for pore scale heterogeneity, are compared with reaction rates computed via a continuum model which employs bulk averaged (porosity, concentration) values.

Results: One of the current challenges facing implementation of large-scale CO_2 injection projects is forming regulations or guidelines that specify the required purity of the injection stream (Pollak and Wilson, 2009). During FY2009, the work has focused on an investigation of co-injection of sulfur dioxide, an important environmental pollutant emitted from electric power plants. With the emergence of carbon capture and geologic sequestration, and the possibility of SO_2 co-injection, the economic favorability of emitting SO_2 to the atmosphere could change.

A primary concern surrounding geologic carbon sequestration is the potential for brine acidification. The presence of co-injectants, such as SO_2, may lead to further brine acidification through the formation of stronger acids. The goal of this work was to estimate the magnitude and time scale of brine acidification for the case of SO_2 co-injection. The potential for brine acidification was investigated for three different SO_2 reaction scenarios: hydrolysis, oxidation, and disproportionation, to investigate the effects of different sulfur-bearing acids. The model scenarios that were studied describe the situation in which SO_2 mass transport to the brine phase is limited by diffusion in the $scCO_2$ phase. One model describes rapid dispersion of SO_2 in a slowly advecting brine phase. The other model investigates diffusive transport of SO_2 in a stagnant brine phase. These represent extreme end cases for transport limitations and are meant to provide bounding estimates of brine acidification, as in reality, a combination of advective and diffusive transport in the aqueous phase will exist. For comparison, we modeled the case of SO_2 phase equilibrium between the entire volumes of $scCO_2$ and brine, which represents the maximum potential basin-scale acidification. To predict brine pH, we developed a geochemical model that simulates aqueous speciation and thermodynamic phase equilibrium of injected CO_2 and SO_2 with brine from a Mississippian carbonate formation in the Alberta Basin, Canada.

Predictions were compared to the case of CO_2 alone which would cause a brine pH of 4.6 under typical pressure, temperature, and alkalinity conditions in an injection formation. In the unrealistic model scenario of SO_2 phase equilibrium between the CO_2 and brine phases, co-injection of 1% SO_2 is predicted to lead to a pH close to 1 with SO_2 oxidation or disproportionation, and close to 2 with SO_2 hydrolysis. For a scenario in which SO_2 dissolution is diffusion-limited and SO_2 is uniformly distributed in a slowly advecting brine phase, SO_2 oxidation would lead to pH values near 2.5 but not until almost 400 years after injection. In this scenario, SO_2 hydrolysis would lead to pH values only slightly less than those due to CO_2 alone. When SO_2 transport is limited by diffusion in both phases, enhanced brine acidification occurs in a zone extending only 5 m proximal to the CO_2 plume, and the effect is even less if the only possible reaction is SO_2 hydrolysis. In conclusion, the extent to which co-injected SO_2 can impact brine acidity is limited due to diffusion-limited dissolution from the CO_2 phase, and may also be limited by the availability of oxidants to produce sulfuric acid.

In addition, pressure-, temperature-, and salinity-adjusted values of the SO_2 Henry's Law constant and fugacity coefficient were determined. They are predicted to decrease with depth, such that the solubility of SO_2 is a factor of 0.04 smaller than would be predicted without these adjustments. To explore the potential effects of transport limitations, a non-steady state model of SO_2 diffusion through a stationary cone-shaped plume of supercritical CO_2 was developed. Simulations for conditions corresponding to storage depths of 0.8 to 2.4 km revealed that after 1000 years, 65 to 75% of the SO_2 remains in the CO_2 phase. This slow release of SO_2 would largely mitigate its impact on brine pH. Furthermore, small amounts of SO_2 are predicted to have a negligible effect on the critical point of CO_2, but will increase phase density by as much as 12% for mixtures containing 5% SO_2.

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Grant: DE-FG02-09ER16017

Structural Basis for Stabilization and Transformation Behavior of Amorphous Calcium Carbonate

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Objective: 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 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: During the initial year of research we focused on refinement of a model structure using the pair distribution function (PDF) obtained from synchrotron total X-ray scattering data for undoped hydrated ACC. We employed the reverse Monte Carlo (RMC) refinement program RMCProfile and collaborated with Andrew Goodwin and Martin Dove (Cambridge University). We considered two types of starting assemblages containing approximately 10,000 atoms: disordered configurations based on the structure of monohydrocalcite (dMHC models) and a completely random initial arrangement of Ca atoms, CO_3^{2-} groups, and H_2O molecules with the same stoichiometry ($CaCO_3 \cdot H_2O$) and same overall density as MHC (Random model). We also employed closest-approach and geometry constraints to avoid unphysically short separations. On convergence, nearly identical and reproducible fits-to-data and individual partial PDFs were obtained for the different starting models (Figs. 1a and b). Because the RMC fitting process is performed in reciprocal space, driven by the Q-weighted reduced structure function, $QF(Q)$, this similarity in real-space (compared to the experimental PDF) is especially encouraging. Further validation for the approach comes from the ability of the model configurations to reproduce all key features of experimental EXAFS data.

Access to partial PDFs (not shown) allowed us to identify the likely origin of various features in the total PDF. In addition to features corresponding to C-O and Ca-O atomic pairs, a distinct feature at 2.8–3.0 Å is interpreted to arise hydrogen bonded O…O correlations. Showing similarities to the hydrogen-bonding connectivities in monohydrocalcite and in ikaite, this finding demonstrates the importance of H_2O in the temporary stabilization of the amorphous phase.

The average coordination for Ca is found to vary only modestly from 5.0 for the dMHC-1 model to 5.8 for the dMHC-2 model, with a value of 5.3 for the Random model. Yet, in all cases the standard deviations are large (1.3–1.6), indicating a significant range of oxygen coordination for Ca. Calcium coordination numbers in crystalline polymorphs range from 6 (calcite) to 9 (aragonite). It is significant that this entire range is represented in the structures derived from both starting models.

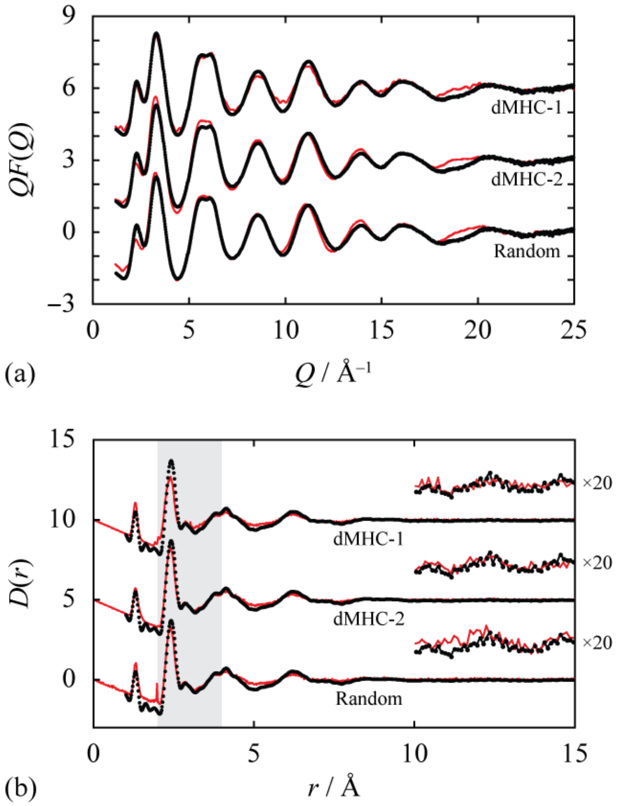

Fig. 1. (a) Reduced structure function from synchrotron X-ray total scattering data (black) and (b) pair distribution function (black). Simulations (red) from RMC refinements using different starting models are superposed.

Another important objective is to identify the origin of the medium-range order in ACC. We note that the broad PDF oscillations extending to ~15 Å (Fig. 1b) are reproduced in all RMC models, which suggests that the MRO does not involve an array of small MHC-like domains. The two correlations consistently responsible for these long-*r* PDF oscillations across all three models are the Ca–Ca and Ca–O pair correlations. We can rule out a simple hard-sphere-like packing of the Ca coordination environments, which gives Ca-Ca correlations at longer distances than observed in the experimental PDFs. Hence, the RMC refinements indicate some degree of Ca clustering. This further implies the presence of Ca-free regions, which are up to 15 Å in diameter, and presumably occupied mostly by CO_3^{2-} ions and H_2O molecules. This is consistent with our NMR observations showing that a significant fraction of the H_2O undergoes restricted motion. We speculate that the separation of Ca-containing and Ca-free regions suggest a likely mechanism for the kinetic stabilization of the phase in that the addition of charged or polar “solute” species should shield the charge fluctuations, hence delaying the nanometer-scale rearrangements necessary for transformation to crystalline forms.

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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: This work will develop models of subsurface multiphase flow and transport across length scales in the context of carbon sequestration for the purpose of supporting, confirming, and extending a consistent, multiscale, physically-based theoretical description.

Project Description: Theory, computation, and mathematical analysis will be combined to formulate, solve, and validate models that capture the physics of multiphase flow and transport phenomena in porous media across a range of length scales. The multi-pronged approach envisioned will produce the foundational underpinnings of a new generation of multiscale, multiphase porous medium models. The focal point of the research will be the development of a series of models to improve the mathematical description of carbon sequestration. Hierarchical modeling frameworks will be developed for two- and three-fluid phase flow and for two-fluid-phase flow and species transport using the newly developed thermodynamically constrained averaging theory that resolves the deficiencies existing in traditional models. Candidate models will be closed in conjunction with microscale lattice Boltzmann simulation methods of highly resolved systems to guide the development and parameterization of specific forms of permissible closure relations. Modern numerical methods will be used to approximate the resultant macroscale models, which will in turn be verified by comparison to highly resolved microscale simulations and to available high-resolution experimental observations.

Results: This newly funded project will require three years to complete. All aspects of the program will be worked on simultaneously, although particular elements will be highlighted in each year.

- Year 1 will be focused on the theoretical development of a two-fluid-phase flow model and the advancement of lattice-Boltzmann methods needed for microscale simulation.
- Year 2 will involve closure of the two-fluid-phase flow model, development of a macroscale simulator, and validation, verification, and analysis of the model. Theoretical work will also be performed to derive the two-fluid-phase flow model with species transport. Further methods development for microscale and macroscale simulators will also be performed.
- Year 3 will focus on the formulation and closure of the three-fluid-phase flow model, development of a macroscale simulator for this model, and validation, verification, and analysis of the model. Applications of the models developed for the case of geologic CO_2 storage will receive special attention.

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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 of transition metals and uranium in order to help elucidate information on oxidation states and bonding environments.

Project Description: This project concerns reactions between minerals and toxic metal-bearing aqueous fluids. Specifically, we are exploring the mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals. Key techniques used are electron microscopy, x-ray photoemission spectroscopy (XPS), and x-ray adsorption near edge structure (XANES). The project includes major theoretical efforts on the interpretation and prediction of XPS and XANES; the *ab initio* theoretical work is coupled to the experimental efforts.

Results: Our theoretical and computational efforts are in two areas. First, we are engaged in enhancement of our computer programs for the simulations of core-level spectra as required for the accurate calculation of complex core-level spectra. Second, we have analyzed the XPS spectra of MnO and of CeO_2 in preparation for our calculations on the more complex U oxides that are the major objective of our efforts. Furthermore, these systems are of substantial interest.

Two parameters determine the magnitude of our computational efforts. These parameters are the active orbital space of orbitals whose occupation may be varied and the active configuration space where the occupations of the active orbitals in different configurations are specified. In our earlier work, we implemented a general active space algorithm that allowed us to reduce the rate of increase of the number of active configurations by eliminating distributions whose contributions are small. In the present period, we extended the code to allow the use of larger, essentially open ended in size, active orbital spaces. These larger spaces are necessary for the study of lanthanides and actinides where the metal atom d and f shells must be included in the active space. In addition, several steps have been taken to move from proof-of-concept to robust, user-friendly code on supported platforms. In particular, we have initiated a partnership with EMSL at PNNL to place our codes within the NWChem framework and, in the process, remove computational bottlenecks. We are also taking steps to exceed our present limit of being able to mix only ~20,000 configurations in our many-body treatments since this limit is too small for an accurate treatment of charge transfer, essential for our theoretical XPS analyses.

Furthermore, we have a unique requirement to determine literally thousands of states that may steal XPS intensity from the allowed configurations.

We have continued our study of the XPS of the lanthanide oxide, CeO_2. The initial studies of the Ce 4s and 5s XPS have been completed and we have compared our theoretical predictions with recent XPS measurements. As shown in the figure for the Ce 4s XPS, our theory reproduces the relative energies and intensities of the experiment with sufficient accuracy to justify our assignments of the chemical and physical origins of the XPS. We expect to improve our agreement with experiment with additional classes of many-body effects, which we will do as soon as the program enhancements described above have been completed. Similar agreement between theory and experiment has also been obtained for the Ce 5s XPS. This is the first time that *ab initio* results, without parameters adjusted to fit experiment, have been obtained for the XPS of a lanthanide or actinide complex. Our results show that previous assignments based on semi-empirical calculations have not correctly identified the origins of the XPS features in CeO_2. With our results, it is now possible to relate the XPS to the chemical bonding in CeO_2. We have encouraging initial results for the 3d and 4d XPS that especially in terms of explaining differences between the 3 and 4d XPS. However, we need to extend the many-body treatments with the new versions of our programs before we can draw definitive conclusions. Once the performance of our new programs has been confirmed with calculations on CeO_2, we will turn to the simulations for UO_2 with particular focus on the satellites of the main $4f_{7/2}$ and $4f_{5/2}$ peaks. This will be followed by simulations of other U oxides.

In other efforts on XPS simulations, we have essentially completed a study, including the full set of possible single charge transfer configurations, for the 2p XPS of MnO. The changes in the spectra are relatively small indicating that features in the spectra that have been assigned to charge transfer would have to arise from higher order charge transfer excitations or from other mechanisms, not involving charge transfer. These possible origins will be investigated. We have initiated an examination of the apparent XPS spin-orbit splittings of core levels for different oxidation states and different materials. The agreement of observed and theoretically predicted spin-orbit splittings may provide us with a direct measure of the extent that necessary many-body effects have been included in the theoretical models. Finally, we are examining how well the commonly used Russell-Saunders multiplets approximate the coupling of electrons in the open 5f shell of actinide cations. Especially for occupations close to a half filled shell, high spin Russell-Saunders multiplets will lead to XPS multiplet splittings much larger than for filling j-j coupled sub-shells. Thus, these multiplet splittings may provide information about chemical activity.

Advances for the measurement of XPS spectra for U cations are described in the Summary of the Co-PI, Eugene S. Ilton (PNNL).

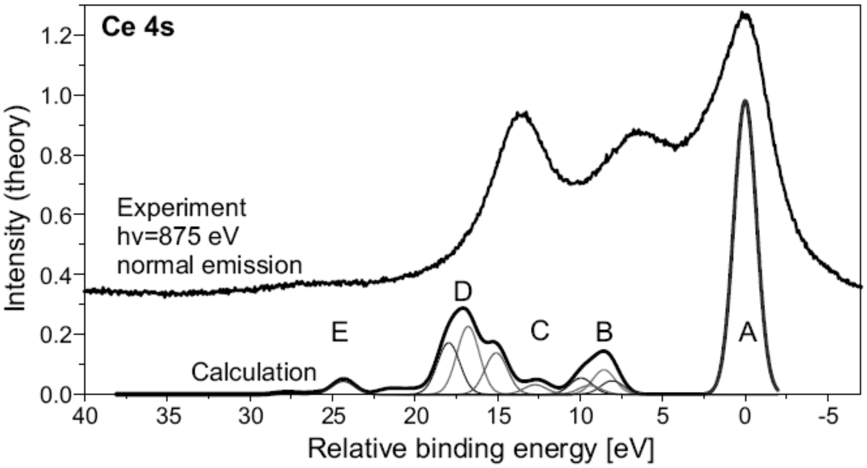

Figure. Theory and experiment for the 4s XPS of CeO_2. The broadened features in the simulation are labeled A-E; the individual contributions and the solid line for all contributions are shown.

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Grant: DE-FG02-06ER15787

Surface Charge Densities and Acidities of Biogeochemically Important Organic Adlayers at Mineral/Water Interfaces Studied by Nonlinear Optics

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Objectives: The project applies nonlinear optics to determine, with an unprecedented sensitivity and dynamic range, the interfacial pKa values, interfacial potentials and charge densities, and the energy densities of tailor-made biogeochemically-important aqueous/solid interfaces in order to test and expand existing surface complexation models that are useful for assessing contaminant transport by computer-based pollutant transport modeling calculations.

Project Description: This project investigates various oxide surfaces and organic ad-layers in a series of experiments and proposes to apply electric double layer models to third order susceptibility for second harmonic generation studies; to image quantitative charge density and surface potentials as a function of time; to introduce interface heterodyne detection into the imaging detection system to improve detection limits; to then build a variety of maps with 0.1 to 1 micron spatial resolution. It will: 1) Apply existing electrical double layer models to the $\chi(3)$ SHG formalism, test them for given heterogeneous scenarios, and expand them; 2) Quantify and image interfacial charge densities and interfacial potentials in real time and directly at the aqueous/solid interface via heterodyne-detected nonlinear optics; and 3) Build heterogeneous kinetic, thermodynamic, structural, and mechanistic parameter maps for interfacial acid-base chemistry and carry out histogram analyses for the heterogeneous processes under investigation to track their spatial and temporal evolution. The results will improve surface complexation models and chemical transport models by incorporating heterogeneous parameters derived from interface-specific kinetic, thermodynamic, spectroscopic, and structural data.

Results: The project has shown that the interfacial acid-base chemistry of silica/water, alpha-alumina/water, and silica/amino acid/water interfaces tracks the bulk pH at low salt concentrations. Initiating pH jumps or anion- or cation-adsorption experiments near neutral conditions does not result in time delays, even at 0.5 M salt concentrations. Instead, we find that the delay times are overwhelmingly controlled by the difference in the initial and final pH values, the salt concentration, and the chemical composition of the alkali halide salt used in the experiments. For common alkali halide salts (Li^+, Na^+, K^+, Cl^-, Br^-, I^-), the time delays increase with increasing extent of cation hydration and increasing anion polarizability, while the rates follow the kinetic salt effect. These findings suggest that the observation of jammed acid-base chemistry at interfaces is controlled by the rigidity of the interfacial water structure, which determines the time delays, and electrostatics, which determine the acid-base reaction rate once it occurs.

The project uses SHG to track the interaction of the environmentally important contaminants barium, strontium, and cadmium, chromate, oxytetracycline, and the nitrate anion with fused quartz/water and the (11bar02) alpha-Al_2O_3-water interfaces at various bulk pH values. Using a dynamic flow system, we assessed the extent of reversibility in the binding process and report the absolute number density of adsorbed cations, their charge densities, and their free energies of adsorption. We also reported resonantly enhanced SHG experiments that show that nitrate, oxytetracycline, and chromate are surface active and report the free energies and binding constants for the adsorption processes. The SHG spectrum of surface-bound nitrate shows a new adsorption band that cuts further into the solar spectrum than nitrate in the aqueous or solid state. Results from measurements regarding the charge state of the alpha-Al_2O_3-water interface as well as the chromium(VI) saturation surface coverages and the pH-dependence of the chromium(VI) equilibrium binding constants are also used to develop a thermodynamic and mass-balanced model that describes the interfacial interactions on the molecular level. Finally, we studied how organic adlayers control the binding of a more complex contaminant, namely the veterinary antibiotic oxytetracycline (OTC). Specifically, four environmentally relevant chemical moieties were covalently tethered to fused quartz surfaces using silane and amide coupling chemistry to survey how amides, polyfunctional binding sites, and phenyl rings that are common in humic acids control OTC binding at pH 8.

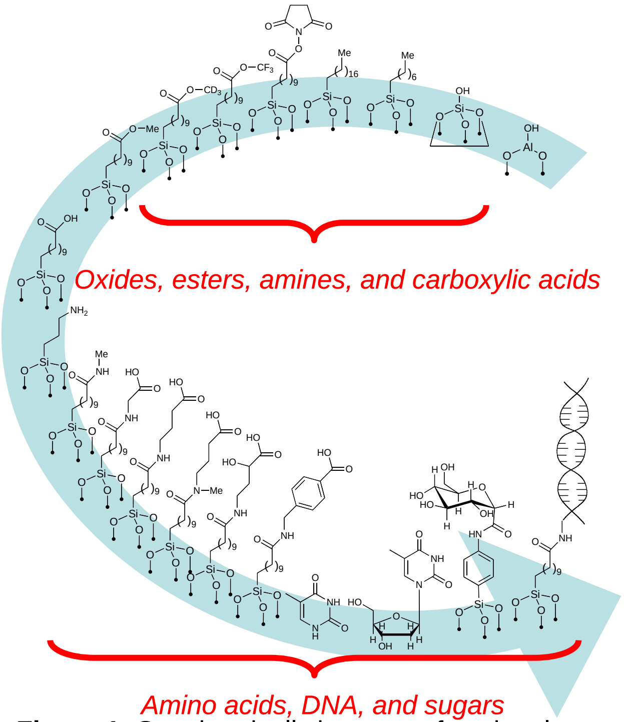

Figure 1. Geochemically important functional groups prepared, characterized, and studied under DOE-BES Grant #DE-FG02-06ER15787

In conclusion, we have used current funding cycle to demonstrate how nonlinear optics, specifically second and third-order optical probes, are highly useful for investigating the interaction of inorganic and organic cations and anions with mineral/oxide water interfaces in the presence and absence of organic adlayers.

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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.

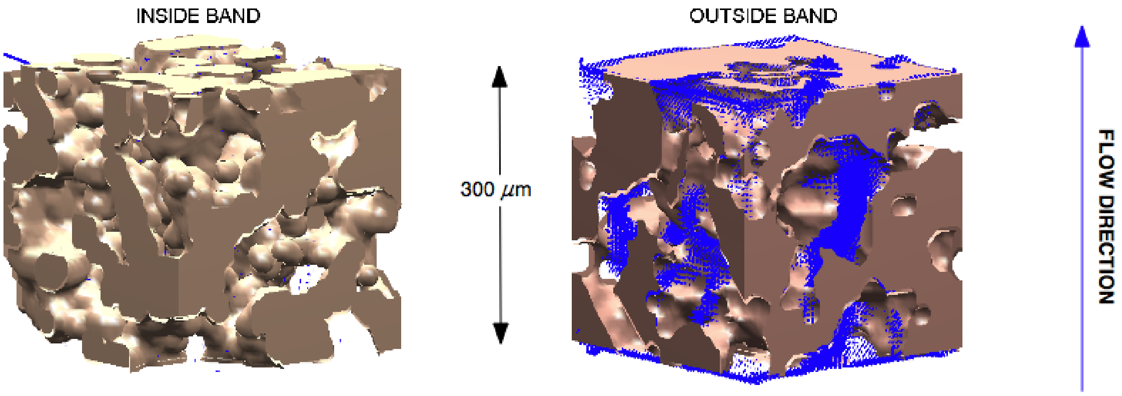

Figure 1. Apparent preliminary results of fluid flow simulations within 3D porous networks using lattice Boltzmann computations inside and outside compaction bands in Aztec sandstones. Blue regions show flow vectors at the grain scale level.

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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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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, 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 (**Allen Lab)**: Research during FY09 primarily encompassed (1) spectroscopy studies of silica surfaces and bulk aqueous solutions to understand the solvation environments and ion pairing parameters, (2) developing the methodology for growing thin films of metal oxides on infrared transparent optics to then be used for vibrational sum frequency generation (VSFG) and infrared spectroscopies, and (3) characterizing the thin oxide films. Results show that silica and iron oxide films of approximately 10 to 20 nm are homogeneously grown on KBr discs. For Fe, we oxidize the films after deposition. Analysis consists of infrared and Xray photoelectron spectroscopy. We are also currently developing methodology for infrared microscopy in transmission mode of the films exposed to aqueous solutions, with normalization using the 2100-2200 cm^{-1} water combination band since this band is relatively insensitive to the solute. The free silanol peak of the surface of amorphous silica has also been examined using polarization VSFG studies. We have determined that at ~40 % RH, the free silanol bond maintains an orientation of ~ 26 degrees from the surface normal, pointing into the vapor phase, even after a 50% reduction in number density upon water vapor adsorption.

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Grant: DE-FG02-06ER15819

Efficient Inversion of Multi-Frequency and Multi-Source Electromagnetic Data

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Objectives: The primary project objective is to develop more efficient inversion algorithms for electromagnetic (EM) geophysical data, taking advantage of some special features of inverse problems in which data are collected at multiple frequencies, or with multiple sources. A secondary objective is to develop a modular system for EM inversion, in order to (1) provide a test-bed for experimentation with new inversion algorithms; (2) to allow inversion schemes to be readily adapted for testing with different source/receiver configurations; and (3) to allow advances/modifications in other aspects of modeling or inversion methodology to be more rapidly incorporated.

Project Description: Electromagnetic (EM) geophysical data used for imaging the subsurface are commonly collected at multiple frequencies, or with multiple source geometries. As a result, inversion methods based on gradient based minimization of a penalty functional can be very costly in terms of computation. In particular, each forward solution (to evaluate data misfit) and each gradient calculation (to derive the next search direction) requires solution of one forward problem for each frequency/source (transmitter). We have been exploring hybrid schemes which combine features of an iterative conjugate gradients (CG) search scheme with a Gauss-Newton (GN) scheme, which traditionally requires computation of the full data sensitivity matrix. The key idea underlying our approach is that each search step in a CG type scheme implicitly generates data sensitivities (essentially columns of the Jacobian) for a series of linear data contrasts, one for each transmitter. If the coefficients of the data contrasts, and the corresponding data sensitivities are saved, a GN type scheme can then be used to solve the regularized inverse problem in a data subspace. This data subspace is always at least as large as the subspace implicit in a CG type search scheme, and potentially much larger, making the hybrid schemes potentially more efficient.

To more effectively explore these ideas we have developed a modular system for EM inversion. Our approach has been to focus first on a simple (two-dimensional magnetotelluric; MT) problem as a specific example, but to develop the code using an object oriented approach, independent of details of this specific problem. The top level of modules implements gradient calculations, and the specific inversion algorithms we are testing. These are implemented in an abstract way, to allow generalization to other problems. In parallel, modules have been developed for a general class of 3D EM inverse problems, with initial focus again on MT. One specific feature of the system is that the model parameter is treated as a purely abstract data type—i.e., objects which represent the unknown model parameter have only private attributes, which are not referenced by any of the modeling or inversion modules except through methods that are within the module. This programming approach greatly simplifies support of multiple model parameterizations, since we can guarantee that no modules depend on details of the model parameter representation, or its implementation. In particular, this will be useful for implementing constraints, physically based model parameters (e.g., making resistivity a function of other physical parameters and inverting for these), and decoupling the solution grid from the model parameterization.

Results: Principal accomplishments during FY09 include: (1) We completed implementation of inversion code for the 3D MT problem within the framework of the modular system. The organization and implementation of the modular system was further refined in conjunction with this effort, and we have applied the inversion to synthetic and real data sets. (2) A fairly general model covariance module has been developed, allowing for spatially variable model smoothing, freezing of model parameters for hypothesis testing, and “tears” to allow for rapid variations of conductivity across a fault or other geologic boundary. (3) We have developed a parallel version of the modular system using MPI on a small cluster. This was done within the framework of the modular system so that the same parallel inversion code can be used for a range of (multi-frequency) problems. An initial application of the parallel 3D MT inversion has been completed. (4) Development of new inversion approaches appropriate for multi-transmitter problems have been further developed, with coding of modules for a cross-well problem nearly complete. Our approach is based on using, but not storing, the full Jacobian. Multiplications by this matrix can be constructed using the forward solutions for each transmitter, and the adjoint solutions for each receiver. These can be pre-computed and stored, and hybrid Gauss-Newton/Conjugate gradient methods used to solve efficiently the linear sub-problem. Parallelization of the scheme is a current focus of our efforts. (5) Our 3D finite difference modeling code has been refined to compute forward solutions using a secondary field formulation. This increases accuracy of solutions for active source problems, and is essential for the cross-borehole application, as well as for marine CSEM.

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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 combining measurements of chemistry, mineralogy, microbiology, and textural analysis at scales from the mineral surface to the watershed to understand changes in the reaction interface during weathering. For example, we are analyzing weathering rinds and corestone/rock fragment size changes as a function of depth in weathering systems. To understand these data, we are developing models for surface evolution at the mineral grain scale, rind formation at the clast scale, and particle size variation versus depth at the profile or watershed scale.

Results: At the mineral surface scale, we are evaluating experiments where samples of forsterite were exposed to solutions containing various concentrations of dissolved Mg and Si. Experiments were run for time periods that were sufficient to ensure development of steady-state topography of the mineral surface. The surface roughness was analyzed using BET gas adsorption. These data will be used to understand the nature of the relationship between dissolution rate and chemical affinity for forsterite.

We are also using neutron scattering to investigate opening of porosity in low porosity rocks during weathering. Neutrons can penetrate bulk rock samples and probe the interior structure (pores vs. mineral matrix). Neutron scattering techniques were used to investigate features ranging from 10 Å to 10 µm in size within three rock types (granite from Puerto Rico, basalt from Costa Rica, shale from Pennsylvania, USA).

For basalt, granite, and shale, the surface area and porosity increase as weathering depletes primary minerals. For all three lithologies, the bedrock has low porosity, with most of the pores not accessible to rock-water interaction. During weathering, dissolution of minerals gradually increases the porosity and connectedness of the porosity.

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.

At the clast or hand specimen scale, we are investigating the relationship between 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 suggest that weathering rinds are thicker and weathering velocity is rapid where the curvature of the clast is greater. Open system mass balance calculations constrained by whole rock chemical and electron microprobe analyses show a hierarchy of elemental mobility of Ca≈Na>K≈Mg>Si>Al>Fe≈P during formation of the rind. The width of the reaction front is quantified through petrographic analysis (< 2 mm), porosity calculations (1.5-2.5 mm), and chemical analysis (0.4 – 0.8 mm).

At the watershed scale, we have developed a "weathering conveyor belt" model in which bedrock fragments enter the conveyor belt as angular fragments and decrease in size due to weathering until they exit at the ground surface. We compared this model to data describing fragment size versus position in the weathering system for low-porosity metavolcanic rocks in a Puerto Rico watershed weathering under tropical conditions (Fig. 1). The model is based on the assumption that rate of erosion = rate of weathering advance. Model-derived size-elevation curves vary as a function of initial fracture spacing, rate of porefluid advection, and rates of erosion and dissolution. This model is a new way of conceptualizing the weathering interface: the interface consists of rock fragments that vary in size across the weathering zone.

This model and our previously published spheroidal weathering model for a near-by 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.

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 the best weathering case study we have, Rose Hill shale weathering in the Shale Hills catchment at Penn State. The U analysis has given us time estimates for weathering. We are pursuing the use of U disequilibrium analysis also for the Puerto Rico weathering system.

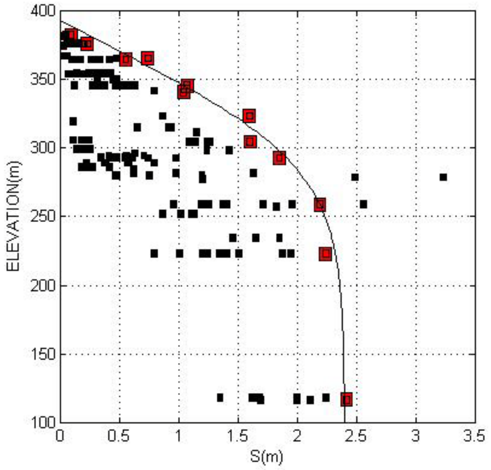

Figure 1. Size of corestones (S, in meters) observed in the Bisley watershed, Puerto Rico, at the land surface as a function of elevation. As predicted by the corestone model shown by the line, corestone size varies with elevation because rock fragments emerging from bedrock weather in the saprolite zone. The model fits the envelope of data shown by the large squares.

Microbial involvement in weathering: All of the models discussed above are purely physicochemical in nature. Given that all weathering involves the presence of biota, we are also in the process of characterizing the microbial biomass and community composition in the Bisley watershed in Puerto Rico to elucidate whether bacterial systems are impacting the weathering interface significantly. Field samples were collected from deep saprolite for microbiological analysis. Cell numbers at sampled depth intervals have been determined by heterotrophic plate counts and direct staining. Culturing in iron-reducing and iron-oxidizing media is in progress. DNA has also been extracted and PCR and clone library construction for sequencing is in progress. We anticipate using these observations to consider how to incorporate biota into weathering models.

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Grant: DE-FG02-05ER15636

Up-Scaling Geochemical Reaction Rates for CO_2 in Deep Saline Aquifers

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Objectives: The goal of the project is to use a combination of experimentation and numerical simulation to bridge the gap between our knowledge of small-scale geochemical reaction rates and rates meaningful for modeling reactive transport at core scales. The focus is on CO_2-water-rock interactions in the context of geological sequestration of carbon dioxide – specifically acid-driven mineral dissolution and precipitation.

Project Description: The work combines (i) spectroscopic imaging and innovative image processing to characterize sedimentary rocks, (ii) development of new pore-scale network models of reactive transport in porous media, and (iii) simulations to examine reaction rate upscaling. Rock specimens came from the Viking formation in the Alberta Sedimentary Basin, provided by the Alberta Geological Survey. Imaging methods include X-ray computed microtomography, backscatter electron microscopy (BSE) and energy dispersive X-ray (EDX) spectroscopy. The dual goals of the analysis of the imaging are to capture the 3D void space network as well as reactive mineral patterns to determine pore contact with individual minerals thereby quantifying meaningful surface areas for use in reactive transport models. Reaction rates computed from network models, which account for pore scale heterogeneity, are compared with reaction rates computed via a continuum model which employs bulk averaged (porosity, concentration) values.

Results: One of the current challenges facing implementation of large-scale CO_2 injection projects is forming regulations or guidelines that specify the required purity of the injection stream (Pollak and Wilson, 2009). During FY2009, the work at Princeton has focused on an investigation of co-injection of sulfur dioxide, an important environmental pollutant emitted from electric power plants. With the emergence of carbon capture and geologic sequestration, and the possibility of SO_2 co-injection, the economic favorability of emitting SO_2 to the atmosphere could change.

A primary concern surrounding geologic carbon sequestration is the potential for brine acidification. The presence of co-injectants, such as SO_2, may lead to further brine acidification through the formation of stronger acids. The goal of this work was to estimate the magnitude and time scale of brine acidification for the case of SO_2 co-injection. The potential for brine acidification was investigated for three different SO_2 reaction scenarios: hydrolysis, oxidation, and disproportionation, to investigate the effects of different sulfur-bearing acids. The model scenarios that were studied describe the situation in which SO_2 mass transport to the brine phase is limited by diffusion in the $scCO_2$ phase. One model describes rapid dispersion of SO_2 in a slowly advecting brine phase. The other model investigates diffusive transport of SO_2 in a stagnant brine phase. These represent extreme end cases for transport limitations and are meant to provide bounding estimates of brine acidification, as in reality, a combination of advective and diffusive transport in the aqueous phase will exist. For comparison, we modeled the case of SO_2 phase equilibrium between the entire volumes of $scCO_2$ and brine, which represents the maximum potential basin-scale acidification. To predict brine pH, we developed a geochemical model that simulates aqueous speciation and thermodynamic phase equilibrium of injected CO_2 and SO_2 with brine from a Mississippian carbonate formation in the Alberta Basin, Canada.

Predictions were compared to the case of CO_2 alone which would cause a brine pH of 4.6 under typical pressure, temperature, and alkalinity conditions in an injection formation. In the unrealistic model scenario of SO_2 phase equilibrium between the CO_2 and brine phases, co-injection of 1% SO_2 is predicted to lead to a pH close to 1 with SO_2 oxidation or disproportionation, and close to 2 with SO_2 hydrolysis. For a scenario in which SO_2 dissolution is diffusion-limited and SO_2 is uniformly distributed in a slowly advecting brine phase, SO_2 oxidation would lead to pH values near 2.5 but not until almost 400 years after injection. In this scenario, SO_2 hydrolysis would lead to pH values only slightly less than those due to CO_2 alone. When SO_2 transport is limited by diffusion in both phases, enhanced brine acidification occurs in a zone extending only 5 m proximal to the CO_2 plume, and the effect is even less if the only possible reaction is SO_2 hydrolysis. In conclusion, the extent to which co-injected SO_2 can impact brine acidity is limited due to diffusion-limited dissolution from the CO_2 phase, and may also be limited by the availability of oxidants to produce sulfuric acid.

In addition, pressure-, temperature-, and salinity-adjusted values of the SO_2 Henry's Law constant and fugacity coefficient were determined. They are predicted to decrease with depth, such that the solubility of SO_2 is a factor of 0.04 smaller than would be predicted without these adjustments. To explore the potential effects of transport limitations, a non-steady state model of SO_2 diffusion through a stationary cone-shaped plume of supercritical CO_2 was developed. Simulations for conditions corresponding to storage depths of 0.8 to 2.4 km revealed that after 1000 years, 65 to 75% of the SO_2 remains in the CO_2 phase. This slow release of SO_2 would largely mitigate its impact on brine pH. Furthermore, small amounts of SO_2 are predicted to have a negligible effect on the critical point of CO_2, but will increase phase density by as much as 12% for mixtures containing 5% SO_2.

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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 sensor swarms within fracture networks. This will be the first application of the physics of sensor 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 initiated 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 are developing a multi-modal imaging method (optical/seismic) to explore the physics of distributing sensors in fractured media. We have begun development of the optical imaging system to monitor nano- and micro- particle swarm location that employs wide-field fluorescence imaging composed of long-working-length optics and two high-sensitivity cooled CCD cameras that perform at the shot noise limit of light detection. We have performed initial testing of the optical imaging system with one camera for fractures with uniform apertures. The swarms consist of a solution of de-ionized water and 25 micron solid soda-lime glass beads (1% by volume).

Results: For initial testing of the optical imaging system, our first experiments were performed on a transparent fracture with smooth walls (uniform aperture) whose aperture was controlled by adjusting the separation between the fracture surfaces. Images of swarm behavior and free stream motion were captured for wall separations of 1 mm, 5 mm, 10 mm, 25 mm and 50 mm. With one camera in the optical system, we tracked the swarm location as a function of position and time (Figure 1a). From the images, we determined both the swarm behavior as well as the free stream flow conditions (Figure 1b). The swarm was observed to move vertically and horizontally in the fracture. The vertical transport of the swarm was arrested by the horizontal free stream currents in the tank. The falling velocity of the swarm and the free stream velocity are affected by aperture, i.e. both velocities decrease with decreasing aperture because of hydrodynamic shearing. The coherence and/or breakup of the swarm is affected by the separation of the surfaces as well as background fluid currents in water.

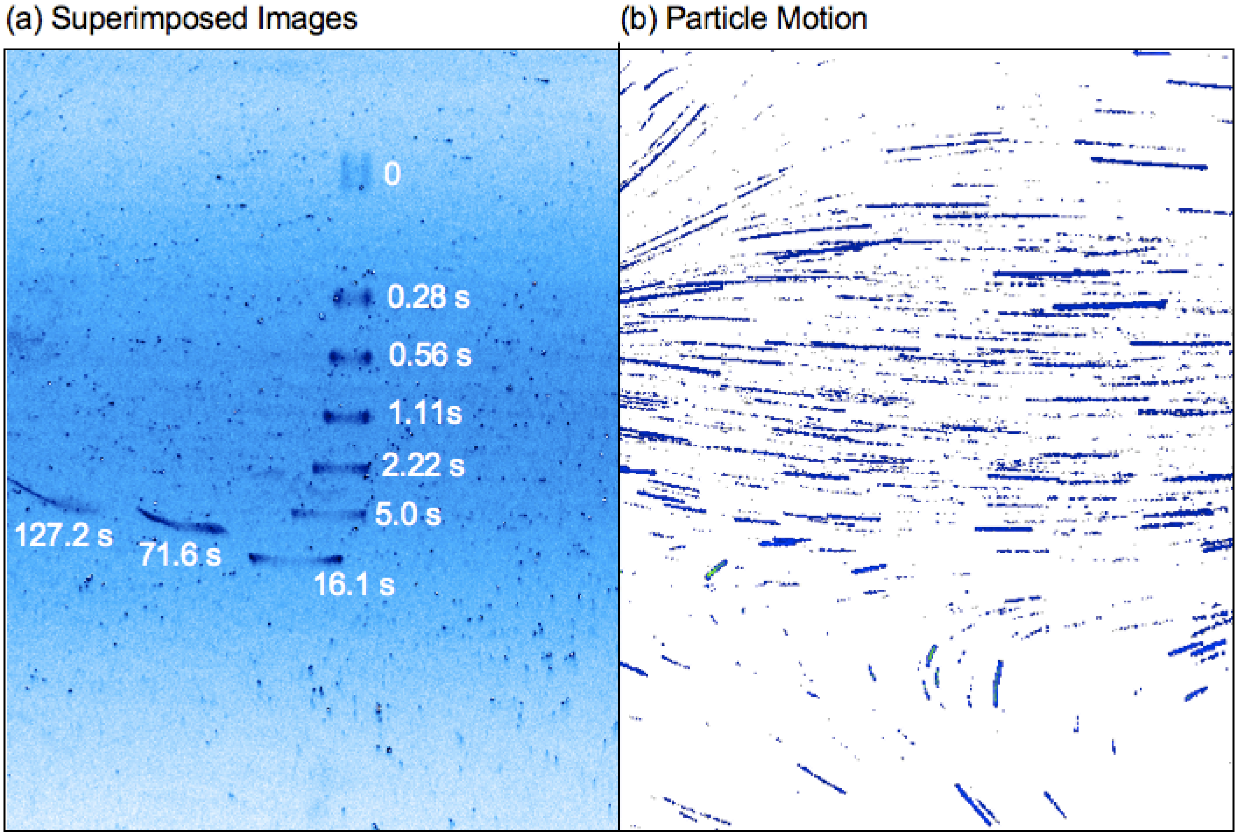

Figure 1. (a) False-colored superimposed images of swarm evolution for selected times as listed in white for surface separation of 50 mm. (b) Extracted free stream motion (fluid currents) captured in the 16 seconds prior to release of the swarm. In both images, a 50 mm by 64 mm regions of the fracture is shown.

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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 grain boundaries in polyphase rocks.

Project Description: During the past year we focused our efforts on characterizing the mobilization and transport of elements along dry grain boundaries. 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, it would appear necessary for isolated minor grains to 'communicate' with one another by chemical exchange through the grain boundaries in order for their compositions to adjust to changing P-T conditions. In a fluid-absent rock, transport of elements must occur by diffusion along pathways composed of dry grain boundaries and grain edges.

Results: An experimental approach to evaluate Fe-Mg interdiffusion along dry grain boundaries consists of two parts: synthesis experiments and diffusion experiments. In synthesis experiments powdered quartz along with components required to form a 'sink' mineral were hammered into oxidized Ni sleeves. Experiments were conducted in a piston-cylinder apparatus at elevated P-T conditions to produce quartzites with an equilibrium microstructure containing ~5% of a minor 'sink' mineral dispersed throughout the rock. The diffusant, introduced during later diffusion experiments, is incompatible in the dominant mineral of the polycrystalline rock but is highly compatible in the dispersed sink minerals. The most successful efforts so far have focused on synthesizing quartzites that contain fayalite as the 'sink' minerals. After synthesis experiments, the rock analog was cut into disks and polished. The polished surfaces of the rock analog were juxtaposed against diffusant sources, and placed back into the piston-cylinder for diffusion experiments. Silicate minerals and MgF_2 diffusant sources were used. The juxtaposition of the quartzite containing a dispersed fayalite against an Mg-rich diffusant source caused strong chemical potential gradients to develop. The only pathway for transport from the diffusant source to the sink mineral was along the grain boundaries. Assuming local partitioning and diffusive equilibrium between sink minerals and 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 grains decreases as a function of distance from the quartzite/ MgF_2 source interface. The fayalite grains that were within ~10 μm of the interface reacted to form enstatite and contain the highest MgO contents at ~15 wt.%. Traverses across fayalite grains that are >10 μm from the source interface have constant MgO concentrations demonstrating that diffusive equilibrium was established between the grain boundary and the sink mineral. 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.

We recently wrote a finite-difference code to help us to better understand the variables that govern grain boundary diffusion in our experiments. The transport of diffusant from the source, through the grain boundaries to the first dispersed sink particle is described by

$$D_{g.b.} \approx \frac{C_{prt} \cdot V_{prt}}{C_{srf} \cdot \delta \cdot t}$$

Where $D_{g.b.}$ is the grain boundary diffusivity, C_{prt} is the diffusant concentration in the particle, C_{srf} is the diffusant concentration in the grain boundary at the source, V_{prt} is the particle volume, δ is the grain boundary width and t is time. The distance term divides out in this equation because on average the particles are considered to be evenly spaced.

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 dispersed sink minerals 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 sink mineral. Due to the strong partitioning and large volume of the sink phase relative to the grain boundary volume, the sink minerals nearest the source interface effectively sequester the majority of the diffusant so that the longer duration experiments do not have longer transport distances. The numerical simulations produce transport and concentration systematics that are identical to those observed in experiments. We have not yet extracted absolute values for grain boundary diffusivity because in the experiments we are unable to measure two essential parameters; grain boundary width (δ) and the diffusant concentration (C_{srf}) in the grain boundaries located at the rock/source interface in the above equation.

Numerous experiments that contained MgF_2 sink minerals and CaF_2 diffusant sources were conducted. Interestingly, the MgF_2 sink minerals did not uptake any Ca from the diffusant source, even when they were in direct contact with the CaF_2. This result suggests that the ionic radius of Ca is too large to exchange with Mg in the MgF_2 structure.

In addition to the polycrystalline experiments, several attempts were made at designing experiments composed of a single grain boundary by joining two polished slabs of quartz with the goal of exchanging components along the single grain boundary between two reservoirs located at each end of the single grain boundary at high P-T conditions. Results from post-experiment measurements demonstrate that significant exchange occurred between the two reservoirs, but extensive fracturing developed during the experiment thus it is unlikely that transport was isolated to any one pathway.

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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 and develops numerical models to capture two types of instability in rocks, namely, brittle faulting and cataclastic flow. Brittle faulting is a form of strain localization whereas cataclastic flow is associated with pore collapse instability.

Project Description: Porous rocks can fail either by shear strain localization or cataclastic flow. Shear localization results from the coalescence of microcracks leading to a tabular deformation band, whereas cataclastic flow is characterized by grain crushing and pore collapse leading in a severely damaged but macroscopically homogeneous compacted continuum. We associate the two types of instability with two distinct bifurcation modes. The first mode, predicted from the singularity of the acoustic tensor, produces a strain rate jump tensor of determinant rank one and defines a deformation band. The second mode, predicted from the singularity of the tangent constitutive operator, is diffuse and produces a full-rank strain rate jump tensor. After identifying the relevant bifurcation mode, we focus on capturing the appropriate post-failure responses.

Results: We focus on shear strain localization and use an extended finite element approach for simulating slow-rate frictional faulting in geologic media incorporating bulk plasticity and variable friction. The method allows the fault to pass through the interior of finite elements without re-meshing. Bulk plasticity is localized to the fault tip, which could be used as a predictor for the initiation and propagation of new faults. We utilize the Dieterich-Ruina "slowness" law formulated in a slip-weakening format and integrated in time using the generalized trapezoidal rule. Numerical simulation of a plane strain compression of a fractured block, described below, indicates that plastic strain concentrates near the crack faces, suggesting potential thickening of the fracture zone.

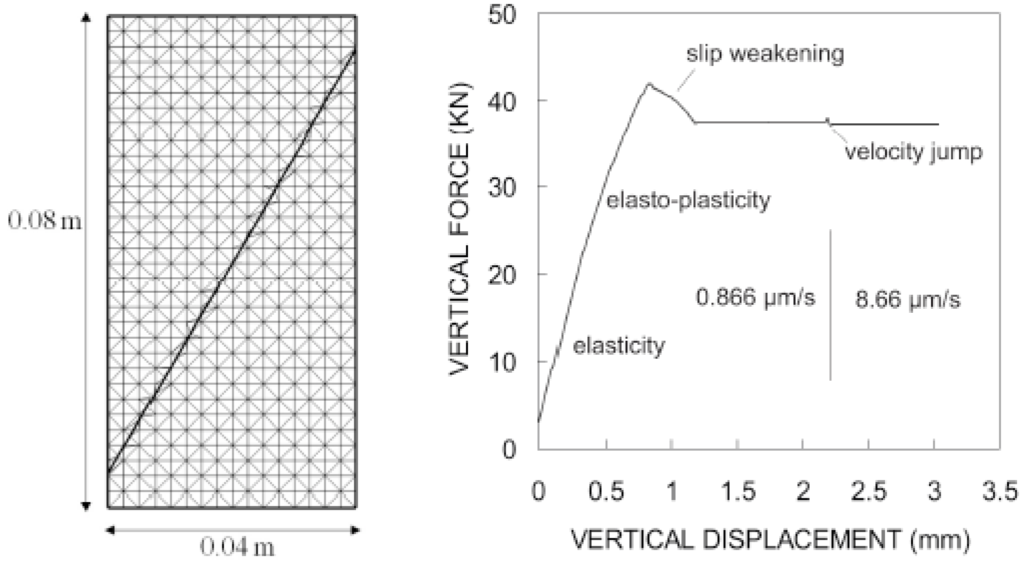

Figure 1. Plane strain compression of a rectangular block with a 60-degree crack: (a) finite element mesh (left), and (b) force-displacement response (right). The simulation includes slip weakening with a velocity- and state-dependent coefficient of friction.

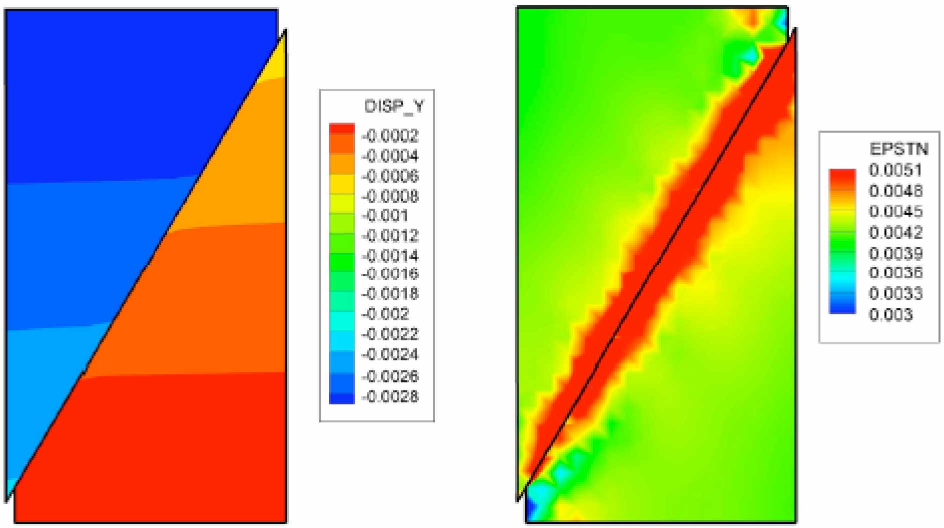

Figure 2. Contours of vertical displacement (left) and cumulative plastic strain (right): The block is 0.04 m wide and 0.08 m tall, and contains a 60-degree frictional crack. It is compressed vertically in plane strain after applying a lateral pressure of 250 MPa on the two vertical faces. The yield zone on the right suggests a propensity of the fracture zone to thicken as the block is compressed. The extended finite element method allows the crack to pass through the interior of finite elements.

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Grant: DE-FG02-03ER15423

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

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Objectives: 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?

Project Description: 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, electrical conductivity, and elastic properties; and (c) compare experimental data with the computed results.

Results: We have conducted a 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).

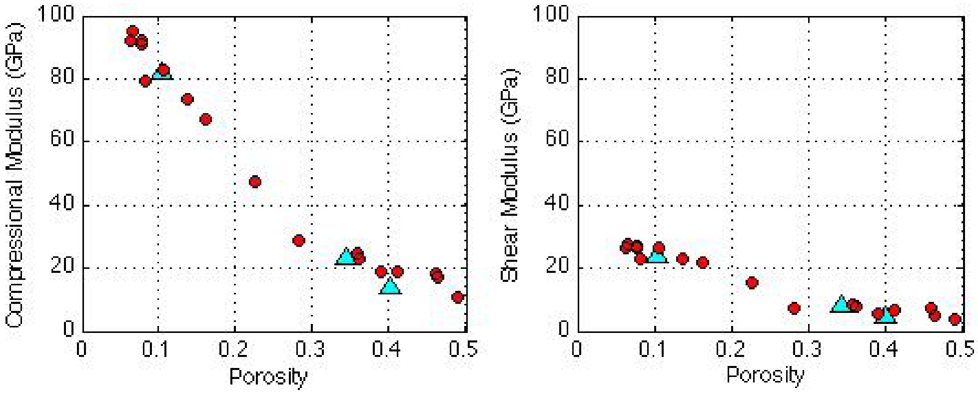

Figure 1. Compressional (left) and shear (right) moduli of micritic carbonate versus its porosity. Blue triangles are lab data just for three samples. From each of these three samples, mm-sized subsamples were extracted, their 3D CT-scans obtained and image-processed to separate the matrix form pores. Each of these three digital objects was then subdivided into 8 subsamples. The elastic properties of these subsamples were calculated (red circles). By so doing, we have expanded and filled the porosity range covered by the original three samples and also produced definite elastic moduli versus porosity trends.

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Grant: DE-FG02-04ER15588

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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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 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.

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: This project began in Sept. 2008. Our experimental efforts to date have centered upon the selection of a micromodel system, identification of suitable fluids, and conducting baseline transient experiments. Our micromodels are etched in silicon and feature a nearly 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 fluid movement. The overall dimension of the micromodels is 5 by 5 cm with 25µm depth of etching. 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 have conducted baseline experiments to ensure that pore-level events are reflected within a physically accurate manner within the micromodel. For example, during drainage accomplished by injecting a viscous nonwetting phase (i.e., a low mobility ratio displacement) into a micromodel that is oriented horizontally, the displacement front should be relatively stable. Pore-level drainage should be controlled by the smallest pore throats of the medium. Figure 1 is a set of representative pore-level images obtained during drainage. The nonwetting phase is n-hexadecane and the wetting phase is dyed blue-green to improve phase contrast. In the images from Fig. 1(a) to 1(c) the nonwetting phase advances causing drainage of the wetting phase. Some wetting liquid remains behind in the smallest-sized pores consistent with the fact that the micromodel is water wet.

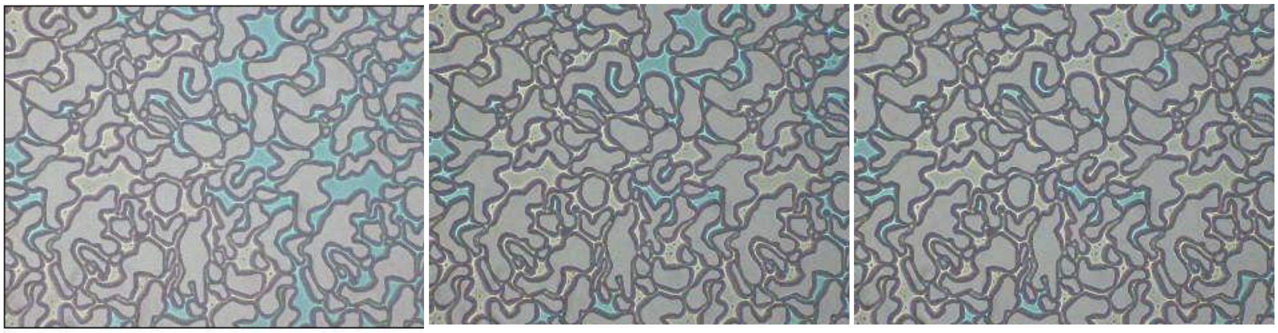
(a) (b) (c)

Figure 1. Representative pore-level results (100X). All images from the same pore space but differ in time by about 1 s per frame. The wetting phase is blue-green and the nonwetting phase is clear. Rock grains are gray.

In the future, we shall conduct a series of unstable drainage displacements under mobility ratio and capillary number conditions that are representative of CO_2 sequestration. Micromodel orientation shall also be changed to vertical to examine the role of gravity at the pore and network ensemble scale. Images are collected at both scales and we work toward appropriate image analysis of experimental results.

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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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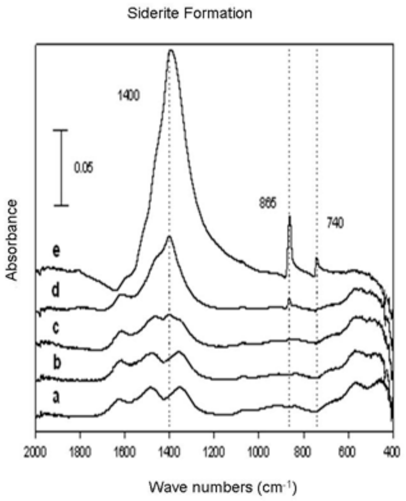
Objectives: The primary goal of this research program is to understand the chemistry that results when supercritical CO_2 ($scCO_2$) with H_2S and/or SO_2 in deep saline formations (DSF) contacts iron bearing minerals. Understanding the complexities the sulfur co-injectants introduce is a critical step 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 DSF. 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 DSF. 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 FY2009 focused on investigating the transformation of the iron oxyhydroxide, ferrihydrite, to siderite ($FeCO_3$) in the presence of $scCO_2$ and aqueous sulfide. Both *in situ* attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and *ex situ* X-ray diffraction (XRD) have been used to characterize the chemistry and resulting phases. The iron oxy-hydroxide ferrihydrite in an aqueous solution containing sodium sulfide in contact with $scCO_2$ at 100^o C reacts within 24 hours to form siderite and elemental sulfur. *In situ* studies of this reaction at 70^o with ATR-FTIR shows that ferrihydrite exists with an adsorbed layer of carbonate. However, the presence of the carbonate adsorbate does not impede the reduction of ferric to ferrous iron and, ultimately, siderite is formed within 1 hour. <u>The accompanying figure exhibits *in situ* ATR-FTIR that investigated the conversion.</u> Spectra a-d were obtained in 30 min intervals. Spectrum e was obtained after 18 hrs of reaction. Siderite formation (characterized by the 1400, 865, and 740 cm^{-1} modes) becomes noticeable from these data after 1 h of reaction time (spectrum c). Studies are being pursued at present that are moving beyond the intermediate phase ferrihydrite and are investigating the transformation of more stable iron oxyhydroxides, such as goethite and lepidocrocite and iron oxides, such as hematite in the presence of $scCO_2$.



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Grant: DE-FG02-06ER15816

Kinetics and Mechanisms of Calcite Reactions with Saline Water

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Objectives: The general objective of the this research is to determine the kinetics and mechanisms of calcite reactions with saline waters over a wide range of saline water composition, carbon dioxide partial pressure ($p\mathrm{CO}_2$), and modest ranges of T and P. This will be done by studying both reaction rates and solubility from changes in solution chemistry. Also, nanoscale observations of calcite surface morphology and composition will be made to provide an understanding of rate controlling mechanisms.

Project Description: The objectives will be accomplished by studying both reaction rates and solubility from changes in solution chemistry, and making nanoscale observations of calcite surface morphology and composition to provide an understanding of controlling surface mechanisms. The specific tasks necessary to reach the objectives are:

a) Improvement of our Pitzer equation-based ability to deal precisely with the carbonic acid system in complex high ionic strength solutions and at high $p\mathrm{CO}_2$;

b) Determination of how $p\mathrm{CO}_2$, Ca^{2+}, ionic strength and "foreign" ions influence reaction rates;

c) Measurement of distribution coefficients of the common saline water components as a function of solution composition, precipitation rate and temperature, as well as their influence on calcite stability; and

d) Investigation of the influence of the parameters in "b" on apparent kinetic solubility from dissolution and precipitation reactions to determine if the apparent solubility differs when approached from super and under saturation.

This knowledge is needed to predict the geochemistry of carbonate mineral-saline formation water interactions. Calcite-saline water interactions will impart a significant influence on processes affecting the post CO_2-injection development or destruction of porosity, permeability and mass transport in the subsurface. Experimental studies and numerical models for the responses of saline aquifers to injection of carbon dioxide, under repository conditions, point to the importance of reactions involving carbonate minerals even in non-carbonate-hosted formations. It is consequently necessary to understand the complex factors influencing calcite-solution interactions in saline waters. This information will clearly be central to the construction of reliable reaction-transport models to predict reservoir and formation response to injection of CO_2 and movement of saline waters.

Results: The research conducted during the past year can be divided into 3 major areas based on the size range of the processes being considered: 1) macro-scale batch reactor studies of calcite dissolution and precipitation in high ionic strength (I) solutions over a range of I, pCO_2, and T at 1 atm; 2) micro-scale (SEM level) studies of the morphology of overgrowths and nucleated precipitates from a variety of solutions that involved $CaCO_3$ polymorphs in addition to calcite; and 3) nano-scale (TEM level) studies of the mechanism of $CaCO_3$ precipitation on substrates.

A major finding of the batch-reactor studies of calcite dissolution was that at high I the identity of the cation of the supporting electrolyte appears to play a minor role as rates were found to be faster in KCl than NaCl solutions under the same experimental conditions. The most significant finding was $X_{\text{"free" } H_2O}$ plays a significant role in the dissolution kinetics of calcite as water becomes limiting regardless of the temperature (25-55 °C) or the pCO_2 (0.1-1 atm) examined in this study. In addition, it was calculated that approximately 45-50% $X_{\text{"free"}H_2O}$ represents a critical threshold below which dissolution will not occur (or occur very slowly) in undersaturated solutions that may be related to the transition from a two-dimensional to three-dimensional water layer adsorbed on the calcite surface. $X_{\text{"free" } H_2O}$ does not play a major role in calcite precipitation kinetics.

In trying to prepare high ionic strength solutions for precipitation studies, we observed nucleation in super-saturated solutions of a precipitate that had a spherical morphology; by XRD analysis, it was determined to be the $CaCO_3$ polymorph, vaterite. The vaterite converted to calcite in hours to days at room temperature, and the rate of transformation decreased with increasing I ; there was evidence of an increasing importance of aragonite as an intermediate, metastable $CaCO_3$ polymorph at low I, demonstrating the Ostwald step rule. Very regular and smooth (as determined by SEM analysis) calcite crystals and occasionally aragonite were produced, often in apparent contact with the precursor vaterite during transformation. This calcite morphology was not produced on overgrowths on Iceland spar calcite

HRTEM observations found an amorphous calcium carbonate (ACC) surface layer a few tens of nm in thickness from which nanocrystalline aragonite was forming. The epitaxial growth of aragonite on the surface of an aragonite crystal substrate appears to take place by a complex mechanism that does not follow the classic Kossel crystal kink and step movement model for crystal growth. The presence of an ACC layer from which crystal growth occurs may explain the large (about a factor of 2) difference between predicted thermodynamic solubility and “kinetic” solubility of newly formed aragonite.

The unexpected finding of the importance of metastable intermediate calcium carbonate polymorphs during the precipitation of calcium carbonate from high ionic strength solutions provides new insights into the mechanisms involved and points to more complex processes than the relatively simple kink and step model general assumed to control calcite growth. The finding of different results for different calcite growth substrates is troubling in that it raises the question of why this occurs and how comparable observations may be between different laboratories using different calcite seeds or crystals in growth studies.

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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, 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, coupled fluid flow modeling, including compositional and reactive processes 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, compositional and geochemical effects. We performed 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. Using field data from a CO_2 injection enhanced oil recovery pilot project, we plan to develop a systematic workflow for the detection and location of CO_2 movement using fluid flow and seismic data.

Results: During the past year our primary focus has been to apply the streamline-based compositional/geochemical simulator and the data assimilation methods developed in this project to understand the movement of CO_2 in the Weyburn field in Canada, a large-scale CO_2 EOR and sequestration project. The key idea behind the data assimilation methods is to update the geologic models using the actual flow-related observations from the field. Initial geologic models are typically generated using the static information such as well log, core, and 3-D seismic data. Once dynamic data such as production and 4-D seismic become available, the geologic models need to be updated such that the numerically simulated results using updated reservoir models honor the observed dynamic data. We have used the Ensemble Kalman Filter (EnKF) to reconcile the geologic models for the Weyburn field with the CO_2 injection, oil flow rates and pressure data. The advantage of the EnKF is that we can update the geologic models on a near real-time basis as the field data becomes available. This calibration is important and relevant for sequestration for a variety of reasons. First of all, we must understand the reservoir volume swept by the injected CO_2. Secondly, the end of the CO_2 injection sets the initial conditions for the predictions of long term sequestration potential. In our research we have focused on three important elements of the EnKF: optimal initial ensemble member selection while maintaining the desired spread in their dynamic response; covariance localization to remove spurious covariance calculations based on limited ensemble size; and preserving geologic realism during model updating. Well-specific black-oil or compositional streamline trajectories that are generated from the velocity field, computed during flow simulation with little additional expense, are used for covariance localization. **Figure 1a** shows the three-dimensional view of the mean permeability of the ensemble of initial geologic models for the Weyburn field. **Figure 1b** shows the initial mean permeability profiles for layer 4 from Marly, layer 10 from upper Vuggy, and layer 24 from the lower Vuggy zone. **Figure 2** shows the updated mean permeability field for the same layers after assimilation of the pressure and flow rate information from the CO_2 injection period. It is clear that the initial geologic models significantly underestimate the permeability heterogeneity in the reservoir. This would have led to erroneous predictions of the injected CO_2 movement.

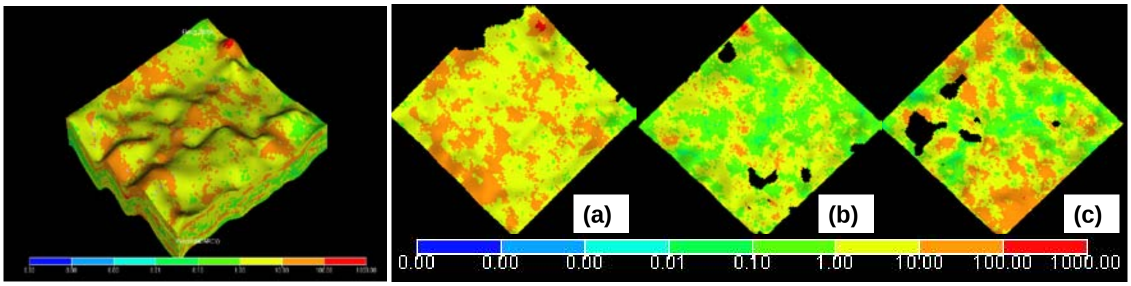

Figure 1. (a) 3-D view of the initial ensemble mean permeability for Weyburn field. (b) Initial permeability (in md) for layer 4 - Marly, layer 10 - Upper Vuggy, and layer 24 - Lower Vuggy.

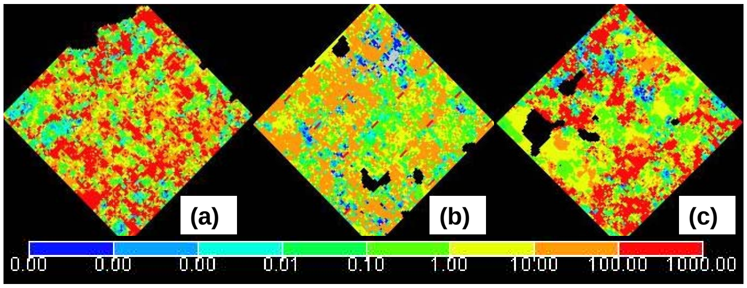

Figure 2. Updated mean permeability (in md) after data assimilation using localized EnKF for layer 4 - Marly, layer 10 - Upper Vuggy, and layer 24 - Lower Vuggy.

Our research efforts also continue to develop our insights into the pressure dependence of the seismic properties of fractured rock with several new advances. The general approach relies on the application of asperity deformation models that describe the behavior of the rock in terms of a distribution of asperities on fracture surface. These asperities, modeled as cylindrical rods that resist the compression or shearing of a fracture, then control the pressure dependence of the seismic velocity. This phenomenological model is much simpler than many theoretical approaches that attempt a more explicit description of fractures, with only three or four parameters. It therefore has the potential of providing more effective implementations on field-scale reservoir models where detailed descriptions of fractures and pore fluids may not be possible.

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Grant: DE-FG02-04ER15496

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

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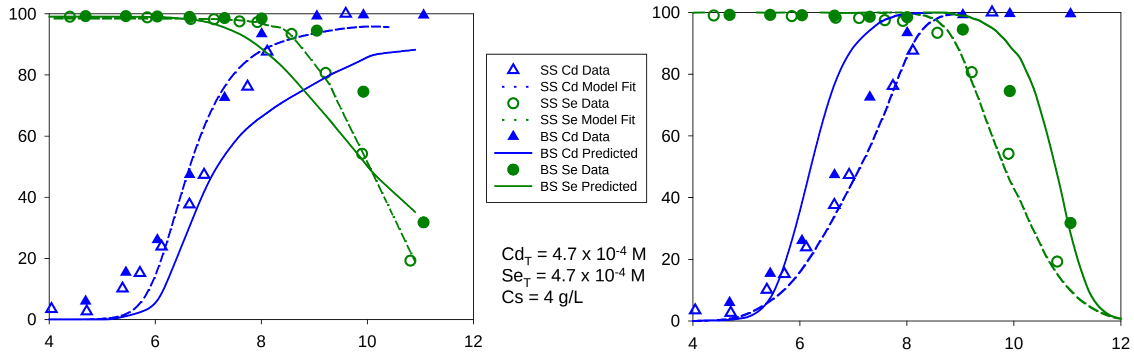
Objectives: The objectives of this research are to develop an approach for predicting the types of metal surface complexes that form on mineral surfaces by focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models to predict 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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Grant: DE-FG02-03ER15430

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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Grant: DE-FG02-03ER15430

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 CO2 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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Grant: DE-FG02-07ER15900

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.

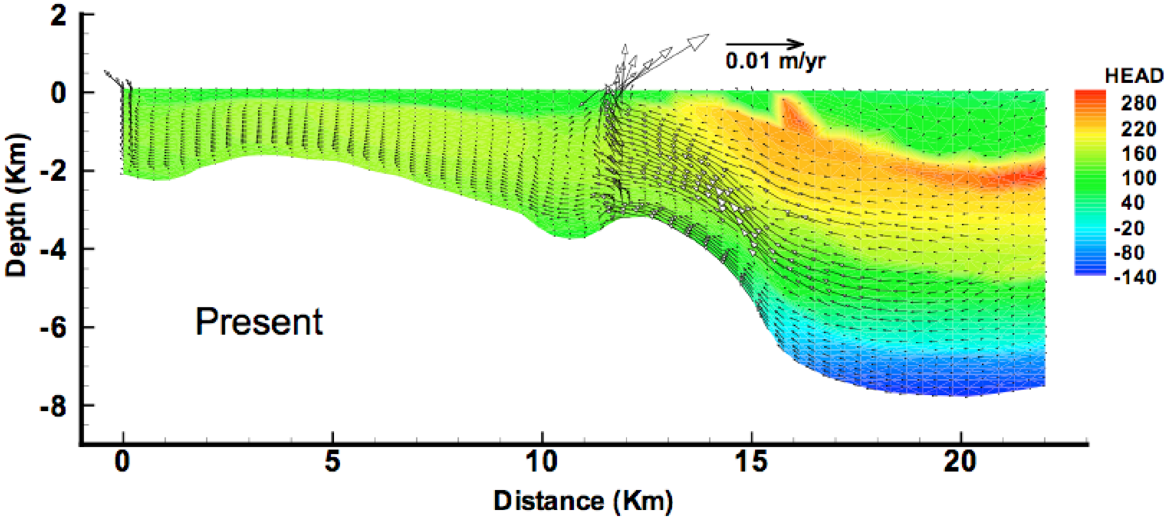
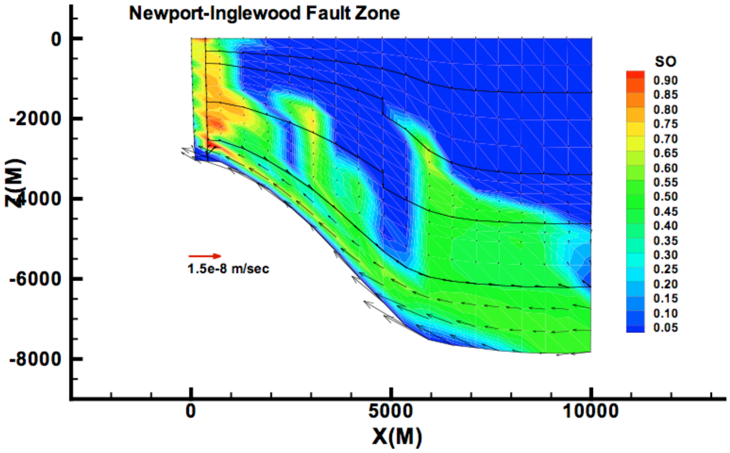


Figure 2. Zoomed view of petroleum saturations and flow patterns near area of discharge.



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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 calcite. 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 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.

Results (selected) for FY 2009:

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 Elhadj et al (PNAS, 2006) 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. ***(PNAS, pending minor revision).*** 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. (*JACS*, 2009). Using *in situ* AFM, we directly measure the kinetics of silica nucleation on model biosubstrates under chemical conditions that mimic natural biosilica deposition environments. Relative contributions of thermodynamic and kinetic drivers to surface nucleation are quantified using amine, carboxyl, and hybrid NH_3^+ / COO^- terminated surfaces as surrogates for charged and ionizable groups on silica-mineralizing organic matrices. Amine-terminated surfaces do not promote silica nucleation, but carboxyl and hybrid NH_3^+ / COO^- substrates are active for silica deposition. The rate of silica nucleation is ~18X faster on the hybrid substrates than on carboxylated surfaces, but free energy barriers to cluster formation are statistically similar on both surface types. The findings show that surface nucleation rates are more sensitive to kinetic drivers than previously believed. Further experiments to test the importance of cooperative interactions with patterned NH_3^+ / COO^- substrates, and aminated surfaces with solution-borne anionic species, show that silica nucleation is most rapid when oppositely charged species are proximal. By documenting the synergy that occurs with cooperative interactions between surface groups on these biosubstrates to promote mineral nucleation, these findings reveal (demonstrate) a new type of emergent behavior and reiterate the potential for cooperative interactions between individual molecular constituents.

Peptides enhance magnesium signature in calcite: New insights into origins of vital effects. *(Science, October, 2008).* Studies relating the magnesium content of calcified skeletons to temperature often report unexplained deviations from the signature expected for inorganically precipitated calcite. The mechanistic basis for these measured offsets, or vital effects, remain unclear. The composition of biologic molecules isolated from biominerals suggests that control of mineral growth must be linked to biochemical features. Building on two papers funded by this project that established a relationship between the ability of biomolecules in solution to promote the growth of calcite ($CaCO_3$) and their and hydrophilicity, we hypothesize that because cation incorporation is the rate-limiting step to growth and Mg is more strongly solvated than Ca, then rate-modifying peptides could also lower the desolvation barrier to Mg incorporation relative to Ca, and thereby alter magnesium content. We find that a simple hydrophilic peptide, sharing the same carboxyl-rich character as macromolecules isolated from sites of calcification, increases calcite Mg content up to 3 mol%. Comparisons to previous studies correlating Mg content of carbonate minerals with temperature show that the Mg enhancement due to peptides results in offsets equivalent to 7-14°C. The findings provide a physical basis for anecdotal evidence that organic chemistry modulates the mineralization of inorganic carbonates and suggest a novel approach to tuning impurity levels for controlled materials synthesis.

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 determine if bacterial cell-cell communication (quorum sensing) is involved in *Shewanella oneidensis* MR-1 biofilm formation, and 2) to investigate the dissolution and solubility of nanosulfides as a function of crystal size and aggregation state, and 3) to synthesize nanoparticles of mackinawite (FeS) and characterize their interaction with aqueous oxyanions (e.g. As) and cations (Cu and Co).

Project Description: Our study of bacterial cell-cell communication was concluded in 2008, and summarized in our Annual Report to DOE last year. This study's capstone publication has recently appeared in *Applied and Environmental Microbiology*.

Dissolution reactions of galena (PbS) is responsible for a number of environmental problems, such as aqueous Pb releases which result in the incorporation of this toxic metal into surface water and groundwater. A detailed understanding of the dissolution of galena is an important key to more accurately predicting and monitoring long-term contaminant metal mobility and bioavailability in natural settings. In particular, the size-dependent dissolution of this mineral, the main focus of this study, has never been studied experimentally until now.

In addition, mackinawite (FeS) characteristics have been/will be studied using both solution analyses and high-resolution analytical electron microscopy/spectroscopy techniques. To date, anoxic synthesis and particle characterization has been accomplished.

Results: The non-oxidative dissolution of galena nanocrystals: Insights into mineral dissolution rates as a function of grain size, shape, and aggregation state. Rarely observed nanoparticle dissolution rate data has been collected and explained for an environmentally and industrially relevant nanomaterial (PbS, the mineral galena) as a function of its particle size and aggregation state using high-resolution transmission electron microscopy (HRTEM) and solution analysis. Under identical anoxic acidic conditions (pH 3 HCl), it has been determined that the dissolution rate of PbS galena varies by at least one order of magnitude simply as a function of particle size, and also due to the aggregation state of the particles (dissolution rates measured are 4.4×10^{-9} mol m^{-2} s^{-1} for dispersed 14 nm nanocrystals; 7.7×10^{-10} mol m^{-2} s^{-1} for dispersed 3.1 μm microcrystals; and 4.7×10^{-10} mol m^{-2} s^{-1} for aggregated 14 nm nanocrystals). The dissolution rate difference between galena microparticles and nanoparticles is due to differences in nanotopography and crystallographic faces present. Aggregate vs. dispersed dissolution rates are related to transport inhibition in the observed highly confined spaces between densely packed, aggregated nanocrystals (Fig. 1), where self-diffusion coefficients of water and ions decrease dramatically. This study shows that factors at the nanometer scale significantly influence the release rate of aqueous, highly toxic and bioavailable Pb in natural or industrial environments during galena dissolution.

Extension of Studies in Nanosulfide Research. The TEM observations of this work show that despite the mackinawite (FeS) aggregates appearing amorphous, they are made up of crystalline nanoparticles 3-10 nm in size. Peak broadening of the mackinawite XRD pattern suggests that the crystallites exist at an average size of approximately 7.7 nm. Synthesizing pure nanoparticles reliably at a certain size and shape especially while maintaining strict anoxic conditions is not trivial. It is apparent that although mackinawite can be synthesized as particles less than 10 nm, it has an incredibly strong tendency to aggregate. Studies of nano-mackinawite interaction with aqueous oxyanions and cations are pending.

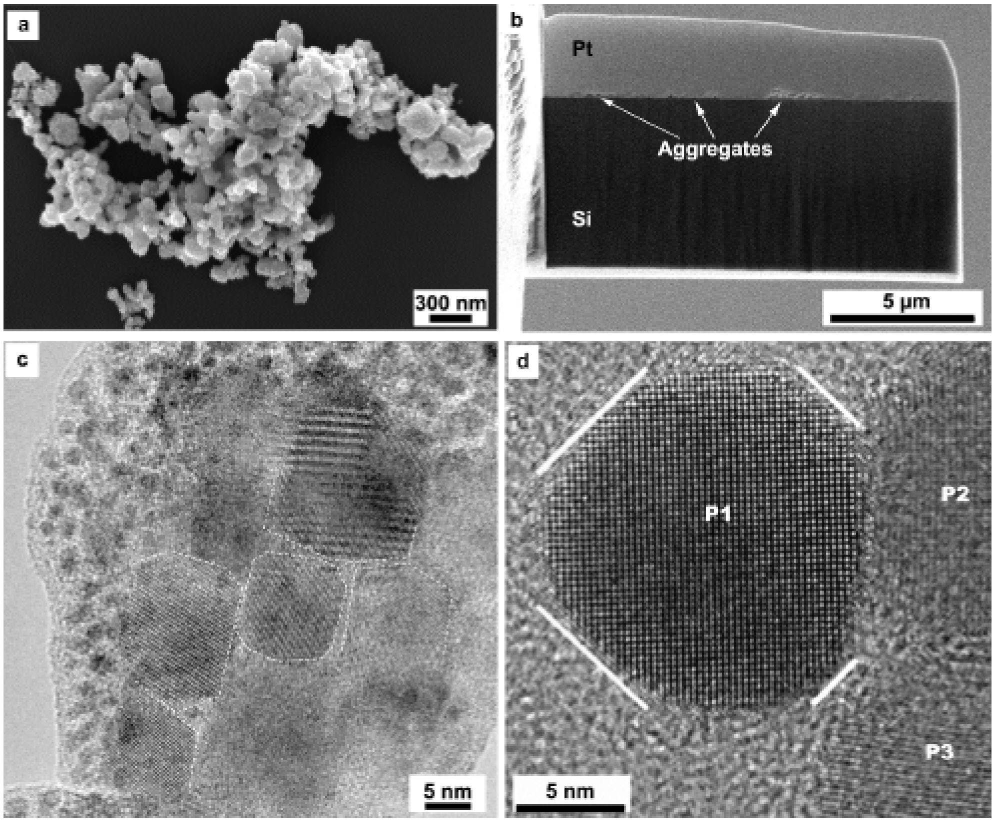

Figure 1. (a) Representative SEM of galena nanoparticle aggregates averaging 240 nm in diameter. (b) A cross-section of the aggregates being prepared by the FIB lift-out technique. (c) HRTEM image of a cross-section of a nanoparticle aggregate. White dashed lines define the edges of galena crystals which are separated by a few nanometers or less. (d) HRTEM image of galena nanocrystal (P1) with adjacent crystals to the right (P2, P3) and open space to the left. {110} faces, denoted by white lines, dissolve much more rapidly (and therefore are larger) on the unrestricted side of the crystal.

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Grant: DE-FG02-07ER15899

Mapping of Temporal and Spatial Phase Transitions of $CaCO_3$ in Echinoderm Skeletons: Key Insights into Basic Mechanisms in Biomineralization

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Objectives: To better 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 include:

(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)** and sea urchin teeth **(objective 3)**, and obtained exciting results, leading to four major publications, in collaboration with Steve Weiner, Lia Addadi, and their group at the Weizmann, where Gilbert spent another month in 2009. All experiments were done using x-ray photoelectron emission spectromicroscopy, scanning electron microscopy and micro diffraction at the Berkeley Advanced Light Source. **(1)** In both sea urchin spicules and teeth 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 never observed a crystal propagation front. The transformation, instead, appears to occurs via secondary nucleation, with crystallinity propagating in connected networks through the amorphous mineral, and each nanoparticle crystallizes only upon contact with an already crystalline one (PNAS 2008, and JACS 2009 under review). We only recently started working on sea urchin spines **(2)** and no major results were observed yet. **(3)** In sea urchin teeth we observed unexpected morphologies and crystal orientations, which may enhance the tooth's rock-grinding performance (PNAS 2009) and its fascinating capability of self-sharpening with use (PNAS 2009, under review).

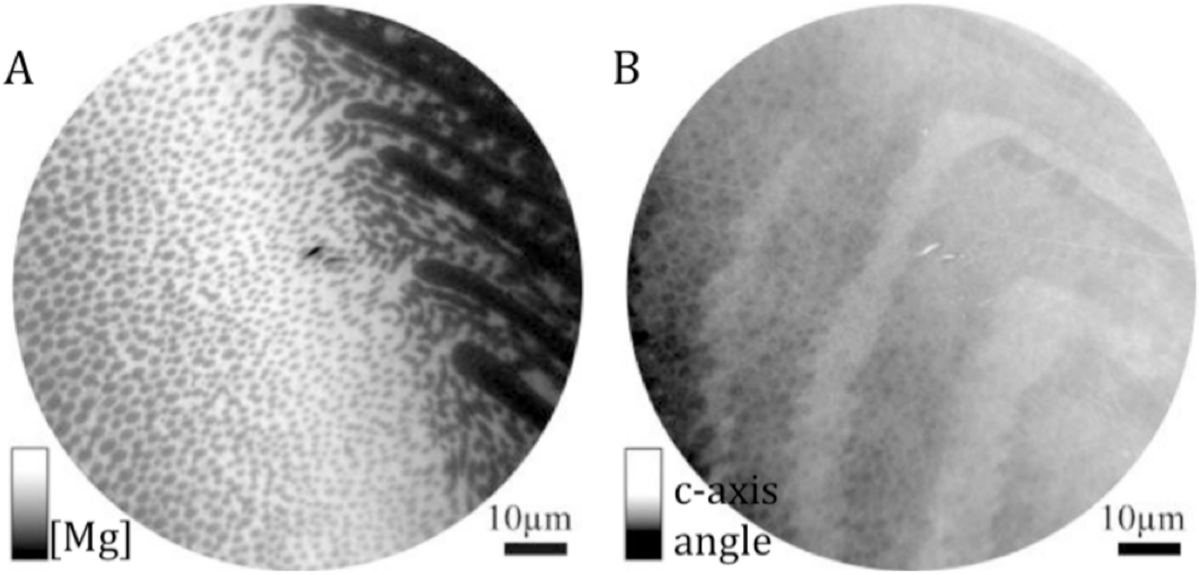

Figure 1: (A) X-PEEM Mg distribution map of the hard and aptly named "stone part" of the sea urchin tooth, as observed in cross-section. With tooth growth this stone part becomes the grinding tip. Low-Mg calcite—dark—in elongated plates and micron-size fibers is visible. Mg-rich calcite matrix—light—cements plates and fibers together, and confers higher hardness to the stone part. (B) Polarization-dependent imaging contrast (PIC) map of the same area in (A), displays different crystal c-axis angles with different gray levels. Uniform gray levels indicate co-aligned blocks of crystals. The blocks, approximately 10-μm wide, have only two orientations, and each comprises a myriad fibers and matrix nanoparticles. Notice the perfect co-alignment of fibers and matrix in each block. Data from PNAS 106, 6048-53, 2009.

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Grant: DE-FG02-05ER15738

Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media

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Objectives: (1) To quantify the grain- and pore-scale physical effects of variable cementation and compaction and relate these to the elastic, inelastic, and hydrologic behavior of granular porous media. (2) To use the resulting data to parameterize Discrete Element Model (DEM) simulations to explore meso- and macro-scale poroelastic behavior.

Project Description: The project scope requires novel approaches to characterizing and exploring the mechanical significance of variable cement in granular porous media. To eliminate the complicating effects of variable mineralogy, we chose to work with quartz-cemented quartz arenites. We are:

1) Integrating microstructural and experimental analyses to relate changes in grain and pore geometries with progressive diagenesis to changes in mechanical and hydrologic behavior.

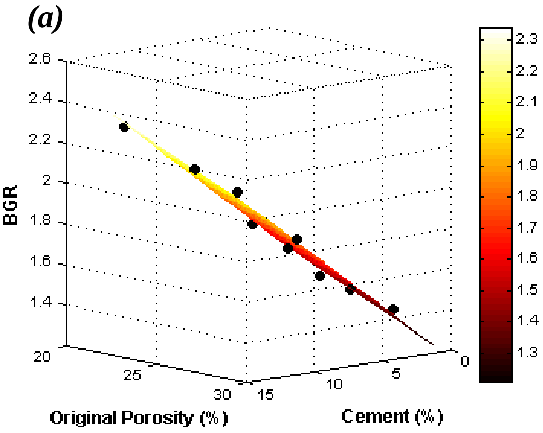
2) Developing quantitative relationships describing the poroelastic response of cemented granular systems to stress by incorporating microscale material response into a DEM.

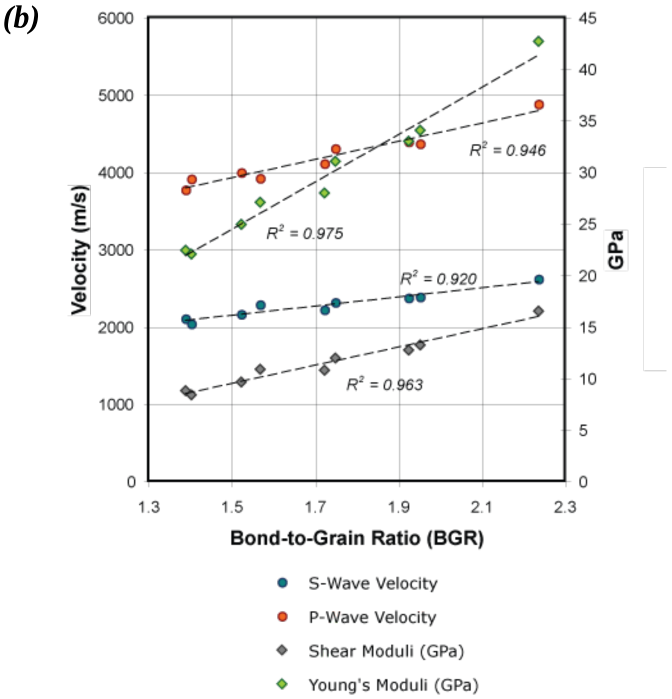
Results: Quartz overgrowths are the most common form of authigenic cements in sandstones and are responsible for significant porosity and permeability reduction and attendant changes in mechanical and hydrologic properties. The distribution of quartz cements is mineralogically and space controlled. Therefore progressive quartz cementation should modify the grain framework in consistent, predictable ways. We have quantified these modifications in a series of variably cemented quartz arenite samples, and shown that their effect on mechanical and hydrologic properties is also consistent and predictable.

To investigate these relationships, the UW group designed and implemented a strategy to integrate detailed microstructural characterization with analyses of ultrasonic velocities, permeability and mechanical properties in the St. Peter Sandstone, a well sorted, well rounded, medium grained quartz-cemented quartz arenite. Samples selected for analysis have cement abundances that vary from < 1% to 16%, final porosities between 8% and 25%, and original porosities between 20% and 30%. To quantify the geometric changes associated with progressive compaction and cementation, detailed back-scattered electron and cathodoluminescent images were collected. Image analysis indicates that the St. Peter Sandstone exhibits typical quartz overgrowth geometries but that cement morphology changes with progressive cementation. Grains in low-cement (< 5%) samples exhibit thin, encrusting layers of quartz with isolated crystal facets and pore spaces are interconnected. In contrast, high-cement (> 10%) samples have an interconnected network of cement with well-defined facets and diminished pore connectivity. Image analyses suggest that with progressive compaction and cementation, the number and length of grain contacts increase and the number of pores increases. However, the number of large, well-connected pores decreases, decreasing pore size variability and permeability exponentially, and systematically altering pore shape. Cement precipitation is more efficient than compaction in increasing grain contact length and altering pore shape. These changes are reflected in systematic variations in S- and P-wave velocities measured on sample cores (Fig. 1).

Compaction and quartz cementation thus alter the 3D framework and thereby impact the mechanical and hydrologic behavior of the sandstone. With increasing diagenesis, elastic moduli increase, compressive strength increases, and permeability decreases. Our research indicates that bond-to-grain ratio (BGR) is consistently one of the best predictors for mechanical and hydrologic properties in the St. Peter Sandstone (e.g., Fig.1b). Therefore, within the St. Peter Sandstone, accurate morphological, mechanical, and hydrologic predictions can be made by knowing the original porosity and cement abundance - parameters that can be relatively easily obtained through point-counting.

Figure 1. (a) Relationship between bond-to-grain ratio (BGR) and compaction (indicated by original porosity), and cement %. (b) Relationship between BGR and P- and S-wave velocities, Young's Modulus, and Shear Modulus.





These empirical relationships informed modeling efforts conducted by the UMass team, which has continued to explore the influence of cementation at both the meso- and macroscale in a series of DEM models where the deformation is driven by pore fluid volume changes. Using realistic BGR values as a proxy for cementation, the theoretical bulk modulus properties from the DEMs with low and high cement content along with estimated permeabilities were input into 2D, axially symmetric, poroelastic continuum models. Poroelastic model results suggest that that deformation behavior is strongly controlled by both the hydrologic and mechanical effects of cement, and therefore cannot be effectively modeled unless both are considered.

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High Precision Ion Microprobe Analysis of $\delta^{18}O$ in Authigenic Quartz

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http://www.geology.wisc.edu/~wiscsims/

Objectives:

1. Improve microanalytical techniques for stable isotope analysis by SIMS and laser.
2. Develop procedures for oxygen isotope analysis at sub-1 to 10 micron-scale by ion microprobe.
3. Evaluate oxygen isotope thermometry in quartz overgrowths and opaline cements as a record of paleoclimate.
4. Determine genesis and timing of porosity-reducing cements in quartz sandstones that form aquifers, fossil fuel reservoirs, and proposed sites for CO_2 sequestration.

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 $\delta^{18}O$ across single crystals and within individual overgrowths at all scales as amall 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 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, 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 $\delta^{18}O$ 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 $\delta^{18}O$ of 1‰ (Page et al. 2007) and analysis of Si and Li isotope ratios (Ushikubo et al. 2008, Richter et al. 2009).

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 & Valley, unpbd.). In contrast to shallowly buried sandstones in Wisconsin, the new results show that buried sandstone cements are zoned by up to 5‰ in δ^{18}O recording growth during burial and heating. These zoned cements are similar to those found by us in the North Sea Ness Fm. (figure, Harwood et al. 2009). Systematic differences are seen with lower δ^{18}O in latest cements deeper in the Illinois basin, indicating higher diagenetic temperatures. Analysis of silicon isotope ratios in quartz overgrowths is underway to evaluate the importance of groundwater silcretes during early cementation.

DOE-sponsored Regional Partnerships, MGSC and MRCSP, are presently drilling 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.

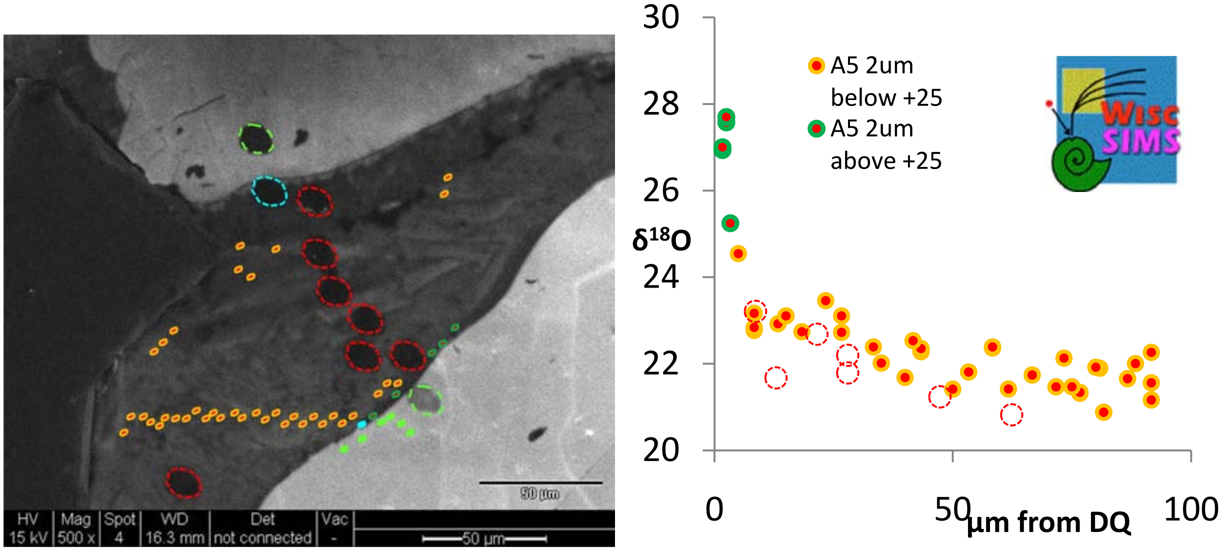

Figure. (Left) CL image of quartz overgrowths (dark) and detrital quartz grains (DQ, bright) in Ness sandstone. Circles show location and size of 2 and 12µm pits from ion microprobe analysis of δ^{18}O. **(Right)** δ^{18}O vs. distance (µm) from the DQ boundary for quartz overgrowths (Harwood et al. 2009). Values of δ^{18}O decrease away from DQ consistent with continued cementation during burial and heating. Note that the largest change in δ^{18}O occurs in early cements within 10 µm of the DQ boundary and can only be resolved with an ultra-small 2µm spot. (f.o.v.=250µm).

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 in controlling the nucleation of individual carbonate polymorphs 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 a 2-dimensional (2D) phase map in the framework of surface energy and epitaxy to illustrate the apparent (as opposed to thermodynamic) stability field of each carbonate polymorphic species on different substrate surfaces.

Results: The project was just started. Preliminary results show that hematite can promote aragonite nucleation, whereas fresh pyrite can enhance calcite nucleation and Mg incorporation.

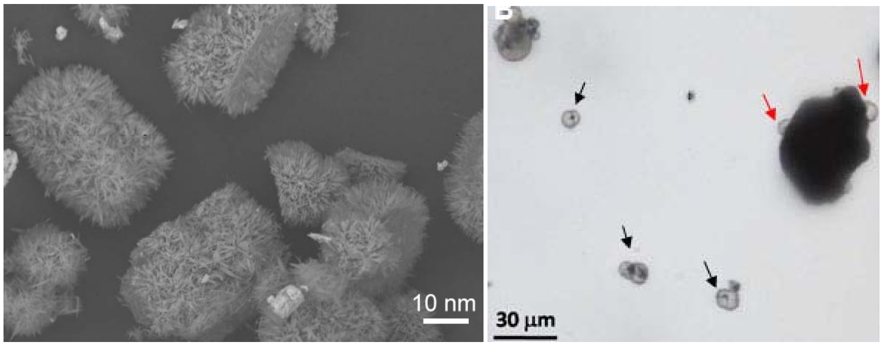

Figure caption: SEM image showing needle-like aragonite crystals grown on hematite polycrystalline cores (left), and petrography microscopic image showing calcite crystals (transparent) preferentially nucleate and grow on pyrite (opaque) surfaces (right).

WOODS HOLE OCEANOGRAPHIC INSTITUTION
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Grant: DE-FG02-06ER15775

Using Comprehensive Two-Dimensional Gas Chromatography to the Explore the Geochemistry of the Santa Barbara Oil Seeps

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R.K. Nelson

Objectives: To further advance our understanding of the geochemical processes that act on oil that travels from reservoirs and seeps onto the ocean floor.

Project Description: The goals of this work are to employ comprehensive two-dimensional gas chromatography (GC × GC) to investigate the geochemistry of the Santa Barbara oil/methane seeps. With the power of GC × GC, we wish to provide unprecedented insights into the processes that act on petroleum in subsurface and surface environments. The results of this work should not be limited to Santa Barbara and ideally can be applied when studying other seeps as well in petroleum exploration and oil spill studies. The Santa Barbara seeps are a natural laboratory and perfect for studying petroleum because of the large volumes of oil seeping, its proximity to critical economic, residential, and recreational areas, and existing collaborative ties with Professor David Valentine at the University of California at Santa Barbara.

Results: In order to compare our field-based observations of biodegradation, we performed a series of aerobic biodegradation experiments in the laboratory. We calculated first order rate constants for naphthalene (N), benzothiophene (BT), and their alkylated analogs (1–4 carbon substituents (C1–C4)) in oil-laden marine sediments from a natural seep. Rate constants were used as proxies for microbial preference, which follows: naphthalene> C1N> C2N> C1BT> C2BT> benzothiophene> C3BT> C3N> C4BT >C4N (Figure 1). The application of GC × GC further enabled separation and quantification of multiple structural isomers for C2N–C4N and C2BT–C4BT, with 7–12 isomers resolved for each C2N–C4N, and 4–7 isomers resolved for each C2BT–C4BT. A strong isomeric biodegradation preference was noted within each of these compound classes, with rate constants varying by as much as a factor of 2 for structural isomers of the same compound. The simultaneous and first-order biodegradation rates observed for 92 compounds resolved in this study, including both *n*-alkanes and aromatic hydrocarbons, lends support to the concept of broad-scale metabolic specificity during aerobic biodegradation of petroleum as observed in the field.

This is the final year of this project, and it has met or exceeded the proposed research goals.

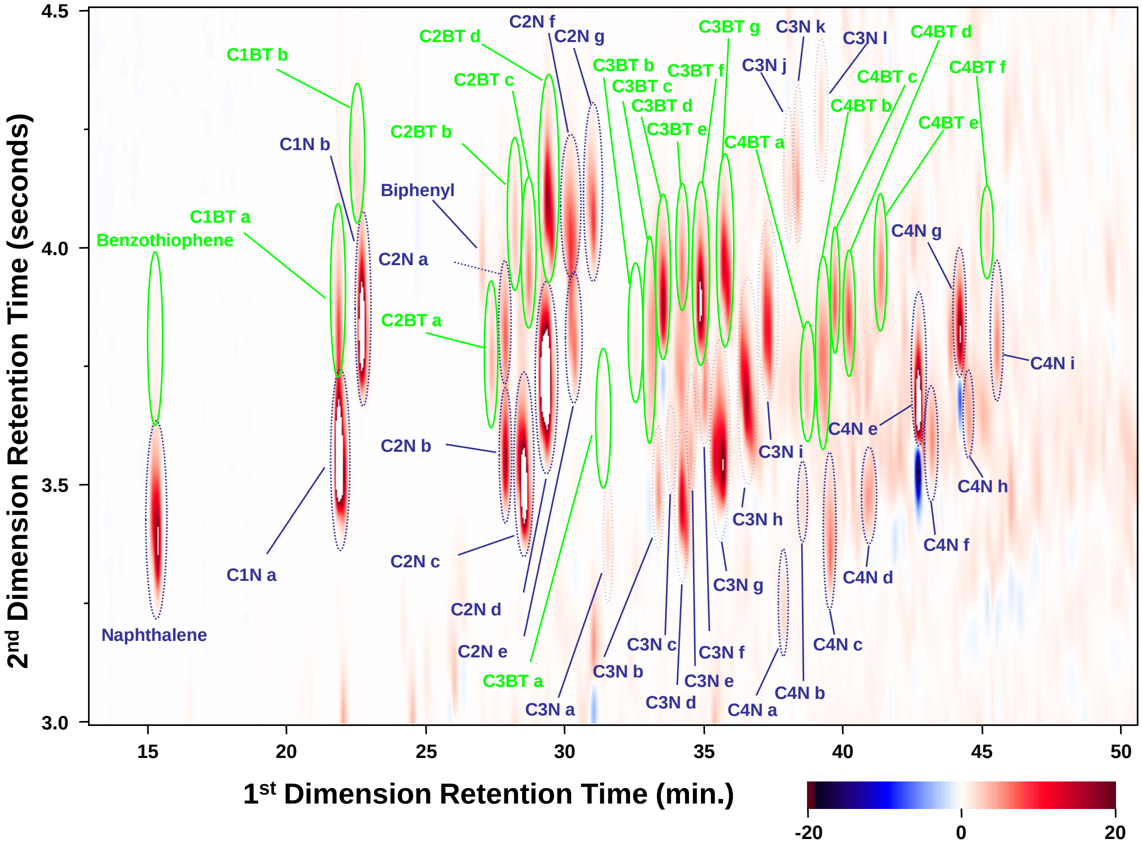

Figure 1. Annotated difference chromatogram produced by subtracting GC×GC-FID chromatograms of the t = 109 day incubation sample from the initial t = 0 day incubation sample. The base-plane appears white, while compounds at a higher concentration in the t = 0 sample than the t = 109 day incubation sample appear red (i.e., those that were biodegraded). Compounds with little or no change in concentration in both samples do not appear. The compounds circled and labelled in blue are naphthalenes and those circled and labelled in green are benzothiophenes.

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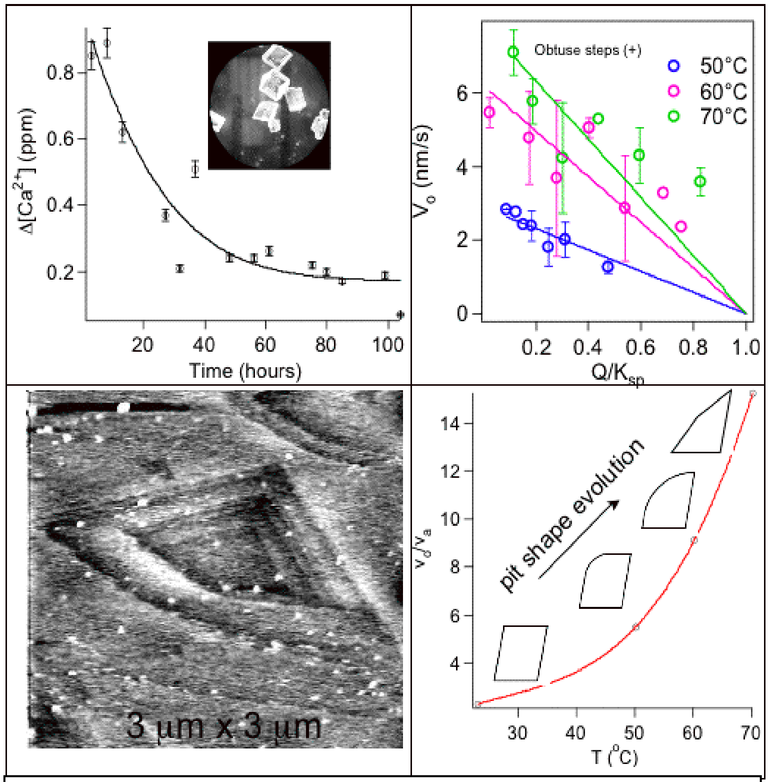
Objectives: We seek to address several problems of critical importance to understanding geochemical processes that occur during the geologic sequestration of CO_2. Specifically, we want to understand the geochemical behavior of the CO_2-aqueous fluid-rock system under the near-equilibrium conditions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

Project Description: 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: **Macroscale dissolution:** We have designed, built and applied new calcite crystallizers capable of producing gram quantities of calcite in 0.3-0.5 mm sizes in approximately 2 weeks (see inset of upper left figure). Pseudo-macroscale dissolution experiments on these calcite crystals were conducted in a small column flow-through reactor. Despite a very short reactor residence time of 10 minutes, dissolution rate data (at 60°C using a near-equilibrium input solution with Q/K_{sp} = 0.25) show that, the dissolution rate decreases with a relaxation time of 30-40 hours (upper left fig.). The long relaxation times are consistent with predictions based on our work during the previous DOE project and suggest that the calcite topography undergoes a slow evolution from the as-prepared surface topography to a pseudo-steady-state topography characteristic of the fluid conditions. This so-called "topographic relaxation" is a process that is highly impacted by sample history.



Upper left: Near-equilibrium macroscale dissolution rate vs. time (pH = 8.5, 60 °C) on large calcite crystals (see inset, 2.5 mm image dia.). **Upper right:** Step speeds using in-situ HAFM (pH = 8.5). **Lower left:** HAFM image showing pit shape at 70°C. **Lower right:** Calcite pit shape is T-dependent, shows decreasing role of acute steps at high T. Step speed anisotropy vs. T shows obtuse step speed is most important at high T.

Microscale (HAFM) dissolution: In experiments conducted in parallel to the macro-scale work above, in-situ Hydrothermal AFM (HAFM) investigations of calcite dissolution at near-equilibrium conditions have provided, for the first time, step speeds as a function of temperature (50-70 °C) and saturation state (Q/K_{sp} = 0.1 – 0.9) (upper right fig.). The speed trends for "obtuse" steps, steps that are generally considered more reactive than the "acute" steps, follow expected trends, but a lack of temperature dependence in the "acute" step speed data (not shown) is not fully understood at this point but could indicate important surface protonation steps, whose equilibrium constants could explain small apparent activation energies. On the microtopographic scale, the temperature dependences are largely responsible for the etch pit shape changes that occur (lower left and right figs.) with increasing temperature and the relatively rapid increase in the "obtuse"/"acute" speed ratio. Importantly, given the typical crystal size of 200 µm, the measured step speeds near Q/K_{sp} = 0.25, and in the context of the topographic relaxation model of Bose et al. (2008) which predicts a relaxation time approx. equal to d/v_s (d is the crystal size and v_s the step speed), we estimate a relaxation time of 22 hours.

With the predicted and observed relaxation times in close agreement, there appears to be a strong relationship between step speeds and macroscale system relaxation.

The implication of these observations in the context of geologic CO_2 sequestration is that kinetic models based on macroscale studies that have not fully accounted for microtopographic controls on reaction rates may be inaccurate on short time-scales (months-years). Long-term predictive models based on similar macroscale results therefore may have an amplifying effect on short-term inaccuracies.

UNIVERSITY OF WYOMING
Department of Geology and Geophysics
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Grant: DE-FG02-06ER15825

Waveguide Scanning Photocurrrent Microscopy (WaSPM): A New Molecular Imaging and Characterization Tool

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Objectives: Our objective is to construct a microscope on the basis of the wavelength-dependent photocurrent response of an iron oxide-coated scanning probe tip interacting with the evanescent light at a waveguide-solution interface. The purpose is to image molecules (such as proteins) at the 10 nm scale.

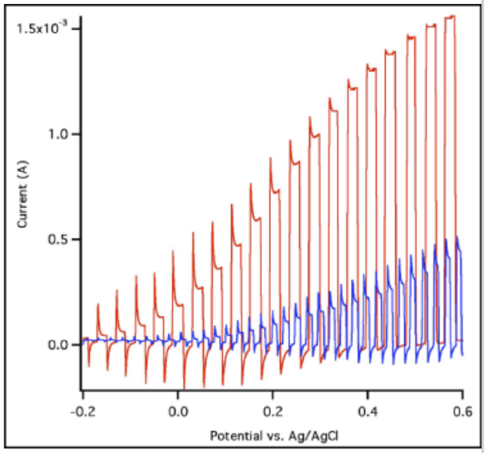
Project Description: The construction of the waveguide microscope depends on the successful accomplishment of a number of preliminary steps, including the manufacture of photosensitive tips using various techniques, and testing these tips for their ability to scatter light out of an evanescent light field at the interface between air and a waveguide in which in-coupled light undergoes total internal reflection and their ability to generate photocurrent. We are using chemical vapor deposition (CVD) techniques to form iron oxide (hematite) nanoscrystalline films doped with Si that produce substantial photocurrent. Instead of making ultrasonic spray pyrolysis films, we have included within the scope of research the production of MnS and WO_3 films by CVD as alternative approaches if the hematite films prove to be less efficient that ultimately needed at low light intensities.

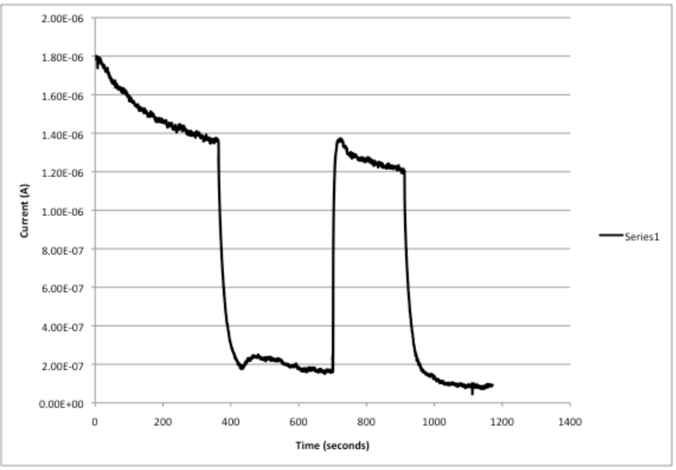
Results: We have prepared the necessary photosensitive tips for the proposed Waveguide Scanning Photocurrent Microscope (WaSPM), and completed a series of photocurrent and transient photocurrent studies related to the photoelectrochemical behavior of the iron oxide active coating on the WaSPM tips. We have had our machine shop build several key parts of the WaSPM, but we ran into technical difficulties with the scanning probe microscope control computers that require replacement or repair.

Because of these delays with the scanning microscope controllers, we decided to develop new photocurrent-generating tip ideas for the WaSPM until the scanning hardware was repaired and available. Thus, we investigated a natural system consisting of a pyrite (FeS_2) photocathode coupled to an iron oxide photoanode. In this configuration, light passes through the hematite (a-Fe_2O_3) before illuminating the pyrite. Electrons promoted to the hematite conduction band by incoming short-wavelength light can combine with holes in the pyrite valence band created by absorption of longer wavelength light by the pyrite. In other words, this configuration creates at natural "tandem cell" with the thermodynamic ability to oxidize water molecules and to reduce protons to hydrogen (among other possible reduction reactions).

The plots on the next page illustrate the main points of the research completed this year. Below, left, is a plot of photocurrent versus potential on the Ag/AgCl scale. The data were taken in chopped light while a voltammogram was being run. The data shown in red corresponds to one of many samples of hematite grown by the CVD process to built in our lab in which the feed gasses were free of water vapor. In contrast, the data in blue stems from samples grown by CVD under identical conditions to the dry samples, except that the feed gas was water-saturated. First, the photocurrent is much higher for the dry film than for the wet film, and second, the location of photocurrent transients – the "spikes" in the data that occur each time the light is turned on or off – are shifted electrochemically. These "spikes" are most likely a consequence of the accumulation of photogenerated holes at the valence band edge near the surface.

Finally, we include (below, right) some chopped-light data for the hematite/pyrite tandem cell idea. In this particular case, we ran the tandem cell under slightly basic conditions. The tandem cell is generating well over 1.0 microamps of current. Quite apart from any possible role in the WaSPM, these observations have implications for natural systems. First, hematite can act as a photocatalyst for water splitting. Second, the pyrite can act as a photocathode lead to the light-driven reduction of aqueous compounds in contact with the pyrite. We believe that this result has implication for potential remediation strategies as well as for the WaSPM.





UNIVERSITY OF WYOMING
Department of Geology and Geophysics
Laramie WY 82071

Grant: DE-FG02-06ER15823

Redox Interaction of Cytochromes and Bacteria with Oxide Surfaces: Probing Redox-Linked Conformation Change

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Objectives: The objective of this research is to better understand the role of conformation change in electron transfer from cytochromes to minerals, a process that underpins respiratory metal reduction by bacteria in nature and in bioremediation strategies, including reductive immobilization of radioactive contaminants.

Project Description: This project aims to better understand how outer-membrane and other cytochromes from dissimilatory metal-reducing bacteria regulate electron transfer from organism to minerals or to metal solutes. In particular, conformation change is directly related to protein enzymatic function. We compare the electrochemical behavior of isolated proteins with that of whole-cell suspensions. We focus on cytochromes from two well-characterized organisms, *Shewanella oneidensis* MR-1 and *Geobacter sulfurreducens*. These bacteria are directly implicated in electron transfer to metals and are thus of great interest not only in natural redox cycling of metals but also in bioremediation strategies for contaminant metals including Cr, U, Tc, Np, and others of interest to the U.S. Department of Energy. We are using a combination of electrochemical, scanning probe microscope, optical waveguide lightmode spectroscopy (OWLS), and quartz crystal microbalance (QCM) techniques to detect structural changes in adsorbed cytochromes.

Results:

1) We completed an electrochemical study of isolated and purified OmcA and MtrC (courtesy of Dr. Liang Shi of PNNL), as well as of both wild-type and OmcA, MtrC, and OmcA+MtrC deletion mutants of *Shewanella oneidensis* MR-1 under aerobic and anaerobic conditions (with courtesy of Catherine Reardon, PNNL). This work has been published.

2) We completed a comparative Optical Waveguide Lightmode Spectroscopy (OWLS) and Quartz Crystal Microbalance with Dissipation (QCM-D) study of OmcA, MtrC, STC, and other cytochromes in order to detect changes in the density and solvent content of adsorbed cytochromes in the oxidized vs. reduced states. Our findings show:

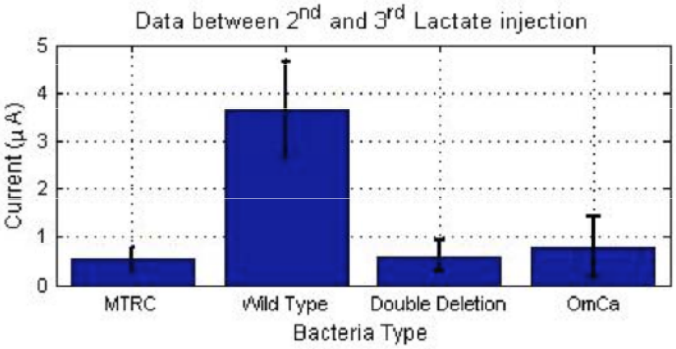
a) Oxidized MtrC desorbs readily from oxide surfaces in response to dilution into protein-free buffer, whereas OmcA does not. These roles reverse when the cytochromes are reduced.

b) MtrC and OmcA are very low density proteins in the adsorbed state – of the total adsorbed mass, only about 23% (MtrC) and 18% (OmcA) is polypepetide and cofactors in the protein. The remainder of the adsorbed mass is the water and solutes that adsorb to the surface in association with the protein. Protein solvent content is larger than reported for most other proteins.

c) The density of periplasmic cytochromes was much high than the density of outer-membrane cytochromes. This was true across species boundaries insofar as it was true of proteins from both *Geobacter sulfurreducens* and *Shewanella oneidensis* MR-1.

d) We completed a study of oxidized vs. reduced cytochromes that allowed calculation of the density of the adsorbed proteins. The density of the periplasmic cytochrome STC was much higher than that of outer membrane proteins, but decreased substantially upon reduction. In contrast, MtrC was less dense in the reduced form. The density of OmcA was about the same in the reduced form as in the oxidized forms.

3) We completed a microbial fuel cell study using the same organisms (wild type and deletion mutants) used in the electrochemical study reported above. This study is unique because we made microbial fuel cells using oxide anodes rather than the graphite felt anodes used in other MFCs. Thus, our study provides a much more "realistic" measure of currents from organisms to oxides such as might be encountered in natural systems. The results are consistent with impaired electron transfer capabilities in all mutants compared to the wild type organism. Results in the form of a histogram are shown at right ("MTRC" and "OmCa" refer to mutants deficient in MtrC and OmcA, respectively).



YALE UNIVERSITY
Departments of Geology & Geophysics and Physics; Program in Applied Mathematics
New Haven CT 06520

Grant: DE-FG02-05ER15741

Freezing in Porous Media: Phase Behavior, Dynamics and Transport Phenomena

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Objectives: The premelted liquid layers on ice are ubiquitous and important aqueous films. They exist over a wide range of thermodynamic and chemical environments, from the depths of glaciers to stratospheric ice clouds and are particularly important in the dynamics and thermodynamics of soils. Premelted films exist in all classes of solids, where they facilitate crystal growth from vapor and the coarsening of polycrystals. Many experiments have demonstrated that the melting temperatures of materials are depressed below their bulk values, T_m, in porous media. Our objectives are to understand the role of premelting in controlling the volume fraction of liquid water in subfrozen model and actual soils and then quantify their underlying role in influencing the dynamical and transport phenomena that drive frost heave and related porous media behavior in the natural environment.

Project Description: Our approach involves advancing the tenets of the condensed matter physics of the system using theory and experiment and ultimately to bring these advances to bear on the environmental setting. Our experiment investigates the notion that a particle in a partially frozen porous media should undergo Brownian motion within its premelted jacket. As the sample temperature decreases, the premelted layer will shrink and the diffusion constant characterizing the particle's motion should increase. We use Dynamic Light Scattering (DLS) to determine the diffusion coefficient as a function of temperature. DLS encompasses a group of non-invasive optical techniques that have been employed widely in the study of microscopic dynamics of soft condensed matter. All DLS methods involve studying coherent light scattered by a sample. As the light passes through the sample, it is scattered by many different particles. Each scattering event introduces a phase shift, which in the image plane, produces an interference pattern called speckle. As the scatterers move, the phase shift induced by each one changes and the speckle pattern varies in time. The time required for the intensity of a particular speckle spot to become decorrelated from its initial value is related to the effective diffusion coefficient of the particles. Our experimental approach is to use a form of DLS called x-ray photon correlation spectroscopy (XPCS) to explore the dynamics of silica particles frozen inside pure ice at a uniform temperature. The experiments are done at the Advanced Photon Source at Argonne as our modality of DLS. Our theoretical approaches vary widely, from the theory of multiple scattering to the statistical mechanics of confined media. We also bridge the gaps in scale from the pore scale to the effective medium scale to study problems that have direct scaling connection to the natural environment.

Results: The premelted liquid film that forms around a foreign particle within a subfreezing solid facilitates the motion of the particle the influence of temperature and concentration gradients. Our study, of phenomena that underlie the bulk properties of frozen soils and particle laden hydrate regions takes place using a troika of theory, the DOE's APS and our laboratory studies at Yale. We have used nearly monodisperse silica spheres of a size small enough to experience Brownian motion as a simplified version of soil but offering several benefits over actual soils. First, the spherical shape and relative monodispersity simplify interpretation of the light scattering results. The use of silica particles allowed us to control the amount and type of dissolved ionic species and avoids complications associated with clays but we have also studied bentonite and montmorillanite in our lab at Yale and data from other experiments in our theoretical work. Because of our previous success in showing that a dilute clay suspension can be treated like a binary alloy with the particles playing the role of the solute, our work this FY benefitted substantially on several fronts. (1) Since having submitted the renewal proposal we tried an entirely new methodology of imaging our samples at the APS called Near Field X Ray Microscopy. The method was originally developed for optical microscopy with the idea being to capture the scattered X rays very near where they exit the sample thereby avoiding substantially interference before they reach the detector; attempting to "beat" the diffraction limit. This has provided us with unprecedented plan view X ray movies of the dynamics of our samples and immediate confirmation of two of the hypotheses outlined in our proposal. We can literally see the polycrystallinity of our quenched sample form in real time (image size 0.4 mm^2) and watch the grain boundary coarsening as well is the redistribution of the particles into grain boundaries, veins, nodes and trijunctions. As far as we are aware, no such observations have been made and the success of the method will have broad implications and utility for a wide range of fields. (2) Both the XPCS and SAXS work, also taking place at the APS, revealed that the particle dynamics bear a relation to the aging dynamics of glasses and gels. Whence, in combination with the real space visual information given by the Near Field method, we understand that particle clusters form during freezing and undergo a highly coupled form of Brownian motion, likely seen as a combination of regions of high particle density and those of low particle density as the X rays are transmitted through the sample. (3) Because of our ability to treat all colloidal suspensions as binary allows we have been able to understand lensing and pattern formation as a form of morphological instability, and we continue to link the theoretical underpinnings of two limits that have traditionally been considered as distinct. We have now studied the morphological stability of a nonequilibrium ice–colloidal suspension interface, and have applied the theory to bentonite clay. An experimentally convenient scaling was employed to take advantage of the vanishing segregation coefficient at low freezing velocities, and when anisotropic kinetic effects are included it was shown that the ice/colloid interface is unstable to travelling waves. The potential for traveling-wave modes reveals a possible mechanism for the polygonal and spiral ice lenses observed in frozen clays. We further studied the system using a weakly nonlinear analysis to discover a long-wave evolution equation for the interface shape containing a new parameter related to the highly nonlinear liquidus curve in colloidal systems. We have explored a number of the implications of these results for the frost susceptibility of soils, the fabrication of microtailored porous materials and the geometric structure of the frozen host material in a soil.

DOE/OBES Geosciences Research: Historical Budget Summary

(Thousands of dollars)

ON-SITE INSTITUTION	FY05	FY06	FY07	FY08	FY09
Argonne National Laboratory	535	758	461	506	700
Idaho National Laboratory	50	50	60		
Los Alamos National Laboratory	1320	963	1050	415	670
Lawrence Berkeley National Laboratory	3240	2939	4063	4416	4880
Lawrence Livermore National Laboratory	1335	1141	1270	1172	850
Oak Ridge Institute for Science and Education		105	12		
Oak Ridge National Laboratory	2075	1750	1750	1850	1820
Pacific Northwest Laboratory	860	910	975	980	1935
Sandia National Laboratory	980	975	1130	1170	965
total, on-site	10395	9591	10771	10509	11820
total, off-site	10492	9544	9869	9605	9341
total, operating	20887	19135	20640	20114	21161
total, equipment					
Total GEOSCIENCES	20877	19135	20640	20114	21161
OFF-SITE INSTITUTION					
Alabama, Univ. of (Dixon)		47	48	48	48
Alabama, Univ. of (Dixon)			58	60	63
American Chemical Society (Criscenti)				3	
American Society for Microbiology (Colwell)	5				
Arizona State Univ. (Shock)	101				
Arizona State Univ. (Hervig/Williams)	132	135			
Boston Univ. (Klein)	130	134		145	152

Caltech (Stolper)		167	172	177	
Caltech (Wasserburg)	200				
Calif., Univ. of Berkeley (Banfield)	200	200	200		
Calif., Univ. of Berkeley (Banfield)	153	123		177	
Calif., Univ. of Berkeley (Helgeson)	167		100	100	
Calif., Univ. of Berkeley (Wenk)	150	150	150		
Calif., Univ. of Davis (Navrotsky)	194	197	215	221	226
Calif., Univ. of Davis (Rustad)	78	82	85		
Calif., Univ. of Davis (Rustad)	136	137	68	69	70
Calif., Univ. of Davis (Casey)	319		135		170
Calif., Univ. of Davis (Rundle)	143	151		156	163
Calif., Univ. of Irvine (Detwiler)					139
Calif., Univ. of Los Angeles (Harrison/McKeegan)	79				
Calif., Univ. of Santa Barbara (Boles)	79	95	95	83	
Calif., Univ. of Santa Barbara (Gibou)				190	190
Calif., Univ. of Santa Cruz (Wu)	318	327			
Calif., Univ. of San Diego (Weare)		269		138	
Chicago, Univ. of (Sutton/Rivers)	600	697	718	739	761
Chicago, Univ. of (Sutton)					422
Chicago, Univ. of (Sutton)	125	148	139	138	282
Chicago, Univ. of (Richter)	138	143	148	174	180
Clark Univ. (Kudrolli)		59	54	55	68
Clay Minerals Society (Cygan)			10		
Clay Minerals Society (Ross)				5	
Colorado School of Mines (Batzle)	114				
Colorado School of Mines (Tsvankin)	150		75		
Colorado School of Mines (Snieder)		97	101	106	

Colorado School of Mines (Benson)			79	82	86
Colorado School of Mines (Scales)					142
Colorado, Univ. of (Spetzler)	55	58	60	62	
Connecticut, Univ. of (Torgersen)		32	34	35	22
Florida, Univ. of (Ladd)	155	108	111		194
George Washington Univ. (Teng)	98		48		31
George Washington Univ. (IPA Lesmes)	150	6	5		
Georgia State Univ. (Elliott)	22				
Georgia Tech (Stack)			210		
Gordon Res. Conf. (Hirth)		10		10	
Harvard Univ. (Martin)	81	96	99	102	
Hawaii, Univ. of (Jahren)					108
Houston, Univ. of (Weglein)	101		51		
Idaho, Univ. of (Wood)	10				
Idaho State Univ. (Magnuson)		88	90	93	
Illinois, Univ. of (Kirkpatrick)	248	216			
Illinois, Univ. of (Bethke)	270		135	138	142
Illinois, Univ. of (Bass)				151	155
Illinois, Univ. of Chicago (Sturchio)	62	51	53	54	60
Illinois, Univ. of Chicago (Nagy)	145				
Indiana, Univ. of (Schimmelman)	119	141	133	128	
Johns Hopkins Univ. (Garven)	88	124			
Johns Hopkins Univ. (Veblen)	205	205	250	250	250
Johns Hopkins Univ. (Sverjensky)	153	158	163	176	180
Johns Hopkins Univ. (Jahren)		101	105		
Louisiana State Univ. (Dutrow)	9				
Maryland, Univ. of (Tossell)	99				

Maryland, Univ. of (Zhu)			130		106
Mass. Inst. Tech. (Evans)	235	304	318	328	344
Mass. Inst. Tech. (Rothman)		160	168	172	160
Mass. Inst. Tech. (Durham)			40	42	43
Massachusetts, Univ. of (Boutt)	145		41		
Michigan State Univ. (Kirkpatrick)				230	
Michigan Tech Univ. (Turpening)	144				
Mineralogical Society of America (Speer)		35	10	10	
Mineralogical Society of America (Speer)		5		10	
Minnesota, Univ. of (Kohlstedt)	39	176	185	192	200
Missouri, Univ. of (Appold)				107	86
NAS/NRC (Schiffries/DeSouza)	90	90	90	90	90
NAS (Linn)	200				
New England Res. (Brown)	100				
New Mexico, Univ. of (Weissmann)				15	15
NY, City Univ. of CC (Koplik)		107	109	110	94
NY, City Univ. of CC (Makse)		85	100	100	100
NY, State Univ. of Stony Brook (Schoonen)		87	83	85	91
NY, State Univ. of Stony Brook (Wong)	128	125	128	132	
NY, State Univ. of Stony Brook (Lindquist)	64	87	66		
NY, State Univ. of Stony Brook (Reeder)					165
North Carolina, Univ. of (Miller)					200
North Texas, Univ. of (Bagus)	35	35	50	50	50
Northwestern Univ. (Rudnicki)	123	113	114	119	
Northwestern Univ. (Geiger)	3	49	50	52	121
Northwestern Univ. (Andrade)				304	110
Ohio State Univ. (Allen)	42	44	80	79	83

Oklahoma, Univ. of (Elmore)	47				
Oregon State Univ. (Egbert)		98	95	104	
Penn State Univ. (Brantley)	174	176	223	261	274
Princeton Univ. (Peters)	114	160	169		
Purdue Univ. (Pyrak-Nolte)		288		117	163
Renesselaer Polytech. Inst. (Watson)	208	215		199	199
Society of Exploration Geophysics (Smith)		5			
South Carolina, Univ. of (Wilson)	54	54			
Stanford Univ. (Borja)	99	102	110	110	110
Stanford Univ (Knight)	146				
Stanford Univ. (Nur)	217		207	221	229
Stanford Univ. (Pollard/Aydin)	261		273	264	272
Stanford Univ. (Tchelepi)				208	215
Temple Univ. (Strongin)		91	83	87	94
Texas A&M Univ. (Morse)	135	157	149	153	
Texas A&M Univ. (Datta-Gupta)	140	143	142	145	
Texas, Univ. of (Katz)	75	78	75	78	84
Texas, Univ. of (Laubach)	227	197	241	264	246
Tufts Univ. (Garvin)			227		
Virginia Tech (Rimstidt)	124				
Virginia Tech (Dove)	178	226	250	202	245
Virginia Tech (Hochella)	98	122	127	143	149
Virginia Tech (Hochella)				4	
Wisconsin, Univ. of (Goodwin)	108		73		
Wisconsin, Univ. of (Valley)	210	217	234	239	248
Wisconsin, Univ. of (Gilbert)			325		159
Wisconsin, Univ. of (Xu)					74

Woods Hole OI (Zhu)	50	61			
Woods Hole OI (Seewald)	177	184			
Woods Hole OI (Reddy)		157	164	172	113
Wright State Univ. (Higgins)	73	98	110	115	105
Wyoming, Univ. of (Eggleston)	46				
Wyoming, Univ. of (Eggleston)		154	131	122	
Wyoming, Univ. of (Eggleston)		100	102	105	
Yale Univ. (Rye/Bolton/Ague)	157				
Yale Univ. (Wettlaufer)	115	100	100		
Yale Univ. (Berner)	130	130			
Yale Univ. (Bolton)			77		
Other		1			
OFF-SITE TOTALS	10492	9544	9869	9605	9341