

Summary of FY 2008 Geosciences Research

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FORWARD

The Department of Energy's 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 other offices. The 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 Earth science beyond DOE. 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. The summaries in this document, prepared by the investigators, describe the scope of the individual projects. The Geosciences Research Program includes research in the two broad areas of geophysics and geochemistry. 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 research is foundational to progress for the Department of Energy's long-range technological needs. Because of the variety of the research needs in the different applied DOE programs, fundamental approaches with multiple potential applications are favored. 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. 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 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. Activities in the Geosciences Research Program are directed toward building the long-term fundamental knowledge base necessary to provide for energy technologies of 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. The Earth is a source for energy and mineral resources, and is also the host for wastes generated by technological enterprise. Viable energy technologies for the future must contribute to a national energy enterprise that is efficient, economical, and environmentally sound.

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 through better collection and analysis of rock physics, seismic, and electromagnetic 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; and tracking of mineral-mineral and mineral-fluid processes using isotopes.

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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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 $\sim\text{\AA}$ -resolution, primarily in studies of ion adsorption, and also in pursuing advances in interfacial X-ray based analytical techniques.

Measurements of Rb^+ and Sr^{2+} at the orthoclase (001)-aqueous interface revealed that Rb^+ adsorbs in the K^+ site as an “inner-sphere” (IS) species; Sr^{2+} adsorbs at a substantially larger height indicating that it is an outer-sphere species (OS). These results demonstrate that the distribution of cations between IS and OS species is determined in part by the characteristics of the mineral surface.

Adsorption thermodynamics of Rb^+ and Sr^{2+} at muscovite were measured. The cation coverage and average cation height were measured. These results revealed: that the IS and OS Sr^{2+} species observed at muscovite have similar adsorption enthalpies; and a pH-dependent hysteresis of the cation coverage

for both ions, resulting in a net reduction in the saturation coverage with an OS-dominated Sr^{2+} adsorption geometry.

The image contrast mechanism for X-ray reflection interface microscopy (XRIM) was determined. These results show how the step direction (up/down) can be determined so that the XRIM images can be converted to reveal interfacial topography. A new formalism for calculating image contrast was developed that will be used to optimized future instruments.

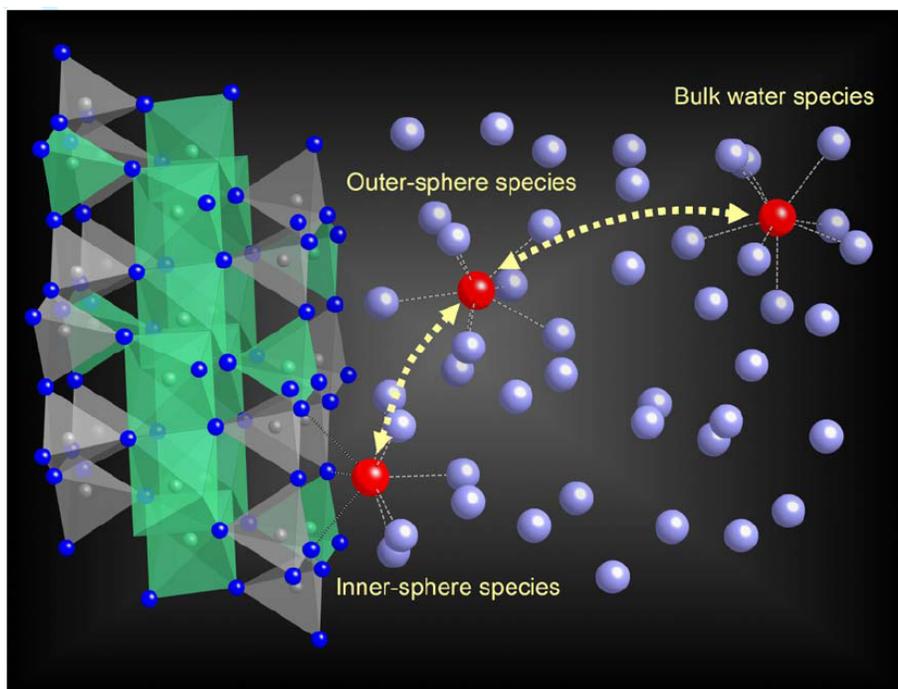


Figure: Schematic (side view) of cation adsorption at the muscovite (001)-aqueous interface. The image illustrates the change in ion hydration geometry associated with a transition between outer-sphere and inner-sphere species, which is inferred to be a major factor in controlling the partitioning between these two species.

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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: A manuscript titled "Simple kinetic Monte Carlo models for dissolution pitting induced by crystal defects", by Paul Meakin, Kevin M. Rosso and Svetlana Yanina, was finalized and submitted for publication to the Journal of Chemical Physics. This paper, which describes new, very efficient, solid-on-solid Monte Carlo algorithms and their application to mineral dissolution, has now been accepted.

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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: The newly expanded 512 processor cluster (3.7 Teraflops) was utilized at the 90+ percent rate. The cluster was configured to address two general research areas, Geophysics and Geochemistry. In Geochemistry the cluster supported clay mineral geochemistry (applying spin-polarized density functional theory (DFT)) to examine and compare the structures of different species and geochemical transport problems (Rate Controls in Chemical Weathering). In geophysics the cluster was used support 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.

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.

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 U–Th/⁴He ages on olivine phenocrysts from late Quaternary basalts. The approach employs abrasion to remove the outer rinds of olivine crystals, which eliminates ⁴He 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. New measurements of 80 to 200 ka basalts have been directly compared with Ar-Ar ages and show that U-Th-He may provide more reliable ages for lavas of this age. 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.

(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 are 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.

(3) *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 1 to 5% organic carbon. In these sediments, even though the biogenic calcite is generally unstable, the $\delta^{44}\text{Ca}$ of pore fluids indicates that there is virtually no calcite dissolution over millions of years. This contrasts with sediments that are nearly pure biogenic calcite, in which calcite dissolves and re-precipitates at rates of 10^{-5} to 10^{-8} yr⁻¹ depending on age. The suppression of calcite dissolution is linked to the presence of clays and organic material, and suggests that the surfaces of the calcite crystals are modified. The effects have implications for geologic carbon sequestration and for reconstruction of past climate changes from sedimentary records.

(4) *U-series alpha-recoil as a nanoscale probe of natural systems:* (²³⁴U/²³⁸U) of fine-grained sediments show systematic effects suggesting that alpha-recoil associated with the decay of ²³⁸U is primarily responsible for ²³⁴U depletions in minerals. Because the rate of ²³⁴U 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.

(5) *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 CO₂. Correlated variations among total CO₂, 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 $\delta^{44}\text{Ca}$, consistent with non-equilibrium processes occurring during calcite precipitation. This is the first use of Ca isotopes to study calcite precipitation from hydrothermal fluids.

(6) *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 $\delta^{13}\text{C}$ of biogenic methane produced at atmospheric pressure and seafloor pressures of ca. 500 atmospheres.

(7) *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.

Physicochemical Controls on Unsaturated Flow and Transport in Geological Media

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Objectives: The flow of water and transport of chemicals through variably saturated soils and geologic formations is strongly dependent on the water content, with flow and transport rates at low saturation levels controlled by water films. Basic properties of water films in unsaturated media remain poorly understood. Latest work on this project tests the hypothesis that film flow rates scale in proportion to grain size.

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. Experiments on flat mineral surfaces and monodisperse sands are being conducted to test models for adsorbed water film equilibrium and transport. Model predictions are being developed and experimentally tested using microscopic (film-scale) and bulk (porous medium) approaches. Direct measurements of film thickness are obtained in a small suction plate chamber by equilibration with aqueous solutions under sub-atmospheric pressures. The chamber is placed in front of an X-ray beam (National Synchrotron Light Source X26A, and Advanced Photon Source 13-ID-C) 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. These hard X-ray synchrotron sources permit efficient X-ray fluorescence monitoring of ionic tracers in water films within sealed environmental control chambers. Larger scale measurements of film-controlled hydraulics in porous media are being conducted in flow cells packed with monodisperse sands, regulated within ranges of matric potential where thin aqueous films separate pendular rings of water at grain-grain contacts.

Results: Because there are more adsorbed water films per unit volume in unsaturated media of finer grain size, it has been suggested that film flow is more efficient in such systems. This conjecture is an extension of the familiar phenomenon of cross-over in the unsaturated hydraulic conductivity relations of sands and clays; where sands are more conductive at higher (near-zero) potentials but at more negative potentials drain to become less conductive than clays. We have addressed this problem through combining considerations of adsorbed film thickness-potential relations, film hydrodynamics, and capillary scaling. This analysis shows that, in the Langmuir limit of low ionic strength films, the bulk unsaturated hydraulic conductivity scales in proportion to the square-root of the characteristic grain size. Thus, film flow is less effective in finer-grained unsaturated media, despite having a greater density of transmitting surfaces. The equation derived for the bulk unsaturated hydraulic conductivity also contains an inverse-cubic dependence on ion valence, thus predicting an eight-fold greater film flux of monovalent solutions than divalent solutions at the same potential. Experimental testing of this equation is further motivated by the fact that it contains no adjustable parameters. However, predicted flow rates and times required for establishing local equilibrium conditions indicate difficult experimental challenges. Predictions of scale- and valence-dependence are currently being tested in bulk systems consisting of monodisperse packs of quartz sands (0.1 to 2.0 mm), infused with dilute KCl and MgSO₄ solutions.

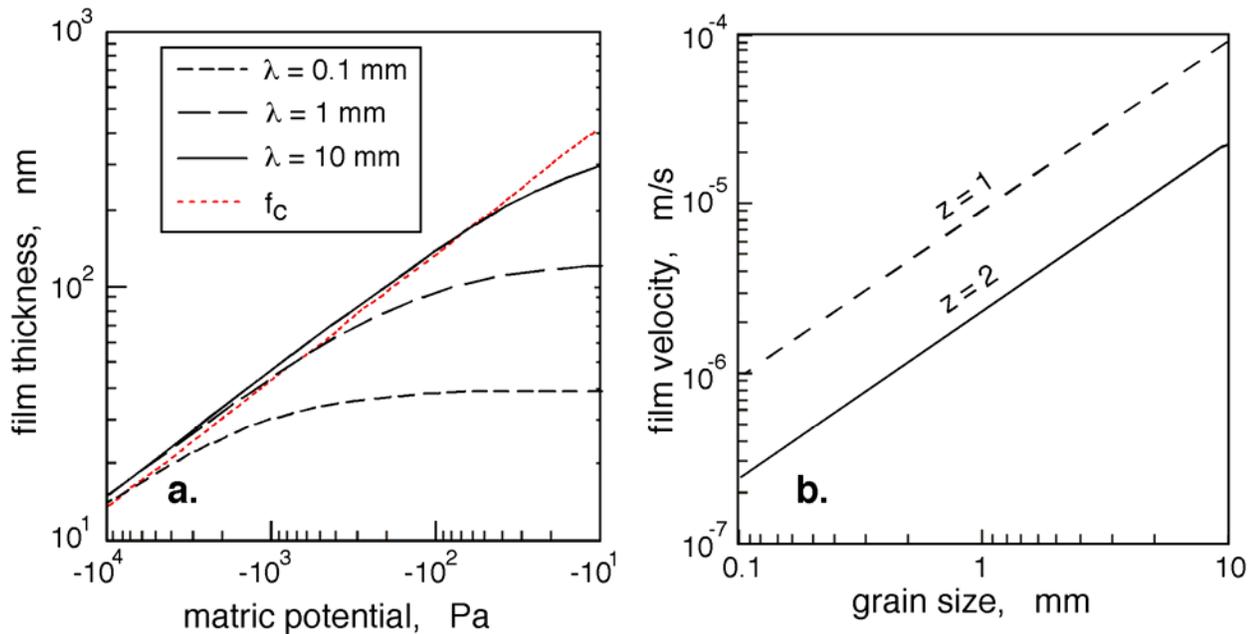


Figure 1. Water film characteristics at low ionic strength (Langmuir-limit). (a.) Water film thicknesses for dilute 1:1 ($z = 1$) solutions on grains of different size (λ). Intersections of film thickness curves with f_c occur at critical potentials, below which films control flow. (b.) Dependence of film velocities on grain size, at critical matric potentials, showing predicted ion charge influence.

Clay Mineral Surface Geochemistry

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Objectives: The overall objective of this project is to investigate the chemical properties of clay mineral nanoparticles (layer type minerals) at molecular scales using computer simulation methods. Current research focused on the metal-binding properties of bacteriogenic MnO₂ nanoparticles, which are layer type Mn oxides, using quantum mechanical calculations.

Project Description: Many bacteria produce layer type Mn(IV) oxides (birnessite, MnO₂), which are known to impact a broad range of geochemical processes mainly through their high capacity for metal sorption. An important structural characteristic of these oxides is the presence of Mn(IV) cation vacancies whose charge deficit is typically compensated by metal cations or protons. The vacancies in birnessite have long been identified as strong adsorption sites for transition metals. Zinc has been observed to form both tetrahedral (Zn^{IV}) and octahedral (Zn^{VI}) triple-corner-sharing surface complexes (TCS) at the Mn(IV) vacancy sites in birnessite. The octahedral complex is expected on the basis of the local coordination environment of Zn in the mineral, chalcophanite (ZnMn₃O₇·3H₂O), but the reason for the occurrence of the four-coordinate Zn surface species remains unclear. We addressed this issue using spin-polarized density functional theory (DFT) to examine and compare the structures of the Zn^{IV}-TCS and Zn^{VI}-TCS species. Our DFT geometry optimization calculations, performed with the code CASTEP, required massively-parallel supercomputing resources of the National Energy Research Scientific Computing Center (NERSC).

Results: Structural parameters obtained by DFT geometry optimization were in excellent agreement with available experimental data for Zn-birnessites, including chalcophanite (Figure 1). Total energy, magnetic moments, and electron-overlap populations obtained by DFT for isolated Zn^{IV}-TCS revealed that this species is stable in birnessite without the need for Mn(III) substitution in the octahedral sheet and that it is more effective in reducing undersaturation of surface O at a Mn vacancy than is Zn^{VI}-TCS, thus making it somewhat more stable. Comparison between geometry-optimized chalcophanite and a hypothetical monohydrate mineral, ZnMn₃O₇·H₂O, which contains only tetrahedral Zn, showed that the hydration state of Zn significantly affects birnessite structural stability. This comparison made possible uniquely by DFT geometry optimization suggested that H-bonds are stabilized for octahedral Zn by linking the interlayer Zn through water molecules, whereas tetrahedral Zn is stabilized by H-bonds with adjacent octahedral sheets that alter the sheet registration, thereby compensating for having no H-bonds between neighboring Zn. Our DFT study provides insight into the occurrence of Zn^{IV} and Zn^{VI} surface complexes at Mn vacancies in hexagonal birnessite, demonstrating that Zn^{IV} forms stronger chemical bonds with O of a Mn(IV) vacancy site than Zn^{VI} does. This is consistent with experimental observations of the predominance of Zn^{IV}-TCS at low loading of sorbed Zn in birnessite. Comparison between ZnMn₃O₇·3H₂O and ZnMn₃O₇·H₂O, which have a high Zn/Mn ratio, suggested that the occurrence of Zn^{VI}-TCS along with Zn^{IV}-TCS in birnessite may be more related to interactions of Zn ions (e.g., through H-bonding) with neighboring Zn ions or with adjacent Mn octahedral sheets than it is to the existence of Mn(III) substitution or Zn bond strength differences.

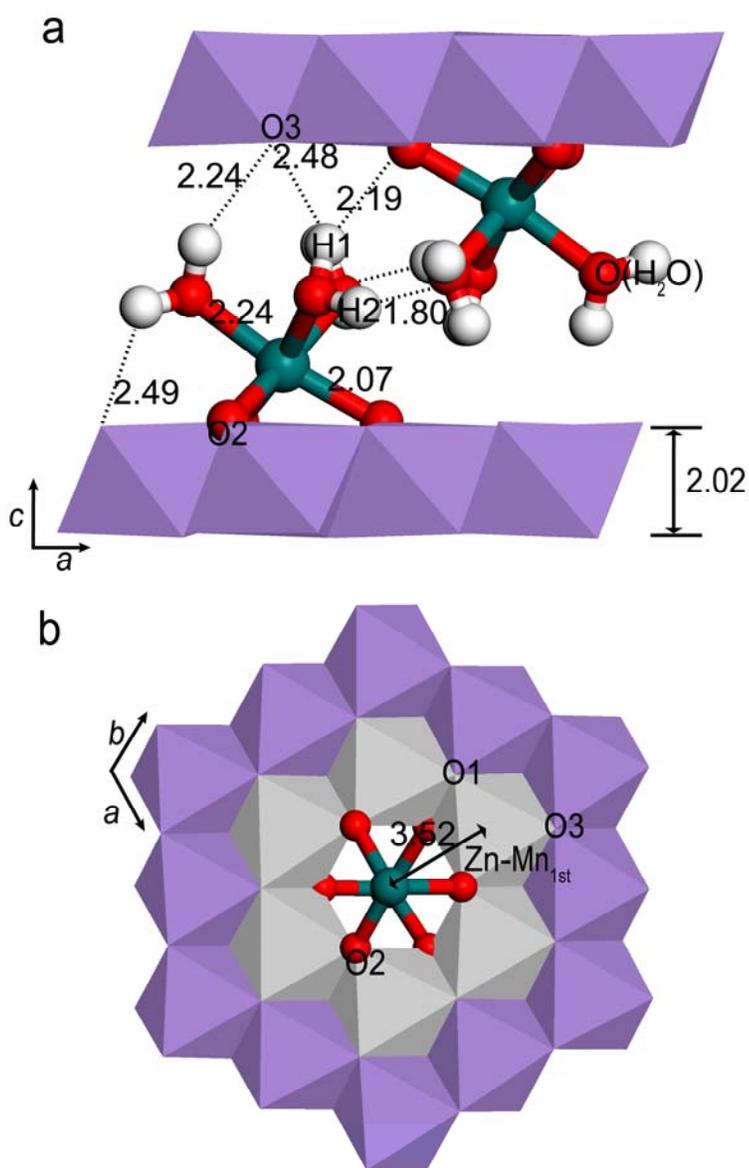


Figure 1. Visualization of the geometry-optimized structure of ZnMn₃O₇·3H₂O (chalcophanite), viewed perpendicularly to (a) the *c*-axis and (b) the *ab* plane (Red: O; White: H; Teal: Zn; Purple octahedron: Mn(IV) octahedron). Zn-O, Zn-Mn, and H-bond distances (dotted lines) and sheet thickness are given in Å. Water molecules are omitted for visual clarity in (b), where the double-headed arrow indicates the distance between nearest-neighbor Mn (Mn_{1st}) and Zn. Gray represents Mn_{1st} octahedra. The labels O1 and O3 identify O bonded to three Mn (O_{3Mn}), whereas O2 identifies O bonded to two Mn and one Zn (O_{2Mn}).

Rate Controls in Chemical Weathering: A Reactive Transport Approach

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Objectives: The objective of this project is to increase our understanding of the controls on reaction rates in natural porous media and to quantify the rates of precipitation and nucleation of important secondary mineral phases in soils and aquifers, a critical deficiency in current hydrogeochemical models. The present lack of understanding limits our ability to develop effective bioremediation schemes for contamination cleanup, to develop predictive models for CO₂ sequestration in deep aquifers, and even to determine the fundamental controls on the rates of chemical weathering, an important long-term regulator of atmospheric CO₂ levels.

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 22°C, 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 and to the Shale Hills Critical Zone Network site in Pennsylvania.

Results: Dissolution and precipitation rates of low defect Georgia kaolinite (KGa-1b) as a function of Gibbs free energy of reaction (or reaction affinity) 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

$$R_{diss} \left(\frac{\text{mol}}{\text{m}^2\text{s}} \right) = 1.15 \times 10^{-13} \left[1 - \exp \left(\frac{-\Delta G}{2RT} \right) \right]$$

In contrast, long-term precipitation rates showed a linear dependence on solution saturation state that is generally consistent with a two dimensional nucleation growth mechanism following the equation

$$R_{ppt} \left(\frac{\text{mol}}{\text{m}^2\text{s}} \right) = 3.38 \times 10^{-14} \exp \left[-\frac{181776}{T^2 \ln \Omega} \right]$$

Measuring precipitation rates at room temperature and circum-neutral pH conditions is difficult if not impossible to carry out experimentally, but it appears to be possible to use of data from field systems to constrain rates under these conditions. Reactive transport calculations of coupled albite dissolution and kaolinite precipitation using the code *CrunchFlow* were carried out for conditions broadly similar to those investigated by White et al (2008) at the Santa Cruz chronosequences to attempt to constrain kaolinite precipitation rates at a pH of about 7. A flow rate of 0.088 m/yr, volume fractions of albite and kaolinite of 15% and 10% respectively, and specific surface areas of 0.43 m²/g and 11.83 m²/g for albite and kaolinite respectively were assumed for the calculations, which were then carried out to 65,000 years (the approximate age of the youngest terrace at Santa Cruz). In the calculation, a modified rainwater with a pH of 5.73 infiltrates the sandy material (porosity = 40%) under partially saturated conditions. Using the kaolinite precipitation rate determined in this study at pH 4 along with the rate law for albite proposed by Hellmann and Tisserand (2006), the reactive transport calculations predict that the pore water composition will remain close to equilibrium with respect to kaolinite (log Q/K_{eq} ~ 0.1), while albite remains far from equilibrium (Figure 1). However, the results at circumneutral pH (6-8) depend critically on the pH dependence of kaolinite precipitation rates. If the pH dependence is significant (e.g., a dependence ≥ 1), then the decrease in the kaolinite precipitation rate as the pH increases could have marked effect on the weathering rate of albite. This can be evaluated by simulating the same system using slower rates for kaolinite precipitation. As the kaolinite precipitation rate constant decreases from 10⁻¹⁵ mol/m²/s (log k = -15) to 10⁻¹⁶ mol/m²/s (log k = -16), the simulations predict that the kaolinite supersaturation will rise substantially, while the feldspar approaches equilibrium more closely (Figure 1). The simulation results most closely match the field data when a rate of 10⁻¹⁶ mol/m²/s is used, suggesting that an dependence of the kaolinite precipitation rate on pH of about 1 is appropriate.

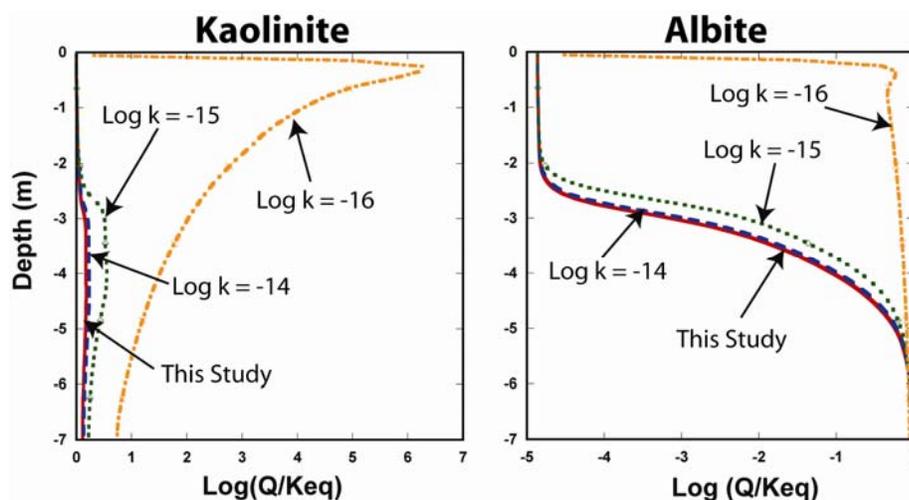


Figure 1: Reactive transport simulations of kaolinite and albite saturation state in the Santa Cruz chronosequences. The best match with the data is provided by a $\log k_{\text{kaolinite}}$ of about 10^{-16} mol/m²/s, suggesting a pH dependence of about 1 for the precipitation rate. The profile marked as “This Study” corresponds to the rates determined in the laboratory at pH 4.

Nanoparticle Aggregation in Natural Aqueous Systems

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Objectives: The project goal is to achieve a quantitative understand of the way that aggregation, and aggregate morphology affects the accessibility and effective reactivity of the surfaces of natural nanomaterials in the environment. Nanoscale oxide and oxyhydroxide minerals play important roles in adsorbing and sequestering aqueous ions including nutrients such as phosphates and contaminants such as heavy metals. These materials are typically subjected to natural flocculation events upon formation that reduce the nanoparticle surface area that is accessible by aqueous ions. In prior research, we demonstrated that aggregation pathway affects pore geometry and consequently the rate and extend of metal ion uptake by the nanoparticle surfaces. Crucially, however, no quantitative relationship exists between simple measures of aggregate structure (e.g., porosity or surface area) and sorption capacity. We proposed that aggregation principally retards the diffusion of aqueous ions, requiring kinetic modeling.

Project Description: We synthesized a suspension of approximately 6 nm iron oxyhydroxide nanoparticles and formed dense aggregates by subjecting the suspensions to drying and rehydration. We used small-angle x-ray scattering (SAXS) to characterize the pore morphology of aggregates. Three-dimensional models the aggregates that are consistent with the SAXS data were generated using numerical approach described by Hedstrom et al., *Langmuir* **20**, 1535 (2000). The models were transformed into 2D slabs and we implemented a novel lattice Boltzman (LB) method capable of simulating diffusion and sorption processes. As shown in **Figure 1b**, the new LB scheme is able to

model the simultaneous diffusion and adsorption of aqueous ions in pore networks of arbitrary complexity.

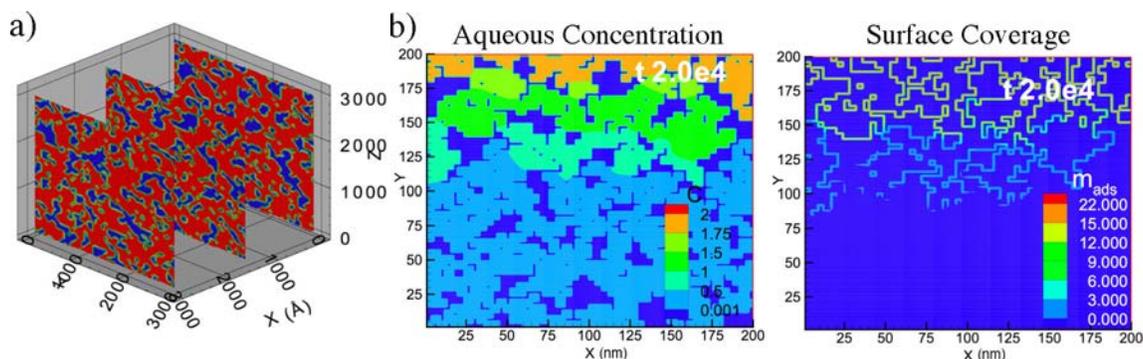


Figure 1. (a) Slices through 3D model of nanoporous aggregate structure derived from SAXS data. Solid aggregate (red) and water pores (blue) (b) 2D images of lattice Boltzmann simulations of copper ion diffusion and sorption within nanoporous aggregates. A constant copper concentration is imposed at the top, and the left image shows the diffusion front that is propagating downwards. Solid regions are shown dark blue. The right image shows the copper coverage on the solid surfaces.

Results: By performing lattice Boltzmann (LB) simulations of aqueous ion diffusion within models of nanoparticle aggregates derived from the SAXS data, we showed that solute transport is retarded by the tortuous pore morphology by over two orders of magnitude. Moreover, adsorption and desorption processes further attenuate uptake and release of metal ions by nanoparticle aggregates. This work will lead to better understanding the relationship between aggregation and effective surface reactivity.

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

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

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

interface. Variations on these techniques also yield specific information such as the redox state of surface atoms, or the lifetimes of particular surface species.

Results: Our most recent work focuses on the hematite, goethite, diaspore and corundum surfaces. For hematite we are interested in the surface variations produced by acids or bases, as well as the geometry of sorbed species like arsenate or silicate. Both CTR and GUXAS results have shown that the geometry of monomeric silicate sorption is as a bidentate complex with strong surface attachment. Molecular dynamic simulations and *ab initio* calculations have verified the relative stability of the experimentally deduced topology. For the goethite surface we found that the surface is relaxed from the bulk, but also has two distinct layers of ordered water at the termination (Figure 1). The water has a structure similar to that of ice XI, and our analysis is able to deduce the local dipole moments so that a direct comparison with PS-SFVS is possible. Analogous surface refinements are in progress for the aluminum-analog of goethite—diaspore. Our surface SFG water studies show that the pH point of zero charge (PZC) for clean corundum (0001) faces is ca. 6.3, rather than the ca. 9.0 measured for corundum powders. Continuing work suggests the differential is due to the types of Al hydroxyl sites exposed in powders. The silicate/hematite work is vital to an understanding of how the reactivity of natural Fe oxide surfaces changes in varied environments, and whether effective remediation approaches for particular pollutants are efficacious. The goethite and diaspore work are crucial to the application of surface complexation modeling with accurate molecular parametrization. For example, current models assume bulk-goethite like structure for the interface, which we show is not accurate. Work in progress will compare the interface structures and interface water of goethite and diaspore, as well as changes due to acid-base treatments.

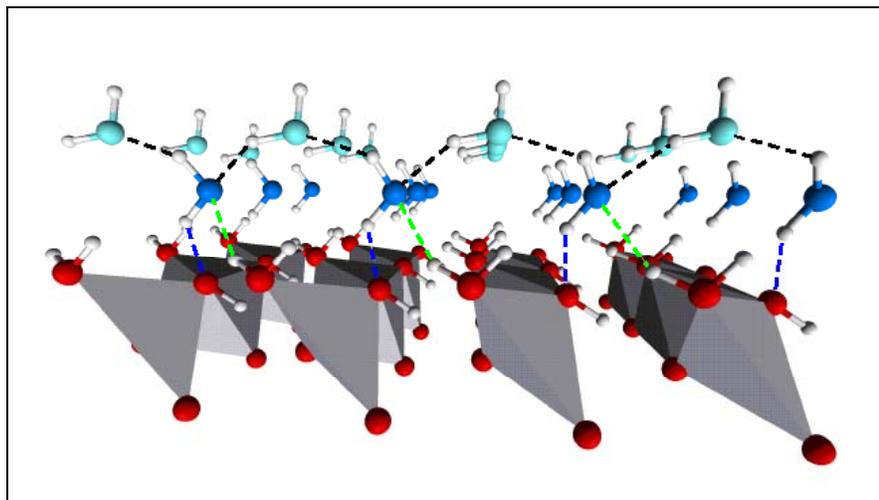


Figure 1. CTR-determined model for the (100) Goethite surface with two layers of ordered water and two surface hydroxyl sites. Dashed lines indicate the positions of hydrogen bonds. The water layer closest to the surface is bound by the $-OH$ acceptor site (blue), and by the $-OH_2$ donor site (green).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

How Does Nanoparticle Structure Control Interfacial Phenomena?

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Objectives: Our past work has shown that nanoparticles differ in structure and strain depending on their precise chemical environment. It is also anticipated that structure, strain and reactivity may change as a function of size. Our investigations aim to characterize possible differences in sorption mechanisms as a

function of Fe oxyhydroxide (goethite and ferrihydrite) nanoparticle size, growth rate, and degree of aggregation.

Project Description: Our studies are done using a combination of molecular probes, bulk measurements, and thermodynamic measurements. Some of the analysis is done in concert with molecular dynamic simulations. For nanoparticle size and shape we employ small angle x-ray scattering (SAXS) and dynamic light scattering (DLS), while the specific molecular nature of surface species is determined with extended x-ray absorption fine structure spectroscopy (EXAFS). Other aspects of nanoparticle structure are determined via determination of pair correlation functions with high energy wide angle x-ray scattering (WAXS). The x-ray measurements are done at the APS (Advanced Photon Source) and SSRL (Stanford Synchrotron Radiation Laboratory) synchrotron sources.

Results: Most recent work has focused in two areas.

1) The nucleation and initial growth of nanoparticles on quartz and other single crystal surfaces have been studied as models for how natural surfaces become either activated or passivated by such nanoparticle development. We developed a grazing-incidence SAXS technique which allows examination *in situ* of the initial phases of nanoparticle growth under bulk water solution, the first time this has been accomplished. The technique has been used to study heterogeneously-nucleated iron oxyhydroxide nanoparticle formation on quartz as a function of solution ionic strength, iron concentration and temperature. We find very strong dependence of the early nanoparticle size and shape on ionic strength, and a changeover in growth mode as size increases. Surface features such as steps and terraces have an effect on nucleation at the earliest stages, with nucleation tending to occur on terraces near steps. After initial nucleation, secondary nucleation events occur on already nucleated particles, leading to a different growth topology.

2) The effect of different ligands on the structure of ZnS nanoparticles show well-defined regimes of behavior depending on the strength of the ligand-zinc bond (Figure 1). Strongly bound ligands like water have a dramatic effect on the surface, reducing strain throughout the nanoparticles, while weakly bound ligands like methanol allow considerable strain to persist post formation, creating a well-defined core-shell structure. Intermediate strength bound ligands show a weaker core-shell topology. These effects have now been studied by combined experimental measurements and MD simulations, with excellent agreement. Analogous experiments are in progress with TiO_2 nanoparticles.

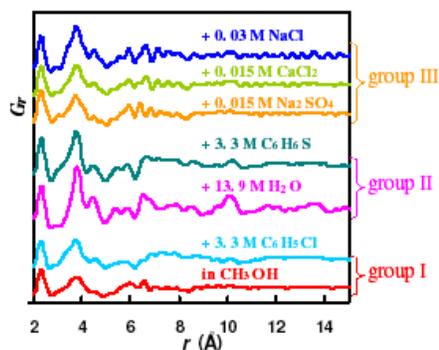


Figure 1. Pair correlation functions for ZnS nanoparticles as a function of different types of surface ligands. The groups represent strong binding (group III: NaCl, CaCl₂, Na₂SO₄), medium strength binding (group II: C₆H₆S, H₂O), and weak binding (group I: CH₃OH, C₆H₅Cl). The structural order in the nanoparticle is a function of the binding strength, e.g. methanol ligation leads to strongly distorted surface structure and considerable structural strain, while Cl ligation allows surface relaxation and less overall strain.

Imaging Electronic and Atomic Redistribution during Redox Reactions at Surfaces

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Objectives: A number of important geochemical reactions are activated by electron transfer at mineral surfaces. Processes include reductive and oxidative dissolution, coupled redox-sorption of complexes, respiration of surface-associated biota, photoactivated reactions, and electrochemical cell reactions. Our research focuses on electron-transfer initiated dissolution reactions, which are important drivers for acid mine drainage development and pollutant transfer in the environment. The actual electron transfer is faster than can be studied by currently available means, but the series of succeeding relaxation steps can be probed to elucidate much of the reaction mechanism.

Project Description: In reductive dissolution electrons are transferred from solution species via shared surface ligands to surface metal ions, like Fe(III), producing surface Fe(II) species. The Fe(II)-O bonds at the surface must lengthen from this reaction, introducing surface vibrations and a general expansion of the surface. This localized strain may act to limit the numbers of Fe(II) that can be produced at the surface, depending on the rate of electron transfer within the mineral. We wish to measure the rate of Fe(II) buildup on Fe oxide surfaces and the ultimate concentration limit, as well as surface and bulk conduction rates. These processes are slower than electron transfer, but for investigation microsecond to picosecond time-resolution is necessary. We are conducting such experiments at the APS (and soon also at the ALS) starting with observations of Fe(II) creation from a photostimulated ligand attached to Fe oxide nanoparticles and single crystal surfaces. A femtosecond laser system activates electron transfer from the ligand, and the synchrotron x-rays detect the result at variable delay times after the excitation. This is a “pump-probe” experiment. Part of the project includes development of fast surface diffraction methods using new 2D pixel detectors, and custom designed software.

Results: Our first static experiments at the APS beamline 13ID showed proof of concept with respect to electron injection from the organic ligand alizarin red into the (1-102) hematite surface. A significant amount of surface Fe(II) is produced within minutes of exposure to the dye. We observe the Fe(II) by collecting surface diffraction data via the (10L) crystal truncation rod. Our first time-resolved experiments at the APS beamline 11-ID using nanoparticle maghemite 11-ID showed measureable Fe(II) creation in 2 nm with eosin Y surface ligands with a time delay of 154 nanoseconds, but no similar effect using alizarin red. In these experiments the nanoparticles were studied in a continuously refreshed slurry, and the near Fe K-edge x-ray absorption spectra was collected (Figure 1). The static results with large single crystal hematite surfaces, when compared with earlier thesis work, suggest that significant concentrations of sorbed Fe(II) are not stable for long time periods, but convert quickly to structural Fe (III) which fills up typically vacant metal sites on the surface. This conversion rate is unknown, but may be accessible when full time-resolved experiments commence.

Another complex issue with such experiments is the possibility of laser heating damage created by the pump pulse. We examined this thoroughly by using different laser spot sizes and pulse totals while continuously monitoring sensitive positions on one off-specular truncation rod. A noticeable drop in rod intensity signaled a change in atomic positioning. These experiments showed that heating effects were

observed only after a large number of pump pulses, so that the typical pump-probe experiments we plan should not be limited by laser damage, even if the same sample spot is used. Follow up experiments will detail the processes by which heat is dissipated after each pulse.

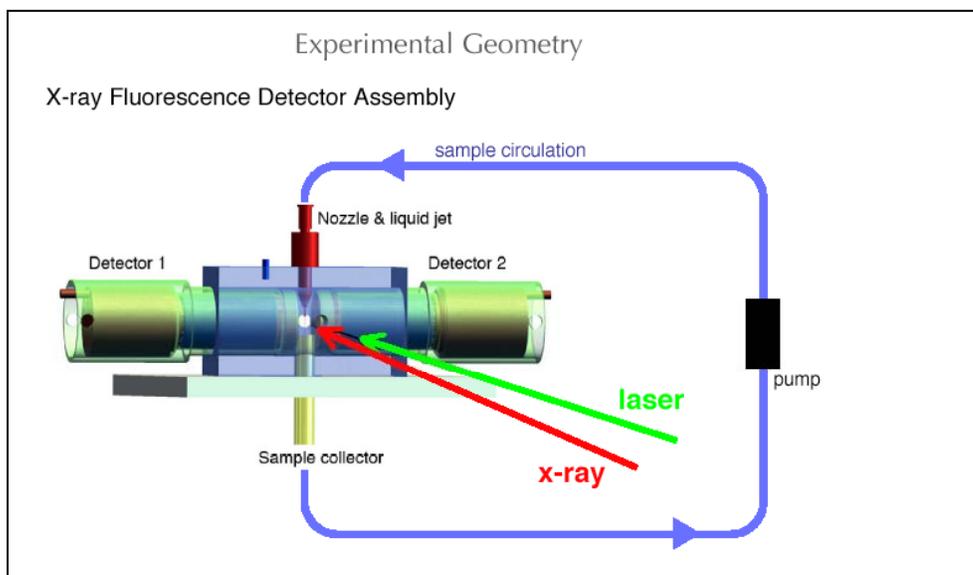


Figure 1. Scheme for studying electron injection into nanoparticles using laser pump-x-ray probe technology, and a continuous moving slurry sample. The actual laser and x-ray beams are co-incident and excite the same liquid stream volume. Laser intensity is typically 1.0 millijoule, with maximum repetition rate of 1.4 KHZ. Experimental setup is at the APS sector 11 ID-D.

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 CO₂ 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-CO₂ interaction along a flow path as part of planned CO₂ pilot injection tests, 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 CO₂-Injection:*

The primary sites being considered for underground sequestration of anthropogenic CO₂ 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 CO₂ 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/H₂O volume ratio. Noble gases are well suited for chromatographic separation studies because they exhibit a smooth increase in solubility by a factor of ~10-15 from Ne to Xe and are

chemically inert with very low concentrations in most rocks and minerals, minimizing the effects of potential water-rock interaction. During and after CO₂ injection, temporal and spatial changes in the isotopic compositions of various solutes (e.g. Ca, Sr, Pb, C, O) are expected to trace the occurrence and rates of mineral dissolution and precipitation driven by changes in the chemical attributes of the water-rock system as a result of CO₂ injection.

Results: *Isotope Tracers and CO₂-Injection:*

Our initial work has focused on gas-water interaction using noble gases as phase-partitioning tracers. For proof of concept, a noble gas monitoring project was conducted as part of a CO₂ sequestration experiment in the Frio Formation in the Gulf Coast South Liberty Field, Texas in which noble gases along with other tracers were injected along with the CO₂ stream and monitored downstream. A significant difference in the peak arrival times for Kr and SF₆ was observed leading to an inferred integrated aqueous phase saturation of ~32-45%. If the rate limiting step for equilibrium partitioning between the CO₂-water phases, then the degree of aqueous saturation implies a characteristic length scale for the water phase of ~10-100 cm, consistent with CO₂-water fingering. The pilot test demonstrated the utility of phase-partitioning tracers, such as noble gases, in defining reservoir environments and processes relevant to geologic sequestration of CO₂. Currently we are formulating field projects in support of the SECARB and WESTCARB demonstration projects and measuring the solubility partitioning of noble gases between CO₂ and water at the P and T conditions appropriate for deep sequestration.

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, CO₂ 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 (³⁶Cl) and radiogenic noble gases (⁴He and ⁴⁰Ar) were measured to assess the residence time of old groundwater in the Nubian Aquifer of the Western Desert of Egypt. A systematic increase in the amount of radiogenic ⁴He that accumulated in the groundwater along the inferred flow path confirmed the age progression indicated by the ³⁶Cl/Cl ratios, but a flux of external radiogenic ⁴He equivalent to ~3.5 times the in situ production rate of the aquifer is required to reconcile the ⁴He accumulation ages with those determined from ³⁶Cl. Furthermore, a divergence of the oldest sample (~650 kyr) from a linear trend between the ³⁶Cl age and the amount of accumulated ⁴He suggests the external ⁴He flux is not constant along the entire flow path. We are expanding this line of research to include other radio-chronometers, such as ⁸¹Kr, by investigating old groundwater from aquifers of the mid-continental United States. An initial suite of samples collected from springs and wells predominately across Kansas and Missouri have analyzed and a second suite has been collected.

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.

Project Description: In addition to experiments involving diffusion in silicate melts (described elsewhere in this volume by Richter et al.), the project also involves determining the magnitude of isotope fractionation of dissolved species by diffusion in water and using these to validate molecular dynamics calculations for the relative mobility and isotopic fractionation of Ca, Mg, K and Li. The experiments use a simple diffusive system that acts as a Rayleigh fractionator. The system consists of a small spherical container that communicates via a small tube with a much larger volume in which it is immersed. We fill the spherical container with a solution of the dissolved salt of the element to be measured for kinetic effects, and allow diffusion to the larger volume of initially pure water. Different diffusive pairs are run for different length of times, after which the run products are measured for their isotopic composition by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) (or by TIMS as appropriate). The resultant data from the experiments provides determinations of the relative diffusivities of elements or isotopes.

Results: In our previous research, we found no measurable diffusive isotopic fractionation of magnesium, but small but well-resolved isotopic fractionation of both Li and Cl (Richter et al., 2006). Molecular dynamics (MD) calculations by Ian Bourg and Garrison Sposito have reproduced these results (Bourg and Sposito, 2007). From the simulations they suggest that the small isotopic fractionation we observed for diffusion in water compared to that in silicate melt, is related both to the number of water molecules in hydration spheres around the dissolved ions as well as the residence time of water in the inner hydration shell.

Our measurements of experiments involving diffusion of K in water have demonstrated fractionation of the $^{41}\text{K}/^{39}\text{K}$ ratio of up to ~ 8 ‰ relative to the starting solution (Fig. 1). The data indicate a fractionation factor of 0.9979 ± 0.0001 , representing the ratio ($D^{41}\text{K}/D^{39}\text{K}$) of the relative diffusivities of ^{41}K and ^{39}K ions in water. Similar experiments for Ca isotopic fractionation by diffusion in water (Fig. 2) reveal a much smaller but resolvable fractionation effect. The data indicate a fractionation factor (for $^{44}\text{Ca}/^{40}\text{Ca}$) of 0.99956 ± 0.00005 . These values agree well with results of MD calculations by Bourg et al. (in prep) indicating values of 0.9976 ± 0.0009 and 1.000 ± 0.001 for $D^{41}\text{K}/D^{39}\text{K}$ and $D^{44}\text{K}/D^{40}\text{K}$ respectively. Compared to Ca^{2+} , this would be consistent with a lower charge density for the K^{1+} ion, and implies a shorter residence time for H_2O in the hydration sphere of K^{1+} .

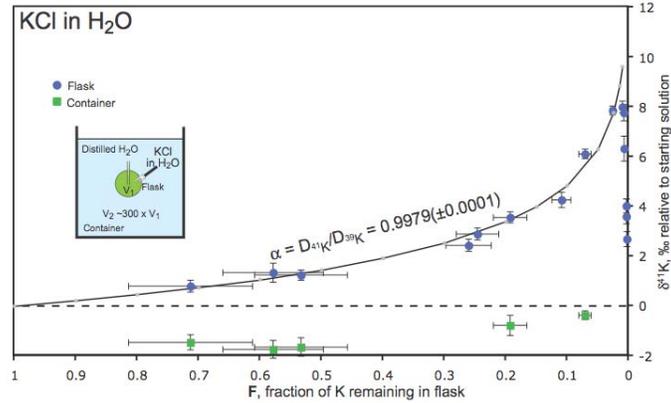


Fig. 1. Plot of $\delta^{41}\text{K}$ against F , the fraction of K remaining in the source reservoir (V_1), for experiments regarding the diffusion of K^+ in water. Inset shows a cartoon of the experimental set up. Results for flasks run up to $F \sim 0.02$ indicate an isotopic fractionation factor of 0.9979 ± 0.0001 , which was used to calculate the black curve. Experiments run past $F=0.01$ have been affected by the finite volumes of the sink (V_2) and source (V_1) reservoirs. The green squares are data for the companion containers for the flasks, and show the expected isotopically light K diffusing from the flask to the container volume.

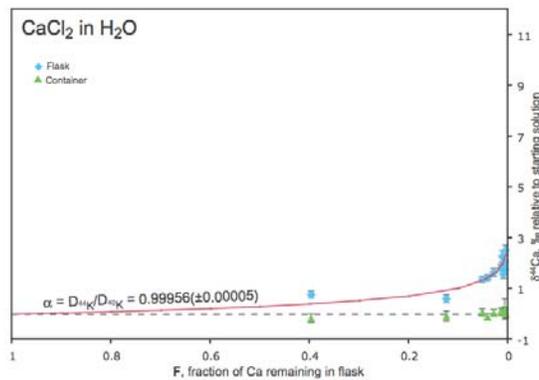


Fig. 2. Plot of $\delta^{44}\text{Ca}$ against F , the fraction of Ca remaining in the source reservoir (V_1), for experiments regarding the diffusion of Ca^{2+} in water (similar set up as shown in inset to Fig. 1). Results for flasks run up to $F \sim 0.01$ indicate an isotopic fractionation factor of 0.99956 ± 0.00005 , which was used to calculate the red curve. Experiments run past $F=0.005$ have been affected by the finite volumes of the sink (V_2) and source (V_1) reservoirs. The green squares are data for the companion containers for the flasks, and show the expected isotopically light Ca diffusing from the flask to the container volume. The scale is similar to Fig. 1.

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: In the first year, we conducted a series of seismic anisotropy measurements in granular sediments using a special compaction cell equipped with ultrasonic transducers. Packs of water (or brine)-saturated spherical glass beads, silica sands (with both smooth and extremely rough surface textures), and halite crystals were compacted, and the resulting evolution of seismic velocities and anisotropy was determined. The glass bead and silica sand tests were conducted as a function of cyclic compaction stresses up to 8 MPa. Because of the large friction between the grains, the seismic properties of the sand samples changed dramatically compared to the glass-bead sample, after the first cycle of loading was applied. The halite compaction experiment was conducted under a constant temperature and stress (25°C and 0.5 MPa). A porosity reduction of up to 6% was observed in the sample within 3 weeks, owing to the pressure dissolution. During the sediment compaction, both P and S wave velocities increased monotonically with reducing sediment porosity. However, all the samples exhibited decreasing S-wave anisotropy with compaction (porosity reduction), while P-wave anisotropy showed the opposite behavior (anisotropy increase). This result is somewhat inconsistent with what we observed previously, and the cause of this behavior is under investigation. An example of the seismic anisotropy evolution for the halite sample is shown in Figure 1.

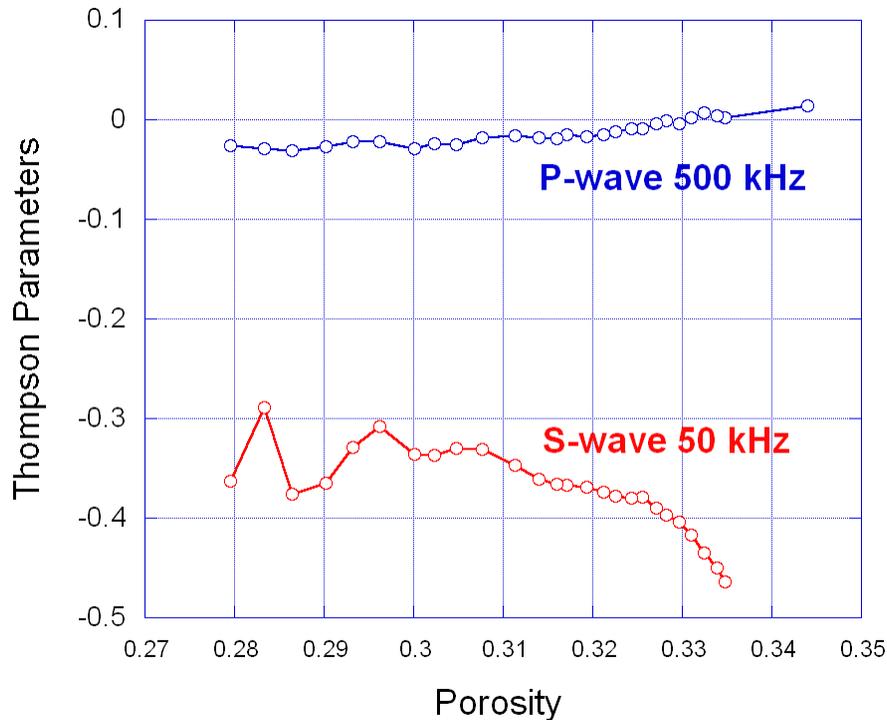


Figure 1. Evolution of transverse seismic isotropy during pressure-dissolution-induced compaction of a halite pack. The blue and red circles indicate the Thompson's ϵ and γ parameters respectively (for P-wave and S-wave anisotropy). With compaction (reducing porosity), P-wave anisotropy increased in magnitude while S-wave anisotropy decreased.

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.

Results: One area of effort during FY08 was testing solutions of the boundary value problem for scattering of elastic waves by a spheroidal inclusion that had been developed in the previous year. This involved developing and testing the numerical accuracy of a small library of computer subroutines for calculating spheroidal eigenfunctions over a large range of parameter values. This phase of the research was nearly completed and a paper describing the method and results is also close to completion. The incorporation of these results into the composite media method that had been previously developed should be straightforward.

Good progress was also achieved on the task of calculating synthetic seismograms in three-dimensional media. A general and flexible method was developed for describing earth models that have both smooth and abrupt variations in material properties and the equations for dynamic ray tracing were solved and implemented in computer programs for these types of models. The remaining step is to incorporate these results into the Maslov integral method.

The scope of the research was slightly expanded during the past year to accommodate specific applications to geothermal problems. This involved the development of a new approach to small seismic sources that treats an earthquake as the failure of asperities. The theory for elliptical asperities was developed and the problem of dynamic interaction of multiple asperities was also solved. Computer programs that implement this new approach were developed and these are now being tested. A paper describing these results is also nearing completion.

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 wavefields, 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 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 CO₂. 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 unequivocal models. Joint inversion of such data is a better approach and allows for an objective testing of different geophysical parameters (conductivity, velocity, density) and their fluid property interrelationships on experimental data. The types of electromagnetic, seismic and gravitational data to be considered include, controlled

and natural source electromagnetic measurements, amplitude and travel time seismic data sets, gravitational vector fields and corresponding gradiometer measurements.

Results: Because the grids used to simulate electromagnetic (EM), seismic and gravity data are different, due to the respective methods differing resolving power, it makes sense to impose an independent grid for the joint imaging of the different types of data. Underlying grids used to simulate the EM, seismic and gravity fields are distinct and grid transfer operators are required to (1) transfer material properties from the common imaging grid to the respective simulation grids and (2) map the gradients of the cost functional for the different data types from the simulation grids to the inversion grid. Grid-transfer operators for the EM and gravity problems have been developed. Corresponding operators for the seismic problem have yet to be developed, but will be based upon the well known Backus averaging relationships. We have demonstrated this concept in the context of 3D controlled electromagnetic inversion and we believe this provides the framework to make joint 3D imaging practical.

3D gravity and gradiometer simulators have now been developed and tested. These simulators have now been incorporated with a massively parallel 3D EM field simulator and will ultimately provide an algorithm for joint geophysical imaging. In this algorithm we have also implemented a cross gradient constraint to link the geophysical properties for structural similarity on the common imaging grid. This constraint has also been generalized for seismic velocity and will be enforced in the inversion process using as a penalty scheme, where the objective functional to be minimized is penalized if the cross gradient constraint is not sufficiently satisfied. The inversion update is also to be obtained using gradient based descent methods with a simple line search so large scale geophysical image and data volumes can be efficiently treated. For the seismic problem we have completed the initial development of a 3D Eikonal simulator for travel time data. This simulator also provides the derivatives of the travel time data with respect to discrete seismic velocity model using a ray tracing methodology. While testing of the seismic simulator is ongoing, results thus far are encouraging.

Once the different geophysical simulators have been coupled, we will direct our attention to investigating the coupled conductivity-velocity-density images for fluid property interrelationships on synthetic and experimental data at controlled sites where verification can be made.

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: Starting FY2008, the focus of the work has shifted specifically to the seismic properties (velocity and attenuation) of unconsolidated grain packs. Attenuation data on sand packs shows there to be more attenuation than the usual Biot theory of macroscopic (wavelength) flow can account for. To explain the additional attenuation, it is first observed that grain packs have a large amount of stress fluctuation over the grain contacts in the packing which results in mesoscopic-scale patches having different frame moduli. We modeled this both with the analytical double-porosity model and our finite-difference modeling of the poroelastic equations. Unfortunately, even when great attention was made to model all parameters properly, not enough attenuation was produced to explain the measured levels of attenuation in sand packs at low confining pressure. Although the mesoscale fluctuations in the frame moduli are large in the grain pack in a percentage sense, the frame moduli are small relative to the modulus of water at low confining pressure and thus significant fluid-pressure fluctuations are not induced by seismic compression.

To resolve the situation, we proposed, in collaboration with Jim Berryman, that perhaps rattler grains are responsible for the missing 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 shaken 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 great detail 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 moduli does not correspond well to the experimental measurements which are closer to 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 rotate 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 bearing stress. This mechanism has been analytically modeled in great detail and can explain the lab measurements. Work is ongoing into obtaining the observed levels of stress fluctuations over the grain contacts via this mechanism.

Last, in the laboratory, we are measuring the mesoscale fluctuation elastic properties on actual rocks. The method is to use a servo-controlled indenter to measure the fluctuations of the “surface” or “indentation” modulus over the surface of planar rock slabs. The apparatus has been built and experiments and calibrations have begun.

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 sub-surface flow properties in a deformable medium. A key feature of this work is the development of new ways to relate changes in geophysical observations directly to flow properties. The ultimate goal is to further our understanding of multi-phase flow in the 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) A trajectory-based method for modeling quasi-static deformation in a poroelastic medium (2) How to use time-lapse Interferometric Synthetic Aperture data to image permeability variations within a reservoir (3) A semi-analytic solution for the modeling of flow in a medium with pressure-sensitive flow properties.

A Trajectory-Based Method for Modeling Quasi-Static Deformation in a Poroelastic Medium -

Using an asymptotic methodology I have derived a trajectory-based solution for pressure and displacement in a poroelastic medium. The technique provides semi-analytic expressions for the travel time and amplitude of pressure changes and deformation. As such, they are useful in treating the inverse problem in which one tries to estimate properties of the medium, elastic moduli and flow properties, using pressure and displacement observations. The method was developed for a medium with variable flow properties and constant geomechanical properties. An extension for layering was also developed. A comparison of the method to a purely numerical approach indicates fairly good agreement. A paper describing this work was published in the *Geophysical Journal International*.

Using Time-Lapse Deformation Data to Infer Permeability - Transient pressure variations within a reservoir can be treated as a propagating front and analyzed using an asymptotic formulation. From this perspective one can define a pressure 'arrival time' and formulate solutions along trajectories, in the manner of ray theory. I combined this methodology and a technique for mapping overburden deformation into reservoir volume change as a means to estimate reservoir flow properties, such as permeability. Given the entire 'travel time' or phase field, obtained from the deformation data, I constructed the trajectories directly, there-by linearizing the inverse problem. A numerical study indicated that, using this approach, one may infer large-scale variations in flow properties. In an application to Interferometric Synthetic Aperture (InSAR), observations were made associated with a CO₂ injection project at the Krechba field, Algeria. Two papers describing this work were published in the journal Geophysics.

Derivation of an Semi-Analytic Solution for Flow in a Medium with Pressure-Sensitive Properties - Using an asymptotic technique I have derived a semi-analytic solution for flow in a medium in which the porosity and permeability are pressure-dependent. The initial derivation presents a one-dimensional solution for linear, cylindrical, and spherical symmetry. The porosity and permeability are assumed to be separable in the medium, in the form of a product of a spatial dependent term and a pressure dependent term. A comparison between a numerical approach, an analytic solution for a special medium, and the new technique indicates the approach recovers the general variation of pressure. A paper describing this work was submitted to the journal Water Resources Research. Some work extending the approach to three dimensions has begun.

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: Presently, 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 significantly depleted with respect to the noble gas concentrations in an assumed air-saturated water (ASW) source

fluid and lack requisite enrichment/depletion factors needed to explain the noble gas inventory in oil field fluids. On the other hand, noble gases extracted from silica spicules from live sponges (*Calyxnicaeensis*) show (1) significantly enriched Ar, Kr, and Xe concentrations ($[^i\text{Ng}]_{\text{sample}}/[^i\text{Ng}]_{\text{asw}} > 1$), (2) very little if any mass dependence in the acquisition and trapping of Ar, Kr and Xe, and (3) 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 depleted with respect to the sponge spicule and fractionated, favoring the heavy noble gases. Furthermore, unlike the sponge spicule, these samples are strongly enriched in Ne. This identifies an important issue: are the differences in noble gas absolute and relative abundances between the sponge spicule sample and the more evolved diatomaceous samples related to (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? We have initiated a collaborative project with Ben Gilbert (Earth Sciences Division, LBNL) measuring noble gases in laboratory-produced nanoparticle agglomerates. Samples of goethite ($\alpha\text{-FeOOH}$) clusters agglomerated under different pH conditions have absolute and relative abundances of the noble gases that are remarkably similar to the organic silica samples discussed above. 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.

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. Inclusions that are very flat fluid-filled or only partially saturated cracks, and/or dry cracks all might produce strong effects on the seismic wave propagation speed, and also on losses via wave attenuation. Results are particularly important therefore in reservoirs containing arrays of vertical fractures containing fluids, and have implications for estimating fluid permeability, and also pore-fluid type and spatial distribution. While working with researchers in the oil industry having extensive experience with numerical simulations of fractured reservoirs, 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 the pores.

Results: Fractures filled with either gas or liquid have been a major focus of the recent work. Some of this research has been published in Geophysics, and further extensions of the work have been recently accepted for publication 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 method of Sayers and Kachanov (1991) for parametrizing the mechanical behavior of fractured systems. The method has been used very little, but has a natural generalization to permit rigorous analysis of fluid effects on fractured systems. The resulting rigorous formulas differ significantly from the usual ad hoc approach taken by most workers in the field. This new approach (with included fluids) shows explicitly and easily how the fluids influence both compressional and shear wave speeds in fractured media.

Density-Driven Brine Convection: A Process for Accelerating CO₂ 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 CO₂ stored in a saline aquifer to the aqueous phase.

Project Description: CO₂ 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 CO₂ 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 CO₂ 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 glass plates that were either flat or featured different kinds of surface roughness. In these experiments, CO₂ is introduced as a gas at ambient conditions atop the water or brine. Dissolution is monitored and visually recorded through pH-sensitive dyes that were added to the aqueous phase. Video recordings of time-dependent patterns of pH change are enhanced through post-processing (Fig. 1). From the visual recordings, quantitative characteristics of the DDC process are deduced, such as number and wavelength of convective fingers, rates of finger advancement and growth, and increase of dissolved inventory with time.

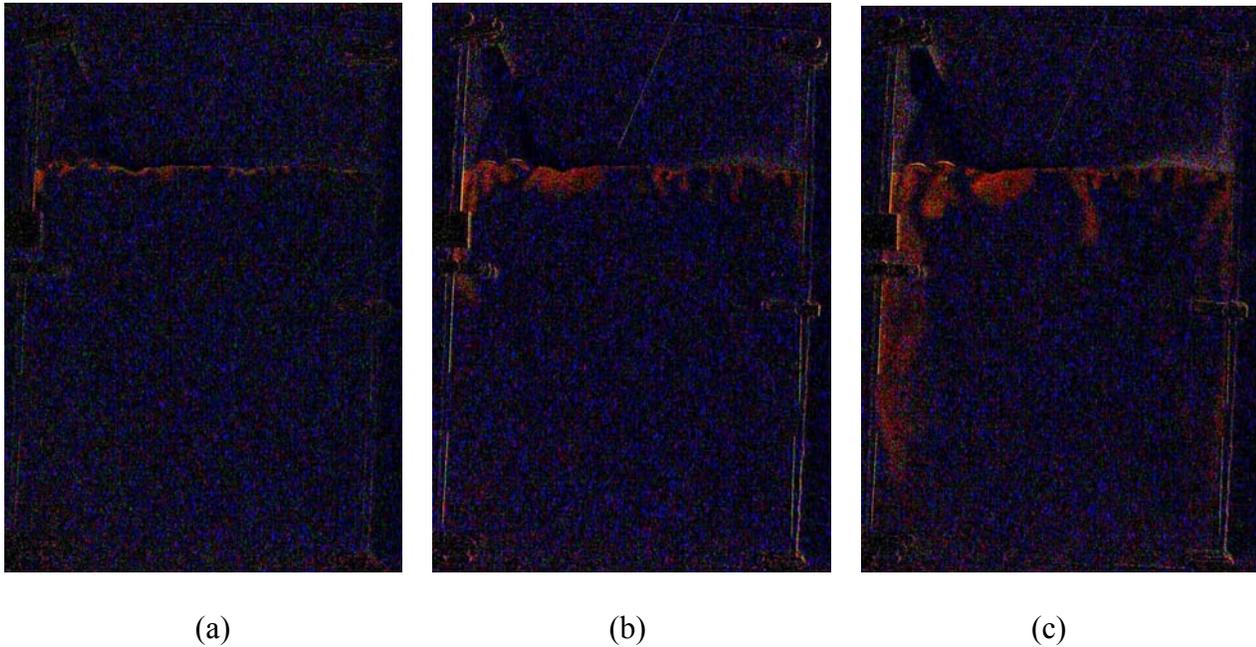


Figure 1. Laboratory visualization of CO₂ dissolution and convection (a - 2 minutes, b - 10 minutes, c - 23 minutes).

Our mathematical modeling efforts focused on adapting our TOUGH2/ECO2N simulator for CO₂ storage to a parallel processing environment. Simulations of the DDC process were performed over a range of spatial scales with resolution down to 0.1 mm, and exploring different hydrogeologic parameters and boundary conditions. Our simulation results show that CO₂ dissolution proceeds through four distinct time periods, as follows.

- 1) At early times, transport of CO₂ away from the dissolution boundary occurs only by molecular diffusion, so that dissolution rate declines with time as $1/\sqrt{t}$, while total dissolved inventory grows as \sqrt{t} .
- 2) This is followed by a period in which convective instabilities begin and grow, leading to a general increase in dissolution rates. These are modulated by significant quasi-periodic variations, as convective fingers partially coalesce and grow.
- 3) The third period is characterized by a continuous downward progression of convective fingers, while total dissolution rates remain constant except for modest random fluctuations of order $\pm 15\%$.
- 4) The final period begins when dissolved CO₂ reaches the lower boundary. At that time, dissolved CO₂ concentrations begin to increase in the upwelling limbs of the convective process, leading to diminished buoyancy force and a gradual decline in dissolution rates.

The final equilibrium state of the system consists of constant dissolved CO₂ concentrations throughout, equal to those applied at the CO₂-brine phase boundary.

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 that form. A long-term goal is to establish the physical basis for biomineralization and accompanying roles of solutes in natural and engineered Earth systems.

Project Description: This work is focused on developing a mechanism-based picture of controls imposed by Asp-rich polypeptides and biomineralizing proteins on the elemental signatures in calcite. We are also probing the transient events and phase evolution during CaCO₃ nucleation at peptide-derivatized templates. In particular, we seek an understanding of the amorphous to crystalline transformation that we recently showed routinely occurs during nucleation at these 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 CaCO₃ nucleation and transformation on peptide derivatized 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: Growth of crystals in biological and geological systems are widely interpreted within classical theories that assume thermal fluctuations of the step are sufficiently rapid to produce an abundance of kink sites for attachment of growth units. Using AFM imaging with true molecular resolution, we have now shown this assumption is invalid for calcite. Instead, steps exhibit low kink density and weak fluctuations. As a consequence, the control of impurities on calcite growth cannot be explained by traditional models based on free energy minimization. By coupling *in situ* AFM measurements of step kinetics with kinetic Monte Carlo simulations of impurity pinning of steps with weak fluctuations, we have found that growth inhibition follows a different mechanism. The formation and spread of new kinks by solute attachment to otherwise complete step edges is blocked by impurity attachment to the steps. This *kink-limited* model offers a plausible explanation for reports of ‘kinetic disequilibrium’ of trace element signatures in calcite and the findings argue for a theory based on weak fluctuations to interpret growth of many common minerals.

We have successfully commissioned our fluid cells and holder for performing *in situ* TEM studies of nucleation from solution (**Fig. 1**). The system exhibits excellent temperature response between 0 and 60°C and has electrochemical control via a working electrode on the gold-coated SiN₄ window through which the electron beam passes. We have developed a sealing procedure that enables to form cells with a thickness between ~100nm and ~1mm. We have shown that, even in 10mm thick cells, we can resolve nanoparticles that are less 5nm in size, follow their diffusion in fluid and observe their growth due to programmed changes in temperature. Most importantly, we have now shown that we can set the operating parameters to induce calcium carbonate nucleation at will on the working electrode and, thus, directly observed nucleation at sub-10nm resolution under conditions of well-defined temperature and chemical potential.

Studies relating the magnesium content of calcified skeletons to temperature often report unexplained deviations from signatures expected for inorganically precipitated calcite. These ‘vital effects’ are believed to have biological origins but mechanistic bases for measured offsets remain unclear. The composition of biologic molecules isolated from biominerals suggests that control of mineral growth must certainly be linked to biochemical features. Building on papers funded by this project that established a relationship between the ability of biomolecules in solution to promote calcite growth and their hydrophilicity, we hypothesize that because 1) cation incorporation is the rate-limiting step to growth and 2) 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 Mg content. In this study, we show that a simple hydrophilic peptide, sharing the same carboxyl-rich character as macromolecules isolated from sites of calcification, increases calcite magnesium content up to 3 mol%. Comparisons to previous studies correlating Mg content with temperature show that the Mg enhancement due to peptides results in offsets equivalent to 7-14°C.

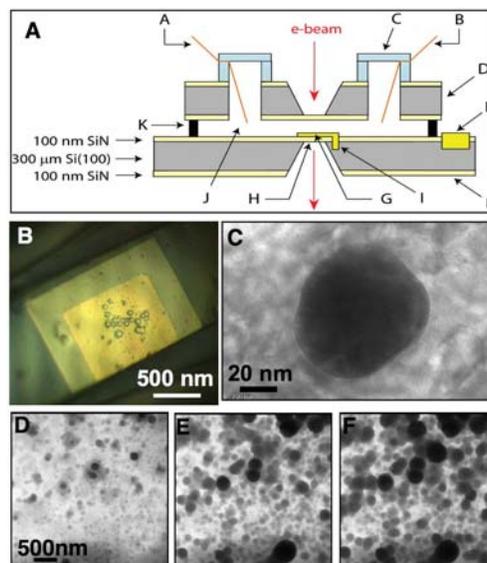


Fig. 1 – (A) Design of TEM fluid cell with temperature and electrochemical control built to investigate surface-directed nucleation at near-molecular scale in real time. Temperature can be varied from 0-60°C and gold electrode on transparent window provides means for inducing crystallization as well as surface for functionalization. (B) Optical image showing calcite nucleation induced electrochemically on electrode in sealed fluid cell. (C) TEM image showing nm-scale resolution of individual gold nanocrystal in sealed fluid cell. (D-F) Sequence of images showing growth of silicone-based colloids.

Fluid Chemistry, Surface Chemistry and Fracture Mechanics: An Investigation of the Connection at the Nanoscale

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Objectives: The project objectives center around two major hypotheses: (1) That the surface chemistry of minerals has a direct influence on fracture mechanics at the molecular scale and (2) that changes in the surface chemistry have a quantifiable influence on the sliding resistance between a scanning probe microscope tip and mineral surfaces. The former objective requires development of new capabilities for the Hydrothermal Atomic Force Microscope (HAFM).

Project Description: The project has two main thrusts toward understanding the principal influences on surface chemistry of carbonate minerals upon exposure to aqueous solutions. These areas include the

elucidation of lateral force contrast mechanisms in mineral/water interface systems and of the coupling processes among fluid chemistry, surface chemistry, and applied stress and the resulting impacts on subcritical crack growth (SCG) and mineral growth/dissolution using *in-situ* scanning probe microscopy (SPM). Our approach is to quantify the friction forces between an atomic force microscope (AFM) probe tip and carbonate mineral surfaces of interest using frictional force microscopy (FFM). In addition, the surfaces are fully characterized using fluid cell AFM measurements of growth and dissolution kinetics and x-ray reflectivity measurements. These methods of characterization allow us to describe both the thermodynamic properties of the surface layers as well as their atomic-scale structure and composition. The FFM measurements then enable us to relate the mechanical surface properties to the chemical and physical properties in a manner that could lead to future applications of the AFM as a surface chemistry-mapping tool with nanometer-scale resolution. In order to achieve the objective of developing improved models for the coupling of fluid chemistry, surface chemistry and mechanical stress at mineral-fluid interfaces, the project will develop a mini-bending jig for the HAFM and make extensive modifications (see Results below) to accommodate the jig and to greatly increase the HAFM scan range. The results from this project will improve our understanding of the surface chemistry of carbonate minerals relevant to surface and subsurface aquifer systems under mechanical stress and on a distance scale (nanometers) that can be computationally modeled at the semi-empirical level.

Results: During this third year of the project we continued our extensive modifications of the HAFM to permit studies of the connection between mechanics and chemistry. In the first two years we developed a mini-bending jig for the HAFM. We redesigned the HAFM to use a longer piezo tube that extends the x-y scan range from 30 to 120 μ and the z-range from 1.2 to 2.3 μ . We devised a new Kalrez[®] membrane shape and used a new composition material for the membrane that has a higher T limit, lower durometer (it's softer), and yet has a lower gas permeability. After calibrating the new HAFM, we made our first real SCG measurements and realtime movies of the process in the HAFM under controlled T, P, and fluid chemistry conditions, including switching fluid composition during an experiment. We redesigned the HAFM to use the new style TopView[©] optical head, that provides the ability to make lateral force measurements (frictional force microscopy) and also allows realtime movie making using the optical CCD camera. The base plate for the optical head was redesigned to use a kinematic mount consisting of 80-pitch screws, allowing fine positioning/focusing of the laser on the tip and to permit flow of cooling water through it. We designed and had manufactured (Watlow) an etched foil heater for the larger flow cell.

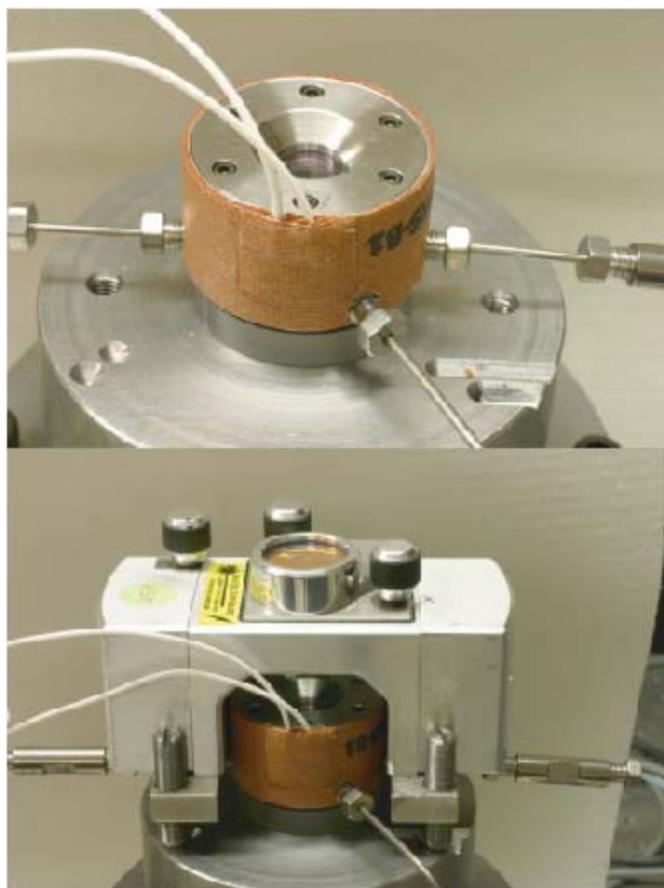


Fig. 1 Etched foil heater for HAFM

This year we used a reactive transport simulator (CRUNCHFLOW, developed by Carl Steefel at LBL) to model the interaction of aqueous CrO_4^{2-} with the mineral barite (BaSO_4). The model was benchmarked against Plug Flow Reactor experiments run as part of PhD research being done by a WSU student. We also completed the testing of the new etched foil heater designed for the HAFM, which was initiated at the end of last year, but completed early this year. Fig. 1 shows the new heater in place on the HAFM. Finally, we began the process of migrating a significant amount of equipment from LLNL into a new lab constructed at LBL. We maintain an office at LLNL and continue to have access to labs and equipment left behind.

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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 CO₂-bearing fluids. This will be achieved through equation of state measurements of H₂O- and CO₂-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 H₂O) and carbon (as CO₂). Despite the essential role of deep fluids in subduction zone processes, the absence of experimental thermodynamic data precludes quantitative modeling of reactions and mass transfer in this setting. The vast majority of aqueous geochemistry studies have been conducted at pressures below ~0.3 GPa, and the widely-used Helgeson-Kirkham-Flowers equations of state for aqueous species are applicable to ≤ 0.5GPa (~ 15km depth). The aim of this project is to determine the sound velocities, equations of state (EOS), and atomic-scale structures of model fluid systems to the high pressures and temperatures appropriate to subduction zones. Brillouin scattering measurements of velocities and EOS on aqueous fluids will be performed to at least 10 GPa and 700° C, and X-ray and neutron scattering experiments will be performed to constrain the atomic-scale structures of the same solutions.

Results: In FY08 we initiated this project and began measurements. 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. In FY08 the LLNL group produced the prototype membrane diamond-anvil cell for use in Brillouin scattering measurements with a ~50° scattering geometry. The UIUC group modified the Brillouin spectrometer to accommodate these membrane cells. The cells were tested and Brillouin spectra were collected jointly by the UIUC and LLNL groups in late FY 08 on compressed CO₂. The cells performed well over a week of measurements and Brillouin data were collected on liquid CO₂ and several solid CO₂ phases (I, II, III). Subsequently, modifications to the diamond-cell design were made to allow for 90° scattering, which will be advantageous for all future measurements.

Reactive Fluid Flow through Variable Aperture Fractures: Permeability Alterations Due to Dissolution

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Objectives: The objective of this project is to explore the local mechanisms that lead to transmissivity alterations in variable-aperture fractures under conditions that cause coupled chemical alteration and mechanical deformation of fracture surfaces.

Project Description: Many energy-related problems involve coupled subsurface processes that can significantly alter the permeability of fractured rock masses. This project integrates experiments in transparent analog fractures with the development of large-scale computational models in which the small-scale physical processes are represented explicitly. Transparent, variable-aperture fractures fabricated by mating a rough glass surfaces with smooth reactive surfaces (e.g., KH_2PO_4 , CaCO_3) allow reproducible experiments in fractures with well-characterized surface mineralogy. Previously developed light transmission methods yield high-resolution ($83 \times 83 \mu\text{m}$ pixels at $\pm 4 \mu\text{m}$ measurement resolution) measurements of fracture apertures over the entire fracture repeatedly during experiments. Computational algorithms developed during this project are built upon a library of scalable routines developed at LLNL for solving large systems of linear and nonlinear equations on massively parallel architectures. Thus, models developed to simulate chemical alteration and mechanical deformation of individual fractures at the laboratory scale (tens of centimeters) can be directly scaled to large single fracture and networks of fractures that are on the scale of tens of meters without using up-scaled constitutive relationships.

Results: Previous experiments demonstrated the influence of mineral dissolution on fracture transmissivity in variable aperture fractures when the fracture surfaces are fixed in space and when a steady normal stress is applied to the fracture surfaces. In FY08, we continued development and evaluation of a parallelized model of fracture flow and reactive alteration. The computational model provides a means for exploring the response of individual fractures to mineral alteration over a much broader range of parameters and larger scales than are feasible in laboratory experiments. Previous theoretical and experimental results suggest that the influence of mineral dissolution on transmissivity alteration will be sensitive to two dimensionless parameters: the Peclet number ($Pe = \langle V \rangle \langle b \rangle / D_m$, where $\langle V \rangle$ is the mean fluid velocity in the fracture, $\langle b \rangle$ is the mean fracture aperture, and D_m is the molecular diffusion coefficient of the dissolved mineral in the aqueous phase) quantifies the relative magnitudes of advective and diffusive transport and the Damkohler number ($Da = k / \langle V \rangle$, where k is the reaction rate coefficient quantifying mineral dissolution at the fracture surfaces) quantifies the relative rates of mass transfer from the dissolving surfaces and advective transport of dissolved species through the fracture. **Figure 1** summarizes results from a computational parametric study of the relative influence of Pe and Da on fracture dissolution and transmissivity alteration. Pe and Da play a critical role in controlling the formation and growth of dissolution channels, which strongly influence transmissivity changes in the fracture. In addition, results point to the difficulty of using laboratory measurements alone to interpret the influence of mineral alteration on field-scale fracture transmissivities.

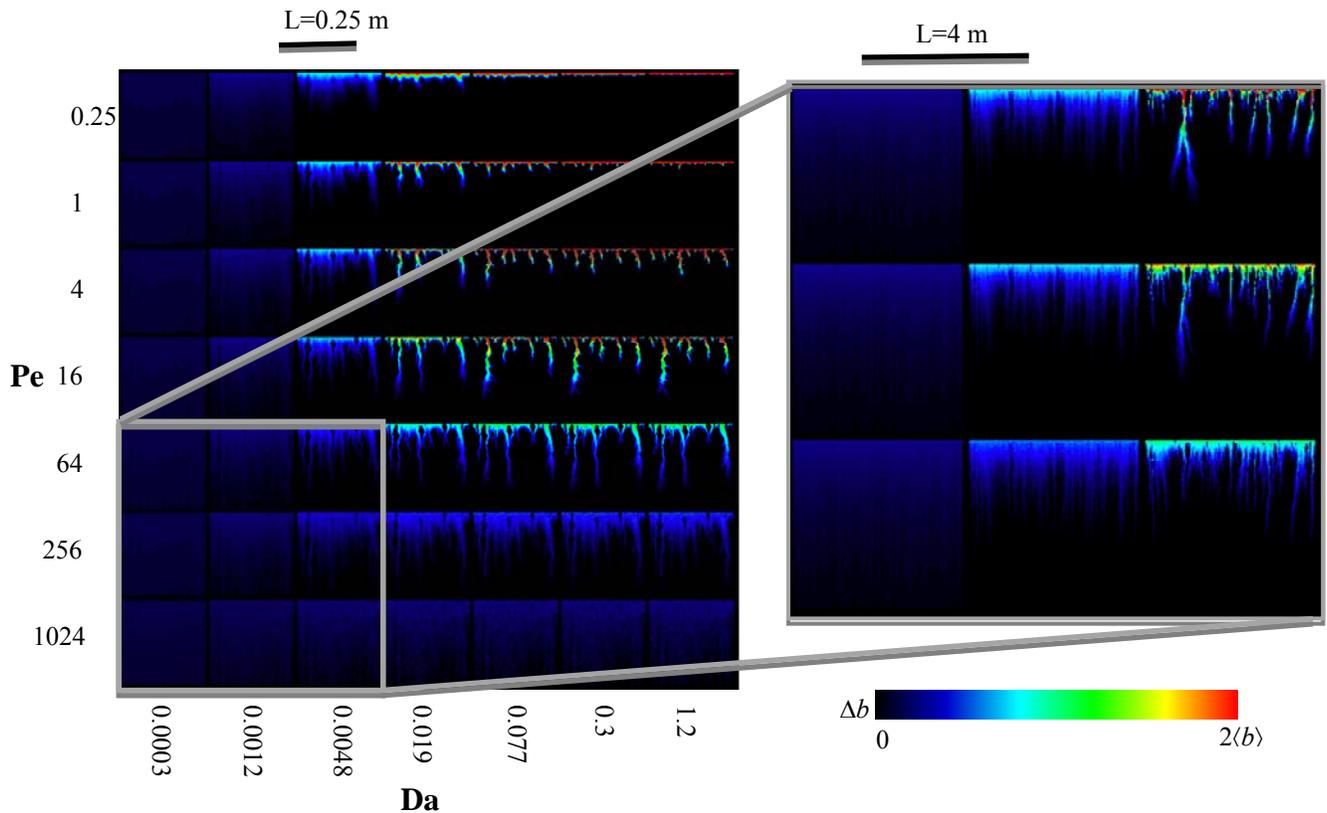


Figure 1: The left-hand frame shows results from 49 simulations in the same fracture for values of Pe and Da ranging over 4 orders of magnitude. Flow of a reactive fluid from top to bottom led to varying dissolution patterns; the images shown for each simulation represent a 50% increase in $\langle b \rangle$. Dissolution behavior ranges from uniform dissolution along the entrance (low Pe and high Da) to relatively uniform dissolution throughout the fracture (high Pe and low Da). The characteristics and growth rate of the dissolution fingers that form at intermediate values of Pe and Da are sensitive to the location in the Pe - Da parameter space. In addition, increasing the scale of the simulations by a factor of 4 (right-hand frame) demonstrates how the channel growth observed in the right-hand frame is influenced by fracture scale. In the region of parameter space that was dominated by uniform dissolution at the lab scale (25 cm fracture), initiation and growth of dissolution fingers is observed in the 4-meter fracture (note the grid spacing in both fractures is 0.5 mm, and the spatial correlation of the fracture aperture fields is identical). These results suggest that in addition to the location within the Pe - Da parameter space, the length of the fracture is a critical parameter controlling the initiation and growth of dissolution fingers.

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

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

Project Description: Characterizing the structural form of Al(III) associated with silicate solids has been the subject of interest for a number of years because dissolved Al(III) is known to inhibit dissolution rates and correspondingly enhance precipitation rates for silicate minerals. In order to determine the reaction mechanisms responsible for this behavior, we use both bulk and surface-selective solid-state NMR techniques to identify the coordination geometry and chemical environment of Al(III). We investigate aluminum sorption and precipitation on amorphous silica and the growth kinetics of aluminum tobermorite. Abstracts to these publications are provided in the Results section.

Results: The following abstracts are presented as a summary of project results.

1) Association of dissolved aluminum with silica: Connecting molecular structure to surface reactivity using NMR

We studied uptake mechanisms for dissolved Al on amorphous silica by combining bulk-solution chemistry experiments with solid-state Nuclear Magnetic Resonance techniques (^{27}Al magic-angle spinning (MAS) NMR, $^{27}\text{Al}\{^1\text{H}\}$ cross-polarization (CP) MAS NMR and $^{29}\text{Si}\{^1\text{H}\}$ CP-MAS NMR). We find that reaction of Al (1mM) with amorphous silica consists of at least three different reaction pathways; (1) adsorption of Al to surface silanol sites, (2) surface-enhanced precipitation of an aluminium hydroxide, and (3) bulk precipitation of an aluminosilicate phase. From the NMR speciation and water chemistry data, we calculate that $0.2 (\pm 0.04)$ tetrahedral Al atoms nm^{-2} sorb to the silica surface and that this amount is nearly constant from pH 4.3-8.2. Once the surface has sorbed roughly half of the total dissolved Al ($\sim 8\%$ site coverage), aluminium hydroxides and aluminosilicates precipitate from solution. These precipitation reactions are dependent upon solution pH and total dissolved silica concentration. We find that the Si:Al stoichiometry of the aluminosilicate precipitate is roughly 1:1 and suggest a chemical formula of NaAlSiO_4 in which Na^+ acts as the charge compensating cation. For the adsorption of Al, we propose a surface-controlled reaction mechanism where Al sorbs as an inner-sphere coordination complex at the silica surface. Analogous to the hydrolysis of $\text{Al}(\text{OH}_2)_6^{3+}$, we suggest that rapid deprotonation by surface hydroxyls followed by dehydration of ligated waters results in four-coordinate $(>\text{SiOH})_2\text{Al}(\text{OH})_2$ sites at the surface of amorphous silica.

2) Transformation of meta-stable calcium silicate hydrates to tobermorite: reaction kinetics and molecular structure from XRD and NMR spectroscopy

Understanding the integrity of well-bore systems that are lined with Portland-based cements is critical to the successful storage of sequestered CO_2 in gas and oil reservoirs. As a first step, we investigate reaction rates and mechanistic pathways for cement mineral growth in the absence of CO_2 by coupling water chemistry with XRD and NMR spectroscopic data. We find that semi-crystalline calcium (alumino-)silicate hydrate (Al-CSH) forms as a precursor solid to the cement mineral tobermorite. Rate constants for tobermorite growth were found to be $k = 0.6 (\pm 0.1) \times 10^{-5} \text{ s}^{-1}$ for a solution:solid of 10:1 and $1.6 (\pm 0.8) \times 10^{-4} \text{ s}^{-1}$ for a solution:solid of 5:1 (batch mode; $T = 150^\circ\text{C}$). This data indicates that reaction rates for tobermorite growth are faster when the solution volume is reduced by half, suggesting that rates are dependent on solution saturation and that the Gibbs free energy is the reaction driver. However, calculated solution saturation indexes for Al-CSH and tobermorite differ by less than one log unit, which is within the measured uncertainty. Based on this data, we consider both heterogeneous

nucleation as the thermodynamic driver and internal restructuring as possible mechanistic pathways for growth. We also use NMR spectroscopy to characterize the site symmetry and bonding environment of Al and Si in a reacted tobermorite sample. We find two [4]Al coordination structures at 59.9 ppm and 66.3 ppm with quadrupolar frequencies of 0.21MHz and 0.10 MHz (+/-0.08) from ^{27}Al 3Q-MAS NMR and speculate on the Al occupancy of framework sites by probing the protonation environment of Al metal centers using $^{27}\text{Al}\{^1\text{H}\}$ CP-MAS NMR.

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 FY08 focused on (1) a series of experiments to evaluate NanoSIMS capabilities to measure gradients in isotopic composition over small spatial scales and (2) the production and characterization of a homogeneous silicate melt/glass containing enhanced concentrations of Pb and U for the thermal diffusion experiments. The high spatial resolution of the NanoSIMS (50 nm) provides a new capability to measure isotope gradients using lateral step scans rather than by the traditional depth profiling approach. A potentially important issue for quantifying isotope gradients is accounting for the Gaussian shape of the primary ion beam. Roughly one-third of the ions strike the sample outside the nominal diameter, potentially degrading the effective spatial resolution and “smearing out” gradients in isotope composition. To evaluate and quantify the magnitude of this effect, we performed NanoSIMS Mg and U isotope ratio mapping of isotopically heterogeneous samples, using a ~250 nm diameter $^{16}\text{O}^-$ primary beam. The results indicate that we can easily resolve differences in Mg isotope composition at length scales of ~200 nm, using *L'image* image processing to remove the effects of beam spread. Preliminary data for U show similar effects; additional studies are currently underway.

In order to study thermal diffusion of heavy elements, we require a homogeneous starting glass containing U and Pb at easily detected levels. To minimize the radiological hazard (and ES&H issues), we use a depleted U-oxide ($^{238}\text{U}/^{235}\text{U} \sim 300$) starting material to seed a silicate glass. Since Pb contained in the starting compounds is lost during melting to homogenize the glass, our current efforts are focused on reintroducing Pb at lower temperatures. Our goal in this work is to see if the large (percent-level) fractionations observed for light elements (Mg, Ca) can be generated for heavy elements by thermal diffusion. Were this to be demonstrated, thermal diffusion could provide an effective way of

intentionally altering the isotopic composition of U-bearing materials so as to make it more difficult to trace their provenance.

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 interconnectness 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 FY08 several significant results were achieved, including two conference abstracts, successful proposals for tomography beamtime at ALS, and an invited departmental seminar at UC Berkeley given by Dr. Heather Watson, a post-doc working on this project. One paper on the electrical conductivity and permeability of extrusive volcanic was submitted to EPSL (with collaborators Wright and Cashman).

A key experimental achievement was the completion of a full series of electrical conductivity measurements on polycrystalline olivine with 0-10 vol% sulfide melt at simultaneous high pressure and temperature in the piston cylinder. The cell and measurement techniques have a high success rate and produce reliable results. Application for a U.S. patent on the electrical conductivity cell was filed.

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. The combination of electrical conductivity experiments of all run products and imaging at the ALS has resulted in the establishment of new cross-property relationships (Figure 1). New collaborations were developed with researchers at the Advanced Photon Source (Argonne National Lab) to make similar micro-tomographic measurements (*in-situ*) on sulfide bearing olivine samples undergoing deformation at high pressures and temperatures. These collaborations expand the scope of geological and physical problems that can be addressed with the current methodology.

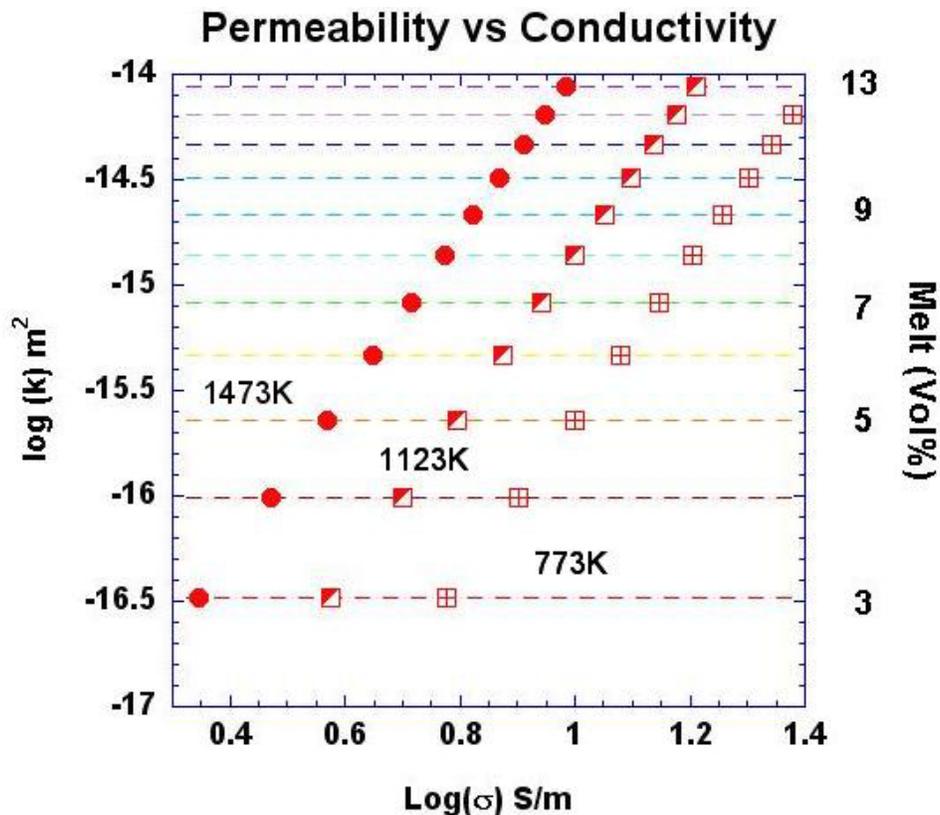


Figure 1: Preliminary relationships developed between melt fraction, permeability and electrical conductivity based on electrical conductivity experiments and permeability calculations from lattice-Boltzmann simulations on tomographic volumes of pre-synthesized samples.

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: We've investigated iron–magnesium exchange and transition-metal trace-element partitioning between magnesium silicate perovskite (Mg,Fe)SiO₃ and ferropericlase (Mg,Fe)O synthesised under lower-mantle conditions (up to 115 GPa and 2200 K) in a laser-heated diamond anvil cell. Recovered

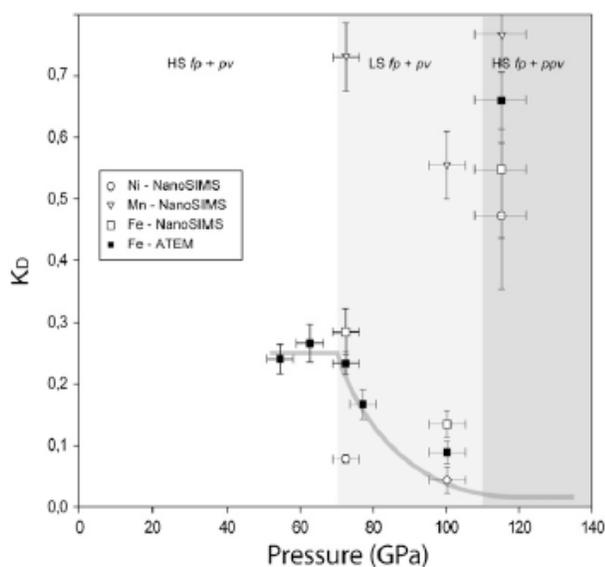


Figure 1. Fe–Mg exchange coefficients between perovskite (pv) or post-perovskite (ppv) and ferropericlase (fp) plotted as a function of pressure. The coefficients published by Murakami *et al.* (2005) and Kobayashi *et al.* (2005) are also shown. The three grey-shaded fields emphasize the stability fields of the successive coexisting phases: High Spin or Low Spin fp+pv (Badro *et al.*, 2003) and LS fp+ppv (Murakami *et al.*, 2004).

samples were thinned to electron transparency by focused ion beam and characterized by analytical transmission electron microscopy (ATEM) and nanometer-scale secondary ion mass spectroscopy (nanoSIMS) (Auzende *et al.* *EPSL*, 2008). Iron concentrations in both phases were obtained from X-ray energy dispersive spectroscopy measurements and nanoSIMS. Our results are the first to show that recently reported spin-state and phase transitions in the lower mantle directly affect the evolution of Fe–Mg exchange between both phases. Mg-perovskite becomes increasingly iron-depleted above 70–80 GPa possibly due to the high spin–low spin transition of iron in ferropericlase. Conversely, the perovskite to post-perovskite transition is accompanied by a strong iron enrichment of the silicate phase, ferropericlase

remaining in the Fe-rich phase though. Nanoparticles of metallic iron were observed in the perovskite-bearing runs, suggesting the disproportionation of ferrous iron oxide, but were not observed when the postperovskite phase was present. Implications on the oxidation state of the Earth and core segregation will be discussed. Transition trace-element (Ni, Mn) concentrations (determined with the nanoSIMS) show similar trends and could thus be used to trace the origin of diamonds generated at depth. This study provides new results likely to improve the geochemical and geophysical models of the Earth's deep interiors.

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High Resolution/High Fidelity Seismic Imaging and Parameter Estimation for Geologic Structure and Material Characterization

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Objectives: This project uses wave-equation migration to improve the quality of information that can be obtained from seismic images. We also seek to exploit the natural advantage of our methods for providing reflection amplitude vs. angle information that can be used to infer *in situ* parameters like rock properties and fluid type and content.

Project Description: High-resolution/high fidelity seismic imaging is critically important for both exploration and production management of energy resources and monitoring of geological CO₂ sequestration. New oil/gas reservoirs are mostly located in complicated geological areas, sophisticated imaging methods for complex structures are needed to pinpoint the targets. We are enhancing our multi-domain seismic imaging techniques for high-resolution/high fidelity imaging. We exploit the natural advantages of our method for providing reflection amplitude vs. angle information that can be used to infer *in situ* parameters like rock properties and fluid type and content. We also are developing imaging methods using multi-component elastic data. High-resolution/high fidelity seismic imaging will help in characterizing the crack distribution, fluid and gas content and changes of reservoir parameters during operation of reservoirs for production or during environmental protection efforts such as those involving nuclear waste disposal, CO₂ sequestration, and groundwater contamination monitoring and remediation.

Results: (1) We developed a novel numerical modeling method to simulate wave propagation in strongly heterogeneous media using a mimetic finite-difference scheme on an unstructured grid. This is the first to introduce the mimetic finite-difference scheme to solve the wave equation. The new method enables us to define arbitrary shapes of geological interfaces including the free surface without any approximation. (2) We improved images of elastic-wave reverse-time migration using a wavefield separation imaging condition and a new approach to handle polarizations of P- and S-waves. We demonstrated that our new migration imaging approach can image vertical faults, which are impossible to image using conventional migration imaging methods. (3) We developed a quantitative method for accurately estimating reservoir geophysical property changes using time-lapse seismic data and elastic-wave sensitivities. Our synthetic studies indicate that the method is more robust than conventional inversion. This will provide a practical and reliable tool for quantitative seismic monitoring for geologic carbon sequestration. (4) A Special Issue on “Computational Geophysics” (Invited Guest Editors: Lianjie Huang and Michael Fehler) was published in January 2008.

Nonlinear Elasticity in Rocks

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Website: www.lanl.gov/source/orgs/ees/ees11/geophysics/nonlinear/nonlinear.shtml

Objectives: This work is focused on addressing a new parameter space of elastic nonlinear behavior. The new parameter space is the nonlinear response of geomaterials to instantaneous or progressive mechanical “damage”, and geochemical change that is manifest by mechanical damage or alternatively, material healing.

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. 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 meso to the macro. The elastic nonlinear response is the most sensitive measure in existence for probing the material mechanical damage state. Impact areas include scientific questions related to volcanism and metamorphism, Yucca Mountain, CO₂ sequestration, reservoir drilling, as well as direct application to monitoring of materials, such as material aging in the nuclear stockpile.

Results: A methodology has been developed to subject rock samples to supercritical CO₂ and nonlinear diagnostics. In initial experiments, we found that carbonate-rich sandstone exposed to supercritical CO₂ shows significant changes in both its linear wave speed and nonlinear elastic response. We first measured the modulus and nonlinear response of a bar of the sandstone under fundamental mode resonance. To obtain the nonlinear response, we conducted resonance frequency step-sweep experiments progressively as a function of the drive amplitude. We created a sequence of resonance curves showing typical modulus softening behavior observed in nearly all rocks, using Nonlinear Resonant Ultrasound Spectroscopy (NRUS). The sample was placed in the pressure vessel where it was exposed to supercritical CO₂ for approximately 1 week. We observed a decrease in the material mass density as well as a decrease in the material linear and nonlinear elastic response. The change in the material nonlinear response was particularly pronounced (Figure). 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, possibly, to healing. If this result is general, then under field conditions of supercritical CO₂ injection/sequestration, changes in permeability networks and fracture healing could potentially be examined and quantified by similar nonlinear acoustic, geophysical methods.

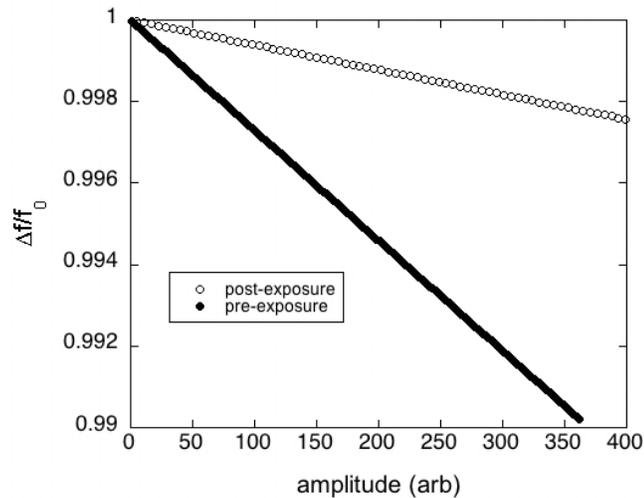


Figure. Nonlinear material response measured by NRUS for a sample of carbonate sandstone before and after being subjected to supercritical CO₂. The change in resonance frequency $f - f_0$ normalized to the low amplitude, linear elastic value f_0 , is compared to the drive amplitude, which diminishes significantly post-exposure. The modulus decreases as well but is a much smaller percentage change.

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 quantify the physical and chemical conditions under which stress waves influence porous fluid flow and sub-pore size (colloidal) particle transport, and obtain experimental data 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. The scale dependence of these interactions being investigated involves microscopic colloid visualization and core-scale fluid and colloid transport. Of particular interest is the mechanism of elastic waves coupling to sub-micron particle (colloid) interactions over a wide range of frequencies (roughly 10 Hz to 10 MHz). 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. Understanding this

phenomenon will allow it to be harnessed for valuable applications, such as enhanced oil recovery and groundwater remediation.

Results: We demonstrated experimentally that low-frequency dynamic stress mobilizes colloids trapped in a synthetic porous medium and causes cyclic variations in the colloid release rate (Figure). Stimulated core transport experiments were performed on a packed column of 1-millimeter Pyrex beads for a suspension of 2-micron fluorescent polystyrene microspheres. Dynamic stress was applied to the sample to investigate how low frequency elastic wave stimulations enhance the mobilization of the captured colloidal microspheres. Cyclical variations in effluent microsphere concentration were observed during stimulation but were absent when stimulation was turned off. Wavelet transform analysis showed these variations to be highly periodic and not correlated with temperature variations in the laboratory or other ambient mechanical disturbances external to the sample. However, pore pressure signals measured in the core showed similar cyclic variations. The behavior is interpreted to be due to periodic downstream plugging of the flow pathways during stimulation. Optical microscopic observations of the Pyrex beads during low frequency flow oscillations revealed that the individual beads rotate, thereby rubbing against each other and scraping the adsorbed microspheres from portions of the bead surfaces. These results support the hypotheses that mechanical interaction between porous matrix grains is an important mechanism in the mobilization of naturally occurring colloidal particles during elastic wave stimulation, and that the subsequent downstream plugging of pore throats can cause complex permeability variations in natural porous systems.

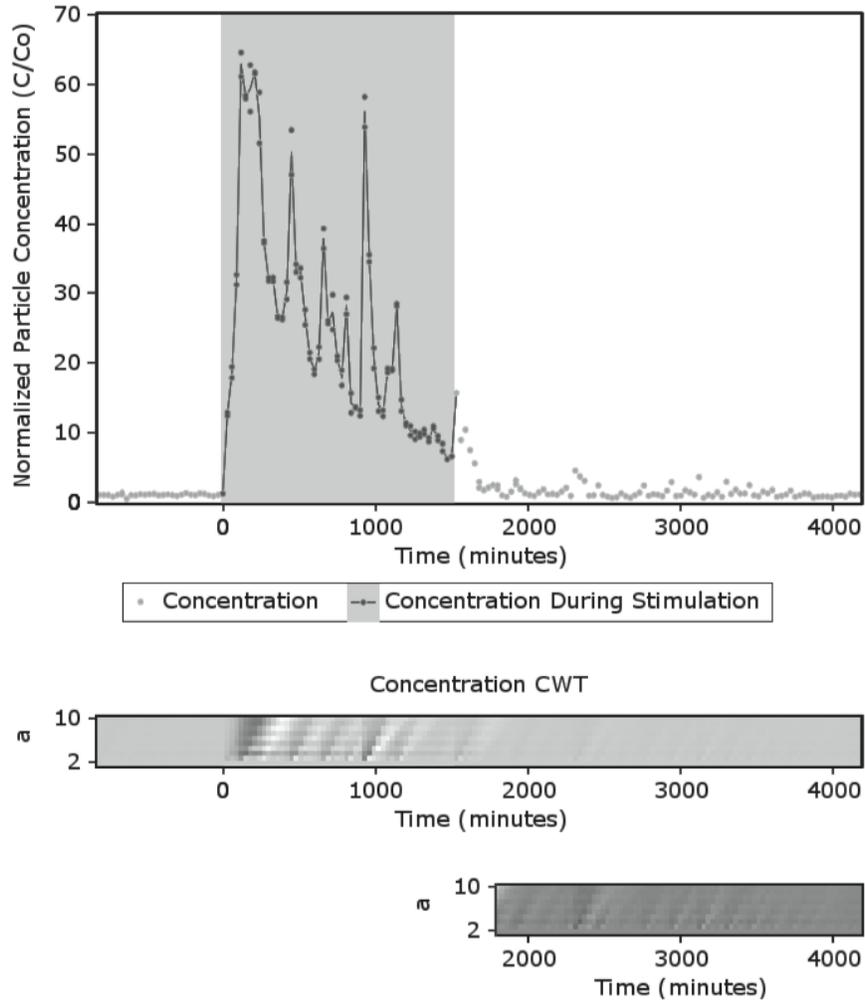


Figure. Effluent particle concentration data (top) and wavelet transform (middle and bottom) for a colloid mobilization experiment. Dynamic stress stimulation at 26 Hz and 360 kPa RMS amplitude was applied at $t = 0$ with duration indicated by the gray region. The wavelet transform (middle) shows the periodic nature of the stimulated concentration peaks, which died out gradually after stimulation was ceased (enhanced image at bottom)

Summer of Applied Geophysical Experience (SAGE)

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Objective: SAGE 2008 provides unique, hands-on training and research experiences in basic and applied geophysics for 25-30 competitively selected undergraduate- and graduate students. This involves developing a broad, community-wide expertise in geophysics, conducting innovative research with students on a variety of important problems, and introducing students to a range of career options in the geophysical sciences.

Project description: SAGE 2008 conducted research in the Santo Domingo Basin to determine the role that the Budaghers fault plays in accommodating deformation along the eastern boundary of the Rio Grande rift system. An east-west-oriented structure, the Budaghers fault lies in a step-over region between two larger, north-trending, synthetic normal faults that form a major continental extension boundary. A second project characterized the depth to the regional water table and identified man-made structures at an archaeological site which served as a proxy for a small-scale environmental-restoration waste-disposal site (Figure).

The geophysical techniques and tools used in these investigations included: seismic reflection and refraction data obtained from a Vibroseis® survey, gravity, time-domain electromagnetics and controlled-source magnetotellurics, ground penetrating radar, and integration with existing aeromagnetics. Six full-time faculty members from LANL and five universities, augmented by several other part-time faculty from a range of institutions and companies, instructed and supervised the students.

Results: Twenty eight students from a wide range of large and small colleges and universities attended SAGE 2008. Participants successfully imaged the subsurface expression of the Budaghers fault, which links the La Bajada and San Francisco faults forming part of the eastern boundary of the Rio Grande rift system. The buried trace of the fault was imaged by SAGE 2007. By integrating SAGE data with proprietary industry seismic data, SAGE 2008 students were able to correlate strata across the Budaghers fault, determine its relationship to other faults in the region and interpret the role that this fault plays in the larger system. In particular, the Budaghers fault is interpreted to be a northward dipping relay ramp which accommodates deformation transfer between two north-trending, synthetic normal faults with down-to-east motion. These larger faults (La Bajada & San Francisco) constitute part of a northeast-trending accommodation zone, transferring offset laterally from the Española to the Santo Domingo basins and ultimately to the very deep Albuquerque basin of the rift.

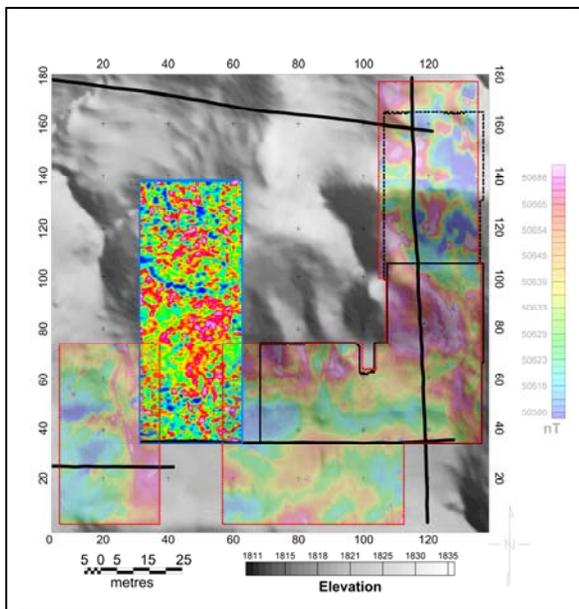


Figure: Topographic map of the San Marcos archeological site overlain by geophysical data sets. Ground penetrating radar, refraction, EM, and forward modeling were integrated to identify kivas, fire pits, and structure walls.

The Uranium Decay Series at a Finer Scale

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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 disequilibria techniques are well-established and valuable tools for geochronology and geochemistry. Such measurements can be made by decay counting; however, there are considerable advantages in using mass spectrometric techniques. The current work represents a mixture of follow-ons to our previous efforts combined with new efforts to provide *in-situ* spatial resolution to U-series studies for geologic materials. Emphasis is on utilizing the multiple ion counting capabilities of the Isoprobe MC-ICPMS for laser ablation measurements. This work provides information on the recent evolution of magmatic systems, human evolution, natural hazard risk assessment, climate change, and the carbon cycle.

Results: Uranium-series geochemistry and geochronology have a wide range of applications in paleoclimatology, volcanology and other disciplines. To further explore these fields, the geoanalytical community has now begun to exploit recent advances in *in situ*, micron-scale sampling via laser ablation-ICPMS. Unfortunately, improvements in instrumentation have generally outpaced development of the appropriate geologic reference materials required for *in situ* U-series work. Our most recent work has focused on characterizing a suite of solid samples for U-series laser ablation applications. Our emphasis has been on obtaining data for uranium and thorium isotopic ratios and elemental concentrations measured in a suite of solid standards from the USGS (e.g., BCR-2G, BHVO-2G, GSD-1G, MACS-1, NKT-2G), as well as those from the MPI-DING series (e.g., ATHO-G, T1-G, StHs6/80-

G). Specifically created for microanalysis, two of these standards are synthetic (GSD-1G, MACS-1) and the remainder are naturally-sourced glasses. They cover a range of compositions, ages (\pm secular equilibrium), elemental concentrations and expected isotopic ratios. The U-series isotopes of some powdered source materials have been previously characterized (e.g., BCR-2, BHVO-2), although there is no confirmation of the same ratios in the glass. We are working to compare bulk measurement of these solid standards via TIMS and solution multicollector-ICPMS to laser ablation data for the solid standards. These new data are necessary to assess the performance of LA-ICPMS techniques which require matrix-matched solid standards for correction of U-series elemental and isotopic ratios. These results from existing, widely-available reference materials also facilitate quantification and comparison of U-series data among laboratories in the broader geoscience community.

Controls on Molecular-Scale Microbial Responses to Metals: Interactions of Bacteria, Metals and Environmental Nanoparticles

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Objectives: This research effort investigates the mechanisms of iron dissolution from minerals as enhanced by the activity of aerobic microbes.

Project Description: The representative aerobic microorganism (*Pseudomonas mendocina ymp*) dissolves iron from mineral surfaces in part with the aid of a reductive process. As described in a report in 2007 (Dhungana et al., *App. Env. Microb.*, **2007**, 73, 3428-30) dissolution was believed to involve a small molecule reductant metabolite, released by the microbe at the mineral surface which reduces Fe(III) to Fe(II). Like siderophores, synthesis and release of the reductant is facilitated by conditions of iron deprivation. It is envisioned that the reductants ultimately act in concert with siderophores to facilitate dissolution of iron from the minerals. Our efforts were twofold: examining the commonality of this reductive process in other aerobic bacteria, and in isolating and chemically identifying the reductant molecule. If this reductant dissolution process can be shown to be generally employed by bacteria in geochemical environments, this would represent a significant advance in our knowledge of mineral dissolution and mobilization processes as mediated by biological factors.

Results: Our initial work focused on *Pseudomonas mendocina ymp*, which was isolated as part of the Yucca Mountain Project from sediment in a surface holding pond of a drilling operation at the Nevada Test Site. We clearly observed an increase in aqueous iron concentrations and bacterial growth rates as mediated by exogenous reductants, as well as co-regulation of siderophore and reductant production in iron-deficient conditions. We have expanded our research to include a panel of other aerobic bacteria. This panel included species that are commonly found in soil environments (*Bacillus anthracis* Sterne, *Burkholderia thailandensis* E264) as well as in other natural environments (*Escherichia coli* K12, *Salmonella enterica* LT2).

Using a standard assay for Fe(II) quantitation after 24 hours growth in iron-deficient media, we examined reductant production in this panel. All aerobic bacteria were observed to produce exogenous reductants (Figure). Furthermore, the bacterial cells themselves also tested positive for reductants, which indicates the species interact significantly with the cell membrane, or are possibly associated with the cell surface. The production of the *P. mendocina* reductant over time also undergoes a burst in

accumulation over the first 24 hours followed by a significant drop over the next 24-48 h (J. DuBois, Notre Dame Univ., personal communication). This is consistent with gradual decomposition of the reductant in prolonged periods of time in iron-deficient conditions, presumably via oxidation or other means which destroys the activity of this species.

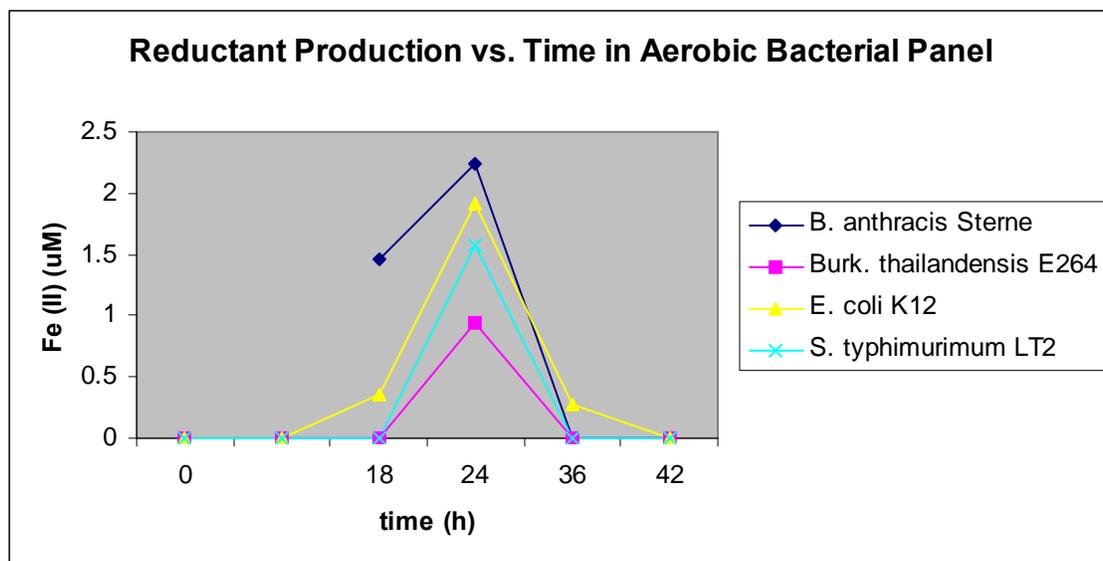


Figure: Analysis of reductant production in iron deficient media vs. time for the bacterial panel. This profile of production over time was reproducible in numerous biological replicates, although the absolute quantification of Fe(II) equivalents in culture was variable.

OAK RIDGE NATIONAL LABORATORY

CONTRACT: OR22725

PERSON IN CHARGE: D. Cole

Nanoscale Complexity at the Oxide/Water Interface

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Objectives: We seek a complete understanding of the complex, nanoscale domain where crystalline metal oxides (including 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 -TiO₂) and cassiterite (α -SnO₂), 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: The pH-dependent charging of cassiterite powder surfaces in NaCl and RbCl solutions, due to proton uptake and release by under-coordinated surface oxygen sites, has been studied and modeled at temperatures of 10-50°C. Electrophoretic mobility studies of the same material were completed at 25-250°C in dilute NaCl solutions. These results have been coupled with surface charge and bonding information obtained from *ab initio* density functional theory and classical molecular dynamics simulations to provide input into a surface complexation model based on the revised MUSIC model. This modeling reveals that both Na⁺ and Rb⁺ form inner-sphere species, as well as outer sphere complexes with charged surface sites. However, Rb⁺ sorbs predominantly at a quadridentate site and a bidentate site, involving either four or two surface oxygen atoms, whereas Na⁺ sorbs at two distinct bidentate sites. The interaction of the cassiterite (110) surface with these ions is distinctly different from the interaction with rutile (110), and this appears to be mainly a result of the somewhat larger unit cell parameters of cassiterite, rather than the difference in bulk dielectric properties between the two phases. However, a fundamental difference between the two surfaces is the much higher acidity of 'terminal hydroxyl' sites on cassiterite, compared with rutile, which represent water molecules that chemisorb atop bare five-fold-coordinated metal atoms on the crystal surfaces. This effect is directly related to the

hydrogen-bonding properties of the terminal hydroxyls with second-layer water molecules and indirectly to the higher polarizability of Ti(IV) vs Sn(IV) atoms at the surface. The net result is that *ab initio* calculations and MD simulations, which indicate much more extensive dissociation of first-layer water at the cassiterite vs rutile surface, are fully consistent with observed pH of zero net proton charge, which is a full pH-unit lower on cassiterite than on rutile.

Previously, we demonstrated that the near-surface structure of sorbed water on both rutile and cassiterite (110) is very similar for the surfaces in contact with bulk liquid water, or with surface water coverage limited to just a few surface layers (at reduced relative humidity). This is an important observation because quasielastic and inelastic neutron scattering studies can be applied to directly probe interfacial water dynamics for mineral nanoparticles with a few sorbed water layers. We have used the backscattering spectrometers at ORNL/SNS and the National Institute of Standards and Technology to probe the picosecond to nanosecond dynamics of water on rutile nanoparticles dominated by the (110) crystal face at total water coverages ranging from 1.5 to 3 structural layers. These results demonstrate that the well-known transition of supercooled water at oxides surfaces, from Arrhenius-type to non-Arrhenius diffusional dynamics, is directly related to the amount of water on the surface, with the transition disappearing at less than two layer coverage. The scattering results at these reduced coverages can be predicted from our classical simulations which builds confidence in this model for predicting a wide range of interfacial phenomena.

We have completed a detailed study of the sorbed water vibrational properties on rutile and cassiterite nanoparticle surfaces using inelastic neutron scattering, in one of the last experiments conducted at the Intense Pulsed Neutron Source at Argonne National Lab. The vibrational properties of the two surfaces are dramatically different at reduced water coverage (below 3 structural layers) and fully consistent with our static *ab initio* and classical molecular dynamics simulations and macroscopic modeling, which indicate that first-layer water on cassiterite is largely in the form of dissociated hydroxyl groups, but in the form of intact terminal water molecules on rutile. Computationally-intensive *ab initio* molecular dynamics simulations are currently running on ORNL's leadership class teraflop computer to directly link computed vibrational properties with the inelastic scattering results. This effort is providing a fundamental understanding and quantitative predictive capability for describing structures, reactions and dynamics at mineral-water interfaces.

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: The high-pressure behavior of brucite and other brucite-type hydrous minerals is of great geochemical and geophysical interest, because these brucite-type minerals serve as a simple, yet useful analog for more complex, hydrogen-bearing oxide and silicate minerals in the deep earth. A neutron powder diffraction study of hydrogenated and deuterated brucite, $\text{Mg}(\text{OH})_2$ and $\text{Mg}(\text{OD})_2$, was conducted at ambient temperature and at pressures to 9 GPa, using a Paris-Edinburgh high-pressure cell. Our data revealed small, yet systematic differences in the structure of brucite under high-pressure environments. The lattice parameter of the a axis, aligned parallel to the planes of Mg-O octahedra, is the same for the two brucites. However, the c axis (along the weak interlayer bonding of the O-D) of deuterated brucite is slightly, but systematically smaller and more compressible than that of the hydrogenated sample. This difference results in a rapid decrease in the c/a ratios of the deuterated sample and the unit-cell volume of the deuterated brucite somewhat smaller than that of the hydrogenated counterpart. The isothermal bulk modulus, pressure-derivative of the bulk modulus, and linear compressibility along the two axes, which are obtained by fitting our data to the 3rd-order Birch-Murnaghan equation, provided quantitative data on the contrasting behaviors of normal and deuterated brucite. Shorter interlayer distances of $\text{Mg}(\text{OD})_2$ under pressure may lead to stronger D-D repulsion than H-H repulsion of $\text{Mg}(\text{OH})_2$, and this could be the reason for the discrepancy observed in the literature studies for investigating the location of H under pressure. Also, the differences in the unit-cell volumes between normal and deuterated brucite provide a first piece of direct evidence that the reduced partition function ratio for hydrogen isotopes of brucite increases with pressure at least to about 10 GPa. The magnitude of this H-D isotope effects is somewhat larger than our previous calculations based on a Kieffer-type hybrid density of state model. These data, along with the fact that the reduced partition function ratio for hydrogen isotopes of water decreases with pressure, suggest rather large pressure effects on hydrogen isotope fractionation in the deep-earth.

The liquid-vapor equilibrium isotopic fractionation of water has been studied by molecular-based simulation, involving Gibbs Ensemble Monte Carlo and isothermal-isochoric molecular dynamics of two realistic models: the extended simple point charge (SPC/E) and the Gaussian charge polarizable (GCP) models. The predicted temperature dependence of the liquid-vapor equilibrium isotopic fractionation factors for $H_2^{18}\text{O}/H_2^{16}\text{O}$, $H_2^{17}\text{O}/H_2^{16}\text{O}$, and $^2\text{H}_2^{16}\text{O}/^1\text{H}_2^{16}\text{O}$ have been compared with the most accurate experimental datasets obtained at our laboratory, to assess the ability of these potential models to describe these small quantum effects according to the Kirkwood-Wigner free energy \hbar^2 -expansion. These simulation results were then used to predict the corresponding vapor pressure isotopic effect for the $H_2^{18}\text{O}/H_2^{16}\text{O}$ and $H_2^{17}\text{O}/H_2^{16}\text{O}$ pairs, compared with experimental data, and two recently proposed correlations. This study suggests that the two water models under consideration are able to describe properly the oxygen isotopic effects on vapor pressure from the triple point to the critical point of water. However, the Kirkwood-Wigner \hbar^2 -expansion cannot handle properly the H/D

substitution because the magnitude of this quantum effect ($\ln \alpha(H/D) : 0.1$) might in principle require the higher-order \hbar^4 - coefficients in the semi-classical free energy expansion.

Rates and Mechanisms of Mineral-Fluid Interactions at the Nanoscale

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Objectives: The objective of this research is to advance our fundamental understanding of rates and molecular-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.

The dissolution rates of quartz, SiO₂ in 0.1 molal NaCl solutions at elevated pH and temperatures of 125-200°C were determined experimentally at very-near-equilibrium conditions using a unique pH-perturbation/relaxation approach in collaboration with Ph.D. candidate, Michael Davis of Penn State University (advisers, Profs. Karl Mueller and Sue Brantley). The unique aspect of this work is the extremely high precision obtainable at conditions very close to equilibrium, due primarily to the high precision of our pH measurements, and the lack of any need to analyze the solutions for total silica, which can be more accurately determined from the measured pH and known starting solution concentrations, using charge and mass balance equations. In addition, we have determined a more reliable value for the equilibrium solubility of quartz in basic solutions, where both uncharged silicic acid, Si(OH)₄⁰, and SiO(OH)₃⁻ are important solution species.

In another collaboration with Penn State (Dr. H. Ohmoto and Ph.D. candidate Tsubasa Otake), we have completed detailed studies of the non-equilibrium transformations between magnetite, Fe₃O₄, and hematite, Fe₂O₃, in mildly-acidic solutions at 100-200°C. Our studies, which also utilized our unique high temperature pH monitoring systems, reveal that transformation of magnetite to hematite readily occurs, even under extremely reducing conditions, due to very slow kinetics of reduction of Fe(III) to Fe(II) in solution, and the rapid precipitation of hematite, perhaps catalyzed by the presence of reduced iron in solution. These results challenge the wide use of these abundant iron oxides as indicators of the

redox state of natural waters, and even the evolution of Earth's early atmosphere, since oxidizing conditions are not required to produce hematite from previously deposited magnetite.

We have conducted experiments of short duration (hour to a few days) to determine the scales of diffusion and recrystallization during hydrothermal alteration for adularia and sanidine. Cation and isotope exchange appear to be coupled, perhaps both taking advantage of defects or fast pathways near the surface, as observed with high resolution transmission electron microscopy. Although recrystallization is a major replacement process, diffusive transport is significant at short times and small distances from the replacement boundary (with Profs. T Labotka, Univ. Tennessee, M. Fayek, Univ. Manitoba and S. Utsunomiya, Kyushu Univ.).

Although a great deal is known about the interaction between water and rhyolitic glasses and melts at temperatures above the glass transition, the nature of this interaction at lower temperatures is much more obscure. For example, on a microstructural scale, extrapolations of high-temperature Fourier transform infrared spectroscopy (FTIR) data to lower temperatures suggests that there should be little or no hydroxyl present in glasses hydrated at low temperature. Comparisons of low-temperature hydration results among SiO₂, obsidian, and albite compositions show distinct differences, and features are present in the spectra that do not occur at high temperature. Analysis of H₂O and D₂O diffusion also suggests that mechanistic differences occur between low- and high-temperature diffusive processes (with Prof. L. Anovitz, Univ. Tennessee).

In hydrology and geochemistry, porosity is arguably the most important physical property of a rock because it provides pathways for water flow or infiltration. Chemical reactions induce changes in porosity that alter the rates of fluid transport and thus potentially the overall rates of reaction. In collaboration with students (Alexis Navarre-Sitchler and Lixin Jin) and faculty (Prof. Sue Brantley) at Penn State, we investigated porosity evolution during weathering of basalt, granite and shale. Micro-computed tomography was used to evaluate changes in porosity with weathering of basalts down to pore sizes of ~4 μm and reactive transport models were developed that demonstrate the importance of porosity evolution in this system. Small-angle (SANS) and ultra small-angle neutron scattering (USANS) data extend our investigation of porosity evolution during weathering down to nanometer size pores, and reveal complex fractal behavior depending on the length scale of the observation.

PACIFIC NORTHWEST NATIONAL LABORATORY

CONTRACT: RL01830

PERSON IN CHARGE: A. Felmy

Reductive Mineralization of Nanometer-Sized Fe(III) Oxides in Grain Coatings and Micropores

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Objectives: Research is evaluating two primary scientific questions. 1.) Can metal reducing bacteria induce the mineralogic transformation of nanometer-sized Fe(III) oxides that exhibit limited physical accessibility to whole cells, such as those that reside in microscopic fractures of lithic fragments or within the three dimensional matrix of a particle coating? 2.) Are mineral transformation pathways equivalent when the respiring cell surface does and does not contact the Fe(III) oxides undergoing reductive biomineralization.

Project Description: Research is using batch suspensions of 2- and 6-line ferrihydrite, the most common bioavailable Fe(III) oxide, and synthetic subsurface sediments where ferrihydrite has been uniformly distributed within intragrain regions of nano-porous silica. Laboratory studies use static and dynamic-flow experimental systems with diffusible chemical reductants (ferrous iron, bioreduced anthraquinone disulfonate) and chemotactic iron reducing bacteria to evaluate whether microorganisms can access iron oxide electron acceptors in intragrain pores that are smaller than the cell, and to identify the nature of resulting reductive mineral products. Abiotic and biotic reduction 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). 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 and microbe-induced changes to the Fe(III) oxides, and to identify the nature and properties of the product phases.

Results: The versatile iron-reducing microorganism MR-1 transformed intragrain Fe(III) oxides in the absence of direct contact through the apparent production of Fe(III) complexing compounds that dissolved the intragrain Fe(III) oxides. The resulting Fe(III) complexes diffused to the grain surface where they were bioreduced, yielding Fe(II) that precipitated as vivianite [Fe₃(PO₄)₂] in unique morphology, often in association with microorganisms and often traversing the porous solid-liquid interface in complex fashion (Figure 1). Mineralization and crystal growth pathways were different when ferrihydrite was not localized to intragrain regions (Figure 2). Ferrihydrite intragrain content, aggregation state, phosphate concentration, and Fe(II) generation/supply mechanism appeared to control whether vivianite; or lepidocrocite, goethite, magnetite, or other solids resulted as primary products. A kinetic, microscopic bioreduction-bioprecipitation model is under development to describe these results, and to provide insights on responsible mechanisms and competitive kinetic reactions.

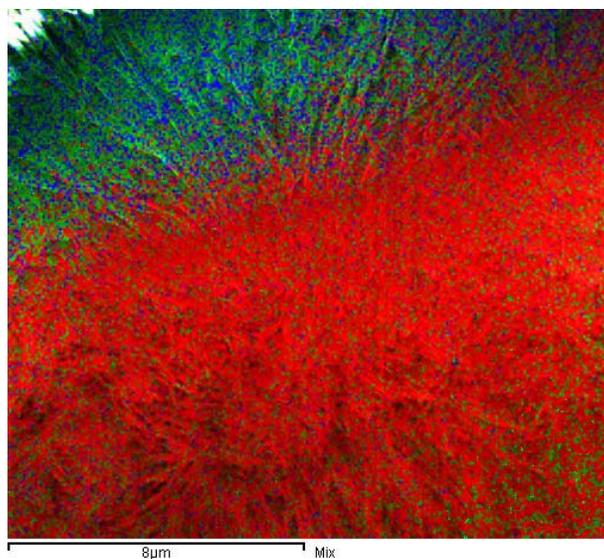


Figure 1. Various types of chemical imaging microscopies are being applied to study the biomineralization of ferrihydrite (green) within porous silica (red). In this focused ion beam thin section (FIB), we observe intragrain dissolution of Fe(III) by biocomplexants, diffusive transport of complexed Fe(III) to the interface (upper left diagonal), and subsequent bioreduction by MR-1 that generates Fe(II) that reacts with phosphate (blue) to precipitate vivianite at the interface (green-blue). Biocomplexants mine the near-surface region of silica first (image center), before working their way to the deeper particle interiors that remain stocked with ferrihydrite (lower right).

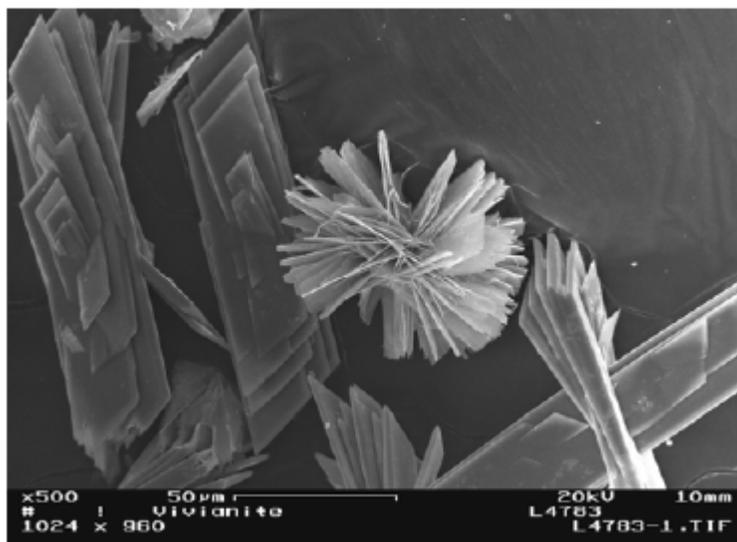


Figure 2. The bioreduction of unprotected ferrihydrite in suspensions with mmol/L concentrations of phosphate leads to the precipitation of macroscopic vivianite crystallites in excess of 50 μm , that differ markedly from those observed in the intragrain system. The initial ferrihydrite is <10 nm in size. Vivianite nucleates on bacterial exopolysaccharide that surrounds MR-1 cells. It then grows rapidly through abiotic means in response to biogenesis of Fe(II) at the ferrihydrite-cell interface and microscopic transport to the growth surface. Crystallite size is a function of the bacterial respiration rate that controls electron flux to ferrihydrite.

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

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Objectives: To provide a molecular level understanding for the prediction the molecular processes involved in microbial metal binding, microbial attachment to mineral surfaces, and oxidation/reduction reactions that can occur at these surfaces and are mediated by the bacterial exterior surface.

Project Description: 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 molecular systems, and predictions of macroscopic geochemical reactions using thermodynamic models. This capability will then be used to gain a fundamental understanding of the processes controlling the lipopolysaccharide (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. Experimental work is carried out to conduct electrochemical measurements on reconstituted outer membranes to determine trans-membrane potentials across the LPS-membrane, and to quantify the adsorption of LPS-membranes to mineral surfaces using atomic force microscopy.

Results: Our molecular model for the LPS membrane for *P. aeruginosa* has been used to study the structural and thermodynamic factors that determine the affinity and uptake of simple, solvated ions. A series of potentials of mean molecular dynamics simulations provided estimates of the free energy profiles for uptake of sodium, calcium, chloride and uranyl ions by the bacterial LPS membrane, with the profile for a water molecule calculated for comparison. Based on these calculations, a compatible classical parameter set for uranyl has also been developed and validated. The uptake of negatively charged ions, such as chloride, is shown to be an energetically unfavorable process, due to the electrically negatively charged character of the surface of the rough LPS membrane, whereas positively charged ions are easily taken up by the polysaccharide layer of the membrane.

Extensive studies have been carried out to investigate the effect of pH on the structure of the LPS membrane with partly protonated phosphate groups, reflecting a slightly acidic environment. External environmental conditions of pH and ionic strength not only determine the form of the ionic species present in the aqueous solution but also the protonation state and, as observed in our simulations, the accessibility of ion interaction sites in the polysaccharide layer of LPS membranes. This is important because, in turn, this will influence the ability of LPS membranes to provide templates for the nucleation of biomineralization processes.

Combined experimental and computation work revealed the hydrogen bonding patterns responsible for selective binding of the amino acid sequence pattern Ser/Thr- hydrophobic/aromatic-Ser/Thr-Pro-Ser/Thr selected as archetype from a library of approximately 3 billion different peptides. The simulations suggest that the presence of proline, a residue of limited flexibility, is essential in defining the three-dimensional framework for the binding.

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 FY08, microscopic examination of the reductive dissolution of hematite (001), (012), (113), and (*hk0*) vicinal surfaces by Fe(II) in the presence of iron chelating ligands revealed that these crystals do not react as historically thought based on macroscopic measurements. Using a combination of electrochemical apparatus to measure surface potential differences, and atomic force microscopy to document surface morphologic changes, we discovered that under conditions of reductive dissolution, surface specific charge density accumulation reactions combined with bulk charge carrier diffusivity create conditions at which interfacial electron transfer reactions at one surface couple with those at another by a current through the crystal bulk. A chemically induced surface potential gradient across hematite (α -Fe₂O₃) crystals is sufficiently high and the bulk electrical resistivity is sufficiently low during reductive dissolution to link dissolution of edge surfaces to simultaneous growth of the basal plane. The finding is important in part because it is a new mechanism and in part because it demonstrates that traditional monitoring of dissolution rates using iron release rates into solution alone does not provide a sufficient basis for determining chemical mechanisms of dissolution. We are currently developing quantitative molecular models to simulate this mechanism, including using accelerated molecular dynamics techniques to probe Fe(II) adsorption mechanisms and kinetics to surfaces of hematite, goethite, and magnetite.

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(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: We obtained the first experimental evidence for the production and stability of sorbed U(V) during heterogeneous reduction of U(VI) by magnetite. These results extend our previous work showing U(V) formation on micas to an entirely different class of minerals and generalizes the potential importance of the intermediate oxidation state U(V) in the reduction of U(VI) to U(IV). U(V) was stable on magnetite surfaces for up to 2.5 months without the formation of U(IV). This latter result indicates that U(V) did not disproportionate on the surface, which excludes such a reduction pathway for the production of U(IV) and suggests that reduction of U(VI) to U(IV) requires two electrons transfers from the substrate. It is possible that the reduction reaction stopped at U(V) due to a slightly non-stoichiometric magnetite surface. The effect of surface stoichiometry and Fe(II) excess or depletion is likely an important parameter for heterogeneous reduction pathways. In other work, it was shown that 2D-correlation spectroscopy is a powerful tool for interpreting XPS data, such as establishing correlations between satellite features and primary peaks in complicated multi-component spectra. This constitutes one of the first applications of 2D-CS to XPS and strongly confirms the identification of unique satellites with different oxidation states of U. Advances in simulating XPS spectra for uranium 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 formation of aqueous carbonate species and their interaction with iron and aluminum oxyhydroxide surfaces which have a high affinity for such species. The interaction of carbonate, bicarbonate, and CO₂ with these materials is highly relevant to the development of processes to sequester CO₂ in the subsurface in order to mitigate its impact on the environment. The isotope fractionation of CO₂ and related species in the gas, aqueous and solid states is a key method to determining the PCO₂ in the atmosphere over geological time scales.

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 nanoparticles. We synthesized such particles by exposing aqueous solutions of ferric iron to various levels of PCO₂, pH and temperatures. The resulting particles were studied by

Temperature-Programmed Desorption (TPD) and Fourier Transform Infrared (FTIR) spectroscopy to follow the sequential desorption of surface- and bulk-bound carbonate with temperature.

Results: The TPD-FTIR experiments enabled a clear distinction between surface- and bulk-bound carbonate in the iron oxyhydroxide particles. Two-dimensional IR Correlation Spectroscopy analysis was used to identify correlations between different sets of discrete surface OH stretches and Multivariate Curve Resolution (MCR) analysis was used to resolve the predominant spectral components (Figure 1). Two dominant groups of hydroxyls were identified on the basis of their differences in proton affinity. Group I hydroxyls appear as two 3698/3541 and 3660/3490 cm^{-1} band pairs. Group II hydroxyls are manifested through the 3648 and 3578 cm^{-1} bands at greater levels of surface proton loading. Group I and Group II were assigned to mostly singly and doubly coordinated hydroxyls, respectively. Stretches arising from triply-coordinated hydroxyls are proposed to be embedded within the dominant O-H band of bulk goethite. A reexamination of (TPD-FTIR) data for goethite and a combined FTIR and TPD study of bulk and surface dehydroxylation and decarboxylation of goethite provided further constraints to this band assignment by identifying important cooperative effects between hydrogen-bonded surface hydroxyls, suggesting that the surface hydroxyls react as interrelated groups rather than individual independent sites.

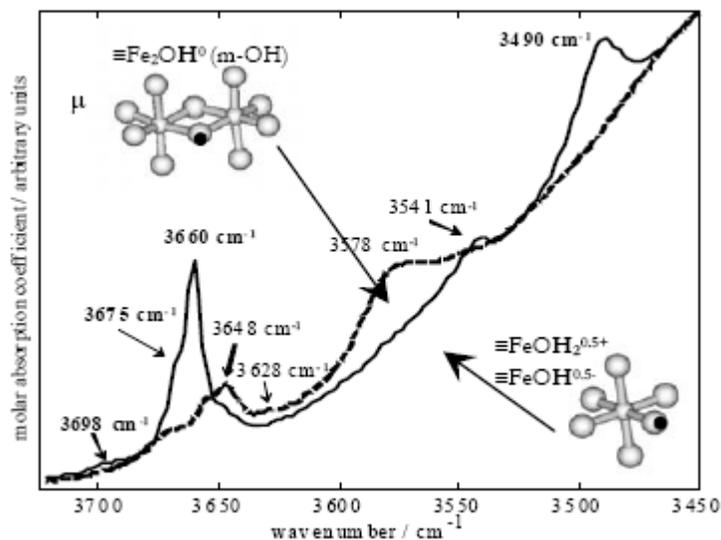


Figure 1. MCR spectra components of ATR-FTIR data for evaporated goethite suspensions identifying the reactive groups associated with the different band assignments.

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

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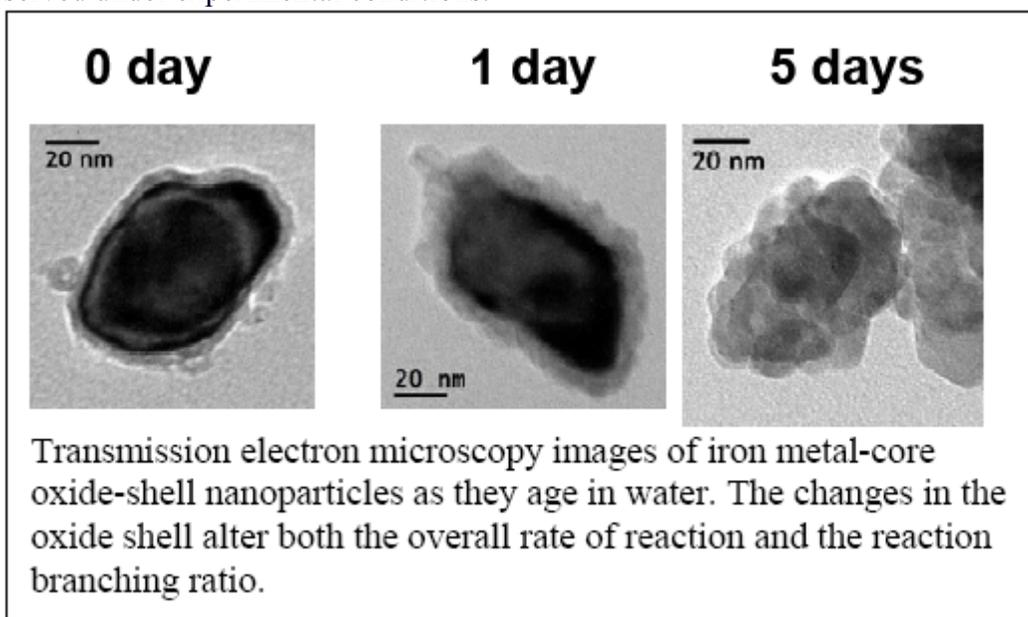
Objectives: The objective of this research is to understand the reaction properties of iron/iron oxide nanoparticles (NPs) and how these properties influence and are influenced by reactions within the NPs (i.e., between the core, shell, and coatings) and interactions between the NPs and the geochemical environment including water, major solutes (inorganic anions), and minor solutes (contaminants).

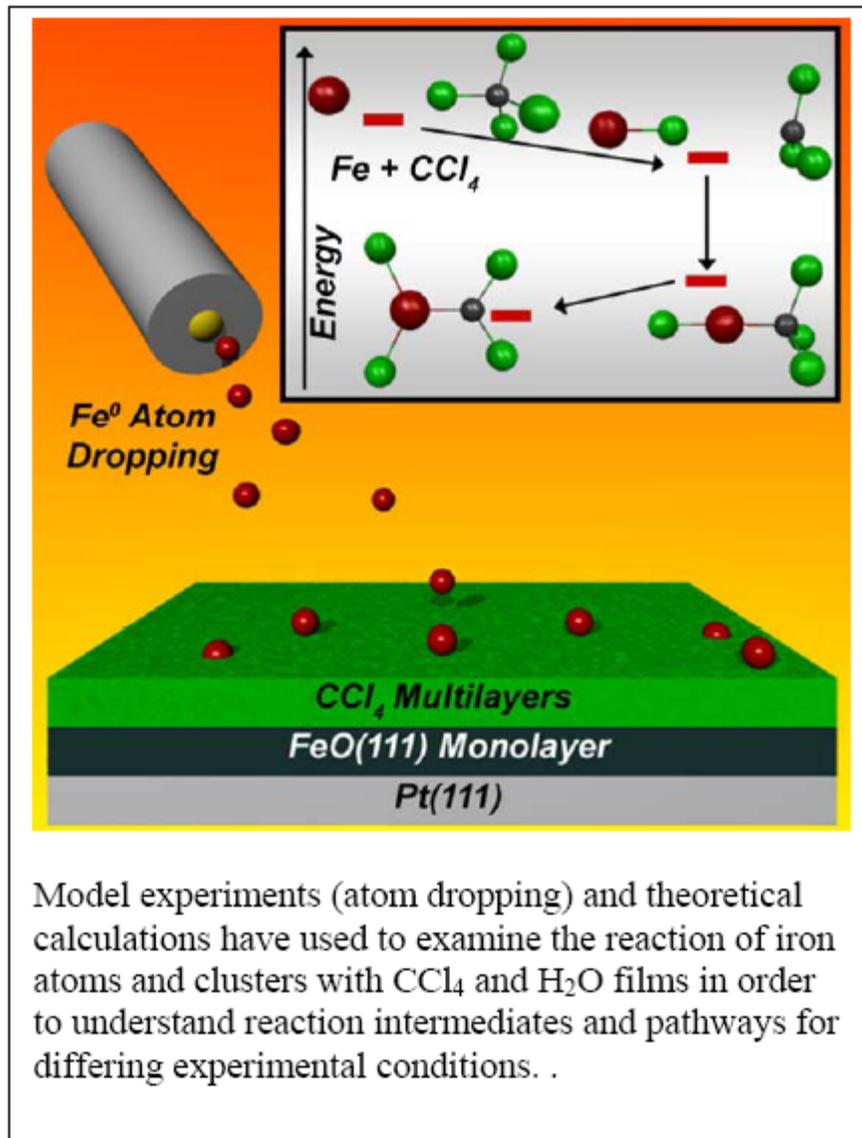
Understanding factors that influence reaction pathways and time dependent behavior are of particular interest. A secondary objective is to use the knowledge gained to "design" NPs for desired lifetime behavior (lifecycle).

Project Description: This project is organized around four major activities: 1) synthesis of well-defined NPs using sputter aggregation, hydrogen reduction and solution processes; 2) 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 as a function of time, and 4) theory and modeling (both computational and experimental) that helps identify reaction mechanisms and reaction intermediates. The project integrates these four activities to achieve the desired understanding.

Results: A combination of *in situ* electrochemical measurements, hydrogen production and batch reaction measurements demonstrated the time-dependence of both reaction rates and reaction pathways of iron metal-core oxide-shell nanoparticles interacting with CCl_4 in water. These measurements in combination with particle characterization using electron and x-ray microscopy and spectroscopy show the dependence of particle properties on the nature and characteristics of the oxide-shell on particle reactive behavior and lifetime. Doping studies suggest that the reaction lifetime and properties of particles can be designed or "optimized." Measurements on metal (Cu, Ni and Pd) doped and undoped nanoparticles highlighted the importance of dopant distribution (within or on the particles) on NP reactivity.

A combination of model experimental and theoretical studies were undertaken to assist fundamental understanding of reaction pathways. The experimental studies involved dropping atoms and clusters of Fe onto H_2O and/or CCl_4 layers and examining the reaction products as a function of metal dose and layer thickness. These experimental studies were complemented by density functional theory calculations of the stability of various reaction products that can be produced in the differing experimental conditions. The calculated stabilities of the reaction intermediates related directly to products observed under experimental conditions.





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 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 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, Al³⁺, Fe³⁺, Cr³⁺, Ca²⁺, and Ni²⁺, 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: Full *ab initio* molecular dynamics (AIMD) simulations are expensive and for many problems compromises must be made in the number of particles to make calculations feasible. Even though the advent of peta-scale computing, along with advances in computation algorithms, is allowing the simulation hundreds atoms routinely, considerably larger particle numbers than is currently feasible need to be used to treat some problems such as the Al₁₃ oligomer. Fortunately, most of the problems that we are focused on are heterogeneous in the sense that there is a region of direct interest which typically has very complicated dynamics (e.g., the ion and most of the solvation region) and a much larger region in which the details of the molecular interactions are not expected to play a decisive role. For such problems QM/MM methodology offers an attractive and computationally efficient way to extend the particle scale (length scale) of AIMD simulations. QM/MM approaches based on local (e.g. GTO's, STO's) basis methods have been used for some time. However, the majority of existing calculations is limited in scope and focus to the structural optimizations of few specifically chosen states along a proposed reaction pathway. This is because the inclusion of dynamics into

QM/MM simulations is determined by the efficiency of the dynamical calculation in the quantum region.

In the last few years we have developed an efficient QM/MM method based on AIMD. This new development has been included in the latest release of NWChem, a quantum chemistry program package developed at PNNL. This method couples our efficient plane wave solvers of Density Functional Theory for the QM region to a molecular mechanics description of a larger region. In FY08, we have extended the QM/MM method to include solid-state molecular dynamics models, and relativistic spin-orbit ZORA corrections. These new developments are being used for a variety of studies, including simulations of solvated oxyhydroxy polymers, the breakdown of the solvated decanoate ion at high pH (with W. Casey, UC Davis), and simulations of the absorption energies of actinides to hydroxylated iron-oxide surfaces (with W. De Jong, PNNL).

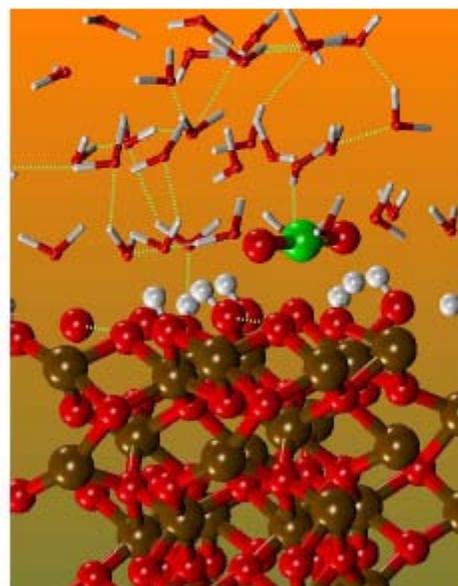
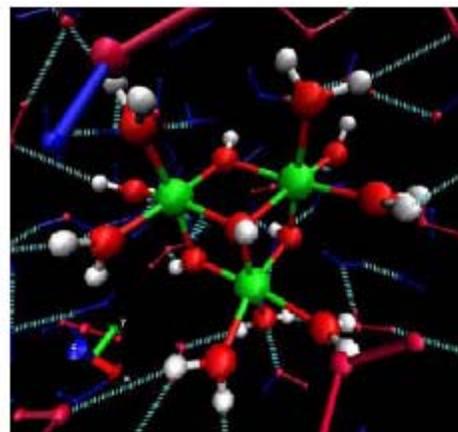


Figure 1: QM/MM simulations of the solvated oxyhydroxy (300°K) polymer $\text{Al}_3(\text{OH})_4(\text{H}_2\text{O})_9$ and solvated actinide species on the hydroxylated Fe_2O_3 surface.

SANDIA NATIONAL LABORATORY/ALBUQUERQUE

CONTRACT: AL85000

PERSON IN CHARGE: J. Merson

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

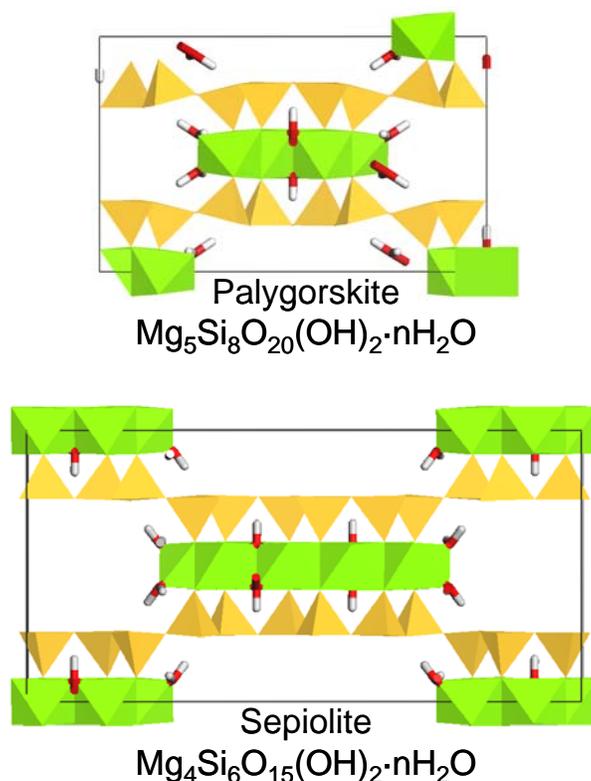
Randall T. Cygan, 505-844-7216, rtcyan@sandia.gov; Jeffrey A. Greathouse, 505-284-4895, jagreat@sandia.gov

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 synchrotron and specialized diffraction 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 sepiolite, palygorskite, talc, and pyrophyllite were investigated using quantum and classical molecular dynamics simulations. The electronic structure simulations are based on plane-wave pseudopotential density functional theory (DFT), which is shown to be sufficiently accurate in predicting the clay mineral structures and vibrational properties. The classical molecular dynamics (MD) simulations, using the CLAYFF force field, reproduce the crystal structures with relatively simple analytical functions that include primarily non-bonded interactions. The DFT results are particularly useful for determining layer hydroxyl structure and dynamics as these properties are difficult to obtain experimentally. The development of second-generation force field parameters for layer (and edge site) hydroxyl groups are based mainly on DFT calculations. Additionally, inelastic neutron scattering experiments were performed at the Los Alamos LANSCE facility to help evaluate the behavior of the water in the channels of the sepiolite and palygorskite materials. The vibrational spectra for water in these phases exhibit a significant librational shift associated with the water molecules residing in different-sized channels. The CLAYFF force field was also used to perform additional large-scale MD simulations of several birnessite minerals. The unique

exchange and adsorption properties of birnessite ($\text{NaMn}_4\text{O}_8 \cdot n\text{H}_2\text{O}$) are related to the charge layer structure and the coexistence of heterovalent manganese in the edge-sharing octahedral layer.



DFT-optimized unit cell structures for the low-water versions of palygorskite and sepiolite indicating the structural hydroxyl groups and the coordinating water molecules in the channels.

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

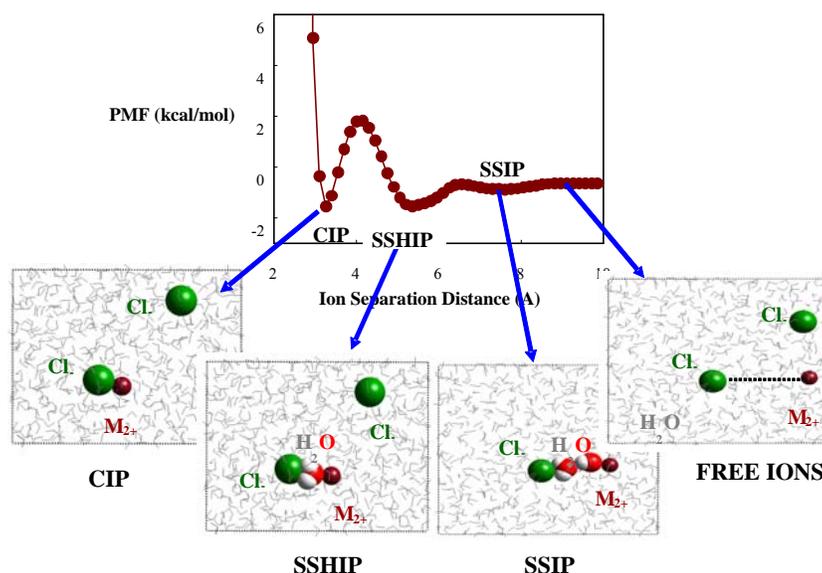
Louise J. Criscenti, 505-284-4357, ljcrisc@sandia.gov; Lynn E. Katz, University of Texas-Austin; Heather C. Allen, Ohio State University

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 past year, we refined our potential of mean force calculations for the alkaline earth metal – chloride complexes in aqueous solution and confirmed that our calculated association constants are the same order of magnitude as those determined experimentally, but do not reproduce the experimental trend with increasing metal ion size. In addition, we refined our surface potential of mean force calculations between the alkaline earth metal cations and the gibbsite basal surface. Our free energy curves suggest that these cations form outer-sphere complexes at the gibbsite surface because there are large activation energy barriers associated with removing the molecules of the cation hydration spheres. Molecular dynamics simulations performed at different temperatures, using the NPT ensemble, confirm that the alkaline earth metal cations bind to gibbsite as inner-sphere complexes at higher temperatures. Free energy curves for the aqueous ion pairs $MgNO_3^+$, $CaNO_3^+$, $SrNO_3^+$, and $PbNO_3^+$ were found useful in interpreting infra-red spectroscopic data from Allen’s laboratory (OSU). Research continued with Wander (Washington State University), to validate and refine the dielectric constant profiles we calculated for three goethite (110) surfaces (charge positive, negative, and neutral) in bulk aqueous solution. Work with Leung (SNL) has focused on using *ab initio* molecular dynamics to calculate surface site acidity constants for silica.



Representative potential of mean force curve for divalent metal cation – chloride pairing in aqueous solution. CIP: Contact ion pair, SSHIP: solvent-shared ion pair, SSIP: solvent-separated ion pair.

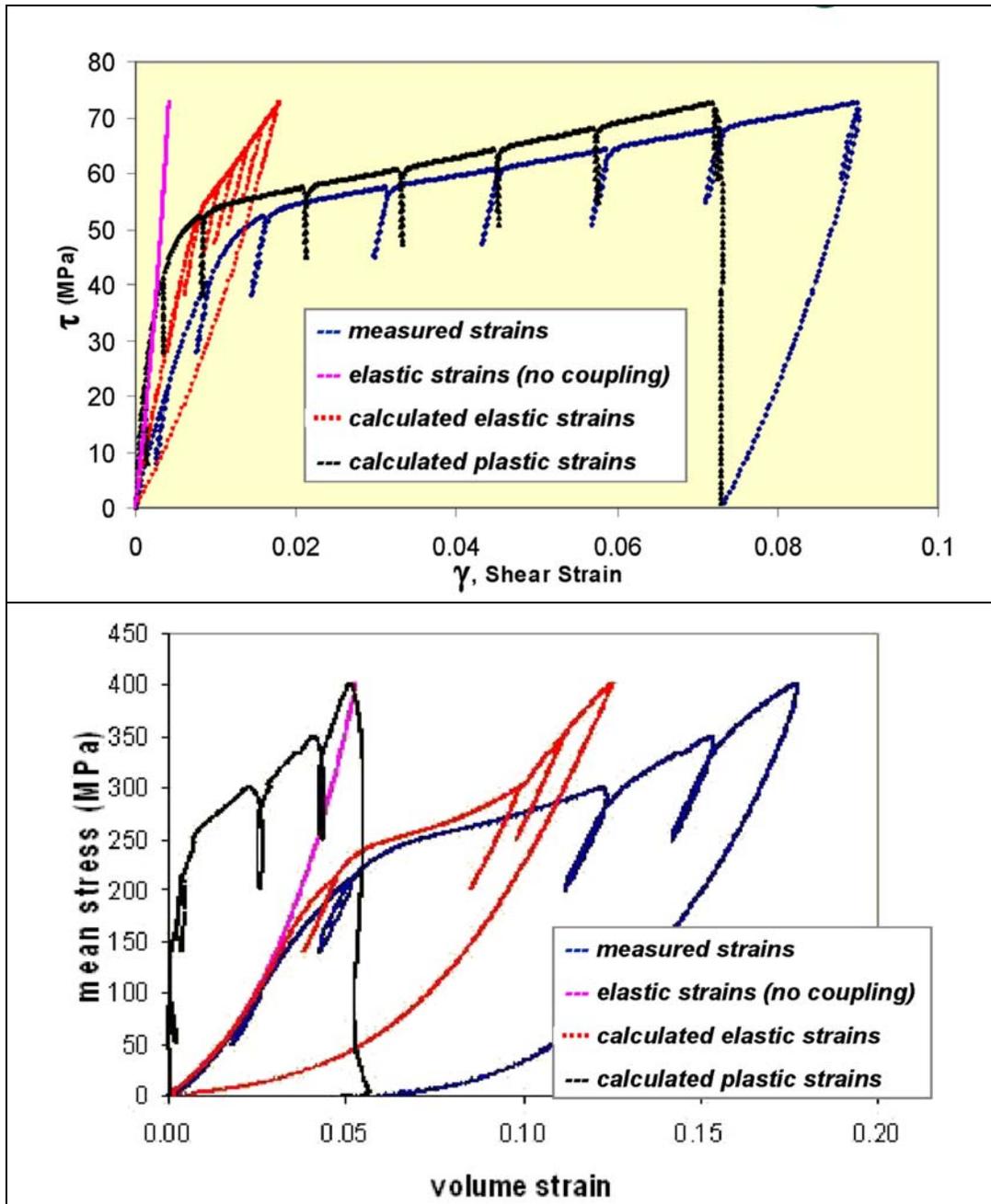
Approaches to Some of the Outstanding Problems in the Heterogeneous Compactive Deformation of Geomaterials

William A. Olsson (retired 6/2006), David J. Holcomb (djholco@sandia.gov, 505-844-2157), John W. Rudnicki, Northwestern University

Objectives: Many porous materials, including some sandstones, exhibit compaction localization, a bifurcation from homogeneous compaction to localized compaction under non-hydrostatic stresses. Compaction localization in porous rock is potentially of importance to industries dependent on extraction or injection of fluids into porous reservoir rocks. Our goal is to elucidate the micromechanical properties responsible for compaction localization.

Project Description: We are furthering this goal by seeking answers to the following questions (1) what are the connections between the various observed modes of localized compaction, (2) why do some porous rocks exhibit localized compaction while other, similar, rocks do not, (3) what controls the propagation modes and (4) which mode or modes are appropriate for describing propagation of compaction bands in geologic settings? We are approaching these questions by focusing on two areas: underlying mechanisms and propagation conditions. To gain some insight into these problems, samples of known, uniform, grain size distributions of St. Peter sand will be deformed in multiaxial compression to investigate the role played by grain size distributions in determining the occurrence of compaction localization in sand. Acoustic emission data will be used to study micromechanisms by examining focal mechanisms and energies of the grain-scale failures associated with compaction in sandstones and unlithified sands.

Results: Our efforts for FY08 continued to concentrate on the analysis of an extensive body of experimental data to produce a consistent picture of the evolution of the constitutive parameters for a sandstone that exhibits shear and compaction localization. The data set contained results from about 30 triaxial tests conducted under either constant mean stress, constant shear stress or constant pressure, with numerous unload loops to determine elastic moduli. The entire stress space available to compressional loading was sampled by the tests. A correct computation of the constitutive parameters β and μ requires separating the observed strains into components resulting from elastic processes and plastic process. Elastic moduli of rock evolve with plastic strain and are also changed by elastic processes, such as crack closure. Therefore separating the strain components necessitates the development of a complete model of the moduli evolution, accounting for the inelastic increment of strain due to modulus evolution and the stress-induced modulus changes. The figure shows the magnitude of the various corrections by comparing the measured strains with the strains after two levels of correction. The simplest correction uses the initial elastic modulus to estimate elastic strain (no coupling). The fully coupled result incorporates both the evolving elastic modulus and the strain increment due to the changing elastic modulus. Analysis of the data set was completed and results will be published. Using the fully corrected plastic strains, the evolution of the constitutive parameters was used to predict the type and angle of localization features, with good agreement with the angles determined by AE event locations.



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 a successful experimental program 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. Both *natural* and *synthetic* grain-cement systems are investigated using novel approaches that provide insight into grain-scale mechanics. To capture this project scope, the project direction is defined by these three specific activities:

- 1) Developing methods for fabricating and testing the mechanical properties of synthetic cemented 2-grain assemblages.
- 2) Integrating microstructural and mechanical analyses to relate physical elements of progressively cemented natural and synthetic systems to their structural response.
- 3) Developing quantitative relationships describing the stress-strain response of cemented granular systems and incorporating that microscale material response into DEM.

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. *We know of no natural system that exhibits this geometry.* Utilizing results generated by the UW group that quantitatively characterized progressive cementation and natural cement morphologies of a quartz-cemented quartz arenite –St. Peters sandstone, this part of the project is investigated the role of specific microstructure parameters that could be measured and seemed likely to be linked to the mechanical response of granular porous media. Two possible parameters are considered in Figure 1, bond-to-grain ratio (BGR) and grain-grain contact length to grain diameter ratio (d/D). In this case, "grain-grain" contact includes the contact of cement overgrowths associated with grains as part of the grain-cement geometries of the granular porous media systems of interest.

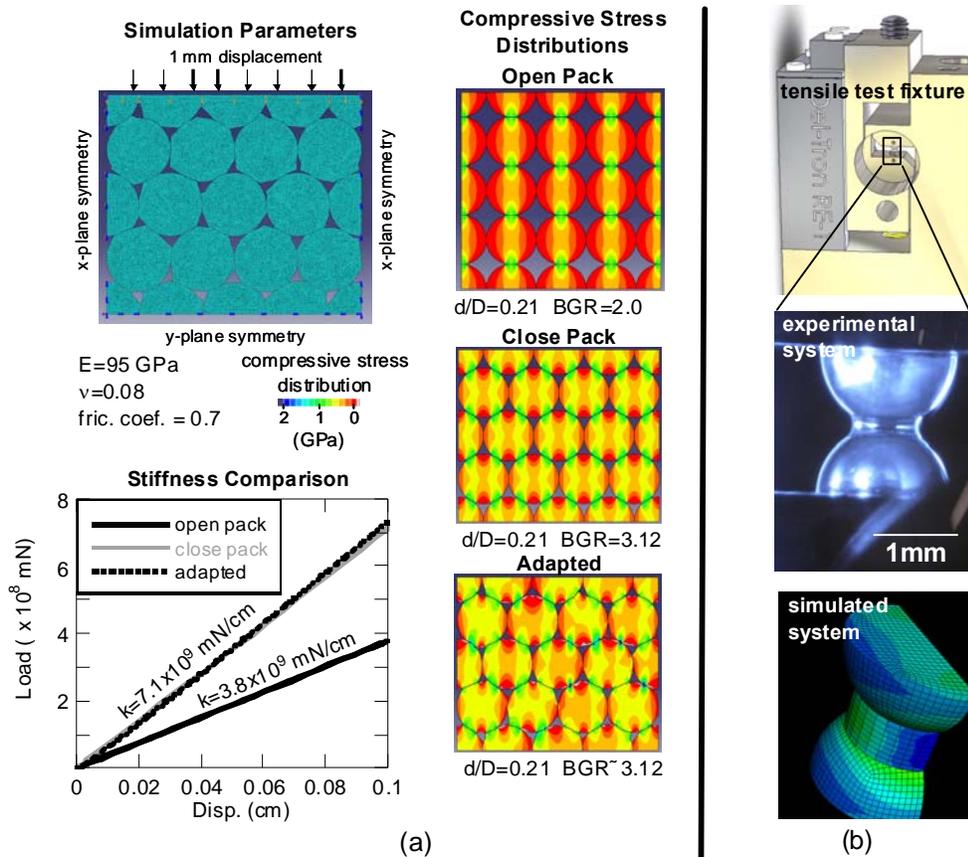


Figure 1 (a) A series of 16 grain simulations demonstrating the role of d/D and BGR microstructure parameters on the stiffness of cemented granular systems. (b) experimental and simulated cemented two-grain assemblies. Experimental system consists of SLS glass beads with ice cement mounted in fixturing configured for tensile testing.

Development of a two grain experimental system using ice as an analogue cement was completed at the end of FY2008. Figure 1(b) illustrated the direct coupling between the experimental system and a simulated system that will be used to better inform cement-bond stiffness necessary for DEM models currently being interrogated at UMass to produce accurate predictions of the bulk mechanical response of cemented granular media.

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

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Objectives: To determine the effects of fluid flow on the growth of solids in fractures.

Project Description: This work continues a previous study of permeability evolution in fractures, by adding numerical modeling for more aggressive conditions of oscillatory dispersion, with precipitation calculations that will be testable by experiment. The numerical simulation involves lattice Boltzmann (LB) calculations. The goal of the simulations is to design experiments capable of testing the models, via growth from gypsum seeds in Hele-Shaw cells. The goal of the project is to determine if precipitation in

fractures will be able to reduce permeability greatly, and thus stop reaction, under real-world conditions found in subsurface storage and pumping.

Results: Previously, it was reported that numerical simulations reproduced the general trend expected for growth in flow; i.e., multicrystalline masses tend to grow into flow, but pronounced fingering is only observable at relatively high Damkohler number ($Da > 10^2$). In the last year, the investigation shifted to a proof of convergence for the LB method, and an analysis of surface tension effects.

A sensitive issue with fixed cell-size automata (or most simulations that do not incorporate adaptive gridding), is the scale independence may not be possible. This potential lack of scalability arises because the minimum finger width decreases as the number of nodes is increased to represent the same physical size simulation. Thus it is possible that the physical minimum finger width may be smaller than the smallest scale allowed by cell size. On the other hand, if the simulation is made very large (many nodes), it becomes prohibitively computer-intensive. Thus it is important to determine the minimum scale for simulating aggregate growth. Figure 1 below shows the effects of scale size on the predictions of centroid displacement – a measure of how much the crystallite mass grows into the flow at fixed model time – for identical Da , Peclet and Reynolds number, but a 4-fold variation in the length of the simulation, and a 64-fold variation in the number of nodes used to represent the simulation. The error bars represent averages over multiple realizations (8 for most sizes). At the lowest sizes, the small width of the channel is known to have an ~10% effect on the accuracy in dispersion modeling. At 200 nodes (in the length of the simulation), the results effectively converge; this is the size used in the current study.

The effect of true surface tension is minimal, at the crystal scale size and supersaturation used in the LB simulations. However, classic models of surface tension effects consider only the role surface tension plays in the instantaneous minimization of energy at the growing interface. Since many natural dendrites and fingers appear to grow by aggregation of pre-formed crystals, the possibility exists that over a small time, pre-formed crystals will settle into a minimal energy position, especially under flow. Work so far indicated that this pseudo-surface tension will cause a greater variation in the nature of the fingering, but will not greatly affect the rate of growth into flow.

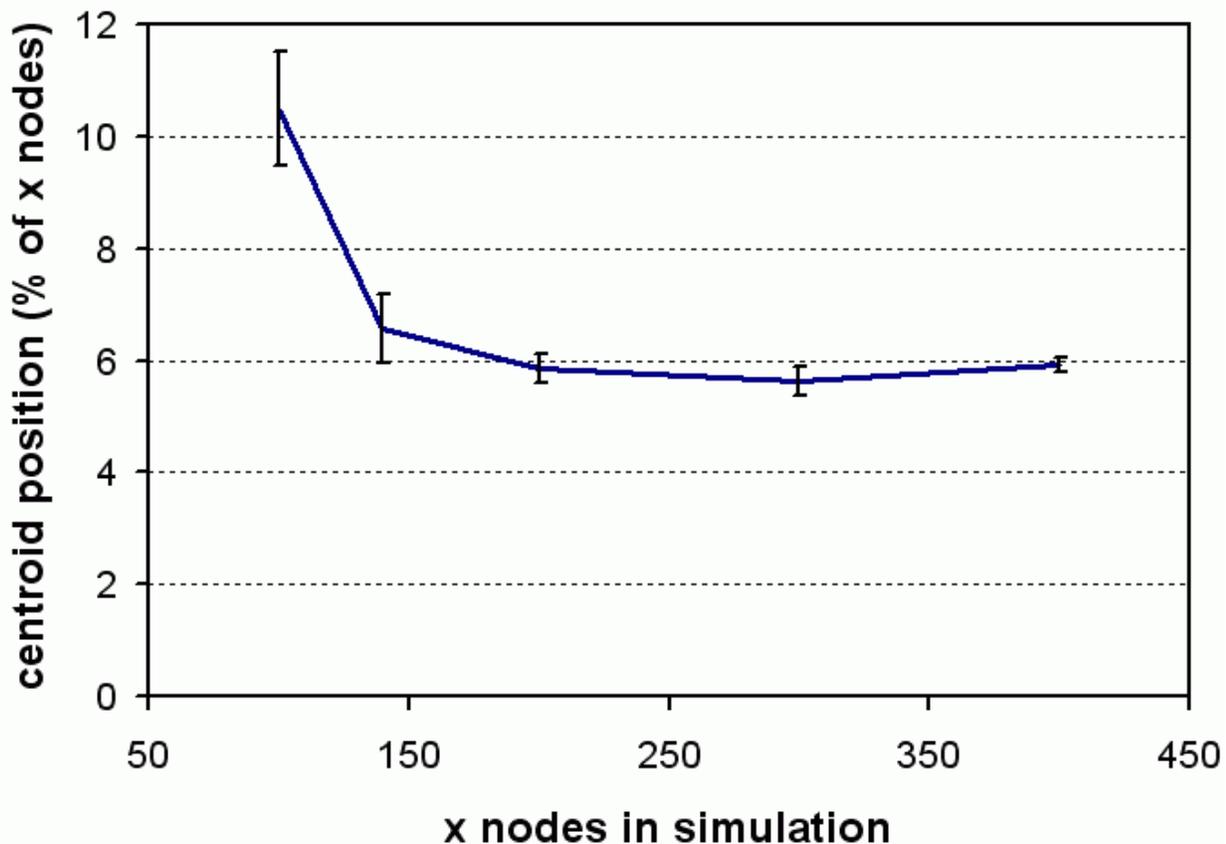


Figure 1. Convergence test. The simulation involves the growth of a multi-crystalline mass into flow; the y-axis measures the extent of the growth at a fixed model time, measured as a percentage of the x-nodes (direction of flow) used in the simulation. Convergence to a constant value is achieved at ~200 nodes. The errors bars represent the standard deviations for multiple realizations, each with trivially varied viscosity and initial conditions.

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 second year of this project, we investigate dispersion characteristics and streamline-based connectivity that are lost when simulating outcrop heterogeneity using geostatistical methods. Initial simulations are based on two-point indicator covariance functions using SISIM; the project has recently expanded this analysis to include multipoint geostatistical methods. A natural aquifer analog was obtained through high-resolution terrestrial lidar (Light Detection and Ranging) scans that capture complex heterogeneity of a braided stream deposit. A semi-automated method segments the lidar scans to create a detailed sand and gravel facies map. This segmented lidar (SL) image represents “realistic” heterogeneity, and is used as a training image to simulate the heterogeneous media.

While dispersion through the SL field shows non-Fickian characteristics, SISIM simulations do not replicate this tailing. We find that disparity in dispersion characteristics can be attributed to differences in velocity variations along individual streamlines (see figure below). These differences can be tracked back to the underlying heterogeneity by measuring the connectivity in velocity and facies along individual streamlines. Even when the SISIM field is highly conditioned (based on 1% of cells in the SL field), the lack of continuous gravel pathways leads to large differences in travel time and dispersion characteristics. Early results using multipoint methods (i.e., Filtersim and Snesim) show that replicating structural patterns seen in the aquifer analog better preserves connectivity and dispersion characteristics of the SL field.

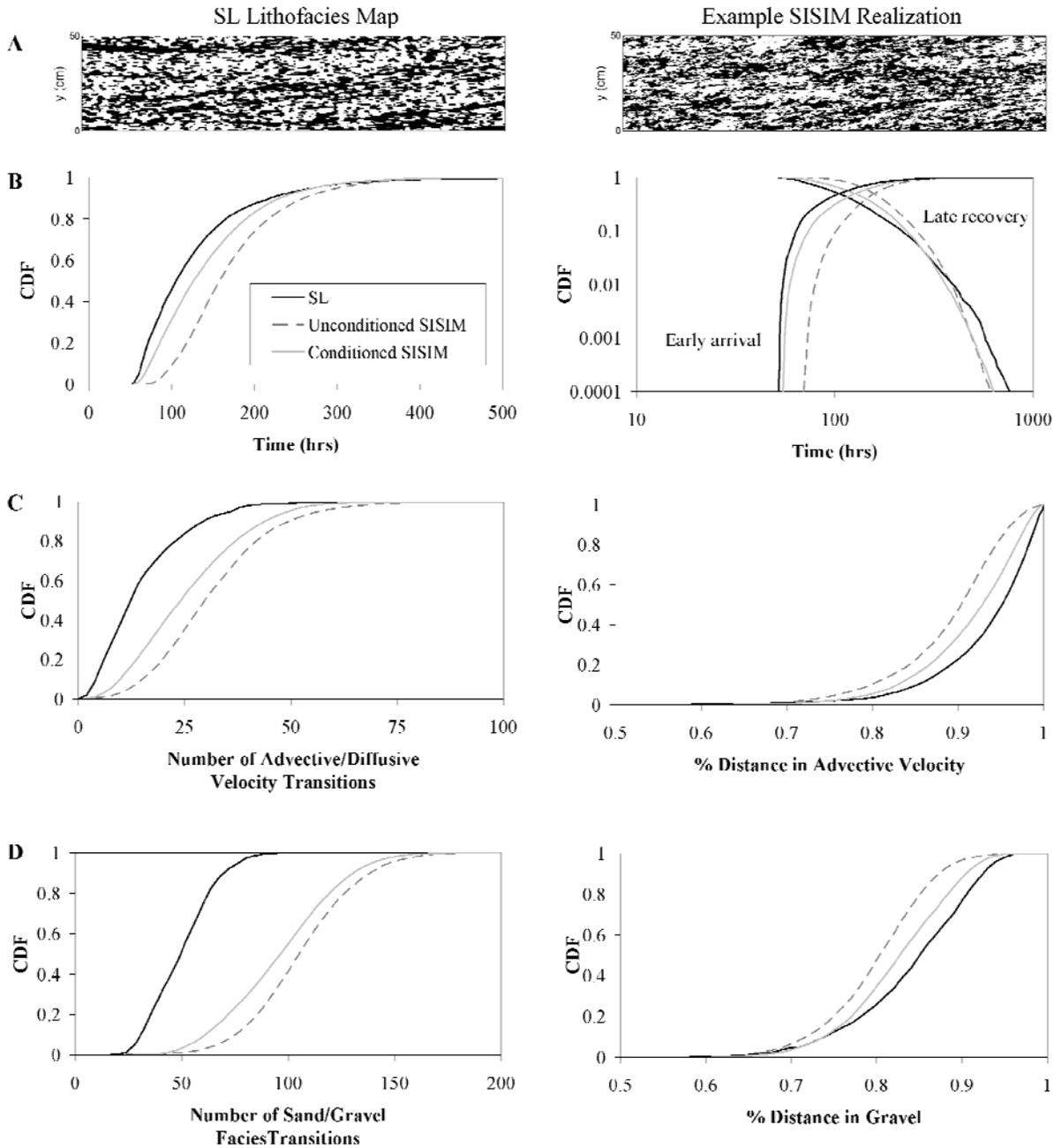


Figure 1: A) SL lithofacies map (left) and example unconditioned realization using SISIM (right). B) Breakthrough curves for SL and SISIM using a linear (left) and log (right) scale. C) Connectivity analysis based on velocity; the number of transitions each particle moves between advective and diffusive dominated velocity (left) and the % travel distance each particle remains in advective velocity (right). D) Connectivity analysis based on facies, the number of transitions each particle moves between sand and gravel (left) and the % travel distance each particle remains in gravel (right).

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

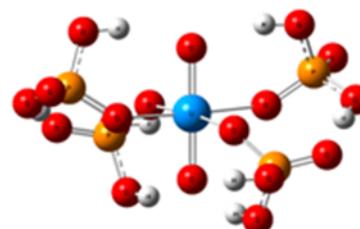
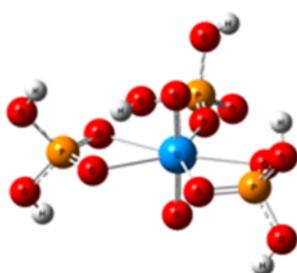
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Objectives: The goal is to develop a molecular level description of the interactions of Gram-negative microbial membranes with subsurface materials. We are developing a molecular level view of microbial metal binding, microbial attachment to mineral 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 the mineral goethite 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: A critical aspect of the identification of actinide complexes are the vibrational frequencies of the actinyl bond. However, even for UO_2^{2+} , the fundamental vibrations are not known. Electronic structure calculations at the coupled cluster (CCSD(T)) level with relativistic effective core potentials and large basis sets have been used to predict the isolated uranyl ion frequencies. The anharmonic effects are larger than the spin orbit corrections but both are small. The anharmonic effects decrease all the frequencies whereas the spin orbit corrections increase the stretches and decrease the bend. Overall, these two corrections decrease the harmonic asymmetric stretch frequency by 6 cm^{-1} , the symmetric stretch by 3 cm^{-1} and the bend by 3 cm^{-1} . The best calculated values for UO_2^{2+} for the asymmetric stretch, symmetric stretch, and bend are 1113, 1032, and 174 cm^{-1} , respectively. The anharmonic vibrational frequencies of the isoelectronic ThO_2 molecule have also been calculated in a similar fashion

and compared to experiment in order to calibrate the UO_2^{2+} results. The ThO_2 frequencies of 807.7, 756.0, and 165.3 cm^{-1} for the asymmetric stretch, symmetric stretch and bend, respectively, are within 1 cm^{-1} of experiment for the stretches. First, second and third pKa's as appropriate have been calculated at the DFT and MP2 levels with a COSMO treatment of the solvation effects for 4 critical sugars in the LPS. These are calculated relative to the values in acetic acid or phosphoric acid as appropriate. The binding of UO_2^{2+} to phosphates is being studied to model uranyl complexation in the LPS as well as to phosphate minerals. A wide range of structures have been explored for up to 4 phosphates in different charge/protonation states as well as with explicit waters of solvation. These structures show evidence for both monodentate and bidentate complexation of the phosphate (Figure) as well as hydrogen bonding to the uranyl oxygens. The relative energetics of the various species are being analyzed.



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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

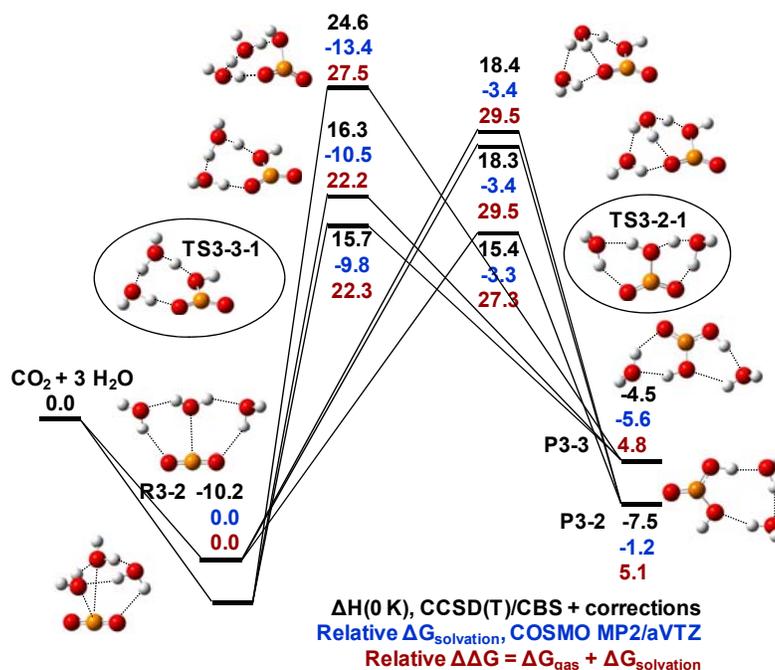
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Objectives: This project addresses key issues of importance in the geochemical behavior of iron oxides and in the geochemical cycling of carbon and iron.

Project Description: For iron, we are specifically studying the influence of carbonate on electron transfer reactions, solid phase transformations, and the binding of carbonate to reactive sites on the edges of 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 CO₂ 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 CO₂ 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 CO₂ in the atmosphere from anthropogenic sources correlate with higher global temperatures. A key constraint on atmospheric CO₂ is the solubility of CO₂ in the oceans. A specific focus of the work is the development of a molecular level description of carbonate chemistry in solution.

Results: Because of the broad geochemical significance of the carbon cycle, controlled, in part, by aqueous carbonate species, we have been studying the reactions in the aqueous carbonate system. The reaction of CO₂ in H₂O leads to a range of reactions relevant to carbon sequestration or to CO₂ clathrate formation. We are focused on the formation of carbonic acid, H₂CO₃ in aqueous solution. Although a consensus has emerged on the active involvement of a water cluster n(H₂O), rather than a water monomer (n = 1), in CO₂ hydration, there has been a debate on the actual number of participating water molecules and the modes of their catalytic action. Using our CCSD(T)/CBS formalism with the COSMO self consistent reaction field approach to treat solvation, we have calculated the potential energy surface for H₂O + CO₂ with up to 4 water molecules. For n = 1, a high energy barrier of ~50 kcal/mol is predicted. For n = 2, a trimeric six-member cyclic transition state with a barrier of ~33 (gas phase) and a free energy barrier of ~31 (solvation) kcal/mol was found. We found 6 transition states with 3 H₂O molecules reacting with CO₂ (see Figure). For n = 3, two low energy reactive pathways are possible. **TS3-3-1** has all three water molecules involved in H transfer in an eight-member cycle. This transition state leads to formation of a structure like an (HCO₃⁻/H₃OH₂O⁺) ion pair. In **TS3-2-1** the third water molecule is not directly involved in the hydrogen transfer but solvates the n = 2 transition state. In the gas phase, **TS3-3-1** and **TS3-2-1** have comparable barrier heights of ~15 kcal/mol relative to separated reactants. **TS3-3-1** is favored in aqueous solution by ~5 kcal/mol on free energy as it has a

larger dipole moment. Bulk solvation reduces the free energy barrier of the first path by ~ 10 kcal/mol for a free energy barrier of ~ 22 kcal/mol at 298 K relative to the complex. There are a wide range of possible structures for $n = 4$ for reactant complexes and transition states. The energetics are similar to those for the $n = 3$ potential energy surfaces. The results for $n = 4$ show that participation of more water molecules beyond $n = 3$ in the cyclic transition will not lower the barrier and could be counter-productive. Gas phase CO_2 hydration with more than 3 water molecules involves the direct participation of 3 water molecules in the cyclic transition state with additional molecules preferring to solvate the complex. These results are the most reliable so far for the prediction of the reaction of water with carbon dioxide and will be used in developing new potentials for the reactions of CO_2 and carbonates in aqueous solutions and on mineral surfaces.



AMERICAN CHEMICAL SOCIETY

Geochemistry Division
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Grant: DE-FG02-08ER15940

Symposium: Advanced Approaches to Investigating Adsorption at the Solid-Water Interface

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Objectives: The primary purpose of this symposium was to bring together researchers who explore adsorption processes at the solid-water interface using different and new techniques including microscopic, spectroscopic, and reflectivity analysis, and both atomistic and molecular modeling. Presentations that tied small-scale studies of the solid-water interface to macroscopic observations and predictive models were encouraged.

Project Description: This symposium was jointly sponsored by the ACS Division of Geochemistry and the Clay Mineral Society, at the 2008 Spring ACS National Meeting held in New Orleans, Louisiana from April 6th through April 10th. It was organized by Louise Criscenti (Sandia National Laboratories), Lynn Katz (University of Texas, Austin) and Heather Allen (Ohio State University). The symposium started Sunday afternoon and ended Thursday morning. It was attended by over 100 researchers. The symposium was divided into six sessions: Adsorption at Oxide-Water Interfaces I, Adsorption at Oxide-Water Interfaces II, Ion Pairing, Water Structure at Solid Surfaces, Beyond Oxides, and Modeling Adsorption in the Field.

Results: Two invited speakers came from overseas: Glenn Hefter from Murdoch University in Western Australia and Tjisse Hiemstra, from Wageningen Agricultural University in The Netherlands. Other invited speakers included: Gordon Brown (Stanford University), William Casey (University of California-Davis), Kim Collins (University of Maryland Medical School), Jeremy Fein (University of Notre Dame), Paul Fenter (Argonne National Laboratory), Stephen Garofalini (Rutgers University), Franz Geiger (Northwestern University), Kim Hayes (University of Michigan), Carla Koretsky (Western Michigan University), James Kubicki (The Pennsylvania State University), Satish Myneni (Princeton University), Nita Sahai (University of Wisconsin), Andrew Stack (Georgia Institute of Technology) and Dimitri Sverjensky (Johns Hopkins University).

Inviting a significant number of speakers insured that a diversity of approaches to investigating adsorption processes were presented, and that lively scientific discussions and exchange ensued. The core of invited talks was complemented by twenty-four excellent contributed talks by students, postdoctoral associates, faculty, and national laboratory scientists. The financial support from the Geosciences Program of the Office of Science greatly helped to achieve the success of this symposium.

BOSTON UNIVERSITY

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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: The first project that we have undertaken is to modify a model first introduced to study self organized critical phenomena and earthquakes to obtain a more realistic model for damage and catastrophic failure. The model begins with a lattice on which each site has a failure threshold, a residual stress and a dissipation coefficient. Stress is initially distributed at random to each site. If the stress is greater than the threshold then the site fails and the stress on the site is set to the residual stress. The difference between the stress on the site at failure and the residual stress has a factor thrown away set by the dissipation coefficient and the remainder distributed to all sites equally within a neighborhood set by the stress transfer parameter R . Here R equal to 1 means nearest neighbor only stress transfer and R large denotes long range stress transfer. When no sights have a stress that exceeds the failure threshold the threshold of each site is lowered to mimic aging and the process outlined above is repeated. After a sight has failed n times it is considered dead. Stress from a failed neighbor site is no longer transferred to a dead site but is transferred instead to the sites that have not died. Catastrophic failure is defined as a

cluster of dead sites that spans the lattice. In the limit where R is “infinite” (in that the neighborhood of each site is the entire lattice), n is one and no stress is dissipated we recover the democratic load sharing fiber bundle model (DLSFBM).

Our studies have produced several important results. These include: (1) Contrary to the assumption made in several treatments of the DLSFBM the system is not in equilibrium. We determine this result by showing that the model is not ergodic. (2) There is a significant difference in the catastrophic failure modes between long and short range stress transfer. In the short range case the cluster of dead sites that spans the lattice is a fractal. In the long range case the failure mode is a nucleation event with a compact object similar to a classical crack. (3) For n and R both large, a situation that corresponds to many important materials, the system organizes itself into stress bands. That is, the sites on the lattice fill bands of stress in a way similar to the way bands are filled in Fermi systems. This has important implications for the catastrophic failure mode. These results are being written up for publication.

In the second project we investigate the evolution of systems quenched into unstable states. This corresponds to the damage problem in which the system is stressed on a very short time scale by something like a shock impulse. Since in many systems damage destroys crystalline symmetry we concentrated on the evolution of unstable states that result in a symmetry change in systems with long range interactions. We found that the evolution took place in three stages which is very different than unstable state evolution without symmetry breaking. In the first stage the original symmetry before the quench is preserved but that the density of the system changes. The second stage has symmetry breaking eigen modes growing exponentially with time and the third stage the eigen modes mix in a fully non-linear evolution. This work has generated two papers. One has been submitted to Physical Review Letters and the second is in preparation.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Division of Geological and Planetary Sciences
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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, H₂O and CO₂, 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 ($D_{\text{H}_2\text{O}}$) in basaltic, andesitic, and rhyolitic melts in order to understand its compositional dependence, including 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. $D_{\text{H}_2\text{O}}$ 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 comparing results from experiments with large and small water concentration gradients. The small gradient experiments consisted of hydration and couple experiments with the extremes of the water concentrations varying by less than ~1 wt. %, whereas the large gradient experiments contained concentrations ranging from 2-4 wt.%. The relationship between $D_{\text{H}_2\text{O}}$ and water content for the large gradient experiments was determined by comparing fits to the FTIR data generated by assuming various functional relationships, including constant $D_{\text{H}_2\text{O}}$, $D_{\text{H}_2\text{O}}$ proportional to water content, $D_{\text{H}_2\text{O}}$ proportional to the logarithm of water content, and $D_{\text{H}_2\text{O}}$ of molecular water constant with immobile hydroxyl groups, as well as direct calculation from the profiles by Boltzmann-Matano analysis. These small gradient experiments allow us to build up this relationship through a series of experiments with different water contents, using Boltzmann-Matano analysis. The small gradient haploandesite experiments are consistent with the large gradient ones at H₂O contents ≤1.5-2.0 wt.%. Over the total range of the large gradient experiments, up to ~4 wt.%, these data indicate that the $D_{\text{H}_2\text{O}}$ – H₂O content relationship is exponential. However, the experiments with higher H₂O concentrations, up to ~6 wt. %, constrain the relationship to be closer to linear. This study has required us to develop a better understanding of how different regression fits to the profiles and noise in the FTIR data affect the determination of diffusion coefficients using Boltzmann-Matano methods. Difficulties of different functions (such as polynomials of different orders, smoothing splines, fragments of Gaussians, and asymmetric sigmoidals) to fit the extremes of the profiles cause variability in the $D_{\text{H}_2\text{O}}$ values

calculated in these regions. Therefore we have concluded that the $D_{\text{H}_2\text{O}}$ values are unreliable in the lowest 10% and highest 20% of the range of H_2O content for any individual experiment. The most consistent function to fit both the hydration and couple experiments is a five-parameter asymmetric sigmoidal function. Random noise added to the best fit asymmetric sigmoidal functions, with the same standard deviations as the fits to the FTIR data, indicate that noise generally contributes about half as much error to the $D_{\text{H}_2\text{O}}$ determination as do the fits to the profiles.

Part 2: We are currently exploring the effects of cooling rate and $f\text{O}_2$ on the occurrence and morphology of P (\pm coupled Al and Cr) oscillatory zoning in olivine. The starting material for these 1-atm experiments is a natural Hawaiian basalt (BHVO-2) to which we've added 10 wt% San Carlos olivine. Oscillatory zoning of P in olivine develops over the entire range of investigated cooling rates and is coupled to zoning in Cr and Al. Times-series experiments show that oscillatory zoning is present even in the first-formed crystals at a given cooling rate. Olivines from specific cooling rates (at QFM) show Cr and P abundances that are positively correlated (the average Cr/P for all of the data is ~ 0.04) and the 1°C and $30^\circ\text{C}/\text{hr}$ experiments produce olivines that have nearly the same range of P and Cr abundances (concentrations of Al in olivine from the slow and fast cooling rate experiments also overlap). At IW, Cr concentration is independent of that of P, suggesting that it is Cr^{+3} that is charge-coupled with P in olivine. Al concentrations are positively correlated with both P and Cr in olivine from our experiments. Cooling-rate experiments on a P-free synthetic analog of BHVO-2 produced olivines with Cr contents at a given Al content that are lower than those from the P-bearing experiments; cooling rate experiments on a Cr-free synthetic analog produced olivines with ranges of P and Al that are similar to those seen in the Cr-bearing experiments. Taken together, the data suggest that multiple substitution mechanisms exist for Al-Cr-P. The presence of oscillatory zoning of P, Cr, and Al in olivines that vary in morphology from skeletal to euhedral (produced by decreasing the cooling rate from 30°C to $1^\circ\text{C}/\text{hr}$) suggests that: (1) diffusion of Al, Cr, and P in the melt at the olivine-liquid interface is slow even compared to growth rates that produce euhedral, faceted olivines, (2) growth rate must be highly variable over short time scales even under conditions of linear cooling. We have also produced X-ray maps of P, Cr, and Al in olivines from different depths from the Kilauea Iki lava lake. All samples, even those from a depth of 246 ft (near the thermal maximum of the lava lake) show fine-scaled, coupled Cr and P oscillatory zoning bands. Although Al zonation was not observed, this may reflect our analytical conditions (we are currently exploring longer dwell times and higher beam currents in an effort to detect Al zonation). Nevertheless, the relative "sharpness" of the Cr and P bands, and the apparent absence of Al banding suggests that diffusion rates for Al in olivine are greater than those for Cr, which in turn are greater than those for P. Coupled with existing cooling rate models for the lava lake, these data may allow us to place quantitative constraints on these diffusion coefficients at temperatures where laboratory experiments would be prohibitively long.

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How Do Interfacial Phenomena Control Nanoparticle Structure?

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Objectives: The objective of this project is to understand how and why the molecular environment at a nanoparticle surface influences the internal structure and properties of the material.

Project Description: Nanoparticles are important components of natural systems, arising as the result of physical, chemical, and biological processes. Due to their small size and enhanced reactivity, they may play unexpected roles in the environment. However, nanoparticles are not necessarily static. Rather, some are able to respond quickly to changes in their surroundings. Thus, prediction of nanoparticle behavior requires understanding of how the presence of molecules such as water, organics and solution pH can influence their structure and surface reactivity. The approach taken in this study is to combine nanoparticle synthesis with experimentation, characterization using a suite of methods, and molecular simulation and other prediction tools. Our work includes synthesis of ZnS nanoparticles with mixed cubic and hexagonal stacking by control of the solution pH; development of a novel method for determination of size-dependent surface free energy of nanoparticles, and study of the atomic structure of ultrafine amorphous TiO₂ nanoparticles.

Results: Surface environments change reaction kinetics, thus can influence nanoparticle structure in a way that cannot be predicted using equilibrium thermodynamics. We have shown that nanoparticulate ZnS with mixed cubic and hexagonal stacking can be synthesized by kinetic control via manipulation of the solution pH. Reaction of zinc acetate with thioacetamide in weakly acidic solutions results in nano-ZnS with mixed stacking whereas reaction in basic solutions results in nano-ZnS in the sphalerite phase. We have developed a statistical model that shows that the mixed stacking is controlled by the relative deposition rates of the ccp and hcp layers during crystal growth, and the relative “sphalerite” and “wurtzite” components of the nanoparticles are determined by these rates. At a higher pH, the ccp deposition rate is higher than the hcp rate and the “sphalerite” component is greater. XRD patterns are simulated based on the predicted structures and were used to interpret the experimental observations.

Determination of size-dependent surface free energy of nanoparticles via x-ray diffraction. We determined the lattice contraction of nanocrystalline anatase (TiO₂) as a function of particle size (~ 4 – 34 nm) using x-ray diffraction and Rietveld analysis. Surface free energy (γ) of nanocrystalline anatase was derived from these data from an integration of the surface stress calculated from the lattice contraction. Our results revealed an unexpected strong size dependence of γ , with a maximum value at around 14 nm. Two opposing factors contribute to the variation of γ with the particle size, the increase of surface energy with decreasing particle size due to presence of more high-energy sites, and the decrease of surface energy due to closer structural correspondence between surfaces and interiors of nanoparticles as the particle size decreases. Our approach may be used to study nanoparticles in cells and other environments where conventional calorimetric measurements of nanoparticle surface enthalpy

are not applicable.

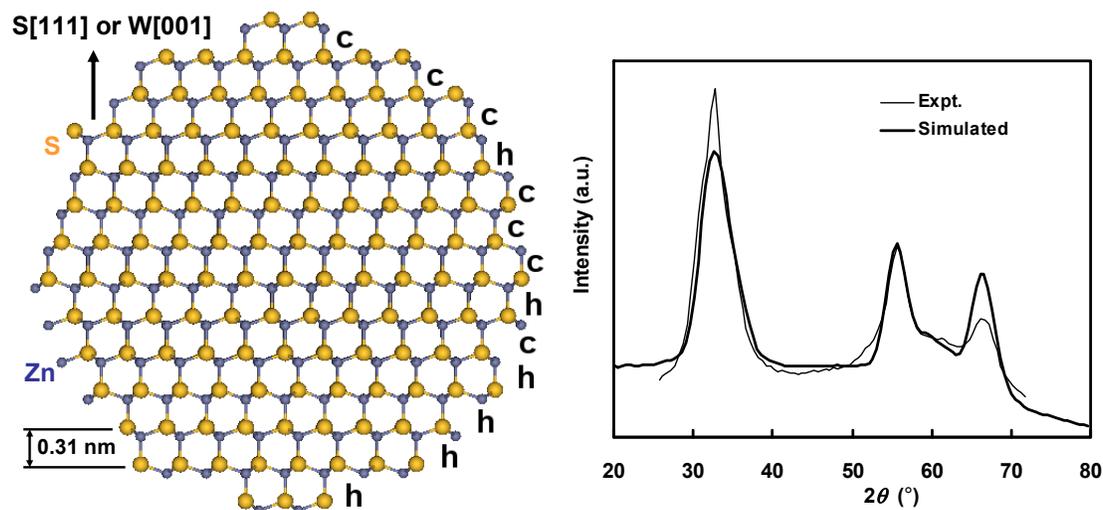


Figure 1. (Left) Structure of a ZnS nanoparticle. The stacking sequence in the particle is (from top to bottom) *cchcchchhhh*. (Right) Comparison between experimental and simulated XRD patterns of ZnS nanoparticles with mixed stacking.

Atomic structure of nanometer-sized amorphous TiO₂. Ultrafine (2 – 3 nm) titania (TiO₂) nanoparticles show only diffuse scattering by both conventional powder x-ray diffraction and electron diffraction. We used synchrotron wide-angle x-ray scattering (WAXS) to probe the atomic correlations in this amorphous material. The atomic pair-distribution function (PDF) derived from Fourier transform of the WAXS data provided the input for reverse Monte Carlo (RMC) simulations of the atomic structure of the small nanoparticles. Input structures for the RMC were obtained by molecular dynamics simulations and X-ray absorption spectroscopy (XAS) simulations were used to screen candidate structures obtained from the RMC. The structure model that best describes both the WAXS and XAS data consists of particles with a highly distorted shell and a small strained anatase-like crystalline core. The average coordination number of Ti is 5.3 and the Ti-O bond length peaks at 1.940 Å. Relative to bulk titania, the reduction of the coordination number is primarily due to the truncation of the Ti-O octahedra at the titania nanoparticle surface, and the shortening of the Ti-O bond length is due to bond contraction in the distorted shell. Core-shell structures in ultrafine nanoparticles may be common in many materials (e.g. ZnS).

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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. Our approach is to embrace some of the complexity of the natural context so as to define the molecular-scale interplay among mineralogy, and microbial activity, and microbial community structure.

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 to use 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.

The research proposed here is relevant to numerous DOE missions in bioremediation of uranium and organic contaminants and energy production (including fuel cells) and will advance fundamental understanding of microbe-mineral and protein-mineral interactions and electron transfer to nanoparticles. In addition, the research will provide new insights into biochemical adaptation by revealing connections between protein variant sequences and the redox potential of electron acceptors required for anaerobic respiration.

Results: This is a newly initiated project and no results are yet available.

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Diffusion/Dispersion Transport of Chemically Reacting Species

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Objectives: The project is concerned with calculation of the thermodynamic properties of biochemical reactions and the characterization of geochemical constraints operating on those reactions. The long-term goals of the research include 1) uncovering basic driving forces shaping the composition of microbial communities in nature and 2) using the relative abundances of proteins or other biomolecules measured in cells or taken from environmental genomes to identify clues to the prevailing geochemical conditions and reaction pathways.

Project Description: Research carried out in 2008 focused on testing theoretical geochemical techniques for computing the metastable equilibrium distribution of proteins as a function of temperature, pressure, pH, oxygen fugacity, and activity of CO₂, NH₃ and H₂S. The work has culminated in a publication and the production of a new software package named CHNOSZ, which aids in calculating the standard molal thermodynamic properties of reactions including proteins, the chemical affinities of the reactions, and the metastable equilibrium activities of the protein in the reactions.

Results: A model system consisting of ten surface-layer proteins from mesophilic, thermophilic and hyperthermophilic was identified so that the computational results could be compared with geochemical data. The calculated logarithms of chemical activities of the proteins shown in the figure are consistent with metastable equilibrium among residue equivalents of the proteins and total activity of residues of 6.3. At low values of the fugacity of oxygen, the protein from the hyperthermophilic organism *Methanocaldococcus jannaschii* is thermodynamically favored. This result is consistent with the submarine hot-spring environment of this organism, which can be exposed to highly reducing and high-temperature hydrothermal vent fluid. The range of relative abundances of the proteins suggests that the approach could lead to testable predictions about coexisting chemical species in metastable equilibrium that might occur in biofilms or other microbial assemblages that are tied to the geochemical surroundings.

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

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Objectives: The goal is to develop a comprehensive model that relates elastic properties of sedimentary rocks, especially their anisotropy, to compositional and microstructural characteristics. These include the orientation distributions of all component phases and the grain and pore space topology. Quantification of texture in shales was the focus of the previous research.

Project description: Understanding geological stresses and anisotropy in sedimentary rocks is critical for seismic exploration. Information is very limited because of the compositional complexities and poor crystallinity of clay-rich rocks. Time-of-flight neutron diffraction spectra and synchrotron hard X-ray diffraction images offer the possibility for probing the internal structure of rocks and quantify micro-to-nano scale stress-induced changes both in natural and experimental samples. Based on observations of microstructures and textures we obtain information about the formation process (sedimentation, compaction and diagenesis) and can link the internal structure to macroscopic physical properties such as acoustic wave velocities. The research spawned stimulating collaborations with experimentalists (Stanford, University of Oslo and Kiel) and theorists (Colin Sayers and Evgueni Chesnokov).

Results: The most exciting and challenging project was to quantify preferred orientation in clay-rich sediments and hard synchrotron X-rays provide enormous opportunities. It is now possible to determine texture patterns of up to six different phases in a complex Opalinus shale from Mont Terri by deconvoluting 2D diffraction images with the Rietveld method. Figure 1 illustrates strong fabrics of illite, kaolinite, chlorite and calcite and a weaker fabric for authigenic illite-smectite. Quartz has a random orientation distribution. A systematic investigation of Jurassic European shales illustrates regular changes with composition and burial depth that can be attributed to compaction. This was verified by investigating texture patterns in experimentally compressed clay aggregates such as kaolinite-illite-quartz and Ca-montmorillonite. From microstructural information anisotropy of physical properties can be predicted by averaging over orientation distributions and then comparing simulations with macroscopic measurements. Predictions of anisotropy are satisfactory but magnitudes of velocities differ, which we attribute to the porosity structure that we are beginning to investigate with microtomography.

A comparison of phyllosilicate textures in shales, metamorphic schists and fault gouge is most revealing. Diffraction images immediately reveal very strong textures for muscovite and chlorite in schists, intermediate textures of kaolinite, illite and illite-smectite in shale and very weak texture in gouge from the SAFOD drill hole (Figure 2). Phyllosilicates in metamorphic schists grew during recrystallization

under stress, in shales they became aligned during sedimentation and compaction and in gouge movements on faults produced randomization.

Residual strains continue to be of concern. We are calibrating stresses for onset of mechanical twinning in quartz as a function of stress and temperature with *in situ* neutron diffraction measurements and could recently document lattice strains in quartz up to 300 microstrains with synchrotron microdiffraction from Laue images. This may provide a new paleopiezometer.

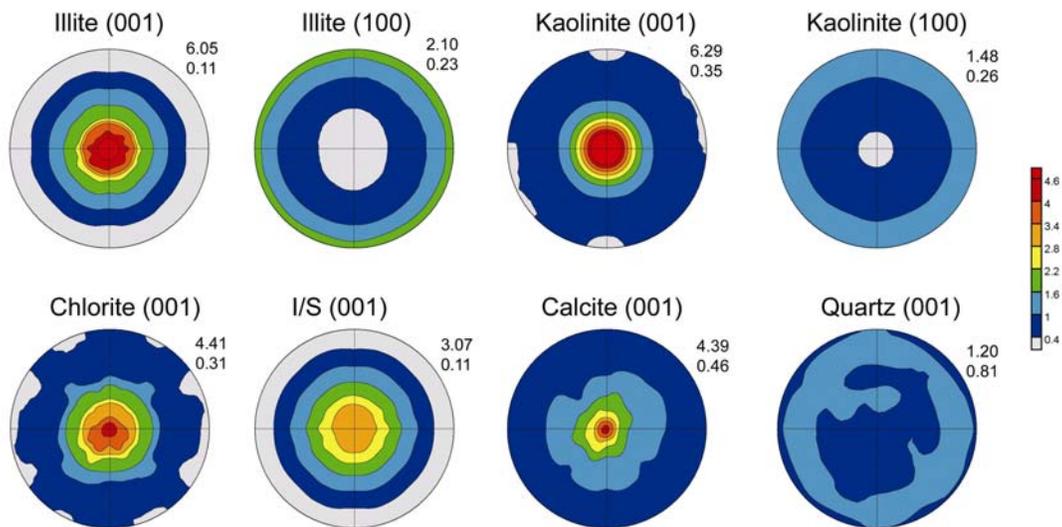


Figure 1. Pole figures of illite, kaolinite, chlorite, illite/smectite, calcite and quartz for Mont Terri shale. Equal area projection. Pole densities are expressed in multiples of a random distribution (m.r.d.). The numbers on the top right side of each projection are maximum and minimum pole densities (in m.r.d.).

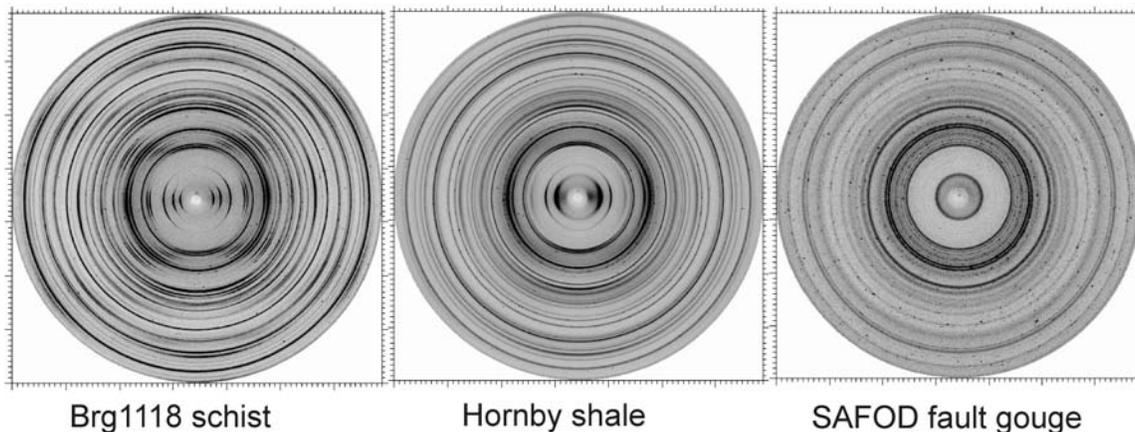


Figure 2. Synchrotron X-ray diffraction images of metamorphic schist (chlorite, muscovite), Kimmeridge shale (montmorillonite, illite/smectite, illite, kaolinite) and SAFOD fault gouge (illite/smectite and illite/muscovite). Intensity variations along Debye rings, particularly those at low diffraction angles immediately reveal the texture strength.

UNIVERSITY OF CALIFORNIA, DAVIS

NEAT ORU

4440 Chemistry Annex

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Grant: DE-FG02-97ER14749

Thermodynamics of Minerals Stable Near the Earth's Surface

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(Thermochemistry Laboratory)*

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 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 have started a study of the energetics of amorphous calcite, an important precursor in biomineralization and possibly in CO₂ sequestration. 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.

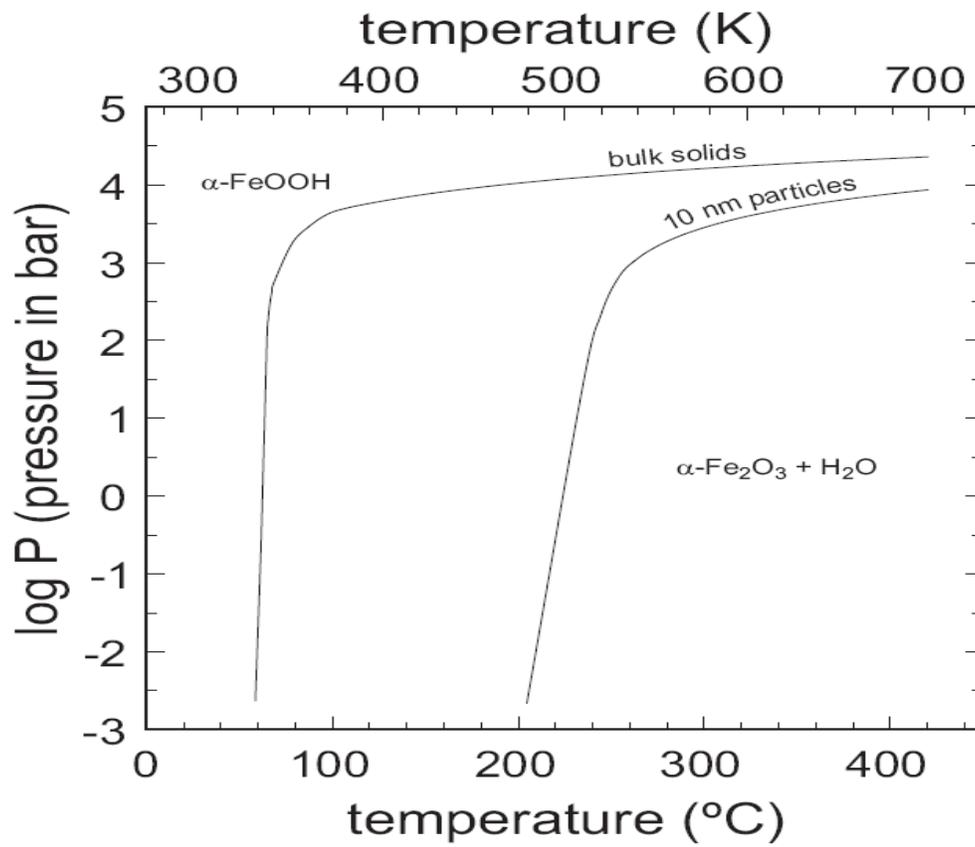


Figure 1. Effect of particle size on the dehydration curve of goethite to hematite plus water

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Department of Geology

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

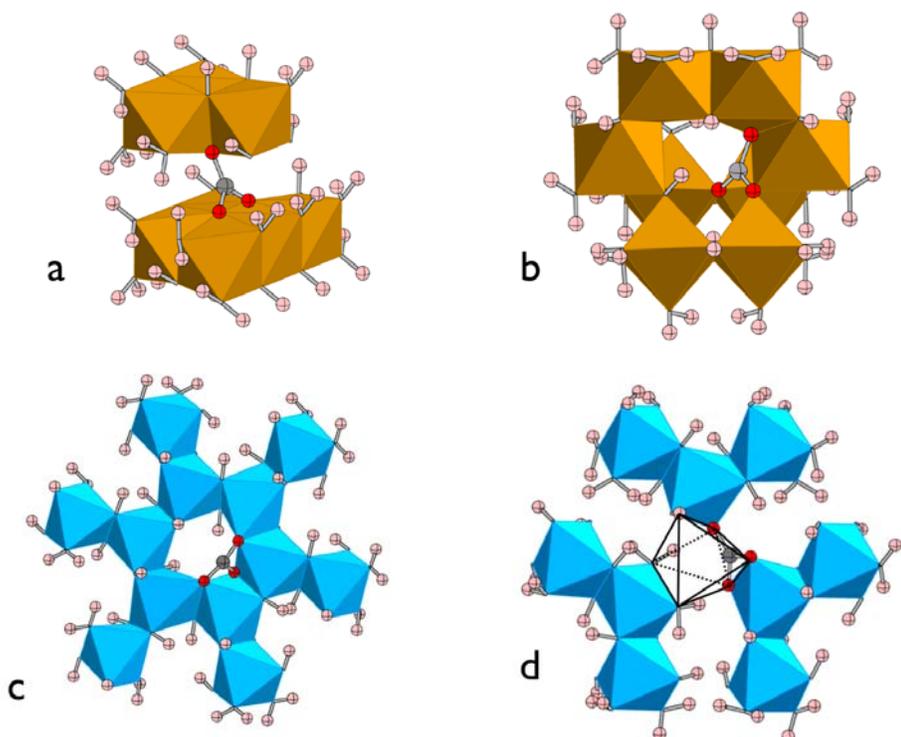
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Objectives: This project addresses key issues of importance in the geochemical behavior of iron oxides and in the geochemical cycling of carbon and iron.

Project Description: The incorporation of CO₂ into soil minerals such as goethite (α -FeOOH) and gibbsite [Al(OH)₃] is one of the major techniques used to infer the pCO₂ of the atmosphere in the geologic past (Yapp, C. J., and Poths, H. Ancient atmospheric CO₂ pressures inferred from natural goethites *Nature* **355**:342-344, 1992). Little is known about how CO₂ defects are incorporated into oxide soil minerals at a molecular level. Understanding the structures of these defects makes it possible to predict their equilibrium isotopic composition, which is a central aspect of the technique of atmospheric reconstruction. Currently, geological evidence suggests that CO₂ incorporated in goethite, CO₂(m), is about 2.5 per mil heavier than CO₂(g). The questions to be addressed are: (1) Why is CO₂(m) so light relative to carbonate in calcite or aragonite which is approximately 10 per mil heavier than CO₂(g)? (2) Do the CO₂ defects all have the same structure, or are there different populations? (3) If there are different populations, would the carbon isotope signatures of these populations be the same, or would they differ? (4) Would large differences be expected for the isotopic signatures of Al and Fe oxide minerals? and (5) Are the equilibrium fractionation factors at the defect sites even relevant, or, alternatively, is the isotopic composition mediated by surface complexes at the mineral-water interface?

Results: *Ab initio* molecular dynamics and quantum chemistry techniques were validated on the aqueous carbonate system and were used to calculate the structure, vibrational frequencies, and carbon-isotope fractionation factors of the carbon dioxide component [CO₂(m)] of soil (oxy)hydroxide minerals goethite, diaspore, and gibbsite. We have identified two possible pathways of incorporation of CO₂(m) into (oxy)hydroxide crystal structures: one in which the C⁴⁺ substitutes for four H⁺ [CO₂(m)_A] and another in which C⁴⁺ substitutes for (Al³⁺, Fe³⁺) + H⁺ [CO₂(m)_B]. Calculations of isotope fractionation factors give large differences between the two structures, with the CO₂(m)_A being isotopically lighter than CO₂(m)_B by ~10 permil in the case of gibbsite and nearly 20 permil in the case of goethite. The reduced partition function ratio of CO₂(m)_B structure in goethite differs from CO₂(g) by less than 1 permil. The predicted fractionation for gibbsite is more than 10 permil higher, close to those measured for calcite and aragonite. The surprisingly large difference in the carbon-isotope fractionation factor between CO₂(m)_A and CO₂(m)_B suggests that the isotopic signatures of soil (oxy)hydroxide could be heterogeneous. Isotope signatures of surface complexes were highly variable, ranging from -18 to -5.1 to +17.5 per mil for bidentate mononuclear, bidentate binuclear, and monodentate surface complexes. The answers to the questions posed above are (1) for goethite, even the heaviest CO₂(m) species is indeed light relative to carbonate in carbonate minerals; (2) High-resolution infrared spectra are in good

agreement with the calculations on both types of defects and indicate that both are present in bulk FeOOH; (3) The different populations have vastly different equilibrium carbon isotope signatures, with the lightest species close in isotopic composition to organic carbon; (4) There are large differences between the equilibrium isotopic composition of CO₂(m) in gibbsite and in goethite, with CO₂(m) in gibbsite being heavier than CO₂(m) in goethite. This differential fractionation needs to be taken into account if both minerals are used to estimate pCO₂; (5) If the isotope fractionation is mediated by surface complexes, the isotope signature is likely to depend strongly on the particular types of surface complexes present, and hence, be a function of pH, surface carbonate loading and the presence of competing anionic sorbents.



The fundamental structures for CO₂(m) found in goethite/diaspore (a, b) and gibbsite (c,d) by the searching procedure. Fe octahedra are brown. Al octahedra are blue. Optimization of both structures results in a carbonate unit shown in ball and stick representation with a grey carbon atoms and red oxygen atoms. Protons are shown in pink. In (d) the edges of the vacant octahedron into which the C⁴⁺ is substituted are outlined in black.

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Grant: DE-FG02-04ER15639

How Do Interfacial Phenomena Control Nanoparticle Structure?

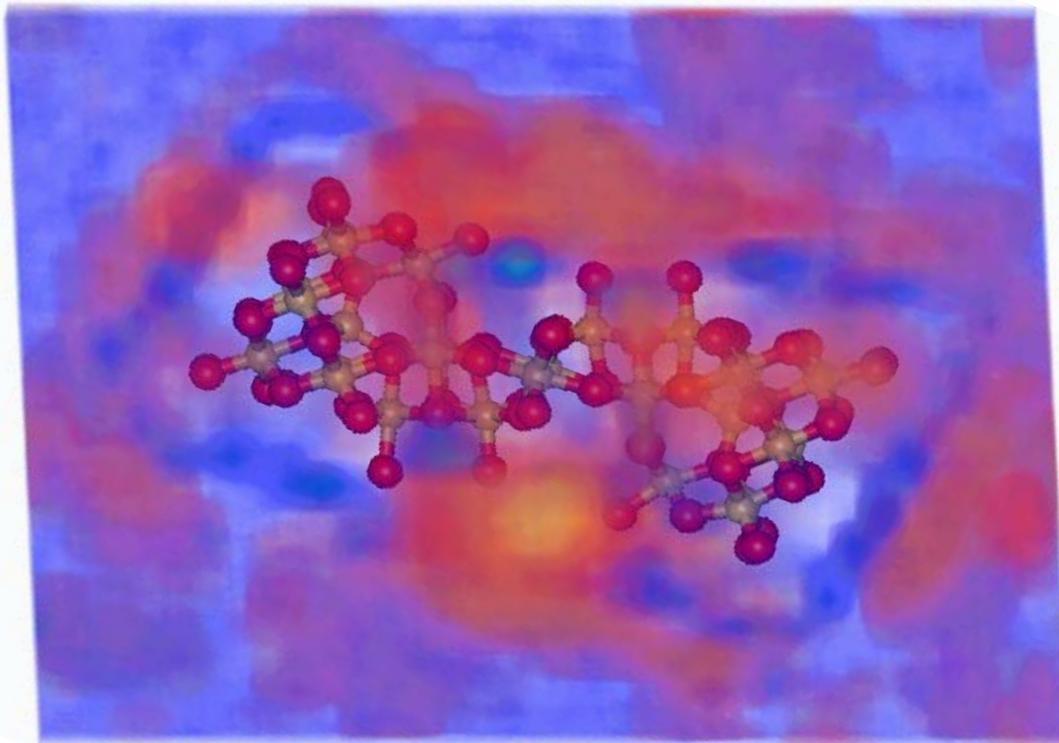
James R. Rustad, 530-754-6021; jrrustad@ucdavis.edu, Jillian F. Banfield (UC Berkeley), Glenn Waychunas (Lawrence Berkeley National Laboratory)

Objectives: This project is focused on the role of solvation and the electric double layer in determining the stabilities of oxide nanoparticles.

Project Description: Amphoteric oxide nanoparticles have pH dependent surface charge. For small ions, such as $\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+}$, the surface charge density is more than sufficient to destabilize the ion into two complexes with approximately 15 Al ions and approximately 9+ charge. In the gas-phase, this is an exothermic process by about 600 kcal/mol. In solution, the nanoparticle will be stabilized through both the dielectric response of the solvent and through the association of background electrolyte with the surface of the nanoparticle. We carried out a series of molecular dynamics calculations of the stabilities of both $\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+}$ (Al_{30}) and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (Al_{13}) in aqueous solution with and without background electrolyte (both perchlorate and sulfate) to test the role of solvation and electrolyte association in determining the stabilities of the nanoparticles.

Results: Both the Al_{13} and the Al_{30} ions were unstable in solution in the absence of background electrolyte. The Al_{13} ion became detached at the μ_4 -oxo sites connecting the central tetrahedral ion to the trimeric capping units, and reached an intermediate state in which bridging dimeric units popped outwards into the solution to accept two additional waters of hydration. In the presence of both perchlorate and sulfate counter ions, the frequency of detachment events at the μ_4 -oxo sites was almost zero on 5 nanosecond time scales of the MD calculations, indicating that the background electrolyte plays an important role in stabilizing the particle, even in aqueous solvent. For the Al_{30} ion, similar behavior was observed. Without perchlorate or sulfate counterions, the Al_{30} ion almost immediately breaks apart into smaller fragments. These simulations underscore the role of solvation forces in stabilizing aggregating oxide fragments. In the absence of these forces, the surface charge accumulated on these particles destabilizes the aggregation process. Furthermore it is probably meaningless to consider the energetics of these particles in the absence of the electrolyte in which they are embedded. The “bulk” energies of the particles, at this scale, are positive, and their stability is entirely determined by the association of the background electrolyte with the proton surface charge.

Density of perchlorate ions (orange) and water molecules (blue) in $\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+}$ (protons not shown). Perchlorate ions are concentrated in the attachment region and mediate the condensation of the Al_{30} ion from smaller Al_{13} units. In the absence of the counter ions, electrostatic repulsion between the two Al_{13} fragments is too strong to result in condensation.



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Grant: DE-FG-02-05ER15693

Proton Exchange Rates and Other Elementary Reactions in Large Aqueous Molecules: A Combined Experimental and Simulation Project

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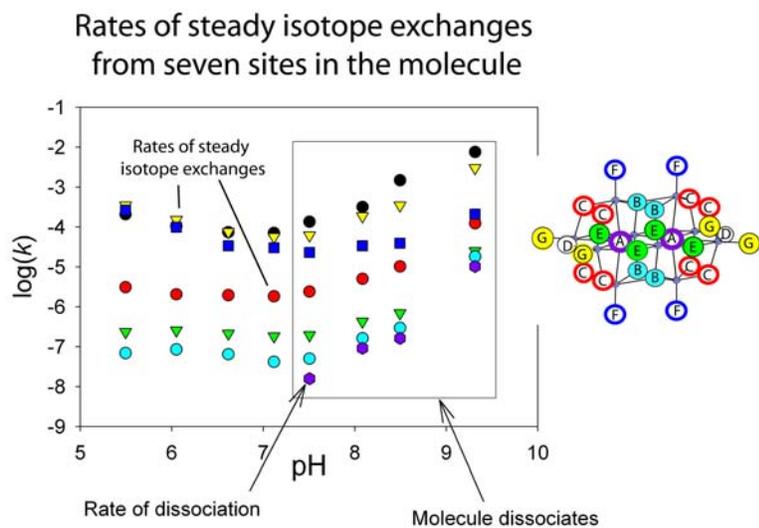
Objectives: We examine isotope-exchange reactions in nanometer-size oxide ions at a fundamental level in order to improve methods of simulating mineral reactions in water.

Project Description: We measure rates of reactions at individual structural sites in nanometer-size ions in water. These ions are chosen not for their immediate geochemical relevance, but for their suitability for detailed study of reactions at the molecular scale. With these molecules, we acquire data at the appropriate scale for simulation and can study systematically some variables that are uniquely important to goals of the DOE. As an example, we study isostructural molecules with, and without, a full shell of f-shell electrons to see how the reactivities differ and how electronic-structure methods can account for the differences.

Results: In recent work we measured rates of steady oxygen-isotope exchange at all seven structural oxygens in the nanometer-size oxide ion with water [Figure 1] as well as the pathways for dissociation. These data are unprecedented in detail. The nanometer-size decaniobate ion [Figure 1] is unique in that it reacts slowly enough in water that one can simultaneously observe steady-state oxygen-isotope exchanges (top) and dissociation pathways (bottom).

The results have led to conceptual advances in both geochemistry and aqueous polyoxometalate chemistry. We find that the entire molecule is involved in the reaction dynamics for isotope exchange; reactions are not local. Isotope-exchange reactions at all structural oxygens are affected by changes in pH, even though this molecule is largely unprotonated. Furthermore, dissociation, which is usually much slower than isotope exchange, leaves much of the molecule intact [Figure] and involves a normally inert and highly coordinated oxygen in the molecule's center. These results are consistent with what we have observed in different, more geochemically relevant systems as well. We find that some reactions affecting minerals, such as exchange of bound for bulk waters, are robust and can be predicted using simple simulations and bonding arguments. On the other hand, isotope-exchange at bridging oxygens are via profoundly counterintuitive pathways.

With similar oxide clusters we can cleanly examine the effect of f-shell electrons on reactivity of oxides in water. The $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(8-x)-}$ and $[\text{H}_x\text{Ta}_6\text{O}_{19}]^{(8-x)-}$ differ only in the presence of an extra full electron shell, including a full shell of $4f^{14}$ electrons in the Ta(V) version. Because of the Lanthanide contraction, these molecules are virtually isostructural yet differ fundamentally in how they exchange oxygen isotopes with solution. Documenting such differences is a fundamental goal of the DOE and presents a clear challenge to computation methods of predicting reactivities for materials with f-shell electrons. The differences are unanticipated and profound.



Pathways for dissociation involve a central normally inert oxygen.

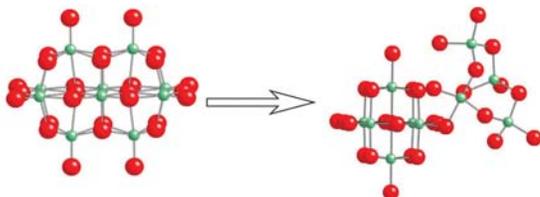


Figure 1: Rates of steady oxygen-isotope exchange (top) in the nanometer-size decaniobate ion proceed by complicated concerted motions. The rates span many orders of magnitude. The colors correspond to different structural oxygens in the molecule. We could separately identify the pathways (bottom) for slow dissociation of this molecule via a combination of NMR and mass spectrometric measurements. The dissociation pathway centers on a normally inert oxygen in the center of the molecule and all isotope exchange rates increase with pH, even though these exchanges are much faster than rates of dissociation of the molecule.

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Departments of Physics and Geology

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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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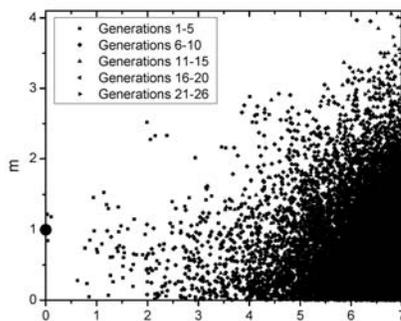
Objectives: To employ computational simulations and statistical field theories for nucleation dynamics to 1) Develop statistical physics models including fully interacting defect and damage fields leading to correlated dynamics of systems with long range elastic interactions and near mean field dynamics; 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 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.

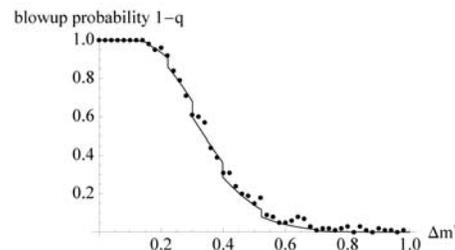
Results: Fully interacting fields of defects and damage are generally not included in most current models for material deformation. Instead, defect density and damage fields are assumed to be non-interacting or dilute, implying a strictly mean field approach. We propose to use statistical physics methods for interacting defect and damage fields, made possible by the construction and use of statistical field theories, to greatly improve our predictive capability for the macroscopic failure of materials. During the past decade, we have formulated and applied a variety of models, methods and techniques to understand the multiscale physics and patterns of deforming rock masses. Our methods and models have been general, and can be applied over a broad range of scales. We have used parallel computational modeling in combination with analysis methods based on modern statistical physics associated with percolation, statistical field theories, nucleation, and phase transitions.

To define a statistical approach to this problem, we will normally begin by writing a free energy functional that connects the microscale with the macroscale processes. Since damage represents a modification of a brittle elastic system, we expect to find that the interactions produce the mean field dynamics characteristic of elastic systems. Sudden transitions in the state of these systems can be understood in the context of first order phase transitions, where the influence of the classical limit of stability, or spinodal, is felt. The appearance of a mean field spinodal leads to a general coarse-grained equation, which expresses the balance between rate of stress supplied, and rate of stress dissipated in the processes leading to surface damage. Our theory has the novel feature that, while the initial nucleation process occurs in a non-classical spinodal mode, the final crack or “droplet” has a classical profile, as a result of the decreasing range of interaction as damage increases. We also compare with laboratory data and show reasonable agreement in certain cases.

As a first example of results using precursors to these methods, we have investigated a branching model (“BASS”) for damage leading to fracture and rupture. To construct such a model, we first consider the more general paradigm of aftershocks following an earthquake, and then construct what is in essence a “time reversed” model. The branching aftershock sequence (BASS) model is a self-similar statistical model for shear fracture (or “earthquake”) aftershock sequences. A prescribed parent shear fracture event generates a first generation of daughter aftershocks. The magnitudes and times of occurrence of the daughters are obtained from statistical distributions. The first generation daughter aftershocks then become parent fractures that generate second generation aftershocks. The process is then extended to higher generations. The key parameter in the BASS model is the magnitude difference Δm^* between the parent fracture and the largest expected daughter fracture. In the application of the BASS model to aftershocks Δm^* is positive, the largest expected daughter event is smaller than the parent, and the sequence of events (aftershocks) usually dies out, but an exponential growth in the number of events with time is also possible. In this paper we explore this behavior of the BASS model as Δm^* varies, including when Δm^* is negative and the largest expected daughter event is larger than the parent. Negative values of Δm^* represent a cascade of damage leading to the eventual primary shear fracture. The applications of this self-similar branching process to biology and other fields are discussed. Shown below is a typical, time-dependent sequence of damage events leading to macroscopic failure.



Simulation of an unstable sequence of events:
Magnitude m vs. nondimensional time T



Probability of “blow-up” plotted
against parameter Δm^*

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

Department of Earth Science
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Grant: DE-FG02-96ER14620

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

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

Project Description: We have mainly targeted active faults and young (Tertiary strata) petroleum fields in southern California for study. Faults include the Refugio Fault in the Transverse Ranges, the Ellwood Fault in the Santa Barbara Channel, and the Newport-Inglewood in the Los Angeles Basin. Subsurface core and tubing scale samples, outcrop samples, well logs, reservoir properties, pore pressures, fluid compositions, and published structural-seismic sections are being studied to characterize the tectonic/diagenetic history and geochemical signatures in carbonate that characterize rapid CO₂ 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 new studies of the geochemical signatures in well scales formed by rapid CO₂ degassing have shown some surprising results. The mineral vaterite, which is an unstable polymorph of calcite, is known to form rapidly in laboratory experiments as micron-scale crystallites. However, within minute to hour time scales it rapidly transforms to calcite. We have found extremely large (up to 300um length) crystals of vaterite in a number of well scales in production tubing from Southern California oil fields. The scales have survived for at least several years.

The vaterite scales appears to have formed in a fundamentally different way than most carbonate scales. The traditional view of carbonate scaling is that the depressuring of a CO₂ charged fluid results in precipitation of calcite. Thus, the oxygen isotopic composition of the calcite is controlled by temperature of crystallization and the oxygen isotopic composition of the fluid that it crystallizes from. Studies by Grace Giles, a DOE funded MS student, show that with *rapid* calcite crystallization the oxygen is up to several per mil more positive than expected for equilibrium due to rapid uptake of the CO₃⁼ molecule from the solution before it can equilibrate with the bulk fluid. In contrast, the oxygen (and carbon) isotopic composition of the vaterite well scales are extremely enriched in the light isotopes. Oxygen isotopic values are 13 per mil lighter than calcite scales and carbon values are 25 to 30 per mil more negative than calcite scales in the same field. These values suggest that the CO₃⁼ molecule is sourced directly from CO₂ gas, rather than from dissolved carbonate ion in equilibrium with an aqueous fluid. Presumably, the Ca ion is provided by a fluid film on the tubing string.

These results are not predicted by conventional geochemical models and demonstrate the potential importance of metastable phases during CO₂ degassing and interpreting isotopic data from well scales. The importance of this finding is relevant to the effects of injection of CO₂ gas in to the formation and the possible effects of leakage of reservoir seals.

We continue to study the South Ellwood fault by examining and acquiring data from Platform Holly in the Santa Barbara Channel. These include fluid composition, shut in well pressure and temperature data, and submarine methane seepage along the fault. Our recent work indicates that surface seepage rates, which are quantitatively measured in steel tents on the seafloor, can be directly linked to the production history of individual wells at Platform Holly that directly underlie the seep collection area. The changes in inflow rates are consistent enough that we are calculating permeability of the approximately one km flow path from the wells to the overlying sea bed. We are also in the process of sampling fluid for elemental and isotopic composition in key wells that have pressure data suggesting that sea water is being drawn down into the underpressured Monterey Formation reservoir at Platform Holly.

In the Los Angeles Basin, Mike Ryan, a current UCSB Masters student, has completed his sampling, petrographic and stable isotopic analyses of carbonate cements associated with the igneous intrusions associated with the north end of the Newport-Inglewood Fault. The igneous body appears to be largely a series of surface flows intruded along the fault. Samples are currently being dated by Ar-Ar methods. Ryan's progress has been slowed by his current status as a pilot candidate in the US Air Force pilot program.

We continue to plan the drilling and coring of the Newport-Inglewood fault near its southern end with monthly visits to Long Beach. Offset tubing strings and thermal anomalies indicate active fluid movement and aseismic creep along the fault in this area. Currently Signal Hill Petroleum, located in Long Beach, California is planning on funding the drilling and coring of the fault zone. Collaborators include Southern California Earthquake Center and Cal State Long Beach. We anticipate that this project will provide a rich dataset for analysis of fault processes.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

Department of Mechanical Engineering

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Grant: DE-FG02-08ER15991

Multiscale Investigation and Modeling of Flow Mechanisms Related to CO₂ 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 CO₂ 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 CO₂ sequestration and other geologic flows.

Results: This project began in Sept. 2008, and thus no results have been obtained to date.

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Grant: DOE DE FG02-06ER15767

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

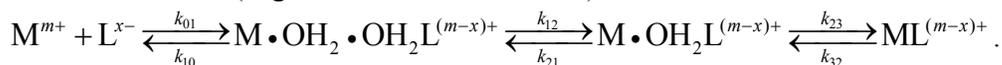
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Objectives: 1st principles simulations methods are being developed and applied to the study of the chemical behavior of metal ions, their counter ions and their oxo-hydroxo hydrolytic polyions in aqueous solutions. The understanding of the aqueous chemistry of these species is essential to the interpretation of processes such as the formation of minerals, the sequestration of CO₂, 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.

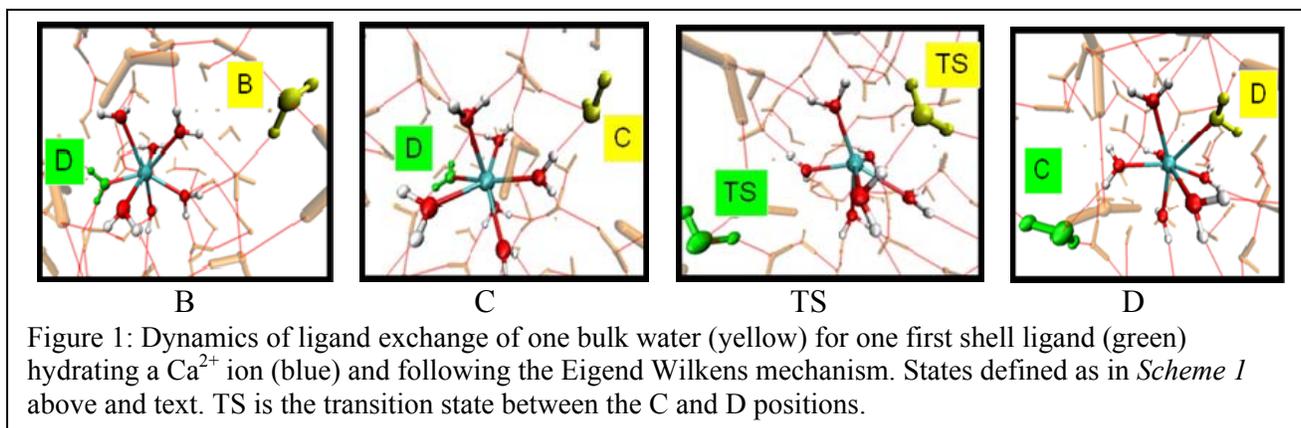
Project Description: The results of this research will contribute to the molecular level understanding of the chemistry of processes such as ore formation, toxic species transport, mineral solubility, and absorption on mineral surfaces for sub-critical to supercritical conditions as well provide for 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, Al³⁺, Fe³⁺, Cr³⁺, Ca²⁺, and Ni²⁺, 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: Ligand transfer in the Ca²⁺-64 H₂O system via the Eigen Wilkens mechanism: One of the most important reactions in aqueous geochemical systems is the transfer of a solute species from the bulk solution to a contact position in the 1st hydration shell of a metal ion or

reactive surface. Reactions with labile ions have been extensively studied by Eigen and others. The putative general mechanism (Eigen-Wilkins mechanism) for these reactions follows Scheme 1,

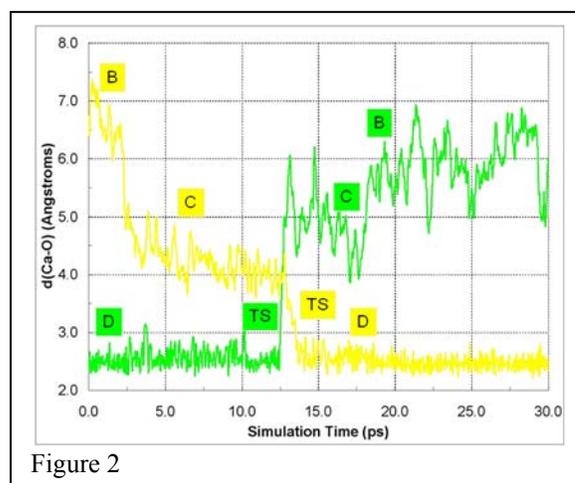


Scheme 1: **A** **B** **C** **D**
 In Scheme 1 **A** represents the reactant Ligand in the bulk water separated by at least two waters, **B** represents the reactant molecule (yellow) coordinated to (entering) the 2nd shell separated from the ion core by two waters (as in Fig.1, panel B), **C** represents the ligand in the second shell separated by a single water from the ion core in an outer sphere complex (Figure 1, panel C) and **D** represents the contact pair product in a inner sphere complex (Figure 1, panel D (yellow)) of the reaction. TS is a



transition state between the C and D states.

For the room temperature Ca²⁺-H₂O system 1st shell residence times are quite short. This is because the Ca²⁺ ion has a fairly loose 2nd hydration shell. However, the dynamics and the interactions in the 1st and 2nd shell are expected to be different and, therefore, require treatment with a 1st principles based theory. This is an ideal system for AIMD simulation studies because the time scales for the reactions are accessible by AIMD simulations. In Fig. 1 the snapshots of the structures of a ligand transfer from the bulk to the 1st hydration shell are illustrated. In this mechanism the reaction is initiated with the exchanging ligand in the bulk (state B). There is then a transfer into the 2nd shell (state C) after sometime the final contact state D is formed passing through a transition state TS. The dynamics of this process are illustrated in Fig. 2. Note that the time spent in the 2nd shell is quite long compared to the transitions from the bulk to 2nd and 2nd to 1st shells. This mechanism is consistent with the presence of a highly structured and relatively stiff 2nd hydration shell.



Methods Developments Results: See PNNL report (Co PI Eric Bylaska):

UNIVERSITY OF CHICAGO

Center for Advanced Radiation Sources

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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 forty seven (247) beam time proposals were received, 231 unique users conducted experiments, and 60 papers were published. Published results included the following (lead collaborators in parentheses). Micro- and nanoscale element-distribution maps indicate that high-field-strength trace elements in metamict zircon were redistributed during alteration by diffusion and by dissolution-and-precipitation processes near microfractures and other fluid channels (A. J. Anderson, St. Francis Xavier University). Metal–oxygen bond lengths of the (ordered) surface Fe atoms of $\alpha\text{-Fe}_2\text{O}_3$ (1_102) reacted with Fe(II) under anoxic conditions were characteristic of Fe(III), providing indirect evidence for oxidation of adsorbed Fe(II) and consistent with recent studies indicating that Fe(III)-hydroxides are effective oxidants for dissolved ferrous iron (K. S. Tanwar, University of Alaska - Fairbanks). Large vesicles were found to represent pathways used by gas to flow non-explosively to the surface indicating the development of an efficient system that sustains persistent degassing in basaltic volcanic systems (D. Baker, McGill University). Short-range ordered aluminosilicates were shown to be relevant for the adsorption of anions, such as CCA-derived arsenate, in natural soils (P. Nico, Lawrence Berkeley National Laboratory). Oxidation state of iron in komatiitic melt inclusions indicated a hot mantle in the Archean (A. J. Berry, Imperial College London). An empirical model, requiring only average particle diameter and porosity as input parameters, was developed to readily estimate air–water interfacial area–water saturation relationships for sandy porous media (M. S. Costanza-Robinson, Middlebury College). Manganese and Zn from liquid fertilizers were found to remain in comparatively

more soluble solid forms in soils, whereas Mn and Zn from equivalent granular sources tended to transform into comparatively less soluble solid forms (G. M. Hettiarachchi, University of Adelaide). Oxidation states of U, Fe and Mn, measured in real-time (400 days) on sediment columns supplied with synthetic groundwater containing organic carbon = 30 mM, showed 80% of the U was reduced to U(IV) with transient reoxidation at about 150 days. Mn(III,IV) oxides were completely reduced to Mn(II) and Fe(III) remained largely unreduced supporting the hypothesis that the reactive Fe(III) fraction was responsible for reoxidizing U(IV) (T. K. Tokunaga, Lawrence Berkeley National Laboratory). Hydrothermal Mo experiments up to 800 °C and 300 MPa indicated that high Mo concentrations can be transported in aqueous solutions and that Mo concentration in aqueous fluids seems not to be the limiting factor for ore formation, whereas precipitation processes and the availability of sulfur appear to be the main controlling factors in the formation of molybdenite (MoS₂) (T. Ulrich, Australian National University).

UNIVERSITY OF CHICAGO

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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: Forty five (45) unique users conducted experiments within the past year and 15 papers were published. Research included the following (lead collaborators in parentheses): (1) Real-time measurements of the effects of organic carbon in changing the oxidation states of U, Fe, and Mn in U-contaminated sediments indicated the reactive Fe(III) fraction was responsible for reoxidizing U(IV) (T. K. Tokunaga, Lawrence Berkeley National Laboratory); (2) X-ray absorption spectroscopy and x-ray diffraction analysis of simulated waste liquid in laboratory sediment columns showed that uranium colloid formation and accumulation at the neutralized plume front could be one mechanism responsible for highly heterogeneous U distribution observed in the contaminated Hanford vadose zone. (J. Wan, Lawrence Berkeley National Laboratory); (3) Pedogenic minerals play an important role in surface soil Pb sequestration, particularly in deciduous forests, and should be considered in any assessment of pollutant Pb mobility. (A. Schroth, Dartmouth College); (4) The influence of phosphate (rock phosphate, biological phosphate, and calcium phytate) and microbial amendments (*Alcaligenes piechaudii* and *Pseudomonas putida*) on U mobility in contaminated sediments and soils was evaluated (A. Knox et al.); (5) Dose-response experiments including μ SXRF were carried out to test the hypothesis that earthworms provide a trophic transfer pathway of roadway-derived Zn in urban systems (S. Lev, Towson University); (6) Studies of natural and synthetic basaltic glasses demonstrated that the oxidation state of iron determined by XANES can be used to infer magma oxygen fugacity with a precision of ± 0.25 log

units in the vicinity of the QFM buffer (E. Cottrell, Smithsonian Institution).

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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.

Project Description: Experiments designed to measure the isotopic fractionation of calcium, magnesium, iron, and lithium by chemical diffusion in natural silicate melts involves diffusion couples with starting materials made from Mid-Ocean Ridge Basalt juxtaposed with a natural rhyolite glass. 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: Table 1 gives a summary of isotopic fractionations due to chemical diffusion between molten basalt and rhyolite and by thermal diffusion (i.e., Soret diffusion) in molten basalt. The basalt-rhyolite diffusion couples are annealed in a piston cylinder apparatus and held at temperatures in the range 1350°C-1450°C for times from 6 minutes to 15.7 hours. The thermal diffusion experiments with homogeneous basalt as a starting material were also run in a piston cylinder apparatus for up to 100 hours. Profiles of major element concentrations were measured with a JEOL JSM-5800LV scanning electron microscope equipped with an Oxford Link ISIS-300 energy dispersive microanalytical system. Trace element profiles and Li isotopic compositions were measured by ion microprobe. $^{44}\text{Ca}/^{40}\text{Ca}$ was measured by double spike thermal ionization mass spectrometry at the Berkeley Center for Isotope Geochemistry. $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{26}\text{Mg}/^{24}\text{Mg}$ were measured at the University of Chicago using a multicollector ICPMS.

The water diffusion experiments were design in such a way that the concentration in a source chamber decays exponentially with time at a rate proportional to the diffusivity of the dissolved salt in water. This allowed the evolving elemental and isotopic concentrations in the source chamber to be interpreted to yield diffusivity ratios with a high degree of precision. Molecular dynamics simulations for the mobility of selected salts dissolved in water were also carried out. Table 2 compares the β exponents (defined in Table 1) for isotopic fractionations of dissolved ions in water determined by laboratory experiment to those from molecular dynamic calculations. Note that with the exception of potassium,

the mass dependence of diffusion coefficients in water are much smaller than for molten silicate liquids (ie., compare the β s in Table 2 to those in Table 1.

Element	σ oxides.	Ω ‰ amu. /100°C	β $D_1/D_2 = (m_2/m_1)^\beta$	β_T $D_T^1/D_T^2 = (m_1/m_2)^{\beta_T}$
Mg	0.0015±1 ^{1,2}	3.6±1 ¹²	0.05±1 ²	0.65±5 ^{1,2}
Ca	0.0006±1 ¹	1.6±1 ¹	0.06±2 ^{2,4}	1.15±5 ¹
Fe	0.0018±1 ¹	1.1±1 ¹	0.03±1 ¹	0.40±2 ¹
Si	-0.0015±1 ¹	0.6±2 ¹	----	0.24±1 ¹
Al	~ 0	----	----	----
O	----	1.5±2 ¹	----	----
Li	----	----	0.215±5 ²	----

Table 1. σ is the Soret coefficient defined as the ratio of the chemical diffusion coefficient D_i of an element to its thermal diffusion coefficient D_T^i . Ω gives the isotopic fractionation by temperature differences in terms of per mil fractionation per 100°C per atomic mass unit difference between the isotopes. The exponent β is used to parameterize the measured difference in the chemical diffusivity of isotopes 1,2 of mass m_1, m_2 .

Solute	β MD simulation	β Experiment
Li ⁺	0.0171 ± 0.0159	0.0148 ± 0.0017
Na ⁺	0.029 ± 0.022	0.023 ± 0.023
K ⁺	0.049 ± 0.017	0.042 ± 0.002
Cs ⁺	0.022 ± 0.014	
Ca ²⁺	0.0000 ± 0.0108	0.0045 ± 0.0005

Table 2. β exponents for fractionation of isotopes of selected elements diffusing in water from molecular dynamics simulations and from laboratory experiments.

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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.

Project Description: We address two aspects of the erosion problem: the “two-phase phenomenon” of water-driven granular flow, and the growth and interactions of channels. We study the former problem in the laboratory and the latter problem in both the laboratory and the field. In both cases we combine our empirical studies with theoretical analysis.

We specifically address the problem of erosion driven by subsurface “seepage” flows. As in the more commonly studied problem of erosion by overland flow, an understanding of the two-phase flow of water and grains is required to predict the conditions under which material is eroded and subsequently transported by rivers and streams. Compared to the case of overland flow, however, the growth of seepage channels is relatively decoupled from topographic roughness. Channel networks driven by groundwater flow instead reflect more purely their competition for water. We seek to better understand the conditions necessary for the initiation of erosion, the mechanisms that govern the growth of seepage-driven channels, and the processes that determine the geometry of seepage networks.

Results: In the last year, we investigated the motion of individual grains in a granular bed driven by a laminar fluid to give us new insights into the relationship between hydrodynamic stress and surface granular flow. A closed cell of rectangular cross-section is partially filled with glass beads and a constant fluid flux flows through the cell. The refractive indices of the fluid and the glass beads are matched and the cell is illuminated with a laser sheet, allowing us to image individual beads. The bed erodes to a rest height that depends on the constant flux. We studied the Shields threshold criterion, which assumes that the non-dimensional ratio of the viscous stress on the bed to the hydrostatic pressure difference across a grain is sufficient to predict the granular flux. We directly verified that the boundary shear stress determines not only the onset of granular flow, but also the granular flux over a roughly horizontal bed in non-steady driving conditions.

In the past year, we have also examined the shape of channel heads observed as a function of slope of the granular bed and seepage rate with precise laser-aided topography. Simple amphitheater and bifurcated channel head shapes are observed similar to those observed in the field. An area driven curvature growth model was developed and compared with laboratory and field channels shapes. The model yields a log cosine form which is in good agreement with preliminary observations.

CLAY MINERALS SOCIETY

3635 Concorde Parkway
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Grant: DE-FG02-08ER15941

Proposal to Support a Joint Meeting of the Clay Minerals Society and the Geochemistry Division of the American Chemical Society – April 5-10, 2008

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Objectives: The primary purpose of the Clay Minerals Society is to stimulate research and to disseminate information relating to all aspects of clay science and technology. Through the 2008 annual meeting in New Orleans, the society offered individuals a means of following the many-sided growth of the clay sciences and of meeting fellow scientists with widely different backgrounds and interests. This was particularly true due to the joint nature of the meeting with the Geochemistry Division of the American Chemical Society. Clay Minerals Society members include clay mineralogists, crystallographers, physicists, chemists, geochemists, soil scientists, agronomists, ceramic scientists, civil engineers, petroleum geologists and engineers, and industrial scientists in fields involving products ranging from catalysts to sorbent materials.

Project Description: “Clays of Demeter: 45th Annual Meeting of the Clay Minerals Society” was held April 5-10, 2008 in historic New Orleans, Louisiana, USA. The timing of the meeting was altered from its usual June date to accommodate holding the meeting jointly with the geochemistry division of the ACS at the national ACS meeting in New Orleans. Approximately 120 – 150 scientists from around the globe attended the meeting and shared knowledge and ideas on the latest advances in clay mineral science while enjoying the historic and musical environs of New Orleans. The meeting included four and a half days of technical sessions, a one-half day awards symposium, and a full day workshop on clay surface redox processes. Details are available at the meeting web site: <http://www.cottey.edu/clay/>.

Results: The technical sessions for the meeting were jointly organized by Brenda Ross of the Clay Minerals Society, and Tim Filley of the geochemistry division of the ACS. The scientific sessions of the meeting kicked off on Sunday morning with the Clay Minerals Society Awards Symposium, which recognized honored members of the Society. Sessions on various clay mineral and geochemistry topics followed over four and a half days and included the following.

- Advanced Approaches to Investigating Adsorption at the Solid-Water Interface
Louise J. Criscenti, Heather Allen, Lynn E. Katz
- Archaeological Clay Source Materials: Their Chemical, Mineralogical, and Physical Characteristics
Sheldon A. Skaggs, Jennifer Webby
- Clay Minerals and Biomolecules
Gözen Ertem
- Clay Minerals and Health

Javiera Cervini-Silva, Lynda Williams

- General GEOC Oral Session
Timothy R. Filley
- General Session on Clays and Clay Minerals: CMS Clay Gumbo
Brenda S. Ross
- Methods for Studying Optical and Electrochemical Properties of *In Situ* Thin Films
Alanah Fitch
- Reactions on Clay Surfaces
Susan L. Brantley, James D Kubicki, Geoffrey M Bowers
- Speciation of Arsenic and Other Trace Elements in Soils and Sediments
Rona J. Donahoe, Dibyendu Sarkar
- The Impact of Hurricane Katrina from an Environmental and Petrochemical Perspective
Lore J Ramillano, Andrew Jackson

One hundred and eighty five oral presentations were scheduled during the technical sessions. Also, forty four technical posters were scheduled on Wednesday at a general poster session. On Monday, a subset of the posters were highlighted at the ACS Sci-Mix poster session. As is customary for CMS meetings, there was a special workshop on Saturday before the formal meeting. The workshop was titled “Clay Surface Redox Processes: Fundamentals and Characterization Techniques”, and was organized by Hailiang Dong. Various administrative meetings and business lunches were held throughout the week of the conference. Finally, there was a special reception for students and new members held on Sunday evening to recognize the future leaders of the society. The financial support from the Geosciences Program of the Office of Science helped greatly to achieve the success of Clays of Demeter.

COLORADO SCHOOL OF MINES

Center for Wave Phenomena

Green Center

Golden CO 80401

Grant: DE-FG02-05ER15739

Prestack Amplitude Analysis of Wide-Azimuth Seismic Data for High-Resolution Reservoir Characterization

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Objectives: The goal of the project is to develop an efficient methodology for prestack amplitude analysis and inversion of multicomponent seismic data acquired over azimuthally anisotropic fractured formations. The project results will be instrumental in seismic characterization and dynamic monitoring of fractured reservoirs. In particular, seismic amplitude inversion will help in estimating the fracture orientation and density, analyzing the local stress field and assessing the capacity of a fractured medium to sequester a fluid.

Project Description: Because reflection coefficients carry local information about the medium properties at the top and bottom of the reservoir, amplitude-variation-with-offset (AVO) analysis can provide a much higher vertical resolution than travelttime methods. The main focus of the project is on the joint AVO inversion of wide-azimuth PP, PS, and SS (if available) data for realistic orthorhombic and lower-symmetry reservoir models. To mitigate amplitude distortions in the overburden, we devised a moveout-based correction for anisotropic geometrical spreading that does not require knowledge of the velocity model. The anisotropic parameters obtained from the amplitude inversion are being used for evaluating the physical properties of heterogeneous, fractured reservoirs.

Results:

1. Amplitude-sensitive semblance analysis for wide-azimuth seismic data.

We developed an amplitude-sensitive semblance algorithm designed to correct for the influence of polarity reversals on moveout analysis of wide-azimuth, long-offset P-wave data acquired over fractured reservoirs. Synthetic tests for transversely isotropic and orthorhombic models show that distortions caused by polarity reversals become more common for long-spread gathers. Conventional semblance produces substantial errors in the normal-moveout (NMO) ellipse and azimuthally varying anellipticity parameter η not just for class 2 AVO (amplitude variation with offset) response, but also for some models with class 1 AVO (Figure 1). Our method helps to flatten wide-azimuth reflection events prior to stacking and azimuthal AVO analysis and provides input parameters for the anisotropic geometrical-spreading correction.

2. Effective reflection coefficients for curved interfaces in anisotropic media.

Plane-wave reflection coefficients (PWRC), routinely used in AVO analysis, break down at near- and post-critical incidence angles and in the presence of significant reflector curvature. To overcome these limitations, we introduced effective reflection coefficients (ERC) for multicomponent data generated by point sources in heterogeneous anisotropic media. If the interface is plane, ERC are close to the exact solution sensitive to the anisotropy parameters and source-receiver geometry; for curved interfaces, ERC provide a practical approximate tool to compute the reflected wavefield. We analyzed the dependence of ERC on reflector shape and demonstrated their advantages over PWRC in 3D amplitude analysis of PP and PS reflection data.

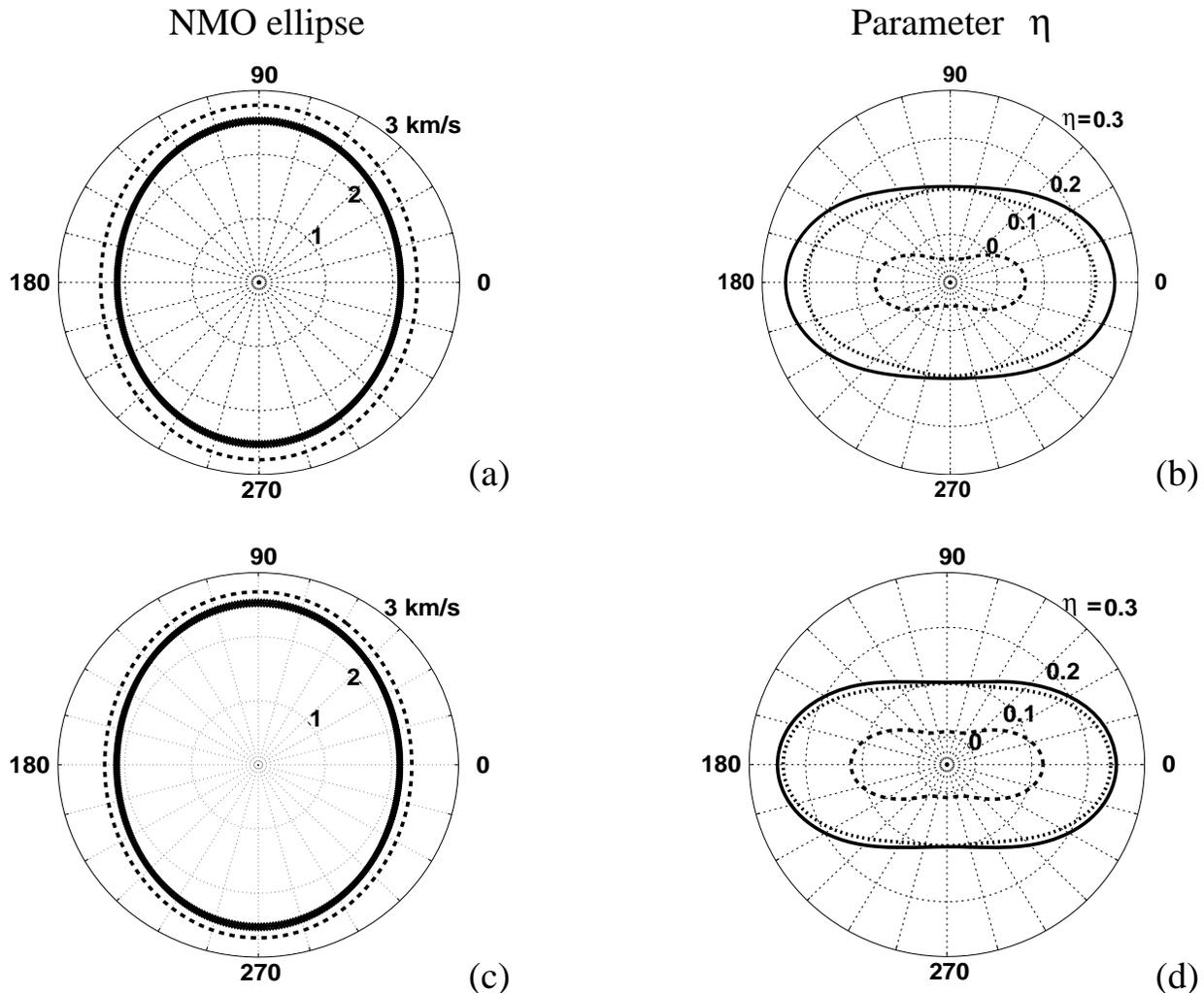


Figure 2: Moveout-inversion results for a wide-azimuth, long-offset P-wave reflection from a boundary between two fractured orthorhombic media. The NMO ellipse and parameter η are shown as a function of azimuth (numbers on the perimeter) measured with respect to a symmetry plane. The event has a class 2 AVO response with the polarity reversal at offset-to-depth ratios between 0.65 and 0.85. The maximum offset-to-depth ratio is two for the top row, and three for the bottom row. The solid lines are the actual NMO ellipses and η -curves, the dashed lines are estimated by conventional semblance, and the dotted lines by our algorithm [the dotted and solid curves on plots (a) and (c) almost coincide].

COLORADO SCHOOL OF MINES

Center for Wave Phenomena

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Grant: DE-FG02-06ER15778

Monitoring the Subsurface with Multiple Scattered Waves and Quasi-Static Deformation

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Objectives: To investigate the use of seismic waves for remote monitoring of temperature changes in the Yucca Mountain nuclear repository. We test this concept using hammer-source seismic data collected during a heating test at Yucca Mountain.

Project Description: This project has concentrated on the processing and analysis of seismic data acquired by a cooperative effort of the US national labs at the Yucca Mountain heated drift experiment of 1998-2002. During this time the experimental tunnel was heated from 100 degrees C to about 200 degrees C within two years, after which the temperature was kept constant for one more year. An array of single-component geophones was operated around the tunnel to detect microseisms, and their calibration shot-records have been processed to relate the changes in observed waveforms to changes in temperature. Our goal is to gain insight into the velocity/temperature relation of the rocks surrounding the tunnel at Yucca Mountain. Knowing this relation makes it possible to monitor the tuff in Yucca Mountain remotely with a “seismic thermometer.”

Results: The original data were contaminated with noise, the first step of the data analysis consisted of filtering the data, and stacking the data recorded within one day over the different shots. The noise level in the processed data is low, this indicates an excellent signal to noise ratio. The wave-forms show systematic changes from trace to trace as the temperature in the rocks surrounding the tunnel changes with time. These two facts combined mean that the data show evidence of systematic and detectable changes in the seismic waveforms as the tunnel is being heated and cooled.

In order to relate recorded data to the temperature dependence of the seismic velocities we carried out spectral element simulations of the seismic waves generated by the calibration shots. We used spectral element modeling because this computational method has the versatility to account for the free surface at the walls of the main tunnel that was heated, and the adjacent tunnel where the calibration shots were placed.

The temperature at the tunnel wall and in several boreholes radiating from the tunnel has been measured. We used this to estimate the temperature distribution in the rock mass surrounding the tunnel. Next we assumed different P-velocity/temperature relations ranging from -0.5%/100 degrees C to -2.5%/100 degrees C. In all calculations we assumed that the ratio of the P-wave and S-wave velocities was determined by the ratio as given in the CRC handbook for granite. This assumption is important because the recorded data were not triggered, in other words, only the differential arrival time of the P-waves and S-waves is constrained.

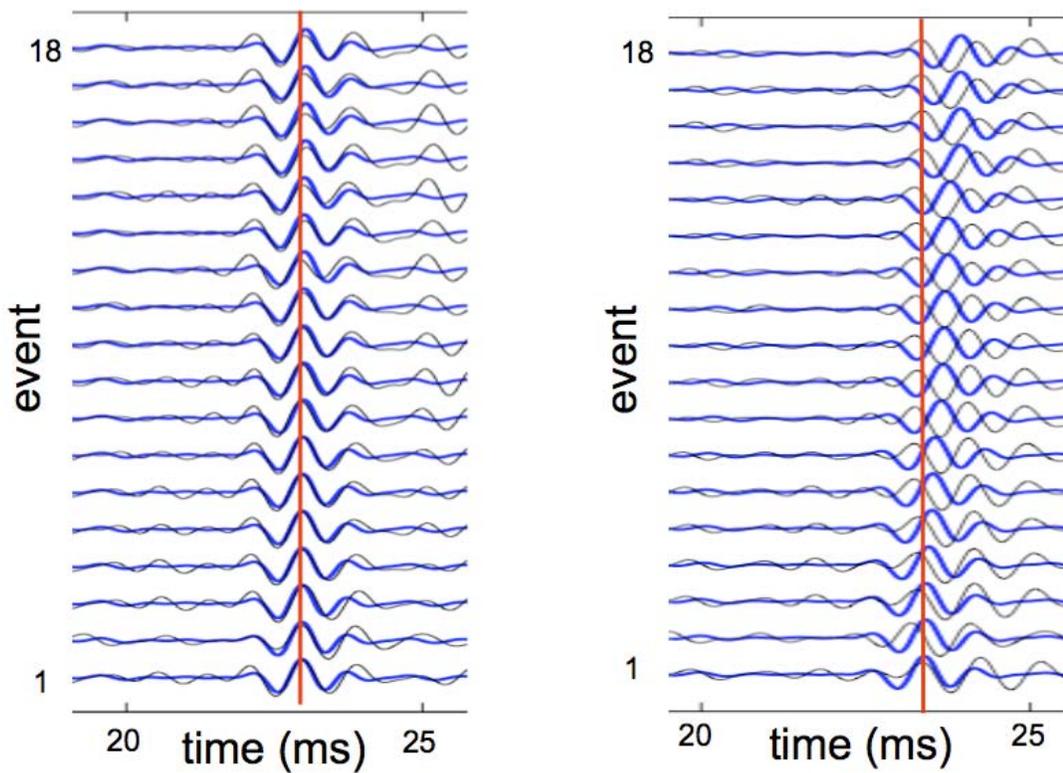


Fig. 1: Shear wave arrival shot and velocity-temperature gradients of $-0.5\%/100$ degrees C (left panel) and $-2.5\%/100$ degrees C (right panel), respectively. Model waveforms are darker, heavier traces. Data is from Channel 4, located below the tunnel opposite from the source. Temperature increases with event number, chronologically from bottom to top. Red line is a marker of constant arrival time.

We compared the waveforms computed for the assumed velocity/temperature relations with observed waveforms with the modeled waveforms. A representative example of arriving shear waves is shown in Figure 1. The traces are recorded over a time of about three years, and recording time increases with event number. Since the temperature increases with recording time, this means that the temperature around the tunnel increases with event number. The observed waveforms in the left panel agree well with the waveforms computed for a velocity/temperature dependence of $-0.5\%/100$ degrees C, whereas, as shown in the right panel, an assumed velocity/temperature dependence of $-2.5\%/100$ degrees C is not consistent with observed waveforms. This indicates that the observed changes in the waveforms with temperature indicate a modest velocity temperature gradient in the host rock at Yucca Mountain of about $-0.5\%/100$ degrees C.

COLORADO SCHOOL OF MINES

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Grant: DE-FG02-07ER15841

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 broken into the following questions: 1) Can multi-scale geologic variability be built in to random fields that are conditioned on measured data?; 2) Do fractures engender upscaled transport that follows the fractional-order transport equations?, and 3) Does high heterogeneity lead to unmixed plumes and reduced reaction rates?

1) Multi-scale variability: We developed four methods to create random K fields that honor 1) the anisotropic fractal scaling that is often observed, and 2) the conditioning (measured) data. Of these four methods, two appear useful at well-studied sites like the MADE site. This model can now be used to generate velocity fields at any discretization and coupled to our previous particle tracking model that solves the spatiotemporally nonlocal transport model. We also showed the exact particle tracking algorithm that corresponds to the most general multi-rate mobile/immobile model.

2) Large-scale transport in fractured rock and fractional ADEs: This year, we investigated whether the parameters for the fractional equation could be discerned from fracture data. It appears that fractures with power-law length distribution $P(L>l) \sim l^{-a}$ with $a < 2$ engender fractional-order transport (Reeves *et al.*, WRR 2008a,b,c) that follows

$$\frac{\partial C}{\partial t} + \beta \frac{\partial^\gamma C}{\partial t^\gamma} = -\nabla \cdot (vC - D\nabla_M^A C), \quad (3)$$

where C is total resident concentration, β is the immobile capacity coefficient, $0 < \gamma < 1$ is the fractal mobile/immobile coefficient, t is time, v is mean velocity, A is the direction-dependent fractional derivative (related to the fracture exponent a), and M is the mixing measure, which is essentially a three-dimensional dispersion coefficient. The link between the transport equation allowed us to make generalizations about the suitability of geologic repositories based on fracture statistics.

3) 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 unmixed 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*, in press). 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.

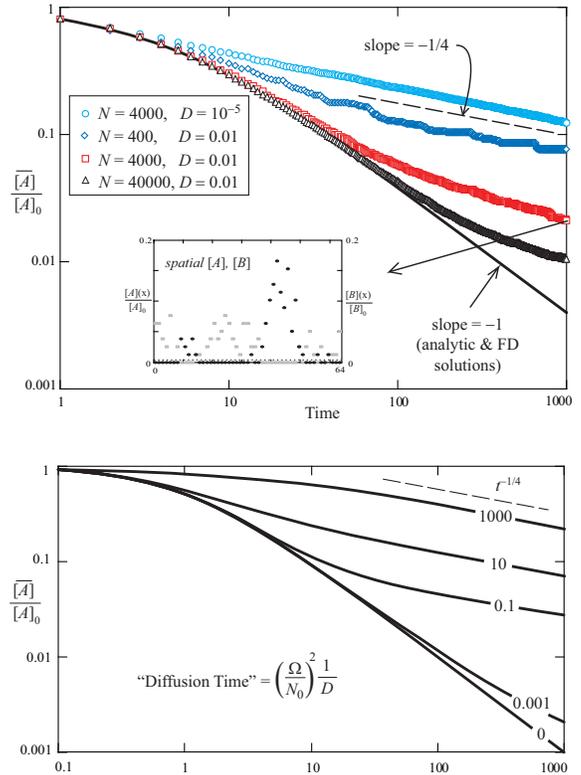


Figure 3. Top: Concentration change simulated by particle models (symbols) and analytic solution to continuum, rate-limited, equations (solid curve). Changes of a single numerical parameter are denoted on the plot. Deviations from the rate-limited solution are due to diffusion-limited reaction. Inset: 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 Wilczek [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) $^2 D^{-1}$.

UNIVERSITY OF COLORADO

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Grant: DE-FG02-06ER15779

Monitoring the Subsurface with Multiple Scattered Waves and Quasi-static Deformation

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Objectives: To investigate the use of quasi static deformation in the detection of changes in the subsurface caused by the infiltration of fluid contaminants.

Project Description: We are exploring a new technology that is based on using low-frequency strain data to monitor changes in fluid saturation conditions in porous media. Laboratory experiments have shown that strain data can reveal changes in complex moduli, which are caused by hysteresis in meniscus movement (changes in surface tension, wettability) when a pore containing two fluids is stressed at very low frequencies (< 10 Hz).

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.

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. Data from three tiltmeters, which had been installed in wells along an East-West line, are being analyzed. Solid Earth tides provide an uninterrupted low frequency deformation to test our theory. We compare theoretical tidal tilts with the tilts measured at the three progressively more distant tiltmeter locations, wells 1, 2 and 3.

Results: Tidal tilts have maximum amplitudes of less than ± 100 nano-radians. We resolve tilts down to 1 nano-radian (1 micron over 1 km). Long-term tilts (many months) resulting from the relaxation of the instrumented wells are on the order of 100 micro-radians, those from routine agricultural activities, such as nearby irrigation, are as large as ± 5 microns and an earthquake in Alaska on November 3rd, 2002 caused a permanent tilt offset of 1 micro-radian. The tidal tilt signals are hidden in this large background noise. Special care is taken in the removal of this background noise.

Previously we used exponential functions to fit the noise, selecting the portions to be fit by hand. We found anomalies that corresponded to the irrigation period with the surfactant. To confirm the anomaly and avoid human bias we developed a series of computer programs that can do the noise removal automatically.

To date we have completed the analysis for all three wells over the period starting on August 18th, 2004 to February 14th, 2005, which contains the period of irrigation with the bio-surfactant. The signals recorded in the field are spliced together, then splined to conform to the theoretical signal at 300s

intervals. To isolate the noise and prepare it for removal, we subtract the theoretical signal from the spliced and splined signal, henceforth refer to as our working signal **S**. Spurious background signals such as spikes and offsets are removed from **S** by applying median filters and offset detectors. The remaining large noise signals, such as those from irrigation or other agricultural activities, are removed individually. We generate a matrix of noise amplitudes by choosing a variable window width and scanning the signal from beginning to end. Each noise amplitude value has associated with it a time and a duration (window width) at which it occurred. Starting in the vicinity, in time and duration, of the largest amplitude we seek a fit for the noise signal. If the fit satisfies our criterion, we subtract the fit from **S** and start over. If the fit is not good enough we select the second largest amplitude and fit in its vicinity. This continues until the remaining amplitudes cannot be fitted anymore within our criteria. Typically we fit noise amplitudes that are larger than the maximum theoretical tides and we accept fits where the standard deviation is better than 10% of the theoretical signal. We compare results from fitting with polynomials only, polynomials and exponentials, and exponentials only.

A comparison of the anomalies for the 6-month period including the irrigation with the surfactant is shown bellow for the two wells nearest the irrigation site. In the figure we show the residuals from the means when amplitudes of the theoretical signals are subtracted from those of the measured and corrected ones. A 14-day sliding window was advanced in steps of 3.5 days and only tidal signals that exceeded 30% of the signals at high tide were used in calculating the means. The data in the figure suggest that indeed the irrigation with the surfactant affected the tidal strain signal. It takes about 2 weeks to see the effect in well 1 and nearly 4 weeks for well 2. It takes about 2 weeks for the irrigation fluid to reach the groundwater.

We are now engaged in noise removal for all three wells for the entire period from October 2002 to April 2005 to see if the apparent effect we see is fortuitous or if it is associated with the surfactant irrigation. The noise levels are particularly high during late spring and the summer months when agricultural activities are at their peak.

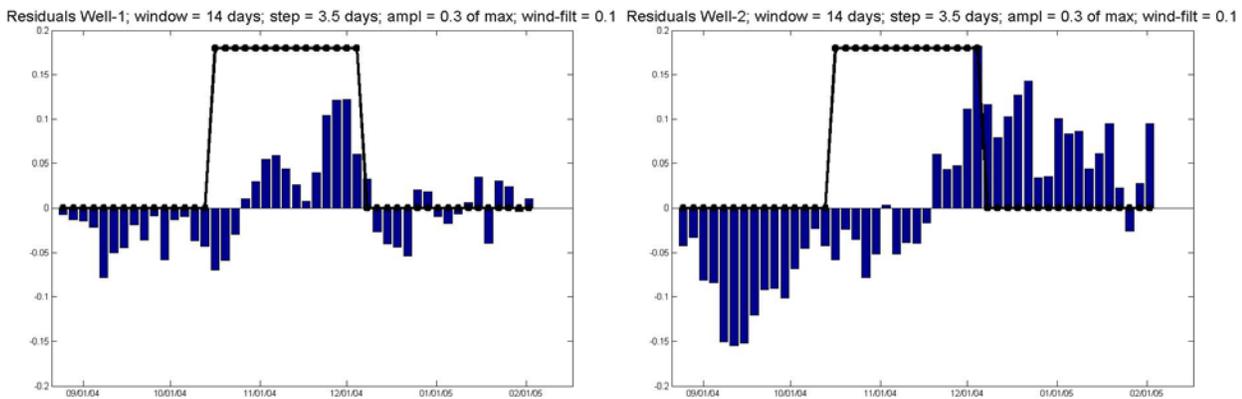


Figure Caption: The effects of irrigation (black line) on the relative amplitudes of the measured and theoretical tilts are shown for wells 1 and 2. The measured signals, which were cleaned and filtered for the selection of the tidal tilt around their 12 to 24 hour periods, are compared with the filtered theoretical signal.

UNIVERSITY OF CONNECTICUT

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Grant: DE-FG02-95ER14528

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

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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: Presently, 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 significantly depleted with respect to the noble gas concentrations in an assumed air-saturated water (ASW) source fluid and lack requisite enrichment/depletion factors needed to explain the noble gas inventory in oil field fluids. On the other hand, noble gases extracted from silica spicules from live sponges (*Calyxnicæensis*) show significantly enriched Ar, Kr, and Xe concentrations ($[^i\text{Ng}]_{\text{sample}}/[^i\text{Ng}]_{\text{asw}} > 1$), (2) very little if any mass dependence in the acquisition and trapping of Ar, Kr and Xe, and (3) 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 depleted with respect to the sponge spicule and fractionated, favoring the heavy noble gases. Furthermore, unlike the sponge spicule, these samples are strongly enriched in Ne. This identifies an important issue: are the differences in noble gas absolute and relative abundances between the sponge spicule sample and the more evolved diatomaceous samples related to (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? We have initiated a collaborative project with Ben Gilbert (Earth Sciences Division, LBNL) measuring noble gases in laboratory-produced nanoparticle agglomerates. Samples of goethite ($\alpha\text{-FeOOH}$) clusters agglomerated under different pH conditions have absolute and relative abundances of the noble gases released that are remarkably similar to the organic silica samples discussed above. 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.

UNIVERSITY OF FLORIDA

Chemical Engineering Department

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Grant: DE-FG02-98ER14853

Pore-Scale Simulations of Dissolution Breakthrough in Rough Fractures

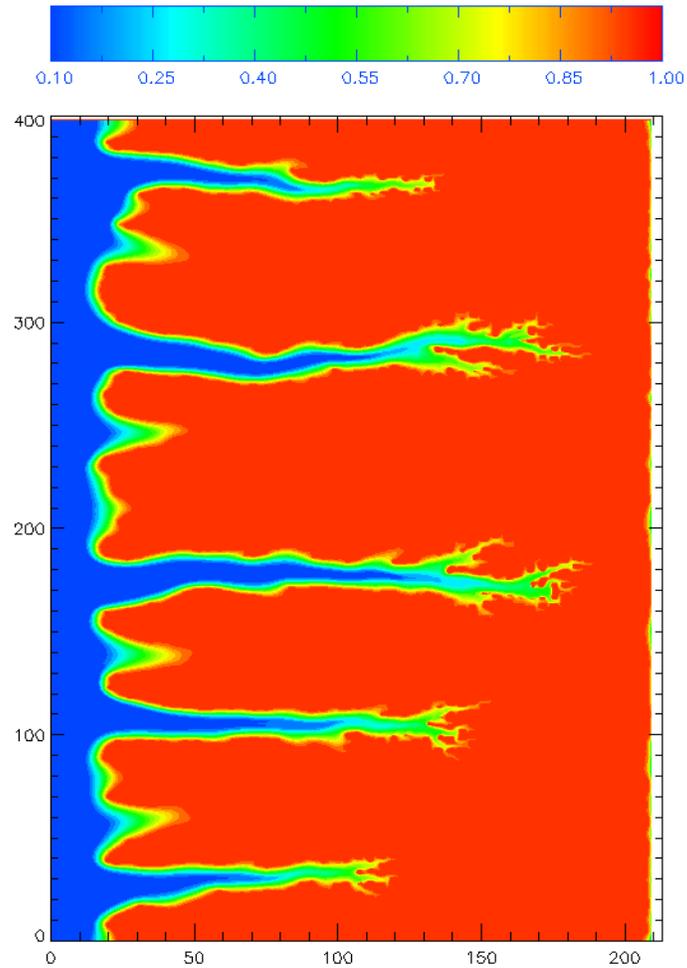
Anthony J.C. Ladd, 352-392-6509, Fax: 352-392-9513, ladd@che.ufl.edu

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: Our microscopic numerical model was previously shown to successfully reproduce the key features of laboratory experiments on the dissolution of an artificial fracture with a well-specified topography. In particular we found very similar channel formation to that observed experimentally under the same flow conditions (Geophysical Research Letters 31:L23606, 2004). We followed up on that work by developing a network model of the interaction between channels (Geophysical Research Letters 33:L205401, 2006).

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. The geometry algorithm forms the core of the new code, allowing us to describe a three-dimensional surface with second-order accuracy, even when there are rapid variations on the scale of the computational grid. Reactive boundary conditions have been implemented in a way that allows for a consistent accuracy, even when a fluid grid point is very close to the boundary surface. The finite-difference solver implements a method of characteristics, rather like the LB algorithm, which gives greatly improved accuracy when the flow is at an angle to the grid. The code is fully parallel and scales well up to of the order of at least 100 processors; we routinely run simulations on 32-64 processors. As an illustration, we show the depth averaged concentration field in an initially homogeneous fracture at $Pe = 10$ and $Da = 1$. A paper describing the new algorithms is in preparation.



We have 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 submitted for publication in the Journal of Geophysical Research.

GEORGE WASHINGTON UNIVERSITY

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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

H. Henry Teng, 202-994-0112, hteng@gwu.edu

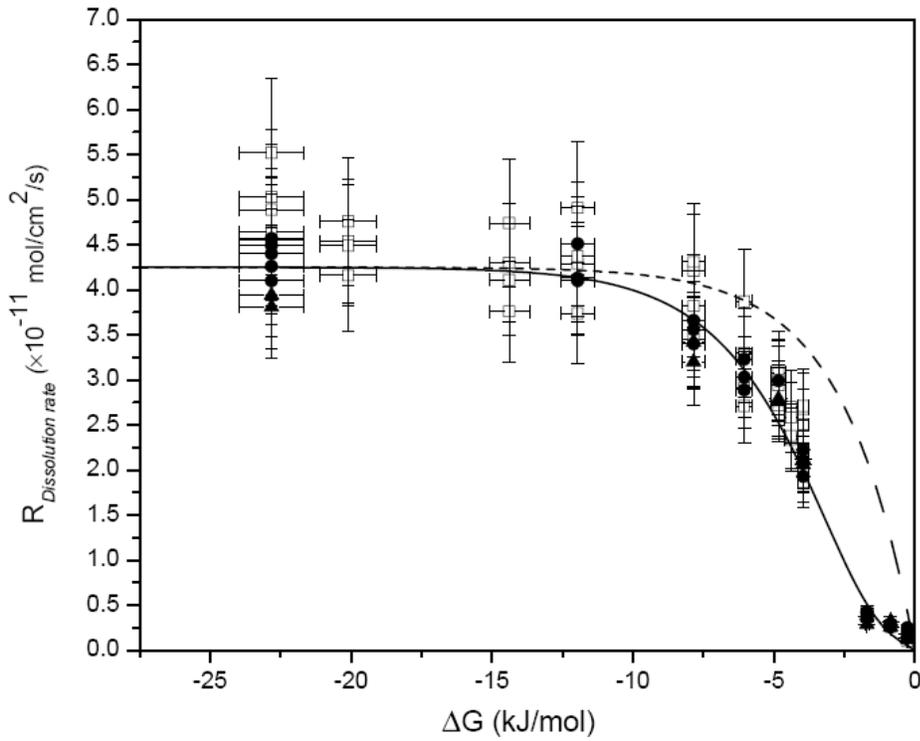
Objectives: To test the combined effect of Gibbs free energy, dislocation density of mineral samples, and the presence of atmospheric CO₂ on the dissolution kinetics of calcite.

Project Description: Carbonate mineral dissolution continues to be at the central front of mineral-water interaction studies due to the emerging need to understand geological carbon sequestration. Previous studies have explored the effect of various individual parameters such as solution chemistry and temperature on the dissolution processes, but left unanswered how those parameters will work together. In this study, we investigate calcite dissolution to test the combinative effect of (1) Gibbs free energy, (2) dislocation density, and (3) atmospheric pCO₂. Mixed-flow experiments were conducted at room temperature (25 °C) in both closed and open (to air) settings using fragmental crystals and powdered samples milled at various time duration (in order to engender different defect densities). We assumed the dissolution behavior will follow the prediction of the classic transition state theory (TST) given in the form of $r = [1 - \exp(-n\Delta G/RT)]$ where r is dissolution rate and n describes the number of rate limiting elementary reactions involved. Compared to a closed system, we anticipated a significant effect of the atmospheric CO₂. We also expected to see a weak impact of dislocation density in the beginning of the dissolution but a strong one at steady state.

Results: Experimental observations show a highly nonlinear dependence of the dissolution rates on the Gibbs free energy. Rather, a sigmoidal model given by

$$r = k_1[1 - \exp(-n(\frac{\Delta G}{RT})^{m_1})] + k_2[1 - \exp(-\frac{\Delta G}{RT})]^{m_2}$$

seems to well fit the measurements with properly adjusted rate constant k and fitting parameter m (see Fig. below) Furthermore, the dissolution rates do not seem to be affected by dislocation density at near and far from equilibrium. In addition, the dissolution rates measured at same saturation conditions are similar regardless the experimental settings, closed or open. These results suggest that: (i) The classic TST model may not be sufficient to depict the relation between dissolution rate and Gibbs free energy for calcite in all saturation conditions. The sigmoidal trend in the R- ΔG relationship indicates that, though the TST rate equation is sufficient to describe calcite dissolution kinetics when $\Delta G < -12 \text{ KJ mol}^{-1}$, it clearly overestimates the dissolution rate when the system approaches equilibrium. (ii) The effect of high-energy surface sites associated with crystal imperfections may be overwhelmed by that of preexisting steps and those generated by dissolution at corners and edges. (iii) The partial pressure of CO₂ under atmospheric conditions bears little importance to calcite dissolution once the saturation conditions of the solutions are fixed.



Experimental measurements of calcite dissolution rates in a closed system as a function of Gibbs free energy of the input solutions. The open squares are fragmental calcite, the solid circles powdered samples milled for 5 min., and the solid triangles powdered samples milled for 60 min. The dash line represents a TST fit and the solid line is a sigmoidal fit.

GEORGIA INSTITUTE OF TECHNOLOGY

School of Earth and Atmospheric Sciences

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Grant: DE-FG02-07ER15901

Barite Growth and Dissolution at the Molecular Scale

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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 FY2008, the MD force-field calibrated last year was used to examine solvation of a large number of barite {001} surface sites important for growth and dissolution and to calculate the kink site formation enthalpy for 10 different kink site formation reactions. Some barium surface sites were found to be under-coordinated to water relative to their sulfate coordination, probably because access by water to those sites is sterically hindered by the presence of the interface. Kink site detachment energies for bariums were found to be endothermic, whereas those for sulfates were exothermic. This suggests that there is a difference in the rates of barium and sulfate attachment and detachment to and from steps, a possibility that is often neglected in experimental measurements. A direct comparison of these calculated formation energies to existing estimates made from AFM step velocity measurements shows that the average after accounting for differences in kinetics is of similar magnitude, but of opposite sign. The source of this discrepancy is not clear as of yet, we are in the process of measuring barite step growth and dissolution as a function of saturation, temperature, and cation/anion ratio and deriving a new crystal growth model.

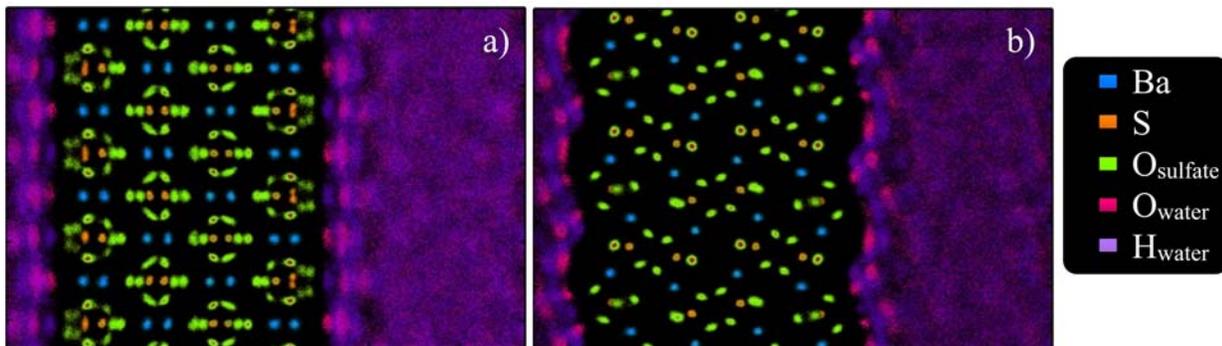


Figure: 2-D histograms of MD simulated $\{001\}$ barite-water interface structure, viewed along the a) $[100]$ and b) $[010]$ directions. The simulation predicts an intricate water structure at the interface, where some oxygens on water are coordinated to surface bariums and some hydrogens are coordinated to surface sulfates.

GORDON RESEARCH CONFERENCES

West Kingston RI 02892

Grant: DE-FG02-08ER15971

2008 Gordon Research Conference on Rock Deformation

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Website: <http://www.grc.org/programs.aspx?year=2008&program=rockdef>

Objectives: The Gordon Research Conference (GRC) on Rock Deformation highlights the latest research in brittle and ductile rock mechanics, with experimental, field and theoretical contributions. The conference serves as a forum for assessing our understanding of rock strength and related physical properties in the Earth. The goal of this conference is to promote a multi-disciplinary and multi-scale assessment of the rheology of earth materials using a variety of techniques.

Project Description: The 2008 GRC on Rock Deformation was held in Tilton, New Hampshire, Aug. 3-8, 2008, organized by Greg Hirth (Chair) and David Prior (Vice-Chair). The theme of the conference was "Real-time Rheology", where geophysical data could be used to address issues such as the frictional behavior of faults, processes responsible for strain localization, the viscosity of the lower crust, viscous coupling between the crust and mantle, and the rheology of the lower crust and mantle. Through the combination of novel analyses of microstructures in naturally deformed rocks with petrologic data, an improved understanding of rheology can be obtained. The structure of the GRC meetings, with their extensive open discussion and free periods each afternoon, distinguishes them from other conference series and is perhaps their biggest strength. They are designed to encourage forward looking talks, so that the emphasis is on new science and the next generation of researchers, rather than providing a series of 'review' presentations. By inviting speakers from across the rock deformation community and beyond, the GRC also fosters new collaborative endeavors in rock deformation. The invited speakers and poster presentations were organized into sessions that covered the dynamics of earthquake rupture, the rheology of the lower crust and coupling with the upper mantle, the measurement and interpretation of seismic attenuation and anisotropy, the dynamics of ice sheets and the coupling of reactive porous flow and brittle deformation for understanding geothermal and chemical properties of the shallow crust. Such topics are important for developing ideas in CO₂ sequestration, geothermal and petrochemical research and the mechanics of shallow faults.

Results: To encompass the elements of these topics, speakers and discussion leaders with backgrounds in geodesy, experimental rock deformation, structural geology, earthquake seismology, geodynamics, glaciology, materials science, and mineral physics were invited to the conference. We invited 18 speakers to address the topical issues listed below, as well as 8 discussion leaders whose role was to encourage participation by all conference attendees, to host the two poster sessions, and to highlight key thematic relationships between the different speakers. We attracted approximately 90 attendees, representing all levels of research career from both the USA and abroad. Although primarily from academic institutions, some participants from the energy and geotechnical industry also attended the conference. The meeting was extremely successful. The agenda is outlined below and posted at:

<http://www.grc.org/programs.aspx?year=2008&program=rockdef>

Earthquakes and the Rheology of the Lithosphere Discussion Leader: **Terry Tullis** (Brown); **Susan Owen** (JPL), "Geodetic constraints on lithosphere deformation and fault mechanics"; **Greg Beroza** (Stanford), "Constraints from Seismology on the Deep Roots of Faulting".

Rheological Properties of Faults during Earthquakes Discussion Leader: **Tom Heaton** (Caltech); **Judi Chester** (Texas A&M), "Geologic perspective on earthquake rupture from field and laboratory studies"; **Yehuda Ben-Zion** (USC), "Collective Behavior of Earthquakes and Faults".

Deformation of Ice Sheets and Glaciers Discussion Leader: **Erland Schulson** (Dartmouth); **David Goldsby**, (Brown) "Creep of Glaciers and Ice Sheets"; **Neal Iverson** (Iowa State), "Viscous and frictional deformation resistance at glacier beds" ; **Sridhar Anandakrishnan** (Penn State), " Slip Slidin' Away: Slow Slip Events (SSE) on the ice streams of West Antarctica"

Seismic Attenuation and Rheology of the Upper Mantle Discussion Leader: **Doug Weins** (Washington Univ.); **Marshall Sundberg** (Brown), "Experimental Constraints on Attenuation in Peridotite: Physical Processes and Implications for Seismology and Rheology"; **Colleen Dalton** (BU), "Seismic Constraints on Upper-Mantle Attenuation"

Deformation and Rheology of the Lower Continental Crust Discussion Leader: **Brendan Meade** (Harvard); **Georg Dresen** (GFZ Potsdam), " Rheology of the Lower Crust - A Lab and Field Perspective"; **Roland Burgmann** (UC Berkeley), "Space Geodetic Probing of Lower Crustal Rheology"; **Alex Copley** (Cambridge), "Using large-scale active deformation to infer crustal rheology"

Linking Mantle Anisotropy and Rheology Discussion Leader: **Neil Ribe** (IPG Paris); **Martyn Drury** (Utrecht), "Anisotropy and rheology of upper mantle rocks"; **Donna Blackman** (IGPP, Scripps), "Tracking deformation of mantle minerals during regional mantle flow and insights available from seismic anisotropy"; **Einat Lev** (MIT), "Anisotropic viscosity in geodynamical flow models"

Looking Forward: Future Directions in Linking Rheology and Reactive Porous Flow Discussion Leader: **Wenlu Zhu** (Maryland); **Steven Karner** (ExxonMobile), "Coupled thermo-hydro-chemo-mechanical processes in crustal rocks: Future directions for applied research involving real-time rheologic constraints"; **Peter Kelemen** (LDEO), "Chemical and physical feedback mechanisms during alteration of peridotite and the potential for enhanced, natural CO₂ sequestration in tectonically exposed mantle"

Poster Sessions 1 & 2 Discussion Leader: **David Prior** (Liverpool)

HARVARD UNIVERSITY

School of Engineering and Applied Sciences and Department of Earth and Planetary Sciences
Cambridge MA 02138

Grant: DE-FG02-03ER15384

Growth and Dissolution of Iron and Manganese Oxide Films

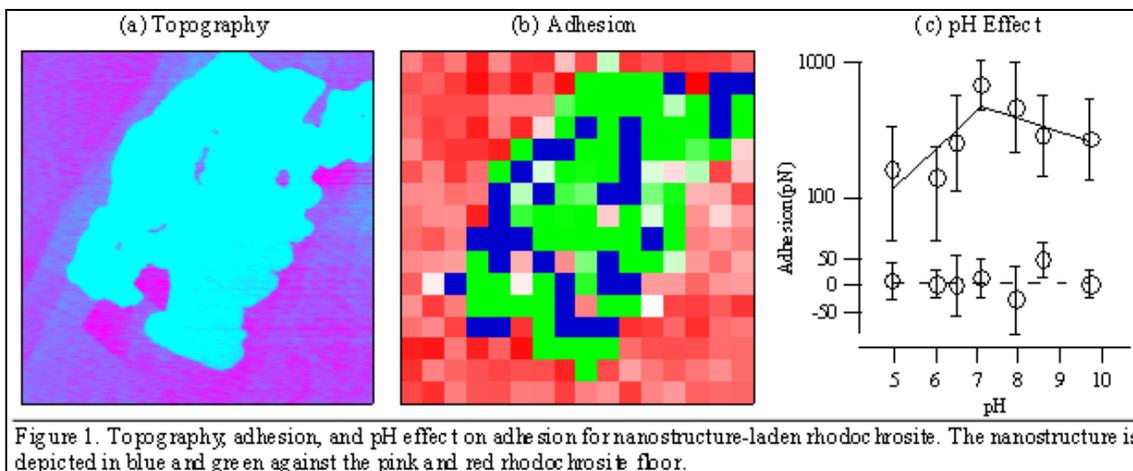
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Objectives: The first objective is to understand the growth and dissolution of Fe and Mn oxide films on mineral surfaces, especially as influenced by the adsorption of other ions. The second objective is to establish how adsorption affects surface 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 oxide films are grown on substrates by the *in situ* oxidation of $\text{Mn}^{2+}(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$ ions by dissolved oxygen. The nanostructures are characterized by their morphology and height using atomic force microscopy. Their electrostatic properties, including surface potential, ion mobility, and interfacial adhesive forces, are characterized using Kelvin probe force microscopy, scanning polarization force microscopy, and force-volume microscopy. Surface potential and ion mobility are studied for variable relative humidity to examine the effects of surface dissolution.

Results: Over the past year, we have characterized the surface-adhesion heterogeneity that Mn-oxide (MnO_x) nanostructures induce on the parent substrate. The observations of surface adhesion forces (Figure 1) in 1 mM NaNO_3 solution from pH 5 to 9.7 show that the oxide nanostructures have different surface adhesion from the rhodochrosite substrate. This surface-adhesion heterogeneity is probed by force-volume microscopy using a charged silicon-nitride probe. On the oxide nanostructures, the net adhesive force has contributions from both van der Waals attraction and electrostatic repulsion. For the most part, the adhesive forces on the nanostructures are dominated by van der Waals attraction and have a maximum at pH 7.1 for $5.0 \leq \text{pH} \leq 9.7$. The modes of the distribution of the adhesive forces are 166 pN at pH 5.0, 692 pN at pH 7.1, and 275 pN at pH 9.7. In comparison to the adhesive force on the oxide nanostructures, that on the rhodochrosite substrate is negligible in the same pH range, suggesting both weak van der Waals attraction and electrostatic interaction with the probe. The quantitative mapping of adhesive force using force-volume microscopy, as demonstrated in this study, can be applied more generally to the study of other nanostructures, leading to improved understanding of their surface reactivities in contaminant immobilization and bacterial attachment.



UNIVERSITY OF HOUSTON

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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. Further, we continue to progress the use of non-linear inverse scattering series methods (specifically, internal multiple attenuation methods) to not only provide new highly capable algorithms, but to provide necessary input for current imaging methods. In addressing the second branch of our research objectives, we have (1) defined and made preparations to enter into a collaborative project with Huang and Fehler at Los Alamos National Laboratory, to identify and address outstanding issues of modeling wave fields in complex media, and (2) progressed the use of the forward scattering series in modeling of post-critical wave phenomena and developed a scattering series based calculation of selected wave field events in complex media.

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. Compromises on the capability and completeness of the computation of that new term were made to allow a realizable result. Those compromises have been removed by the development of new math methods this past year, by Dr. Fang Liu, a research professor in our group, to allow the promise and usefulness of that term to be tested and used on synthetic and field data. 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.

This past year produced another important advance in the imaging project of our research program. The idea was to develop a method for directly imaging at depth, without any direct or indirect (explicit or implicit) need for the velocity model when the earth actually has rapid variations in density, velocity or both. All of the imaging methods that we described in the previous paragraph and that we developed before this past year assume that all rapid variations are due to velocity. We removed that limiting assumption in our inverse scattering series imaging algorithms this past year. That assumption is too often violated in the real earth in areas of exploration interest. Those density change driven and/or dominated reflectors are often at play in layered earth geology especially in shallow reflectors due to compaction processes in deep water plays . Early tests of that new multi-parameter earth direct depth imaging at depth were carried out for a one dimensional acoustic earth. Our plan is to extend these new imaging ideas and concomitant algorithms to a multi-dimensional elastic earth where (at least) three independent parameters can vary, and apply those more realistic and reliable algorithms to field data this coming year. The algorithm uses the strength of multi-parameter methods to only allow reflectors (and primaries) where velocity is one of the parameters that varies into the nonlinear conversation, while maintaining a strength of the single parameter world by outputting a single composite imaged data at each point in the subsurface. The goal is a structural map where reflectors are well located in depth, without the need for a velocity model, but where the output is not for subsequent amplitude analysis at depth , i.e., for migration but not for migration-inversion. We are managing the risk and leaving the more ambitious goal of location and inversion without overburden information, to a next step, after we can achieve location without inversion without any information above the imaged reflector.

IDAHO STATE UNIVERSITY
Department of Biological Sciences
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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 FY08 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 08 include:

- 1) Continued sabbatical leave travel for Magnuson to the University of Wyoming, to work with collaborators Carrick Eggleston and Patricia Colberg. Magnuson performed experiments on c-type cytochromes using the newly acquired Optical Waveguide Lightmode Spectrometer (OWLS). Magnuson presented some of this work at the V.M. Goldschmidt Conference in July 2008, and the Lake Arrowhead Microbial Genomics Meeting in September 2008.
- 2) Studies with OWLS and with Quartz Crystal Microbalance: Previously we examined basic adsorption properties of cytochromes from *Geobacter sulfurreducens*, and after developing experimental protocols, we then examined mineral dependent surface adsorption with OmcB, and an additional cytochrome c, ApcA (from *Acidiphilium cryptum*) for their comparative adsorption properties to glass waveguide surfaces coated with either silicon dioxide, titanium oxide, or iron oxide. Our results were quite intriguing, in that we did in fact observe surface-dependent behaviors. This technique has shown that mineral-specific adsorption of cytochromes c occurs, and that when coupled with quartz crystal microbalance analysis, corroborates protein homology models predicting structure of these cytochromes.
- 3) Fluorescence spectroscopy: One useful development in this area has been the application of cytochrome c fluorescence to detect these proteins directly, without using stains. This tool provides a simple means of extracting cytochrome c bands from polyacrylamide gels for subsequent proteomic analysis.
- 4) Homology Modeling using PHYRE: Using genome sequence data for *Acidiphilium* and *Geobacter*, we have constructed additional homology models of cytochromes c using PHYRE,

SWISS-MODEL, and MacPyMol. Remarkably, models for OmcB and ApcA, and ApcA are predicted to be quite accurate (very low E-value), and usually cover 80-100% of the protein length (Figure 1).

- 5) Continued training of undergraduate researchers (Binita Shakya from Nepal, and Josh Ellis, an Idaho student who is now working with my group as a Graduate Assistant), and continued support of a Research Associate (Mike Swenson).
- 6) Continuation of a collaboration with Dr. John Cort of the the Pacific Northwest National Laboratory-Environmental Molecular Science Laboratory (EMSL). We have collected ^{13}C and ^{15}N spectra of ApcA and are now fitting data and producing an NMR structure. This is a great example of how DOE support helps to foster collaboration with the National Laboratories.

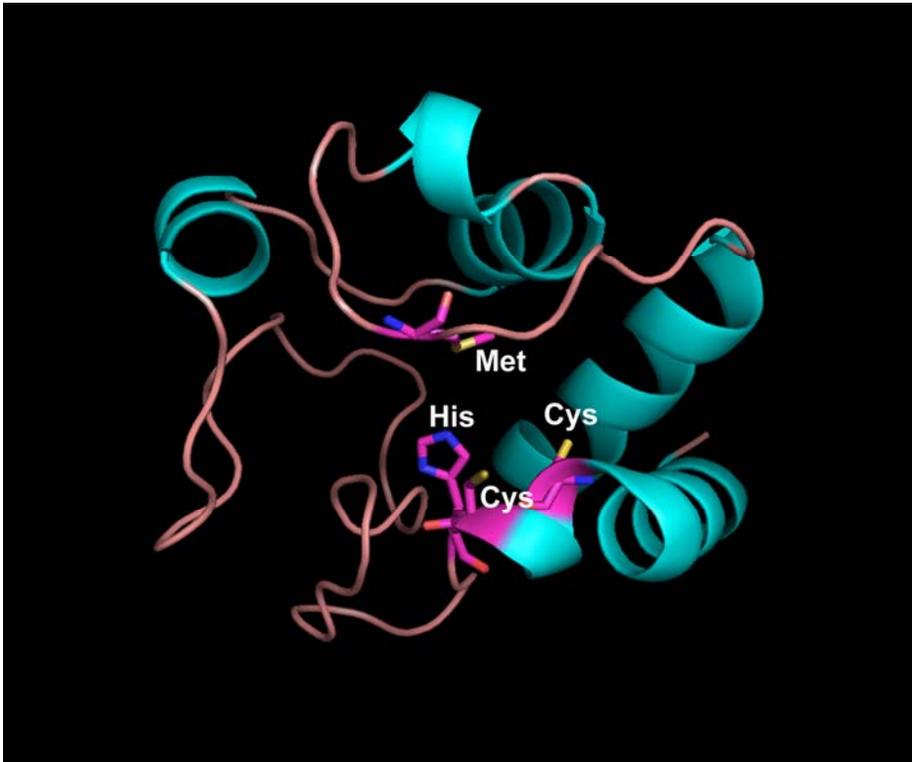


Figure 1. Homology model of ApcA, showing the amino acids making up the heme binding pocket. The model is based on a cytochrome *c2* from *Rhodospila globiformis*.

UNIVERSITY OF ILLINOIS

Department of Geology
1301 West Green St.
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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 advanced techniques in molecular biology (specifically, quantitative reverse transcriptase PCR), combined with *in-situ* sampling of attached microorganisms and dissolved gas concentrations, to address the relationship between the chemical composition of groundwater and its microbial community for the Mahomet Aquifer, the regional water supply for central Illinois. The study will integrate benchtop column experiments, field study, and numerical modeling to address a number of specific questions of current interest: 1) Which microbial populations are active, and at what specific rates? 2) What is the distribution of activity between microbes suspended in the groundwater and those attached to sediments? 3) To what extent do dissolved gas concentrations and volatile fatty acid (VFA, e.g. acetate) concentrations in the groundwater reflect the activity of specific groups of microbes. Results of the study will help establish use of advanced techniques of molecular biology to define not just the identities of microbial populations in the subsurface, and in experiments, but the specific activities of those populations. The results will help reveal the relationship between microbial activity and groundwater quality.

Results: We performed a comprehensive analysis of how the communities of attached and suspended microbes in an aquifer vary depending on the concentrations of sulfate and ferrous iron. Determining that the attached community reflects geochemical conditions better than the suspended, we analyzed the attached microbes from each of the wells we sampled using a PCR-based method, terminal restriction fragment length polymorphism, or T-RFLP, which yields a fingerprint diagnostic of the community. A statistical comparison of the community profiles reveals systematic similarities and differences in the bacterial communities between sites with high and low sulfate concentrations (**Figure 1**). 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 bacterial populations associated with iron reduction on the sediment samplers we used, regardless of sulfate concentration or other

obvious geochemical parameter. This result may indicate that these types of microbes possess versatile metabolisms and do not require ferric iron to live; pure culture experiments seem to confirm this hypothesis.

Using passive samplers for gas and aqueous ions, we demonstrated that wells in the Mahomet can be monitored for spatial and temporal variation in groundwater chemistry without being pumped. We continue to develop the passive sampling component of the project, focusing on monitor wells near production wells in the Mahomet.

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

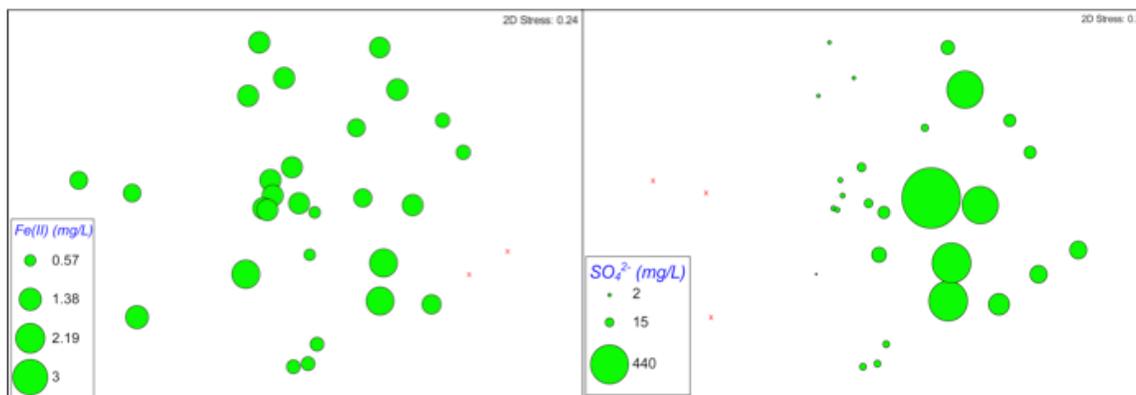


Figure 1. Non-metric plot of Bray-Curtis similarity coefficients for all samples of attached bacteria from the Mahomet Aquifer in east-central Illinois. Distance between symbols is proportional to difference in community composition; symbols radius indicates the relative concentration of Fe^{2+} or SO_4^{2-} in groundwater. Statistical analysis shows a significant difference in communities from high and low SO_4^{2-} wells, but reveals no statistical significance of ferrous iron concentration.

UNIVERSITY OF ILLINOIS

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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 CO₂-bearing fluids. This will be achieved through equation-of-state measurements of H₂O- and CO₂-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 H₂O) and carbon (as CO₂). Despite the essential role of deep fluids in subduction zone processes, the absence of experimental thermodynamic data precludes quantitative modeling of reactions and mass transfer in this setting. The vast majority of aqueous geochemistry studies have been conducted at pressures below ~0.3 GPa, and the widely-used Helgeson-Kirkham-Flowers equations of state for aqueous species are applicable to ≤ 0.5GPa (~ 15km depth). The aim of this project is to determine the sound velocities, equations of state (EOS), and atomic-scale structures of model fluid systems to the high pressures and temperatures appropriate to subduction zones. Brillouin scattering measurements of velocities and EOS on aqueous fluids will be performed to at least 10 GPa and 700° C, and X-ray and neutron scattering experiments will be performed to constrain the atomic-scale structures of the same solutions.

Results: In FY 08 we initiated this project and began measurements. 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. In FY 08 the LLNL group produced the prototype membrane diamond-anvil cell for use in Brillouin scattering measurements with a ~50° scattering geometry. The UIUC group modified the Brillouin spectrometer to accommodate these membrane cells. The cells were tested and Brillouin spectra were collected jointly by the UIUC and LLNL groups in late FY 08 on compressed CO₂. The cells performed well over a week of measurements and Brillouin data were collected on liquid CO₂ and several solid CO₂ phases (I, II, III). Subsequently, modifications to the diamond-cell design were made to allow for 90° scattering, which will be advantageous for all future measurements.

UNIVERSITY OF ILLINOIS AT CHICAGO

Department of Earth and Environmental Sciences
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Grant: DE-FG02-03ER15381

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 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. Measurements of Rb^+ and Sr^{2+} at the orthoclase (001)-aqueous interface revealed that Rb^+ adsorbs in the K^+ site as an “inner-sphere” (IS) species; in contrast, Sr^{2+} adsorbs at a substantially larger height indicating that it is an outer-sphere species (OS). These results demonstrate that the distribution of cations between IS and OS species is determined in part by the characteristics of the mineral surface. Adsorption thermodynamics of Rb^+ and Sr^{2+} on muscovite were measured. The cation coverage and average cation height were measured. These results revealed that the IS and OS Sr^{2+} species on muscovite have similar adsorption enthalpies. A pH-dependent hysteresis of the cation coverage was observed for both Rb^+ and Sr^{2+} , resulting in a net reduction in the saturation coverage and an OS-dominated Sr^{2+} adsorption geometry. Several experiments aimed at examining replacement reactions in alkali feldspar were performed as part of a continuing study. A new design for flow-through experiments having the capability for rapid changes in solution composition was tested for eventual application in hydrothermal experiments.

INDIANA UNIVERSITY

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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 D/H stable isotope ratios of organic hydrogen in sedimentary organic matter during thermal maturation. Evaluate the diagenetic and/or paleoenvironmental significance of D/H ratios in different types of kerogen, specific macerals 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. 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) We are targeting paleoenvironmentally relevant D/H ratios of *n*-alkyl moieties that are physically trapped or chemically bound in kerogen. We liberated *n*-alkanes and alkyl side chains attached to aromatic clusters in kerogen. Two parallel experiments disintegrated the macromolecular matrix of two aliquots of the same kerogen from New Albany Shale using two aqueous media, namely one with $\delta D_{\text{water}} = +1173\text{‰}$, and the other with $\delta D_{\text{water}} = -136\text{‰}$. The resulting pairs of liberated *n*-alkanes expressed about the same level of D-enrichment. This proves that water has no significant impact on compound-specific δD values during the release of these formerly trapped *n*-alkanes, and therefore the *n*-alkanes' δD values are isotopically conservative. D/H ratios of alkyl side chains in kerogen hold great promise for paleoenvironmental studies in kerogens and humic compounds in general.

(2) Coals from 'contact-metamorphic' sequences where magmatic dikes had vertically intersected a coal seam express unusual and steep trends of hydrogen isotopic exchangeability in kerogen and D/H ratios (Figure 1). The observed patterns are remarkably different from all other reported data sets across natural maturation gradients, and we interpret them to be due to hydrologic isolation of coal adjacent to dikes. A manuscript presenting these data has been submitted to *Geochimica et Cosmochimica Acta*.

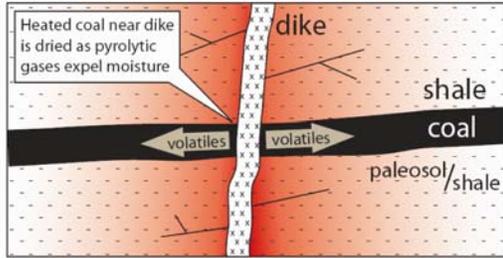
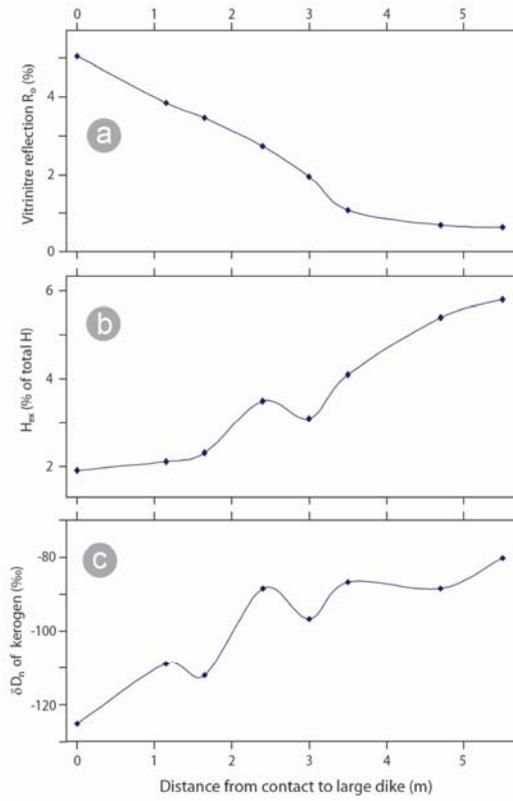


Figure 1: A coal seam was vertically intersected by a magmatic dike (**upper panel**) resulting in rapid heating of coal and generation of steam and thermogenic gases. The highly permeable coal near the intrusion was effectively dried before it reached high enough temperatures for cracking reactions. Shale and paleosol/shale acted as poorly permeable barriers and limited hydrologic connectivity. **(a)** Increasing thermal maturity of coal is quantified by vitrinite reflectance R_o (%). **(b)** Decreasing amounts of exchangeable hydrogen (H_{ex}) in kerogen reflect the loss of chemical functional groups. **(c)** Decreasing δD_n values of non-exchangeable hydrogen in kerogen with increasing maturity contrast with other observations from water-rich environments and thus witness the absence of D-enriched water during heating (Schimmelmann et al., in review).



JOHNS HOPKINS UNIVERSITY

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Baltimore MD 21218

Grant: DE-FG02-89ER14074

Crystal Chemistry of Toxic Metal Sequestration

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Objectives: For FY08, specific objectives center on application of focused ion-beam milling (FIB) to contaminated soils from Hanford 300 Area, investigation of a newly discovered nanoscale zirconium (oxyhydr)oxide, development of electron energy-loss spectroscopy (EELS) methods, and 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, and synchrotron-based techniques.

Results: During this second year of the project cycle, we have leveraged our earlier development of focused ion-beam milling (FIB) techniques for beam-sensitive materials. This has resulted in identification of six classes of solid hosts for uranium in samples of vadose-zone sediments from the Hanford 300 Area. These include metatorbernite $[\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ and coatings comprised mainly of phyllosilicates on sediment clasts as recognized by previous workers (c.f. Catalano et al., 2006; Arai et al., 2007). Newly recognized hosts include: 1) amorphous and poorly crystalline materials that line voids within the basalt fragments that make up more than half of the sediment; 2) Fe- and Mn-oxides; 3) amorphous palagonite surrounding fragments of basaltic glass; and 4) an amorphous zirconium (oxyhydr)oxide found in clast coatings. This work highlights the complex speciation and solid-phase residence of U at the site while helping our collaborators to advance effective modeling of the associated U groundwater plume.

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 some Hanford samples. The phase is intimately intergrown with phyllosilicates in fine-grained coatings found on lithic and mineral fragments in the shallow portion of the vadose zone. EELS reveals a P:Zr atomic ratio of ~ 0.2 , suggesting the phase is either intergrown with minor amounts of a Zr-phosphate or has adsorbed a significant amount of phosphate.

Preliminary results on structural and chemical changes in meta-autunite group minerals under heating and vacuum conditions common in analytical settings have been obtained. Rapid depletion of interlayer cations during EMPA has been characterized and will be integrated with our continuing work using x-ray powder diffraction and Rietveld refinement to probe structural changes during dehydration.

JOHNS HOPKINS UNIVERSITY

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Grant: DE-FG02-96ER14616

Predictive Single-Site Protonation and Cation Adsorption Modeling

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

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

Results: We focussed on describing the attachment of rare earth elements and organic acid anions to mineral surfaces. We take advantage of our recent advance in surface complexation theory that includes specifically accounting for the role of water dipoles during adsorption. Our major goal is to integrate experimental uptake data and spectroscopic results with a predictive model. Using X-ray studies of yttrium surface coordination on titanium dioxide, we have developed a model for rare earth element adsorption many oxides. The results indicate the importance of a single hydrolysis state for rare earth elements on oxide surfaces. Organic acid anions also typically attach to oxides with a state of protonation different from that in aqueous solution at the same pH. However, the organic species typically adsorb in multiple ways, which can be accounted for if experimental data refer to a wide enough range of conditions and if sufficiently general predictive theories are available. Our results indicate that Born solvation theory can help the development of very general linear free energy correlations for both organic and inorganic species. In this way, results for inorganic systems previously studied in this project can help generalize the results for the organic species currently studied.

JOHNS HOPKINS UNIVERSITY

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Grant: DE-FG02-06ER15831

Development of New Biomarkers for Surficial Earth Processes

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Objectives: (*Hypothesis*) - The carbon isotopic composition of the ancient atmosphere ($\delta^{13}\text{CO}_2$) can be reconstructed by measuring the carbon isotope composition of fossil terrestrial plant tissues.

Project Description: We compared the $\delta^{13}\text{C}$ value of land plant tissues isolated from modern fluvial sediments to the $\delta^{13}\text{CO}_2$ value of today's atmosphere.

Results: We sampled sediment at 12 sites along a salinity gradient in the Black River Basin (Southwestern Jamaica), from the coastal plain ($\text{NaCl} = 0.5 \text{ g/L}$) to near its mouth ($\text{NaCl} = 4.4 \text{ g/L}$), which allowed us to evaluate the effect of marine influence on the organic carbon isotope signature, and thus our ability to reconstruct $\delta^{13}\text{CO}_2$ value from TOC. Many properties of the sediment varied systematically with salinity (e.g., mass-percent carbonate, abundance of palynomorphs), confirming a significant and increasing marine influence as we move closer to the mouth of the river. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonate within the sediment also varied systematically with salinity ($\Delta\delta^{13}\text{C} = 9.8 \text{ ‰}$; $\Delta\delta^{18}\text{O} = 3.3$): the increase in carbonate $\delta^{18}\text{O}$ value near the mouth of the river reflected the input of relatively-depleted rainwater upstream; the low values of carbonate $\delta^{13}\text{C}$ value found upstream reflect the influence of CO_2 produced by the decay and respiration of terrestrial plant material. Similarly, the $\delta^{13}\text{C}$ value of total organic carbon (TOC) systematically decreased by approximately 2 ‰ with increased NaCl concentration, indicating the presence of a mixing line between marine and terrestrial organic inputs. In contrast, for leaf and stem isolates, we observed no significant dependence of $\delta^{13}\text{C}$ value on NaCl concentration, suggesting that the isotopic signature of the integrated terrestrial contribution is independent of the salinity of the depositional environment. This work is now *accepted-after-revision* by the journal *Palaios*, additional manuscripts are *in-preparation*.

UNIVERSITY OF MARYLAND

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Grant: DE-FG02-07ER15916

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

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Objectives: The pore structure and transport properties of rocks, including fluid permeability and electrical conductivity, can be altered by a wide variety of diagenetic, metamorphic, and tectonic processes. Our goal is to provide better understanding of the interrelationships among permeability, mechanical properties, and the pore shape, under hydrothermal conditions, in mineral aggregates, with and without reactions.

Project Description: We conduct experimental investigations of the effect of changes in failure modes on transport properties. Specifically, we extend the two-step experiments to a wider range of strain-rates and temperatures, with concomitant permeability measurements. Variations in the time between loading to produce the shear band and the subsequent reloading to produce the compaction band are investigated. We will conduct thorough and detailed image collection and analysis of all deformed samples. Microstructure observations of the pore space in samples before and after alteration will be done using SEM, laser scanning confocal optical microscopy, and the high resolution x-ray CT techniques.

Results: *Faulting associated growth of compaction localization*

Recent field and laboratory studies have demonstrated that different modes of strain localization occur in porous sandstones in response to different stress conditions. Because natural environments often include preexisting heterogeneities that are reactivated during tectonic loading, different modes of strain localization coexist. Zones of localized deformation, either shear- or compaction-dominated features, profoundly affect flow processes. Each deformation mode induces significant permeability changes. In general, shear localization provide conduits for pore fluid discharge, whereas compaction bands induces significant permeability reduction and provides hydraulic barriers, enabling the development of pore pressure excess. We continue the experimental investigation on how dilatant shear localization affects the initiation and growth of compaction localization. In our previous study, we demonstrated that under low confining pressures, deformation in porous Bentheim sandstone samples with pre-existing shear fractures is primarily stable sliding along the pre-existing fracture surface. With increasing confinement, sliding along the fracture surface was inhibited, and compaction localization occurred in the fractured rocks. In collaboration with Drs. Dresen and Stanchits at GeoForschungsZentrum, Potsdam, Germany, we also conducted deformation experiments using 12 piezoelectric transducers (PZT) to monitor acoustic emission and elastic wave velocity. We recently compared our experimental data to the deformation structures of ODP core samples from the Nankai accretionary prism. Our findings include: 1) compaction bands generally initiated at the shear fracture interface and gradually developed into a

series of deformation bands along the fault; 2) The differential stress required to initiate compaction localization in pre-fractured samples are considerably less than that in intact sandstone samples; 3) “Kink-bands” observed in the sediments from the Nankai accretionary prism closely resemble compaction bands developed in our experiments. Understanding the growth of compaction localization provides new insights into the hydromechanical and seismic behaviors of subduction wedges and sedimentary basins.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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Grant: DE-FG02-97ER14760

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

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Objectives: The broad objective of this proposal is to study the interrelationships among permeability, mechanical properties, and the pore structure of rocks under hydrothermal conditions, with and without metamorphic reactions.

Project Description: Each experimental study or calculation was designed to isolate a particular aspect of a natural process, rather than to conduct more complex experiments in which several processes act simultaneously, as often occurs in nature. Our recent work falls into four general categories: A.) the effect of mechanical deformation on transport properties, B.) the effect of thermal loading on permeability, C.) the effect of structural heterogeneity on fluid transport, and D.) some aspects of the methods of measuring permeability in the laboratory.

Results: In previous work, we have deformed aggregate mixtures of quartz and calcite at temperatures from 300-800 K, confining pressures up to 300 MPa, and various pore pressures (argon gas) during isostatic loading ($\sigma_1 = \sigma_3 = P_c > P_f$) and conventional triaxial loading ($\sigma_1 > \sigma_3 = P_c > P_f$). In addition we measured permeability and storativity measurements and measured yield and critical stresses (i.e., the differential stress at the onset of dilatancy) in conventional triaxial deformation tests on Solnhofen limestone at confining pressures of 70 to 200 MPa, from 298 to 473K, and a constant pore pressure of 50 MPa. During the current year, we expanded our pressure solution model of compression of asperities pressed against each other in presence of fluid. Our aim was to investigate the kinetics of stress transfer between unequally stressed contacts and to estimate its effect on the effective global creep law. The results indicate that the transient mechanical response may have time scales as long as hundreds of years and that load transfer, at least in this simple case, can significantly influence the overall mechanical response of the aggregate material. As would be expected intuitively, both creation of new contacts and variations in the contact radius can decrease the overall displacement rate, with creation of new contact being the most effective in rate-reduction. But, the details of the load transfer can often be counter intuitive; and, load transfer can also significantly extend the transient period. Finally, we incorporated our previously devised, single-pipe, Biot slow P-wave propagation model into network simulations. We numerically estimated the dispersion equation for one-, two-, and three-dimensional heterogeneous networks and determined the reduction in wave velocity caused by wave scattering and, therefore, by heterogeneity.

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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.

Project Description: We address two aspects of the erosion problem: the “two-phase phenomenon” of water-driven granular flow, and the growth and interactions of channels. We study the former problem in the laboratory and the latter problem in both the laboratory and the field. In both cases we combine our empirical studies with theoretical analysis.

We specifically address the problem of erosion driven by subsurface “seepage” flows. As in the more commonly studied problem of erosion by overland flow, an understanding of the two-phase flow of water and grains is required to predict the conditions under which material is eroded and subsequently transported by rivers and streams. Compared to the case of overland flow, however, the growth of seepage channels is relatively decoupled from topographic roughness. Channel networks driven by groundwater flow instead reflect more purely their competition for water. We seek to better understand the conditions necessary for the initiation of erosion, the mechanisms that govern the growth of seepage-driven channels, and the processes that determine the geometry of seepage networks.

Results: Our work in FY2008 concentrated on developing an understanding of how the flow of subsurface water shapes the “steephead channels” that drain into the Apalachicola River near Bristol, Florida, on the Florida Panhandle (Figure 1). The channels are cut through 65-m thick surface deposits of sand, and are about 100 m wide and up to 4 km long. Groundwater emerges at the base of each conical channel head.

By combining field observations with physical theory, we have shown that two simple linear response relations suffice to characterize key aspects of the growth and form of the network. The first growth law states that the velocity at which channel heads advance is proportional to the flux of groundwater to the heads. The second states that tip-splitting and side-branching events occur at a rate proportional to the total groundwater flux drained by the network. Remarkably, the dynamics defined by the first growth law is reversible. We have therefore used this property to reconstruct the history of network growth and estimate network age.

We have also addressed the characteristic length scale between channels on developed networks. Our theory predicts the evolution of this length scale, thereby linking network growth dynamics to geometric form.

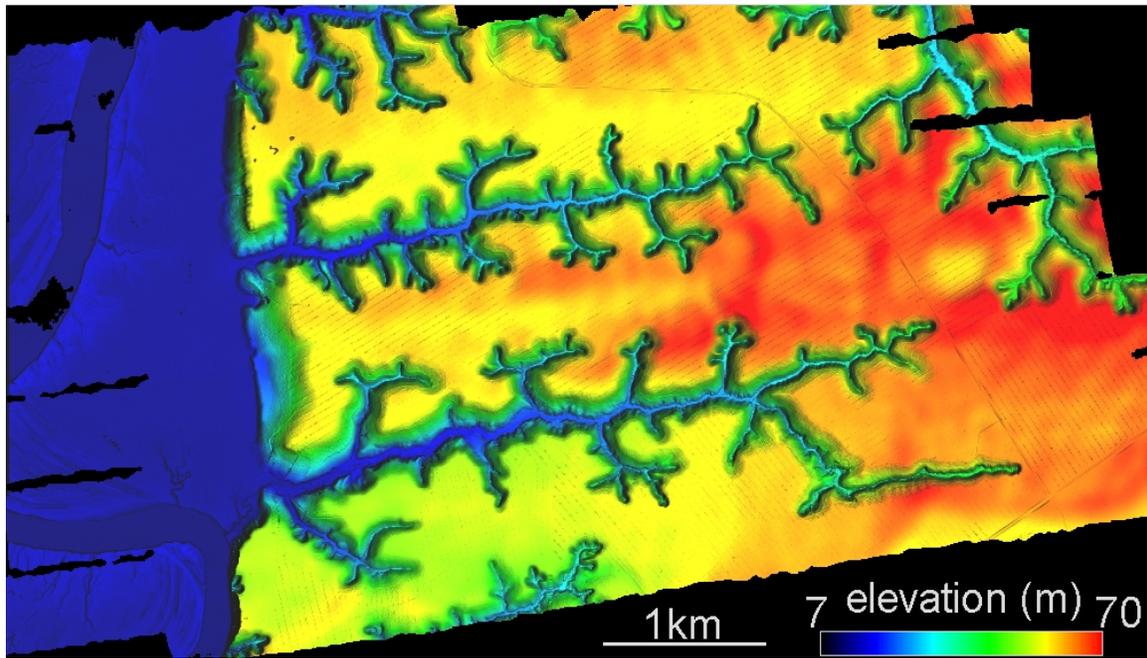


Figure 1: Topographic map of networks of steephead channels draining into the Apalachicola River, located on the Apalachicola Bluffs and Ravines Preserve, near Bristol Florida. Topography is shaded with illumination from the east. Mapping data were collected by the National Center for Airborne Laser Mapping.

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Grant: DE-FG02-07ER15839

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 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 773 to 1173 K and pressures from 6 to 12 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 are well on the way towards collecting the full set of data that describes the strength of olivine from the coolest parts of the lithosphere to warmer temperatures where high-temperature creep mechanisms control strength. Our results indicate that at strain rates near 10^{-5} s^{-1} the flow strength of olivine increases from 2 to 4 GPa as temperature decreases from 1173 to 673 K. These strength levels are generally higher than found in previous work. Also contrary to previous work, the temperature sensitivity over this range is not constant. At lowest temperatures, strength varies little with temperature, but becomes more temperature-sensitive with increasing temperature, eventually matching the value for high-temperature creep. Meanwhile, our colleagues at the University of Minnesota are investigating the evolution of fabric in the deformed olivine samples using EBSD (electron backscatter diffraction). The results indicate a clear change in the dominant slip system with stress, from (100) [001] at high stress to (010) [100] at low stress.

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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-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 requires us to develop methods of appropriately small-scale experimental deformation and structural characterization of granular porous media. We chose to work with both *natural* and *synthetic* grain-cement systems using novel approaches that provide insight into grain-scale mechanics. We are:

1. Developing methods for fabrication and apparatus to test the mechanical properties of synthetic assemblages of soda-lime silicate beads and ice cements.
2. Integrating microstructural and experimental analyses to relate physical elements of progressively cemented natural and synthetic systems to their structural response to stress.
3. Developing quantitative relationships describing the stress-strain response of cemented granular systems and incorporate microscale material response into a DEM.

Results: 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. *We know of no natural system that exhibits this geometry.* Therefore, the U. Wisconsin group has designed and implemented an approach using detailed microstructural characterization and ultrasonic velocities to quantitatively characterize and determine the mechanical impact of progressive cementation and natural cement morphologies in the St. Peter Sandstone, a quartz-cemented quartz arenite. The Sandia team is investigating the mechanical effects of quartz cement geometry, distribution, and abundance in quartz arenites with a series of 2D, plane strain, finite element simulations of two-grain and multigrain arrangements. The 2-grain models demonstrate that as cement bridges lengthen, stress is more distributed, point loads dissipate, and contact stiffness increases, regardless of cement geometry. However, the distribution of stress in the system varies with cement geometry. Increasing cement bond length results in more homogenous stress distribution and greater stiffness in cubic-closest-packed multi-grain assemblages as well. Importantly, this is true even

though the overgrowth model has more than three times the cement and 25% less pore space than the grain-bridging model.

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 (see figure below) 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. Therefore, in coupled problems it is of utmost importance to consider both the mechanical and hydrologic influence of cement on material properties.

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

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<http://www.msu.edu/~kalinich/research.html>

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 2008 we significantly advanced in several new promising research directions along with completion of on-going projects and final publication of work completed in previous years.

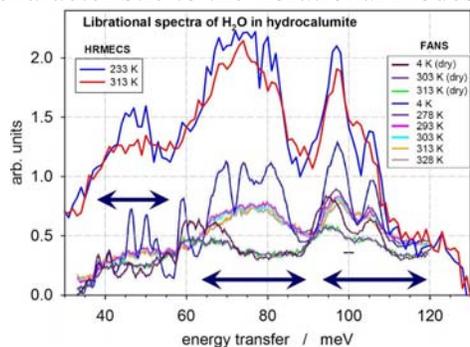
New computational directions focused on modeling proton exchange reactions in aqueous hydroxide and carbonate solutions. Using *ab initio* molecular dynamics (AIMD), metadynamics (MTD), and multistate empirical valence bond (MS-EVB) techniques, we are gradually bridging the gap between rigorous but computationally very expensive quantum-chemical approaches and classical MD simulations, which are much more efficient in modeling large disordered systems relevant to geochemical and environmental applications. AIMD simulations provided, for the first time, new quantitative insight into the structure and dynamics of hydrogen bonding environments for hydrated carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and carbon dioxide (CO_2) and the effects of these species on the structure, H-bonding and dynamical behavior of the surrounding water molecules. The first successful MS-EVB model of the proton transfer involving the OH^- ion has also been developed. In 2008 we initiated a systematic quantitative study of the energetics and structure of adsorption between metal cations, natural organic matter (NOM), and mineral surfaces via calculation of potentials of mean force resulting from these interactions. These calculations are natural extension of our previous MD simulations which semi-

quantitatively allowed us to estimate the effects of metal cations with different charges and charge density on the NOM aggregation in aqueous solutions. New MD simulations were also performed to quantitatively analyze the dynamical behavior of aqueous species at mineral-water interfaces and in nano-confinement within clay interlayers at several characteristic time and length scales, which we investigated simultaneously by our NMR and neutron scattering efforts.

In the ^{39}K NMR studies of K^+ replacement by H_3O^+ at the water-solid interface of synthetic, nanocrystalline muscovite mica, we show that the molar ratio of K^+ initially on the basal surface to H_3O^+ in solution ($\text{K}^+_{\text{surf}}/\text{H}_3\text{O}^+_{\text{aq}}$) is a useful parameter for characterizing and comparing experimental results, that significant K^+ displacement only occurs when $\text{K}^+_{\text{surf}}/\text{H}_3\text{O}^+_{\text{aq}} \leq 1$, and that a majority of K^+ remains as inner- or outer-sphere species within 3-4 Å of the surface for $\text{K}^+_{\text{surf}}/\text{H}_3\text{O}^+_{\text{aq}} \geq 1$. To the best of our knowledge, this work includes the first model-independent spectroscopic evidence of a significant K^+ association with the muscovite surface when $\text{K}^+_{\text{surf}}/\text{H}_3\text{O}^+_{\text{aq}} \geq 1$, the first use of ^{39}K NMR to study K^+ desorption and structure at the muscovite-water interface, the first spectroscopic study of K^+ replacement by H_3O^+ at environmentally relevant water/solid ratios.

In 2008 we initiated investigations of Ca-bearing materials using ^{43}Ca NMR at natural abundant levels of ^{43}Ca (0.145%). Ca^{2+} ion is a major component of natural materials such as limestone, is a key component of the load-bearing phases in cement and concrete, and using ^{43}Ca as a proxy for ^{87}Sr in NMR studies may be the only way to learn about the molecular-level structure and dynamics of Sr^{2+} released from nuclear waste storage tanks into hydrated soil minerals. ^{43}Ca NMR has been considered impractical to date due to the unattractive NMR properties of ^{43}Ca that lead to poor sensitivity and poor spectral resolution. However, by partnering with the High Field Magnetic Resonance User Facility at Pacific Northwest National Laboratory, we have collected preliminary data showing that ^{43}Ca NMR is viable in many complex materials and identified our and the facilities needs to perform even more detailed studies in the future.

In 2008 we have also completed the first series of experiments probing the dynamics of interlayer and interfacial water molecules in layered double hydroxides and clays by inelastic (INS) and quasi-elastic (QENS) neutron scattering techniques using several complementary instruments - HFBS, DCS and FANS at NCNR (NIST) and HRMECS and QENS at IPNS (Argonne National Lab). INS and QENS probe the correlations of H_2O librational and diffusional motions in confined spaces over the time scale significantly different than that probed by NMR, but most directly comparable with MD simulations. In combination with MD results, the neutron scattering measurements for “dry” and “wet” samples of hydrocalumite help to identify three energy ranges (45-55, 65-90, and 90-120 meV) uniquely characteristic to the librational modes of H_2O in the interlayers.



Comparison of INS spectra for hydrocalumite obtained with FANS (NIST) and HRMECS (IPNS) instruments.

MINERALOGICAL SOCIETY OF AMERICA

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Grant: DE-FG02-01ER15127

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Objectives: MSA and GS Short Courses are 2-4 day, in-depth instructional courses, usually given in conjunction with major meetings, and taught by several invited speakers, well-recognized in the field, who also write the accompanying Reviews in Mineralogy and Geochemistry volume. The courses are cogent and concise reviews of the literature and new advances about a subject area.

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 FY2008, with a companion *Reviews in Mineralogy and Geochemistry* volume:

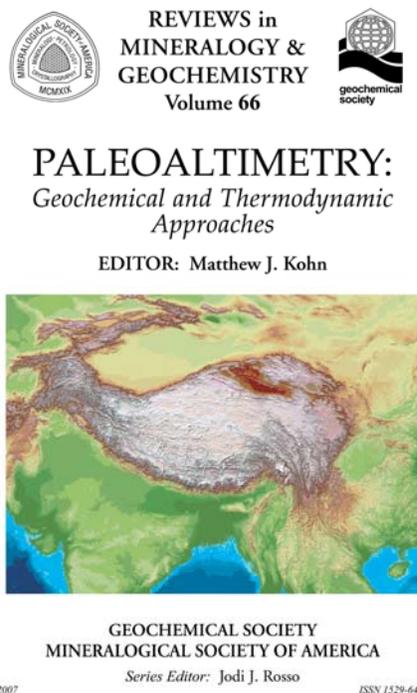
[1] **Paleoaltimetry: Geochemical And Thermodynamic Approaches.** October 26-27, 2007. Convener is *Matthew J. Kohn* (Boise State University). The course had 35 participants (17 students, 6 professionals, and 12 speakers).

Elevation is a direct reflection of the internal force balance of an orogenic system, and consequently paleoelevation histories yield one of the best discriminators of competing orogenic models, particularly for the formation of plateaus. In addition, because elevation reflects the complex interplay between tectonic and climatic processes, changes to elevation have fundamental influences on changes to regional climate, flora and fauna, erosion, and structural and sedimentation styles. That is, elevation changes provide a means of understanding and linking together a wealth of geological phenomena spanning numerous traditional disciplines. The short course was designed to review the principal chemical and thermodynamic means of inferring past elevations, with applications that included geodynamics, geomorphology, paleoclimatology, structural geology and tectonics. The short course focused on 4 general areas: the geomorphologic and geodynamic rationale for studying paleoelevations, proxies for atmospheric properties, radiogenic and cosmogenic nuclides, and stable isotopes.

The introduction to the course considered geomorphology and geodynamics as a rationale for studying paleoelevations. Geomorphologic techniques have advanced rapidly in the last ~5 years, and relict erosion landscapes coupled with quantitative estimates of incision provide first-order estimates of the

amount of surface uplift that have occurred in an area. These results, in turn, are used to test various geodynamic and tectonic models, especially the importance of lower crustal flow. The middle part of the course examined atmospheric thermodynamics and atmospheric pressure proxies as means for inferring elevation, mainly through records of leaf macro- and micro-morphologies, but also from bubble size distributions in vesicular basalts. The remaining ~50% of the course examined in detail the various isotopic techniques that are used for inferring paleoelevations. These included U-Th/He and fission track methods for inferring topographic relief and its evolution, the elevation-dependence of cosmogenic radionuclides, and numerous stable isotope proxies that mainly link either to the elevation-dependence of the $^{18}\text{O}/^{16}\text{O}$ and D/H ratios in precipitation. One exciting highlight of the course included fresh results on calibration of the clumped isotope technique in paleosols for inferring both temperature and precipitation $^{18}\text{O}/^{16}\text{O}$ ratios. These results showed both the problems in blindly using laboratory calibrations of calcite fractionations, yet also excellent promise for refining paleoaltimetric estimates with this method.

The content of the course was geared toward students and professionals interested in paleoaltimetric methods, geodynamics, and tectonics, and provided a lively forum for discussions of geochemical and thermodynamic methods with diverse applications to different mountain belts and tectonic problems. The lecture room for the short course and the first-rate facilities of the Crowne Plaza Hotel (formerly Holiday Inn Denver City Central – one of the GSA preferred hotels) provided an excellent environment for the presentation of the formal course materials and for informal discussions during lecture breaks and meals. The lectures were presented on Friday and Saturday October 26 and 27.



Reviews in Mineralogy and Geochemistry volume 66: **Paleoaltimetry: Geochemical and Thermodynamic Approaches**, Matthew J. Kohn, editor, i-x and 278 pp. ISBN 978-0-939950-78-2. (\$40 non-members, \$30 MSA, GS, and CMS members). Copies were distributed to all short course participants, 648 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 66 is also posted on *GeoScienceWorld*. (GSW) that as of March 2008 had 257 subscribers.

MINERALOGICAL SOCIETY OF AMERICA

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Grant: DE-FG02-08ER15928

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.

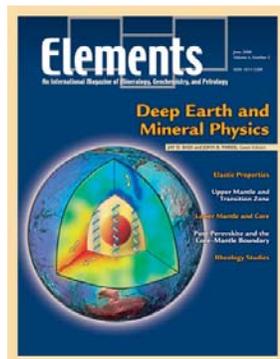
Project Description: The grant was for partial support of two thematic issues of the magazine on "Sequestration of Carbon Dioxide" and "Deep Earth and Mineral Physics".

Results: Publications supported by the grant are:

[1] *Elements* volume 4 number 3 (June 2008) 39 pages in 6 articles devoted to the topic of *Deep Earth and Mineral Physics*. Guest Editors: Jay D. Bass (University of Illinois) and John B. Parise (Stony Brook University)

[2] *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

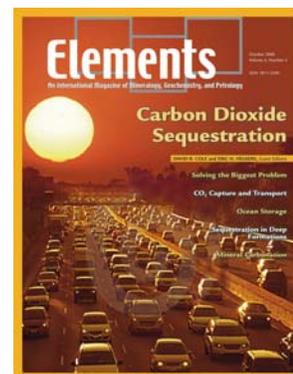
10,595 copies were distributed to individuals, libraries, and societies. The issues are also available on line through GeoScienceWorld (<http://elements.geoscienceworld.org/>) and the *Elements* (www.elementsmagazine.org/) websites.



Deep Earth and Mineral Physics. Mineral physics is concerned with understanding the physical and chemical properties of the condensed matter at extreme conditions, with the goal of understanding the interior of Earth, from the crust to the core, as well as other planetary bodies. DOE has had a long-standing interest in the behavior of matter under extreme conditions as a means of approaching numerous problems related to the environment, climate, energy, and national defense. Understanding the rheology of materials is necessary for modeling convection in planetary interiors, and it is also necessary for approaching problems related to the long-term storage of nuclear waste. High-pressure-temperature equations of state of fluids are needed to

calculate chemical reactions and fluid transport during subduction of slabs into the Earth, and they are also needed for understanding the behavior of fluids in nuclear reactors. The PVT equations of state of solids are needed to determine the density distributions in planets and their total mass, and also needed to understand the behavior of materials under sudden impacts and when shocked to extreme PT conditions.

Sequestration of Carbon Dioxide. The 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 CO₂ into rock formations beneath the surface of the Earth, typically at depths of 1000 to 4000 meters. Although CO₂ is a relatively benign substance, the volume being considered is large. If developed to its envisaged potential, geologic sequestration will entail the pumping of CO₂ into the ground at roughly the rate we are extracting petroleum today. To have the desired impact on the atmospheric carbon budget, CO₂ 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.

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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 objective of this study is to determine the rheological behavior of olivine, the primary mineral in Earth's upper mantle, in order to provide the basis for modeling geodynamic processes.

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 to 15 GPa.

Experiments were conducted at temperatures ranging from 673 to 1073 K and pressures from 4 to 10 GPa. Advanced synchrotron x-rays techniques provided *in-situ* measurements of pressure (i.e., mean stress), differential stress, and strain. These measurements are used to establish the flow behavior of olivine by describing the dependence of creep rate on deformation conditions such as stress, pressure, and temperature.

Results: Following the development of improved testing techniques, we have completed a series of experiments to reach our goal of characterizing with good resolution the rheological behavior of olivine.

Important unresolved issues in geodynamics demand a better understanding of the rheological strength of lithosphere. To determine the flow behavior of olivine under lithospheric conditions, we carried out creep experiments at relative low temperatures (673 - 1073 K) but high pressures (4 - 10 GPa). Our results indicated that the flow strength of olivine increases from 2 to 4 GPa as temperature decreases from 1073 to 673 K. The final touch is in progress for establishing the flow law for olivine at lithospheric temperatures. Meanwhile, we have also investigated the evolution of the fabric in olivine samples deformed at high pressures. Deformation-induced fabrics provide important information for understanding seismic anisotropy in the upper mantle. Our recent EBSD (electron backscatter diffraction) analyses of the fabric of deformed olivine aggregates have documented the influence of deformation conditions (e.g., temperature and stress) on the fabric evolution of olivine at high pressures. Deformation of olivine is dominated by the (100) [001] slip system at low temperatures and high stresses and by the (010) [100] slip system at high temperatures and low stresses.

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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 fault conduit aperture that arise due to local increases fluid pressure caused by fluid generation, disequilibrium compaction, thermal expansion, seismicity, or possibly stress perturbations caused by pumping of hydrocarbons.

The present research consists of developing a numerical model for solitary wave initiation and propagation in a compacting sedimentary basin undergoing hydrocarbon generation, based on Eugene Island geology. The research involves the development of an original computer program that applies theory for the propagation of solitary waves in a conduit embedded in a visco-elastic matrix. This program is to be coupled to the commercial BasinMod-2D® software that enables calculation of multi-phase fluid pressure, flow, heat transport, and deformation in a geologically heterogeneous environment.

Results: The project was begun during FY2008 and has not yet generated reportable results. Project efforts thus far have been directed primarily toward personnel recruitment, purchasing computing tools, and the first steps of developing a numerical solution for solitary wave transport. Experimentation with several finite difference schemes has produced solutions to the governing equations for solitary wave transport that successfully model wave motion for relatively low viscosity contrasts between the matrix and pore fluid. Further work is needed to identify and employ a more robust numerical scheme that will be stable for more geologically realistic viscosity contrasts. However, results generated thus far illustrate how increasing matrix viscosity dampens wave amplitude.

In addition to generating a working numerical solution for solitary wave transport, additional tasks planned for the remainder of the first grant year are to begin developing a model for basin compaction and hydrocarbon generation using the BasinMod software that will compute the fluid pressure field in Eugene Island. These fluid pressure calculations will be coupled to the solitary wave transport calculations and will help to identify regions of overpressure that would be favorable for spawning solitary waves.

NATIONAL ACADEMY OF SCIENCES

Board on Earth Sciences and Resources
500 5th Street, N.W.
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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 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 2008, the Board oversaw 10 studies. Examples of studies underway during FY 2008 are Deep-Time Geologic Records for Understanding Climate Change Impacts; FEMA Flood Maps: Accuracy Assessments and Cost Effective Improvements; National Requirements for Precision Geodetic Infrastructure; and Challenges and Opportunities in Earth Surface Processes. BESR completed 11 studies in FY 2007 and one at the beginning of FY 2008. The results of BESR's studies are published in its peer-reviewed reports. Examples of completed studies include **Minerals, Critical Minerals and the U.S. Economy; National Land Parcel Data: A Vision for the Future; Coal: Research and Development to Support National Energy Policy; and Origin and Evolution of Earth: Research Questions for a Changing Planet.**

During this reporting period, the Board held two meetings. The November 2007 meeting was held at the Beckman Center in Irvine, California. At this meeting, two BESR standing committees, the Geographical Sciences Committee and the Mappings Science Committee, were reviewed. The new report, **Coal: Research and Development to Inform Energy Policy**, was discussed with the chair, Corale Brierley. The BESR members visited the Southern California Earthquake Center and listened to presentations by Tom Jordan and his staff. Most of the meeting was devoted to a roundtable discussion

on Impacts of Coastal Inundation. Speakers included Margaret Davidson (NOAA), Susan Cutter (University of South Carolina), Lynn Utery (USGS), and Don Chambers (University of Texas at Austin). After a lengthy discussion, two study opportunities were identified: (1) Community Resilience Indicators for Decision Support and (2) Sea Level Rise in California. Both potential studies are now in the funding stage.

The June 2008 meeting was held at the Keck Center in Washington, DC. At this meeting, one standing committee, Committee on Geological and Geotechnical Engineering, was subject to a lengthy review. Two new reports were discussed. These reports were **Minerals, Critical Minerals, and the U.S. Economy** and **Origin and Evolution of Earth: Research Questions for a Changing Planet**. Elizabeth Edie (BESR staff) provided an overview of the former and Don DePaolo (University of California, Berkeley) provided an overview of the latter. A major portion of the meeting's open session was devoted to a roundtable on "The Energy Water Nexus." The speakers were Peter Gerick (Pacific Institute), Michael Hightower (Sandia National Laboratory), Robin Newmark (Lawrence Livermore National Laboratory), and Mark Cowing (California Department of Water Resources). Speakers were asked to identify cutting-edge research questions and emerging research opportunities related to the transdisciplinary study of water availability and energy issues, both in the context of increasing social demand for these resources and in the context of predicted climate warming. These included but were not limited to the following sectors:

- (1) The need for and impacts on water associated with novel approaches to carbon-based energy and alternative energy resources;
- (2) The need for and impacts on water in the management of fossil carbon through sequestration and other means;
- (3) The energy demands of supplying water to agriculture, communities, and industry;
- (4) The impact of shifting climate on regional water patterns, and their consequences for land cover, water supply, energy extraction, and power generation; and
- (5) Approaches to assessing the value of water and energy resources through a more complete understanding of their relationship to each other.

Following the presentations, possible transdisciplinary study ideas were discussed.

NATIONAL ACADEMY OF SCIENCES

Board on Earth Sciences and Resources

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Grant: DE-FG02-05ER15664

Grand Research Questions in Solid-Earth Sciences

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Objectives: A National Academies committee was established to frame some of the great intellectual challenges inherent in the study of the Earth and planets. The goal was to focus on science, not implementation issues, such as facilities or recommendations aimed at specific agencies.

Project Description: Over the past three decades, Earth scientists have made great strides in understanding our planet's workings and history. Yet this progress has served principally to lay bare more fundamental questions about the Earth. Expanding knowledge is generating new questions, while innovative technologies and new partnerships with other sciences provide new paths toward answers. The committee canvassed the geological community and deliberated at length to arrive at 10 questions. Some of the questions present challenges that scientists may not understand for decades, if ever, while others are more tractable, and significant progress could be made in a matter of years.

Results: The 10 questions are summarized below.

1. How did Earth and other planets form? While it is generally agreed that the Sun and planets came from the same nebular cloud, we do not know enough about how Earth obtained its chemical composition to understand its evolution or why the other planets are different from one other. Further measurements of solar system bodies and extrasolar objects could offer insight to the origin of Earth and the solar system.
2. What happened during Earth's "dark age" (the first 500 million years)? Another planet is believed to have collided with Earth during the latter stages of its formation, creating debris that became the moon and causing Earth to melt down to its core. This period is critical to understanding how the Earth developed its atmosphere and oceans, but little information is available because few rocks from this age are preserved.
3. How did life begin? The origin of life is one of the most enduring questions in science. The only remaining evidence of where, when, and in what form life first appeared springs from geological investigations of rocks and minerals. To help answer the question, scientists are also examining the sedimentary record of Mars, which predates that of Earth.
4. How does Earth's interior work, and how does it affect the surface? Core convection produces Earth's magnetic field, which may influence surface conditions, and mantle convection causes

volcanism, seafloor generation, and mountain building. However, scientists can neither precisely describe these motions, nor calculate how they were different in the past, hindering scientific understanding of the past and prediction of Earth's future surface environment.

5. Why does Earth have plate tectonics and continents? Earth has plate tectonics, but we still do not know why it started and how closely it is related to other unique aspects of Earth, such as the abundance of water and the existence of the continents, oceans, and life. Moreover, we still do not know when continents first formed, how they remained preserved for billions of years, or how they are likely to evolve in the future.

6. How are Earth processes controlled by material properties? Scientists now recognize that macroscale behaviors, such as plate tectonics and mantle convection, arise from the microscale properties of Earth materials, including the smallest details of their atomic structures. Understanding materials at this microscale is essential to comprehending Earth's history and making reasonable predictions about how planetary processes may change in the future.

7. What causes climate to change—and how much can it change? Earth's surface temperature has remained within a relatively narrow range for most of the last 4 billion years, but has also changed abruptly. Study of Earth's climate extremes through history—when climate was extremely cold or hot or changed quickly—may lead to improved climate models that could enable scientists to predict the magnitude and consequences of climate change.

8. How has life shaped Earth—and how has Earth shaped life? The exact ways in which geology and biology influence each other are still elusive, such as life's role in oxygenating the atmosphere and reshaping the surface through weathering and erosion, and how geological events caused mass extinctions and influenced the course of evolution.

9. Can earthquakes, volcanic eruptions, and their consequences be predicted? Progress has been made in estimating the probability of future earthquakes, but scientists may never be able to predict the exact time and place an earthquake will strike. Geologists are moving toward predictive capabilities for volcanic eruptions, but face the challenge of developing a clear picture of the movement of magma, from its sources in the upper mantle to the surface where it erupts.

10. How do fluid flow and transport affect the human environment? Good management of natural resources and the environment requires knowledge of the behavior of fluids, but we have not yet developed models that can predict the performance of these natural systems. It remains difficult to determine how subsurface fluids are distributed in heterogeneous rock and soil formations, how fast they flow, how effectively they transport dissolved and suspended materials, and how they are affected by chemical and thermal exchange with the host formations.

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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 second year of this project, we continued to use terrestrial lidar (Light Detection and Ranging) to investigate the root causes of non-Fickian dispersion in natural groundwater systems. The UNM contribution to this study focuses on providing realistic images of aquifer heterogeneity through application of interpreted lidar scans and digital photography of outcrop analogs for aquifers. During the first year of the study, we successfully imaged an outcrop area with terrestrial lidar, segmented the image to distinguish sand-dominated from gravel-dominated lithofacies, and assigned hydraulic conductivity (K) values to the different lithologic types for application in groundwater models. Results of this work showed that groundwater flow was focused into the gravel-dominated laminae, bypassing much of the sandier facies. The model results displayed strongly non-Fickian character for solute breakthrough. Over the past year, we focused testing our ability to image and model realistic heterogeneity from outcrops by varying the lidar image collection methods and evaluating additional processing steps for interpreting facies distributions.

Results from the second year efforts show that (1) non-Fickian dispersion character can be replicated at several outcrop analog study sites, where groundwater focusing occurs along coarser-grained laminae; (2) not all outcrop exposures are suitable for lidar interpretation due to limited laser reflection intensity contrast; (3) multiple lidar scans of the same image area must be acquired in order to reasonably identify lithofacies type from reflection intensity mean and variance (the multiple scans generate a more accurate image by allowing us to average out random noise); and (4) 3D models of heterogeneity can be developed by sequentially scraping outcrop faces and collecting lidar scans from each exposed outcrop face. Figure 1 shows an outcrop near Hanford, Washington, that is composed of mixed gravel-

dominated beds and sand-dominated beds. We were able to successfully segment lithofacies from the lidar scan and run groundwater models through the interpreted segmented lidar map. By releasing particles at one end of the simulation and recording travel times to the other end of the simulation, we can see that this heterogeneity results in non-Fickian transport character (e.g., heavy-tailed breakthrough solution).

Because 2D representations of aquifer heterogeneity may result in unrealistic artifacts that could affect overall interpretation of transport results (e.g., effects of dead-end strata that probably extend laterally in the third dimension), we evaluated means to collect 3D analog data by scraping an outcrop at approximately 2cm intervals and collecting multiple scans of each exposed face. Because output from lidar produces a 3D point cloud, this sliced-outcrop approach utilizes the full 3D capabilities of the terrestrial lidar equipment. Placement of known survey markers at scan corners allows for compilation of the data into a 3D volume and will allow us to produce highly-resolved 3D models of heterogeneity. In the upcoming year, we plan to compile additional 3D results and compare these results to transport characteristics that are observed in 2D. All of these results will be used by our collaborators on this project to evaluate other simulation methods for modeling heterogeneity and to evaluate heterogeneity of dispersion parameters in an aquifer.

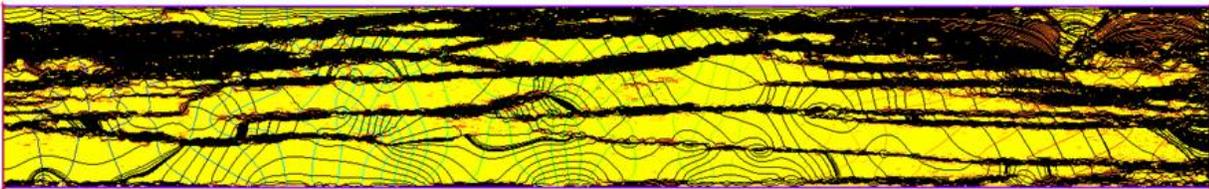


Figure 1: Groundwater and advective pathline simulation results from the high-resolution lidar-based outcrop image of Upper Ringold Formation, near Hanford, Washington. Note the strong focusing of particles into well connected gravel units. This heterogeneity resulted in a strongly non-Fickian breakthrough.

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 Université de Paris - Orsay.

Results: We have studied the flow of two types of complex fluid: non-Newtonian shear-thinning and shear-thickening fluids, and suspensions of spherical solid particles. In the former case, we developed a new lattice-Boltzmann algorithm to simulate fluids with non-Newtonian stress characteristics, and studied their flow in self-affine fracture channels, including finite-Reynolds number inertial effects. Local aspects of the flow fields, such as maximum velocity and pressure fluctuations, were studied, and the behavior of the non-Newtonian fluids were compared to the previously studied Newtonian case. We find a scaling relation between permeability and mean aperture in the low Reynolds number regime, generalizing an earlier result for Newtonian fluids. As the Reynolds number increases, we observe the same sequence of transitions to nonlinearity found in intergranular porous media. Furthermore, the permeability results may be collapsed into a master curve of friction factor vs. Reynolds number shown on the left below, analogous to the well-known Nikuradze correlations for flow in rough pipes, using a scaling similar to that employed for power-law fluids in porous media.

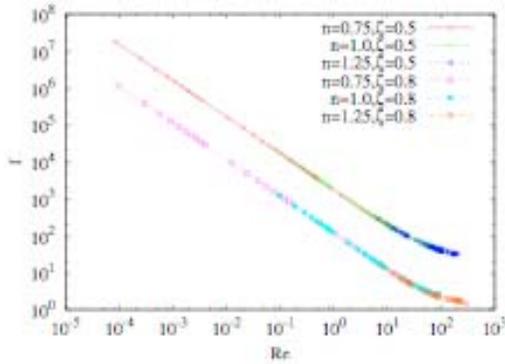
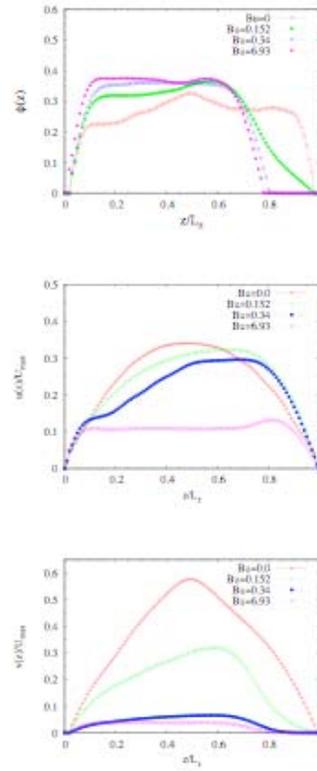


FIG. 11. (Color online) Friction factor of self-affine fracture channels of Hurst exponent $\zeta=0.5$ and 0.8 as a function of Reynolds number defined as in Eq. (14) for power-law fluids with $n=0.75, 1.0,$ and 1.25 .



Concentration and velocity profiles in a sedimenting suspension.

In the suspension case, our first application is to study particulate sedimentation when gravity acts on the system. Using previously-developed lattice-Boltzmann methods for simulating flows containing suspended particles we have studied sedimentation processes in the presence of a finite Reynolds number flow, in some detail for fractures having flat walls, and we have begun to address the self-affine case. We considered three dimensional suspensions of spherical particles at initial bulk volume fractions 0.13, 0.26 and 0.34, particle Reynolds numbers ranging from about 0.02 to 5.0, and buoyancy numbers (non-dimensionalized gravitational force) 0 to 200. To date, only gravitational and contact forces are included, but additional electrostatic and dispersion force attraction mechanisms will be incorporated in future modeling. In the neutrally buoyant case we observe particle migration phenomena and flow field characteristics similar to those found in earlier experiments and simulations. With buoyancy effects included, a three-phase stratified system develops containing clear fluid, flowing suspension and immobile sediment regions. We compute the evolution of the concentration phase boundaries and the various velocity fields; example profiles for bulk concentration 0.26 are shown on the right above. While the results are in qualitative agreement with observation, in this case unfortunately there is even less experimental appropriate data to compare to. Future work will address clogging issues, fracture junctions, and self-affinely rough fracture surfaces.

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK

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Grant: DE-FG02-03ER15458

Study of Damping 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. In order to unravel the origins of dissipation in earth materials from a fundamental point of view, we have developed the concept of a frequency dependent effective mass of a loose granular aggregate contained within a rigid cavity. The effective mass is complex valued; its real part reflects the elastic properties while its imaginary part the dissipative properties of the granular medium. We demonstrate how the distinct features of the effective mass allow the study of some of the mechanisms of damping of acoustic modes, aging and elasticity in granular matter.

Generally speaking, the effective mass exhibits a sharp resonance which we interpret in terms of an effective sound speed describing the elasticity of the material. The imaginary part of the effective mass of shows a broad resonance peak which quantifies the attenuation of acoustic waves in the system. We observe remarkable changes in a humidity controlled environment in the stiffness and attenuation in the medium. By monitoring the effective mass in time, we find a logarithmic aging effect in the resonance frequency as well as an increase of the damping upon humidification and its subsequent drastic decrease upon drying. We interpret these effects as manifestations of capillary condensation occurring between the asperities at the contact surfaces between the grains during humidity-dry cycles. We conclude that,

in loosely jammed granular materials, dissipation of acoustic energy is dominated by the asperities at the interparticle contact surfaces. Therefore humidity drastically affects the attenuation of the material through the capillary condensation of liquid bridges. The large variations in dissipation found in this study demonstrate the conditions for effective particle damping and are relevant to a variety of applications for optimizing attenuation of structure-borne acoustic waves.

Recent studies indicate that the elastic and dissipative properties of granular materials are determined by the contact network structure. Thus, we have studied the structural properties using a statistical mechanics approach based on the volume ensemble for granular materials.

Our results illuminate a diverse spectrum of data on sphere packings through a statistical theory of disordered jammed systems, while revealing new packing states open to experimentation. Our results ultimately lead to a phase diagram providing a unifying view of the disordered sphere packing problem that: 1. provides a statistical interpretation of the important limits of random loose packings (RLP) and random close packings (RCP), 2. predicts their density values in good agreement with experiments, and 3. establishes the concomitant equations of state relating observables such as the average mechanical coordination number Z , entropy, volume fraction and elastic moduli. This classification guides the search for indications of jamming from a systematic point of view, through the exploration of the elastic properties for all jammed states.

STATE UNIVERSITY OF NEW YORK, STONY BROOK

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Grant: DE-FG02-96ER14633

Complexities Affecting the Rate and Mechanism of Pyrite Oxidation: An Interdisciplinary Approach

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Objectives: The primary goal of this research program is to understand the microscopic aspects of pyrite oxidation. Our continuing research strategy is to understand macroscopic observations of pyrite reactivity with an atomic/molecular level view. The results of this research will lead to a better understanding how pyrite reacts in a range of chemical environments.

Project Description: The reactivity of pyrite in anoxic and oxic environments is being investigated by integrating aqueous geochemical and modern surface science techniques. An emphasis of the research is to develop *in-situ* techniques to study the mineral surface on a microscopic level in the presence of an aqueous or gaseous phase.

Results: Research in 2008 focused on the reactivity of co-mingled sulfides. A series of column experiments were conducted to evaluate the influence of co-mingling pyrite (FeS_2) and galena (PbS) on their respective oxidation rate. The extent of reaction was determined on the basis of the rate of metal release. The rate of metal release in co-mingled experiments was compared to those in separate mono-mineralic column experiments. The results are summarized in Figure 1. Note that the rate of pyrite oxidation decreases drastically when it is co-mingled with galena. Conversely, galena is far more

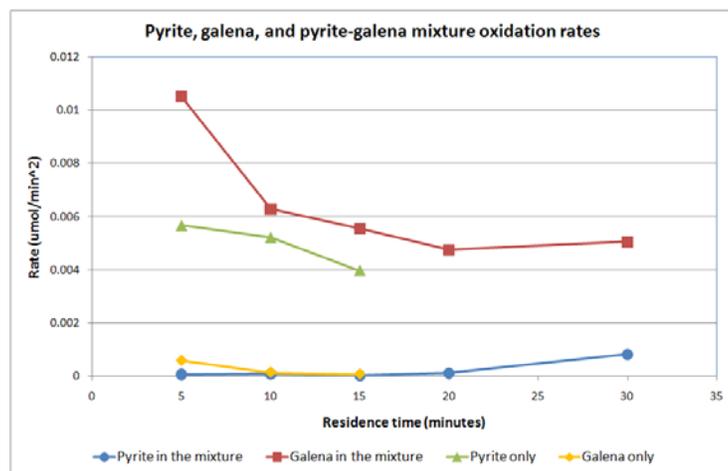


Figure 1. Rates of oxidation of pyrite, galena, and pyrite/galena mixture as measured in column experiments. The advected solution was saturated with oxygen. Rates determined on the basis of iron and lead release data. The oxidation rate is limited by oxygen availability. Hence, at higher residence times the rates do not longer vary with residence time.

reactive in the mixture than by itself. This is consistent with the concept of Galvanic protection. That is, pyrite donates electrons to the oxidant (molecular oxygen) and these electrons are replaced by ones withdrawn from galena. Hence, the galena ‘protects’ the pyrite. Scanning Electron Microscopy observations support these finding. Galena recovered from experiments in the presence of pyrite show a much higher etch pit density than observed on galena surfaces recovered from mono-mineralic

experiments. Based on the electronic structure of common metal sulfides it is expected that sphalerite (ZnS) and chalcopyrite (CuFeS₂) will behave similarly when mixed with pyrite.

The implication is that in mixed waste with pyrite as one of the major component these accessory metal sulfides will oxidize first. Hence, the initial stages of oxidation of a waste pile may see high concentrations of copper, zinc, and lead in the effluent.

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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 soils, sandstones and chinks, and low-porosity crystalline 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 CO₂ 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: (1) Stress scaling of mechanical compaction and strain localization. Compaction bands are a compactant failure mode in porous rock, forming thin tabular structures normal to the maximum compressive stress with negligible shear offset. We systematically investigated the conditions involved in the development of compaction bands in sandstone, including the influence of composition and the geometric attributes of the bands across a range of length scales. Synthesis of field and laboratory data on band dimensions in five sandstones over four orders of magnitude revealed a quadratic scaling relation between the thickness and length of compaction bands. Using an anti-crack/anti-dislocation fracture mechanics model we obtained a scaling relation in which the stress level is inversely proportional to band thickness. This relation provides a mechanical basis for interpreting discrepancies between laboratory and field data, with the implication that the critical strain energy release rate in the field is comparable to laboratory measurements.

(2) Development of 3-D imaging techniques to characterize the evolution of compaction and localization. Statistical and digital image correlation techniques were developed to map out the spatial distribution of inelastic strain and to characterize the influence of bedding on the development of strain

localization. In principle, imaging techniques we have developed can be implemented for computed synchrotron microtomography. We have initiated the design of a rig for this purpose.

(3) Discrete element and probabilistic modeling of compactive failure and permeability evolution. Compactive failure is accompanied by permeability reduction of up to several orders of magnitude, possibly with strong stress-induced anisotropy. A probabilistic damage model was formulated which can realistically capture key attributes of the permeability evolution. In parallel, we used the discrete element modeling to analyze the complex micromechanics of brittle failure and compaction localization in clastic rocks. In particular, we focus on the influence of grain-scale pore heterogeneity. A methodology for simulating grain crushing and pore collapse was formulated, and the model simulations highlight how discrete compaction bands are promoted by grain-scale homogeneity. Current efforts will extend it to a 3-dimensional discrete element model.

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Up-Scaling Geochemical Reaction Rates for CO₂ in Deep Saline Aquifers

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Objective: 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 CO₂-water-rock interactions in the context of geological sequestration of carbon dioxide – specifically acid-driven mineral dissolution and precipitation.

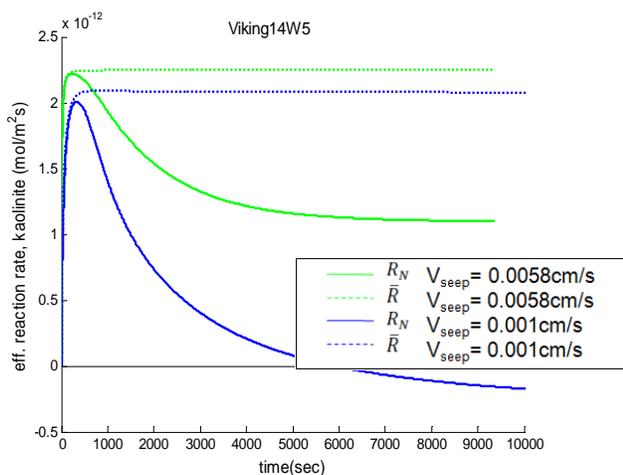
Project Description: The work combines (i) spectroscopic imaging and innovative image processing to characterize sedimentary rocks, (ii) development of new pore-scale network models of reactive transport in porous media, and (iii) simulations to examine reaction rate upscaling. Rock specimens came from 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: During FY2008 we have completed reactive transport network models for two Viking samples, a sandstone and a conglomerate sandstone. A third model, a shaly sandstone, has been built and simulations on it are continuing. The current reactive model involves two minerals, a plagioclase feldspar (anorthite) and a layered clay (kaolinite). The model simulates acid-driven dissolution of anorthite with secondary precipitation of kaolinite. For initial conditions, the spatial distributions of the two minerals in the sandstone samples, as well as accessible surface area for each, were modeled based upon observations of the distribution of pore clays and grain inclusions in the imaged sandstones.

The ratio, β , between the bulk reaction rate for the core as determined by the network model and the reaction rate predicted by the continuum model is used as a measure of the accuracy of such continuum models. For dissolved CO₂ values consistent with target storage basin conditions (input solution pH of 2.9), the anorthite present in the rock dissolves. As the saturation state for anorthite is negligibly small, anorthite dissolution rate is determined predominantly by local pH. As there is small variation in pH throughout the core-scale network, the heterogeneity of the pore network (variations of flow rate, anorthite distribution, chemical concentrations) does not play a large role. Therefore β_A for anorthite is close to unity, indicating that the continuum model does a reasonable job predicting correctly up-scaled reaction rates.

For kaolinite, the situation is drastically different. The kaolinite reaction rate is affected both by pH and by saturation index. As the mineral is initially present in the sample, kaolinite undergoes either dissolution or precipitation, depending on local conditions, with dissolution dominating at higher flow rates, and secondary precipitation dominating at lower flow rates. For dissolution, the reaction rate is dominated by pH, with saturation index values playing a modifying role. Thus for the same reasons as for anorthite dissolution, at faster flow rates when kaolinite dissolution dominates, the continuum model does a reasonable job of predicting correctly up-scaled kaolinite reaction rates, and β_K is close to unity. However, at slower flow rates, when the secondary precipitation of kaolinite dominates, the saturation index plays the dominant role, and network heterogeneity dominates. The continuum model fails completely at predicting up-scaled reaction rates, even to the point of predicting bulk dissolution for kaolinite, when in fact the network model shows secondary precipitation dominating.

First-generation pore-scale network models, which utilized rectangular lattice structures, model network parameters, and random placement of mineral distribution, did predict near-unity values for β_A , and distinctly non-unity values for β_K . However, these first generation models predicted $\beta_K \sim -2 \cdot 10^{-3}$, while our newer models, based upon real rock networks and mineral distribution/surface accessibility, predict values for β_K in the range [-26, 2].



The other significant difference between the first-generation and the new, more accurate network models are in the times to reach steady state conditions. In the first generation models, steady state bulk reaction rates are reached in the order of 10^2 sec. In the new, rock-based models, while steady state bulk rates for anorthite dissolution are reached in roughly the same time span, steady state bulk rates for kaolinite reactions are reached after 10^4 sec. In contrast, the continuum models predict attainment of steady state bulk rates for kaolinite much earlier (see Figure).

Fig. Kaolinite reaction rate vs time for the sandstone sample. R_N – bulk rate as determined from network model. \bar{R} - bulk rate determined from continuum model. Note the network model bulk rate transitions from dissolution to secondary precipitation dominated at the slower flow rate.

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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.

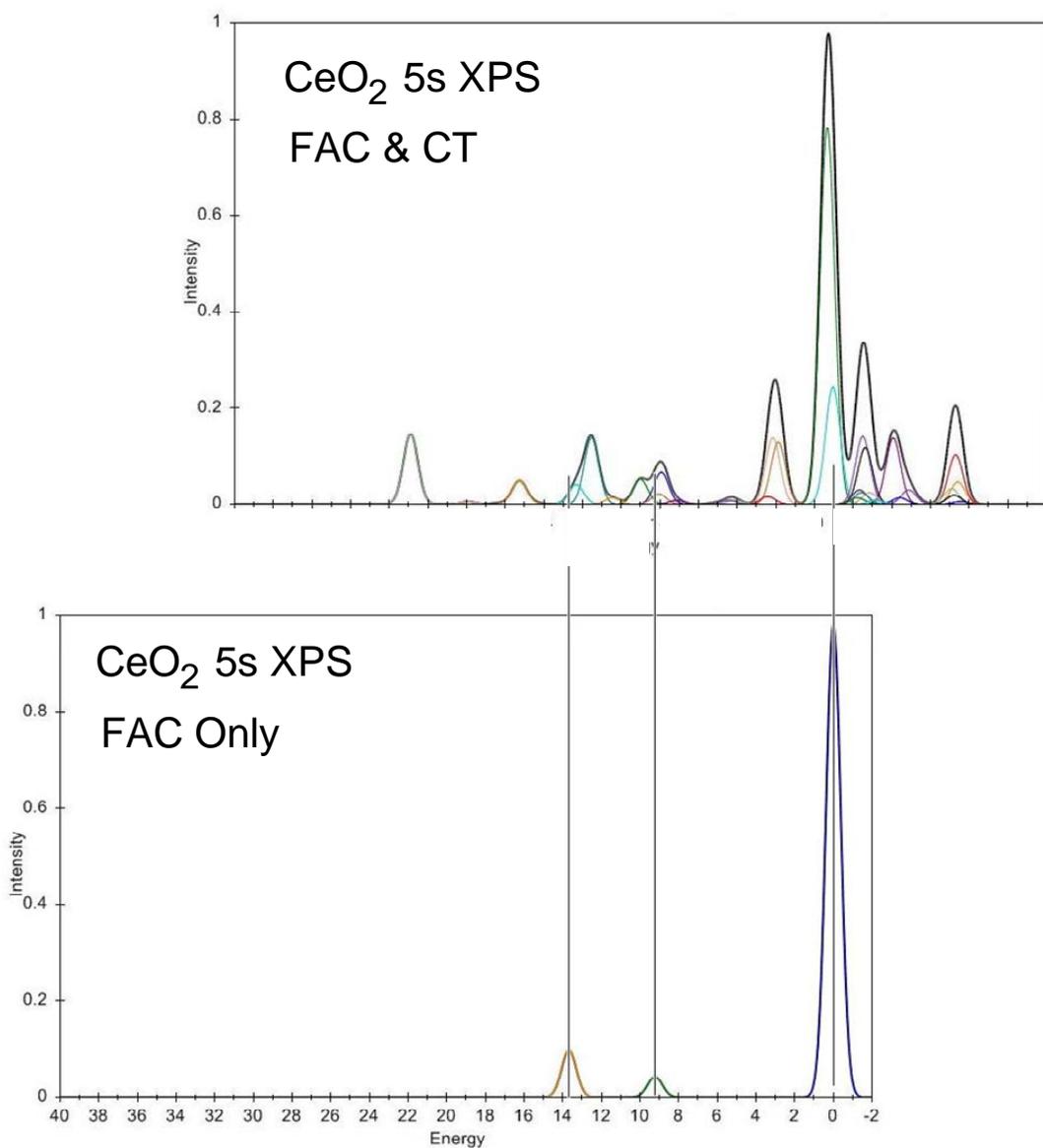
Results: Our results are in two related areas: (1) Software development for the calculation and display of core level spectra. These were needed to achieve our objectives for the theoretical analysis of XPS and XANES. (2) Applications to several materials systems to relate these core-level spectra to materials properties.

In order to study inter-atomic charge transfer, CT, many-body effects in core-level spectra, we extended the way in which we added CT configurations. Initially, the number of configurations that we used increased exponentially when CT was included. We were able to control this exponential growth by grouping the CT in a sequence of single CT, double CT, etc. and selecting only the most important terms. For the comparison of our theoretical predictions with observed XPS and XANES spectra, we needed a graphical display of our theoretical results broadened to include experimental resolution and lifetime. Our previous software had limited options for the broadening parameters and was not directly interfaced with our *ab initio* calculations. We developed PC software where we have flexibility for choosing broadening parameters and we have a direct interface with the PC program.

Our efforts to study many-body effects for different U oxidation states require that we first use our new codes to establish the validity of our methods in simpler cases of CT in transition metal and lanthanide complexes. The results we obtained achieved this objective and were also of interest in their own right. We have extended our understanding of the role of frustrated Auger Configurations, FAC's, a concept that we introduced to describe intra-atomic many-body effects demonstrating the generality of the FAC's and showing how FAC's couple with CT. We have studied FAC and CT many-body effects for MnO, NiO, and CeO₂. For the 5s XPS of CeO₂, our results show an unexpected coupling of intra-atomic FAC's and CT; see the theoretical predictions in the figure below. Our predictions will be tested by our

colleagues at the Fritz-Haber Institute in Berlin with new experiments at the BESSY synchrotron. The criteria and theoretical concepts learned in this work will now be used in theoretical studies of UO_2 .

Figure. The theoretical 5s XPS for CeO_2 modeled by an embedded cluster where the calculated XPS are broadened by a Gaussian of 0.9 eV FWHM. The top figure shows the XPS where both FAC's and CT effects are included; the lower figure shows the XPS with only the FAC's. The spectra are aligned so that the main peaks are at the same position.



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Grant: DE-FG02-93ER14344

Approaches to Some of the Outstanding Problems in the Heterogeneous Compactive Deformation of Geomaterials

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Objectives: To obtain an improved understanding of the factors governing the formation and extension of bands of localized compaction and their effect on subsurface fluid flow with applications to the technologically common problem of storing or recovering fluids from the earth's crust.

Project Description: Evidence from laboratory experiments and field observations on porous rocks (and other materials) has indicated that compaction does not necessarily occur homogeneously, but, instead, is localized in narrow planar zones that are perpendicular to the maximum compressive stress. Because the permeability of these zones is reduced by several orders of magnitude, they present barriers to fluid flow across them. Consequently, their formation in reservoirs or aquifers can adversely affect attempts to inject or withdraw fluids, such as carbon dioxide. Because the zones are narrow, they will be difficult to detect from the surface and, as a result, it is important to understand the conditions for their formation and extension.

Results: Treating shear and compaction band formation as a bifurcation from homogeneous deformation has proven to be a useful framework, but the results are strongly dependent on the material constitutive relations that are used. Comparison of recent observations of failure angle in true triaxial tests with theoretical predictions places constraints on the form of the constitutive model and suggests that neither of the common idealizations, Mohr-Coulomb nor Drucker-Prager, is adequate. Although almost all the analyses and laboratory tests on compaction bands have been done under drained (or dry) conditions, in the field compaction bands are thought to form under saturated conditions. The alternative limiting case to drained deformation is undrained deformation (no fluid mass flux) which may be a reasonable approximation until near the point of band formation. Comparison of the conditions for band formation under drained and undrained conditions suggests that a particularly interesting case occurs when the inelastic volume change is compactive but the pressure sensitivity is positive (yield stress in shear increases with hydrostatic compression). These conditions may occur near the transition of a cap-like yield surface to a frictional yield surface. For such cases, the localization condition for undrained response is met before that for drained response.

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

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Objectives: We apply nonlinear optics, specifically the Eienthal, or $\chi^{(3)}$ method, to determine 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: We determine the interfacial charge densities, interfacial potentials and energy densities of chemically diverse geochemically important tailor-made organic adlayers at mineral/water interfaces with the goal of assessing their affinity towards ionic and neutral aqueous pollutants. Our results improve surface complexation models and chemical transport models by incorporating heterogeneous parameters derived from interface-specific kinetic, thermodynamic, spectroscopic, and structural data.

Results: 1. Tracking Interfacial Acid-Base Chemistry.

We recently reported that acid-base chemistry at aqueous/solid interfaces tracks bulk pH changes at low salt concentrations (Fig. 1). Physical chemistry tells us that acid-base properties at interfaces should track acid-base properties in the bulk under equilibrium conditions. However, charge-balancing at the interface as well as the molecular environments of the bulk and the interfacial species can shift interfacial acid-base equilibria by multiple pKa units from their corresponding bulk solution values. While a molecular-level understanding of these dramatic effects has now emerged for equilibrium, or steady-state conditions, their influence on the time dependence of interfacial acid-base reactions is just beginning to be understood. When we track the $\chi^{(3)}$ response from the fused quartz/water interface as a function of time while transitioning the bulk solution pH flowing

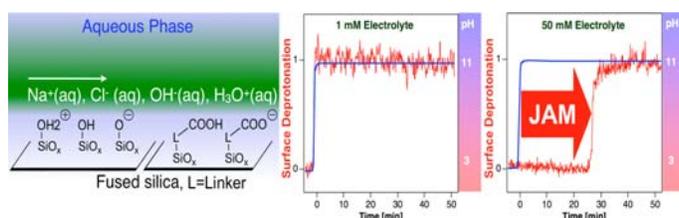


Fig. 1. Using nonlinear optics, we show that acid-base chemistry at aqueous/solid interfaces tracks bulk pH changes at low salt concentrations. In the presence of ten to 100 mM salt concentrations, however, the interfacial acid-base chemistry remains jammed for hours, until it finally occurs within minutes at a rate that follows the kinetic salt effect. For various alkali halide salts, the delay times increase with increasing anion polarizability and extent of cation hydration and lead to massive hysteresis in interfacial acid-base titrations. The resulting implications for pH cycling in these systems are that interfacial systems can spatially and temporally lag bulk acid-base chemistry when the Debye length approaches one nm. *J. Am. Chem. Soc.* ASAP Article (2008).

across the interface from acidic (pH 3) to basic (pH 11) within a few seconds, we find that acid-base chemistry at aqueous/solid interfaces tracks bulk pH changes at low salt concentrations (**Fig. 1**). In the presence of 10 to 100 mM salt concentrations, however, the interfacial acid-base chemistry remains jammed for hours (**Fig. 1**). The same is observed for sapphire/water interfaces and amino acid-functionalized fused quartz/water interfaces. Control studies indicate that mixing conditions, dissolution, impurities, or laser heating or instabilities are unlikely causes for the delay times. Furthermore, 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. The delay time depends on the salt concentration in the bulk aqueous solution, and when the interfacial response finally occurs, its rate follows the kinetic salt effect. For various alkali halide salts and for pH jumps between pH 3 and pH 11, the delay times increase with increasing anion polarizability and extent of cation hydration and lead to massive hysteresis in interfacial acid-base titrations. The resulting implications for pH cycling in these systems are that interfacial systems can spatially and temporally lag bulk acid-base chemistry when the Debye length approaches one nm.

2. Metal Cations. Metal cations are ubiquitous in nature and funding by the DOE-BES-Geosciences program allowed us to expand the scope of our nonlinear optical work to study divalent metal cations at aqueous/oxide interfaces (**Fig. 2**). We focused specifically on metal ions with weak electronic transitions and also those with electronic transitions that are impractical for SHG resonance enhancement due to symmetry constraints of d-d transitions. We thus investigated Ba(II), Sr(II), Ca(II), Zn(II), Mn(II), and Cd(II). Using chemical equilibrium modeling software (ChemEQL, EAWG: Swiss Federal Institute of Aquatic Science and Technology), we paid special attention to the overall charge state and speciation of the metal ion complexes in solution and at the interface, which allowed us to expand the applicability of nonlinear optics from species composed of p-block elements to alkaline earth and transition metal ions. **Fig. 3** shows that at a constant bulk solution pH, specific cation or anion adsorption changes the interfacial charge density. At constant screening electrolyte concentration, the changes in Φ_0 resulting from the changes in the interfacial charge density are reflected in changes in the SHG E-field. Using Gouy-

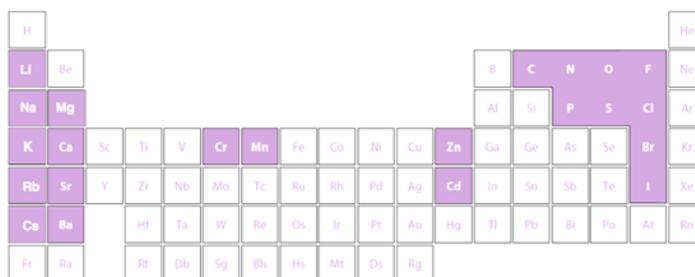


Fig. 2. Adsorbates and substrates containing these elements investigated thus far in the Geiger group using nonlinear optics. *Ann. Rev. Phys. Chem.*, (2009), ASAP Article.

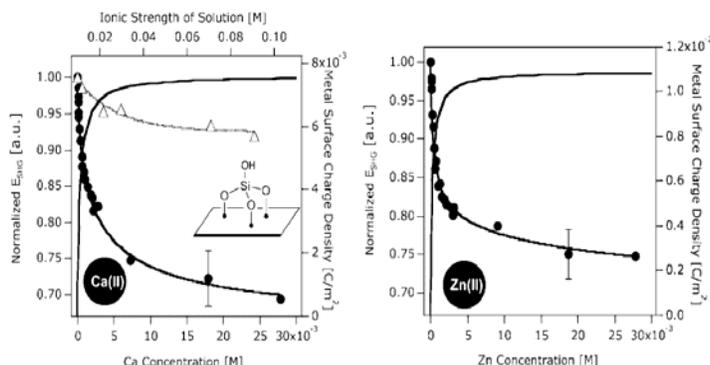


Fig. 3. Adsorption isotherms for Ca(II) and Zn(II) at the fused quartz/water interface. Left axis corresponds to the normalized SHG E-field, decreasing solid curve is obtained by fitting the Gouy-Chapman-Stern model to the adsorption data. Right axis refers to the calculated ascending solid curve representing the surface charge density due to metal adsorption at a given bulk metal concentration [M] for the case of $C_{elec} = 0.01 + [M]$. Results of the NaCl control experiment are plotted in left graph (open triangles) vs. ionic strength (top axis), the dotted line is a guide to the eye. pH = 7. *J. Phys. Chem. C*, ASAP Article (2008), and *J. Phys. Chem. A*, ASAP Article (2008).

Chapman and Gouy-Chapman-Stern theory, expanded to the Triple Layer model, in which the adsorbing metal cations are placed at the β -plane, the data is analyzed and yields the binding constants, rate constants for adsorption and desorption, and the absolute surface charge density of the surface-bound ions. This method is particularly useful for studying charged adsorbates with weak electronic resonances, and for quantitatively assessing their absolute surface coverages. We then used the information derived from our experiments to obtain retardation factors with very high sensitivity, specifically for the highly mobile species barium, strontium, and cadmium, which, insofar as our laboratory measurements mimic geochemical conditions, show R_f values ranging between 1.00005 and 1.01 for silica-rich soil.

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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. Figure 1 shows a schematic of the proposed framework.

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 Advanced Photon Source in Argonne National Lab. Also, the hierarchical computations at the specimen level will be validated using the aforementioned techniques in samples of sandstone undergoing deformation bands.

Results: No results to report yet (project started on September 1, 2008).

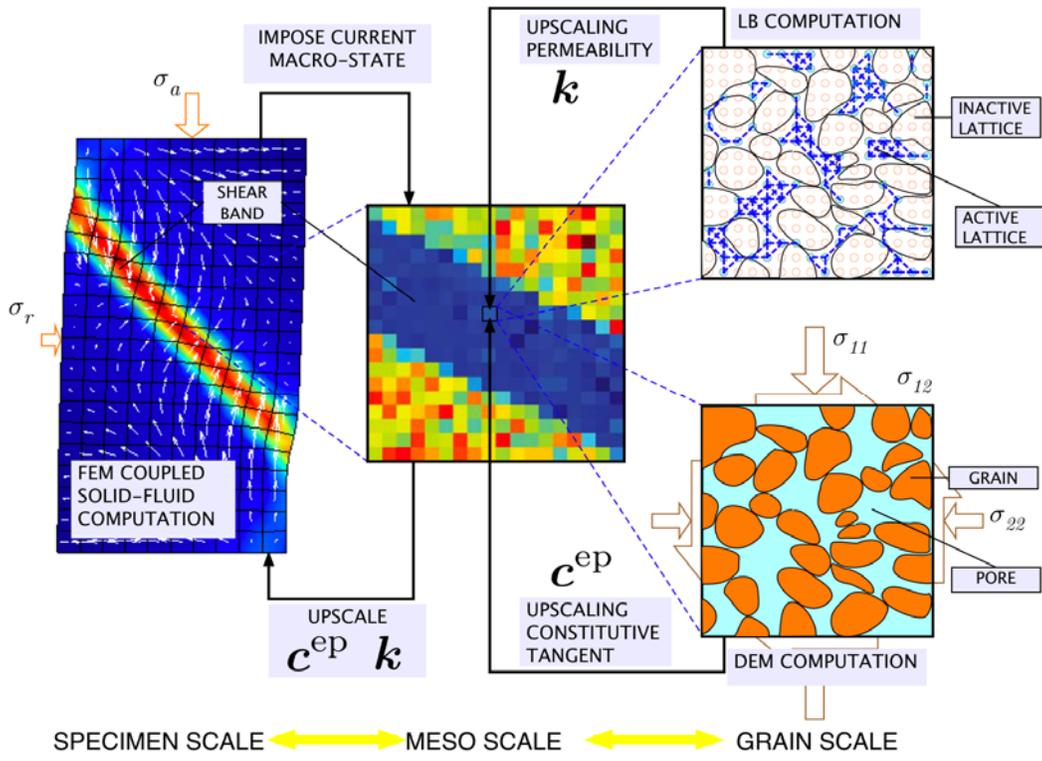


Figure 1. Schematic of multiscale framework to predict deformations in fluid-saturated rocks.

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

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Objectives: The objective of this research is 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 and vibrational sum frequency generation spectroscopies (XAS, VSFG), and molecular modeling to investigate the potential formation of ternary metal-anion complexes at mineral surfaces in different solution compositions over a range of surface coverages. XAS provides data on how the metal binds to the surface (monodentate, bidentate) and VSFG provides data on the anions adsorbed with the metals, polyatomic anion orientation in some cases, and water structure at the mineral surface. Molecular modeling supports data from both spectroscopic techniques by providing information on water structure at the surface, the surface sites for metal-binding and the orientation of any associated ions, and the relative energetics of different surface complexes. We initially focused on investigating water structure and Sr^{2+} , Co^{2+} , and Pb^{2+} adsorption from NaCl , NaNO_3 , and NaClO_4 solutions onto quartz, amorphous silica, corundum, and gibbsite.

Results (Allen Lab): This past year, we have made significant progress on understanding water mediation of ion pairing in the bulk and at the air-water interface. Nitrate interfacial segregation and ion pairing characteristics with the dications has been the focus. Raman and infrared spectroscopic investigations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Pb^{2+} with NO_3^- in aqueous solutions have focused on the level of ion pairing, solvent-separated, solvent-shared, and contact ion pairing. Magnesium ions have unique character that changes the air-water interface structure with respect to nitrate. We observed that the repulsion of the interface for magnesium allow the nitrate anion to be relatively free from its Coulombic effects. Nitrate itself approaches the interface, but is not overly surface active. The water structure for magnesium, calcium, and strontium is strongly perturbed, more than what we would have predicted based on Raman and infrared studies of their bulk environments. We are continuing our studies of nitrate salts, and have just begun working on oxidized sulfur and selenium salts.

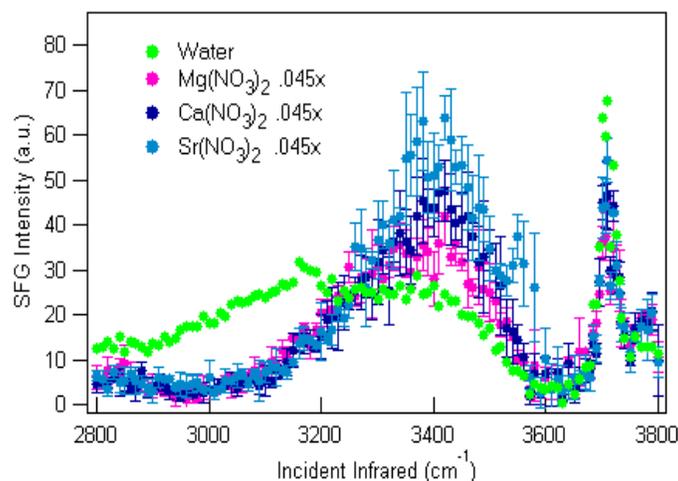


Figure 1: Vibrational sum frequency spectra in the hydrogen bonding and free OH stretch region of aqueous $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, and $\text{Sr}(\text{NO}_3)_2$ solutions obtained from the air-aqueous interface. The hydrogen bonding network is disrupted more than in the bulk (Raman and infrared spectra not shown) illustrating the magnified perturbation at the air-water interface from these solvated ions. It is not completely understood why strontium has the largest effect, although there is correlation with increasing polarizability of the cation, albeit much smaller than for similar studies by our group on sodium halides.

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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 FY08 include: (1) Development and initial testing of our first 3D application, to the 3D MT problem. The same inversion modules now work for two problems (2D and 3D MT) with quite different structure. In the course of this effort a number of details in the organization and implementation of the modular system were significantly refined. (2) We have begun work on parallelization of multi-frequency EM inverse problems using MPI on a small cluster. We are attempting to implement the parallelization at the top (generic) level of the modular system, so that the same parallel inversion code can be used for a range of problems. (3) A manuscript on the modular system is in preparation. This manuscript, which is nearing submission, includes a detailed mathematical derivation of a common framework for data sensitivity calculations, applicable to a wide range of specific EM methods, and different numerical modeling approaches. (4) Development of new inversion approaches appropriate for multi-transmitter problems have been developed. Our analysis shows that the full Jacobian for such problems can be constructed using one forward solution for each transmitter, and one adjoint solution 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. Coding and testing of this approach will begin soon. (5) Our 3D finite difference modeling code is being refined to compute forward solutions using a secondary field formulation. This will increase accuracy of solutions for active source problems in particular, and is essential for the cross-borehole and marine CSEM applications that we intend to work with in the coming year.

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Rate and Mechanism of Transformation of Bedrock into Saprolite During Spheroidal Weathering

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Objectives: We hypothesize that the mechanisms of transformation of cohesive bedrock to disaggregated saprolite involve coupling between chemical, physical, and microbial processes driven by the fluxes of water and reactants into bedrock.

Project description: We are developing a model for water influx and reaction at the bedrock/saprolite interface and testing it on several rock types, including quartz diorite weathering in Puerto Rico. We are using geochemical mass balance methods, microbiological studies, and methods from fracture mechanics to develop a model to predict the rate of spheroidal weathering and other bedrock-transforming reactions, and hence the rate of production of saprolite in this and other settings. Because spheroidal weathering is a phenomenon that occurs on almost every rock type in almost every climatic regime, our model will be useful for bedrock systems globally.

Results: Work has been published on advanced 1-d models of reaction & transport without fracturing. The model captures the emergence of steady-state weathering profiles under a condition of constant rate of erosion. Both numerical and approximate analytical results have been obtained. Regimes of local-equilibrium, transitional, and kinetic-controlled behavior have been characterized and compared to field observations.

We have also developed and field-tested a weathering conveyor belt model which uses approximate first-order descriptions of weathering rate and chemistry within the weathering profile. This model studies the evolution of a random distribution of initial joint-bound block sizes as these bedrock “particles” move upward through the weathering zone, eventually leaving exposed corestones at the erosional surface. We have obtained initial results for the stresses generated due to reaction; these lead to a substantial elastic strain energy that drives cracking that defines spheroidal macro-fractures.

In weathering quartz diorite, the first visible reactions deepest within pristine rock are the oxidation of biotite and the dissolution of plagioclase. Microscopic and spectroscopic results reveal that hornblende does not dissolve or oxidize within the ~45-cm thick spheroidally weathered zone, but dissolves completely within the 7 cm spanning the rindlet-saprolite interface. Oxidation of Fe(II) within biotite crystals in the rindlets was observed, as well as a loss of K^+ that increased with distance from the corestone. The loss of interlayer K^+ permits sorption of water. These effects expand the lattice, which is inferred to cause spheroidal fracturing. XANES spectral fits demonstrated that observed Fe(III)-rich zones are oxidized biotite and not precipitated Fe(III)-(hydr)oxides or other Fe(III) phases.

Microbial abundance in the diorite increases near the saprolite-bedrock interface. As bedrock weathers, ferrous iron is released from silicate minerals, providing electron donors for autotrophic iron-oxidizing

bacteria. These bacteria fix CO₂ and provide organic carbon substrate for other organisms. At the base of the soil profile directly above the quartz diorite corestones, direct cell counts reveal that total microorganisms increase relative to numbers in the overlying matrix. Confocal laser scanning microscopy images of saprolite demonstrated consistent associations between live cells and amorphous minerals but not with quartz. Coupled environmental SEM and TEM analyses indicate that bacteria are associated with weathering biotite and the weathering product halloysite. Iron-oxidizing bacteria have been cultured from the regolith-saprolite interface. Also, 16S rRNA clone libraries from saprolite DNA include the known iron oxidizer *Acidithiobacillus ferrooxidans*. PCR primers have been developed for functional genes encoding iron oxidase (*iro*) and rusticyanin (*rus*) in *A. ferrooxidans*. These primers will be used on DNA extracted from saprolite and cultures to document the presence of these genes in the microbial community growing at the bedrock-saprolite interface.

To interpret microbial populations within the context of weathering reactions, we developed a model for estimating growth rates of lithoautotrophs and heterotrophs based on measured substrate fluxes. The calculations and observations are consistent with a model wherein electron donor flux driving bacterial growth at the saprolite-bedrock interface is dominated by Fe(II), i.e., autotrophic Fe(II)-oxidizing bacteria support heterotrophic activity, leading to bedrock disaggregation and saprolite formation.

These observations on weathering quartz diorite from Puerto Rico are now being extended to weathering of metavolcanics in a neighboring watershed (Fig. 1). We have begun measuring microbial biomass in saprolite lying above the metavolcanic bedrock using similar approaches to our work on the quartz diorite. In addition, we are analyzing extensively weathered low-porosity granitic or basaltic rocks from Hawaii and 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 where the curvature is greater. Open system mass balance calculations constrained by whole rock ICP-MS and electron microprobe analyses across the clast show a hierarchy of elemental mobility of Ca≈Na>K≈Mg>Si>Al>Fe≈P from the unweathered core to the rind. The width of the reaction front is quantified through

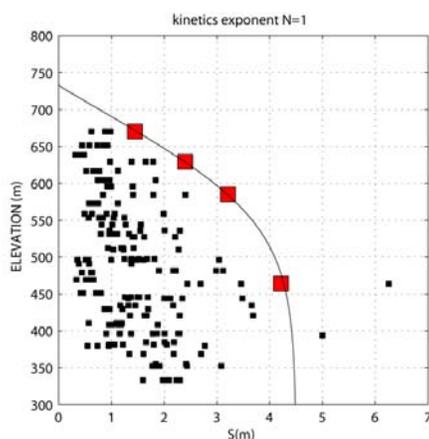


Figure 1. Size of corestones (S , in meters) observed in the Bisley watershed, Puerto Rico, as a function of elevation. As predicted by the corestone model shown by the line, corestone size varies with elevation because rock fragments emerging from bedrock weather in the saprolite zone. The model fits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

petrographic analysis (< 2 mm), porosity calculations (1.5-2.5 mm), and chemical analysis (0.4 – 0.8 mm). The reaction front is wider where the curvature is lower and the weathering velocity is rapid where the curvature is greater.

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Up-Scaling Geochemical Reaction Rates for CO₂ 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 CO₂-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: During FY2008, the work at Princeton has focused on (1) completing the development of algorithms for interpreting 2D images, and (2) addressing a new research question related to the effects of co-injection of SO₂ in the context of CO₂ geologic sequestration. In this summary, we report on the first of these.

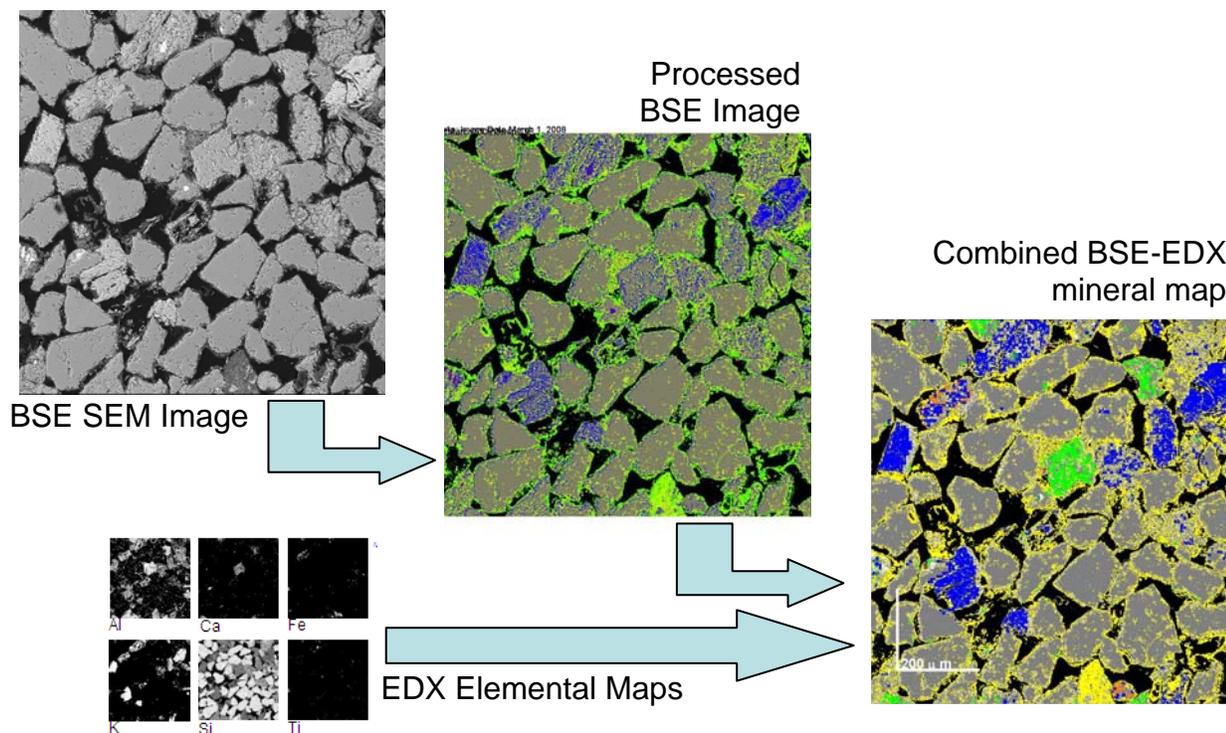
The major challenge with reactive transport modeling in consolidated media is accurate characterization of surface area, and the apportionment of this surface area to reactive minerals. Existing methods of quantifying mineral surface areas for consolidated media at best are imprecise and at worst are not valid because they do not account for obscured grain surfaces by clay minerals, inaccessibility of reactive minerals due to matrix cementation, and inaccessibility of reactive minerals due to presence as grain inclusions.

Through a combination of Backscattered Electron (BSE) scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis of thin sections, we have developed a novel image analysis method to quantify the accessibility of minerals to formation fluids in sedimentary sandstones. The main

goal is to determine the extent to which mineral accessibility is well represented by measures of mineral abundance, such as volume fraction. This provides insight on how uncertain are the estimates of surface areas that are often used in reactive transport and reaction path models in the context of deep sedimentary formations.

In Peters (2008, “Accessibilities of reactive minerals in consolidated sedimentary rock: An imaging study of three sandstones”, *Chemical Geology*, in press), we present a study of three different sandstone specimens from the Viking formation in the Alberta sedimentary basin. BSE imaging was used and a segmentation algorithm was developed to study the relationships between mineral abundances and mineral accessibilities, as measured by the extent of pore-to-mineral contact. This allowed us to broadly classified minerals into three categories: kaolinite, quartz, and “reactive” minerals. We concluded that if a mineral volume fraction is used in reactive transport modeling as a proportional measure of accessible surface area in consolidated sandstones, the reaction rates are likely to be overestimated by three to five times.

We extend this work in Bowman and Peters (2008, “A New BSE-EDX Method to Quantify Mineral Abundance and Accessibility in Sandstones”, manuscript in preparation), in which high resolution BSE images are interpreted together with EDX elemental maps, which have high accuracy in mineral identification. In this method, we are not limited to broad classification of minerals. We are able to quantify specific mineral types, and draw conclusions about accessibility for the particular minerals that are important in the context of interactions with acidic pore fluids as will occur in CO₂ geologic sequestration. One such image is shown below.



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Self-Assembling Sub-Porosity: The Effect on Fluid Flow and Seismic Wave Propagation

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Objectives: The objective of this proposal is to determine the effects of sub-porosity in a fracture on seismic wave propagation through fractured rock. The principal focus will be on experimentally determining the link between the frequency-dependent seismic properties of fractures and length scales associated with the presence, morphology and spatial distribution of a sub-porosity that affect the hydraulic properties of a fracture.

Project Description: To achieve the proposed research objectives we will determine the effect of micro-scale phenomena on macro-scale measurements of fluid-solid phase distribution and seismic wave propagation, and determine the relevant seismic attributes that indicate a sub-porosity within the fracture. Creation or destruction of sub-porosity within a fracture affects length scales associated with the geometry of the fractures. The size of the geometric length scales relative to the seismic wavelength determines the scattering response of the fracture. The spatial correlations in fracture geometry relative to the scale of the field-of-view affect the collection of the energy of scattered waves. An acoustic lens system was used to produce a pseudo-collimated wavefront with a controllable beam diameter to set the field of view to 5 mm, 20 mm and 60 mm. This experimental approach was used on two limestone samples, each containing a single induced fracture, and an acrylic control sample. Fluid flow and seismic measurements were made on the fractured samples for the following conditions: water-saturated, after reactive flow and after grain/particle (microsphere) transport.

Results: Our analysis focused on the seismic response for a fixed aperture with different sub-porosity created by single or multiple layers of beads. The acoustic response depends critically on the length scales associated with the layers (bead diameter, layer thickness), the aperture of the fracture, and seismic wavelengths. The structure of the sub-porosity affected the time-frequency response of the transmitted seismic waves. For layers formed by successive deposition of beads smaller than a wavelength, the spectral response showed strong stop-band behavior. Good agreement was found between the information provided by the stop-band behavior (e.g., size of the grain in the fracture, the impedance contrast between the grains and fluids in the fracture) and the experimental parameters, suggesting that the spectral response of an in-filled fracture provides information about the infill material. Effective stiffness as a function of frequency was used to determine the dominant scattering regime produced by the sub-porosity (Figure 1). When the grain size is comparable to a wavelength, a frequency-independent effective stiffness is observed. Sub-wavelength grains produced a divergence of effective stiffness at low frequencies because the signals were not attenuated. For short-wavelengths, sub- and multiple wavelength bead sizes produced a linear dependence of fracture specific stiffness on frequency, essentially approaching the ray regime.

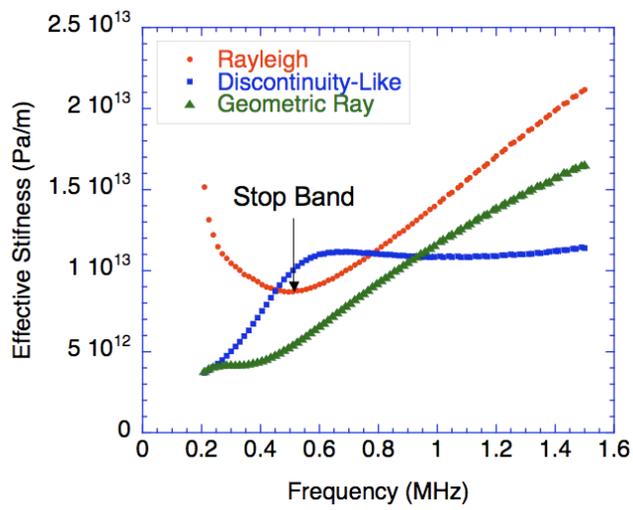


Figure 1. The dependence of effective fracture stiffness on frequency enables the delineation of the scale structure associated with a sub-porosity, i.e. grain size and layering relative a wavelength.

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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: Grain boundary diffusion has been characterized through a new experimental approach that involves transporting a diffusant from a source material along dry grain boundaries where it is incorporated into sink minerals dispersed throughout a polycrystalline rock analog (Fig. 1). The dispersed sink approach involves two steps: (1) synthesis of polycrystalline rock analogs that have sink phases dispersed throughout a matrix with an equilibrium microstructure, and (2) diffusion experiments in which the rock analogs containing dispersed sink phases were placed against a source material containing a diffusant that is compatible in the dispersed sink phase but incompatible in the minerals that comprise the polycrystalline matrix. Two different quartzites were synthesized at elevated P-T conditions in a piston-cylinder apparatus to characterize Fe-Mg interdiffusion along dry quartz grain boundaries; one containing ~5% fayalite (Fig. 1a) and the other containing ~10% enstatite sink minerals (Fig. 1c).

After synthesis experiments, rock analogs were cut into slabs and polished. The polished surfaces of the rock analogs were juxtaposed against diffusant sources, and placed back into a piston-cylinder apparatus for diffusion experiments. The Fe and Mg sources were polished slabs of MgF_2 , San Carlos olivine (~ Fo_{90}) and MgO (Fig 1a). In some experiments diffusion couples were formed by placing polished slabs of the fayalite- and enstatite-bearing quartzites against one another (Fig. 1c). The juxtaposition of source and sink materials caused strong chemical potential gradients to develop. The only available pathway for transport from the source to the sink phases was along the grain boundaries. After the diffusion experiments, diffusion couples were sectioned and the sink phases were analyzed for the diffusant using an electron microprobe (Fig 1b, d). The time integrated grain-boundary flux can be evaluated by measuring the total number of diffusant atoms accumulated in the sink in a given time. Assuming local partitioning and diffusive equilibrium between sink phases and grain boundaries, the

diffusant concentration in the sink phases will reflect (i.e., be proportional to) the concentration profile of the diffusant in the grain boundaries throughout the bulk sample.

Microprobe analyses and back-scattered electron images of the sink phases demonstrate significant and efficient transport of diffusants along the quartz grain boundaries (Fig 1). In an experiment in which a slab of fayalite-bearing quartzite was placed against MgF_2 and run at 1125°C for two hours, MgO contents of the fayalite grains show that Mg was transported $\sim 200\ \mu\text{m}$ from the diffusant source. This transport distance suggests an effective grain boundary diffusivity on the order of $10^{-12}\ \text{m}^2\text{s}^{-1}$. Interestingly, the 8 day experiment does not show significantly greater transport distance, but at a given distance from the source/quartzite interface, the fayalite grains from the longer experiments have a higher concentration of MgO . Preliminarily we suggest that the grain boundaries become 'saturated' in the diffusant, effectively shutting down grain boundary transport. Similar processes may be important in the preservation of diffusive halos surrounding minerals in natural rocks. In experiments that placed a fayalite-bearing quartzite against an enstatite-bearing quartzite, the MgO content of fayalite grains $\sim 30\ \mu\text{m}$ from the interface is the same as that of the starting material. Compared to the diffusion experiments that used MgF_2 , MgO and San Carlos olivine sources, the characteristic transport distance is approximately an order of magnitude smaller. This preliminary result suggests that grain boundary transport may be source concentration dependent.

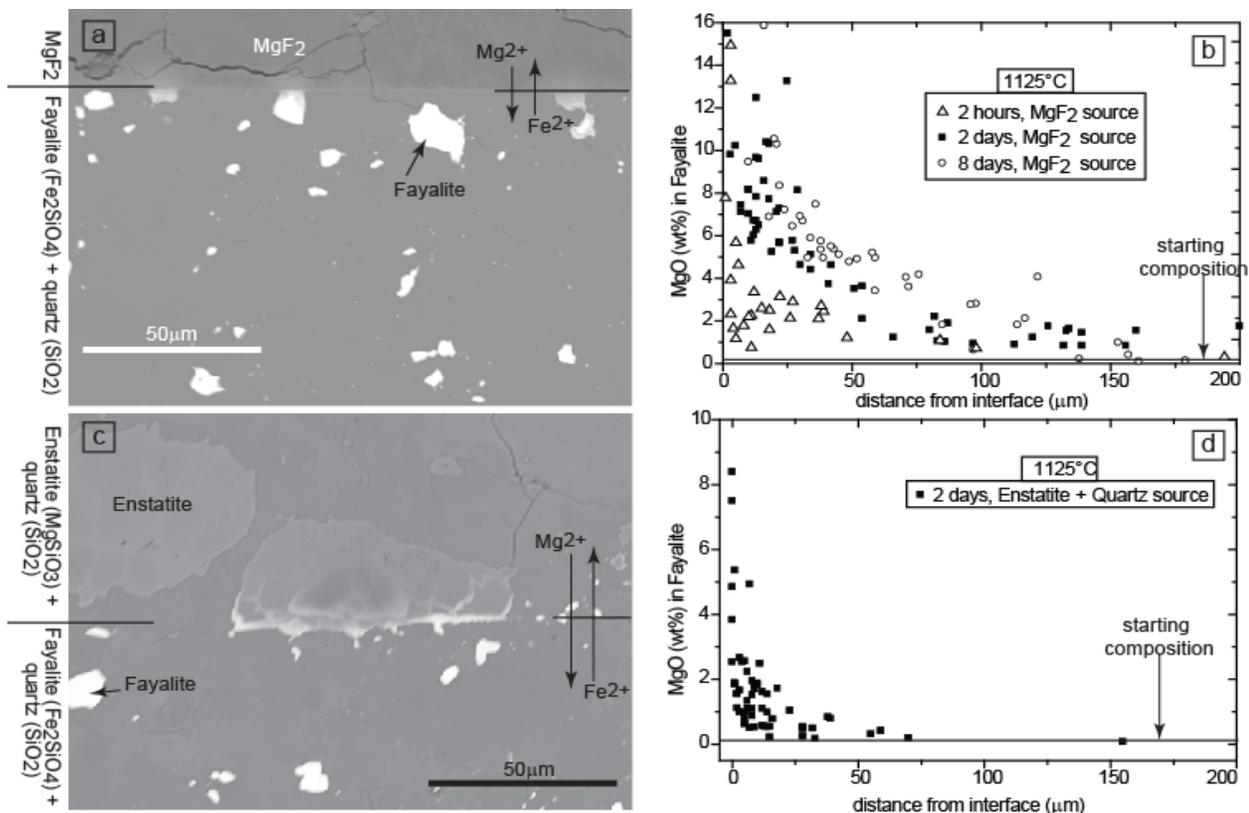


Figure 1. Backscattered electron images (a, c) of diffusion couples and MgO contents of isolated fayalite grains (b,d) in quartzite as a function of distance from the quartzite/ Mg -source interface. Arrows labeled with Mg^{2+} and Fe^{2+} show directions of diffusion.

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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: The focus of Year 2 of the project was to develop a large deformation finite element model for brittle faulting post-failure response of geologic materials. The model may be used to investigate complex stress distribution and deformation patterns surrounding a fault. We utilized the extended finite element method and represented the fault as an embedded discontinuity with frictional interaction on the contact faces. Figure 1 shows an application example in which used the method to simulate thrust faulting due to tectonic compression.

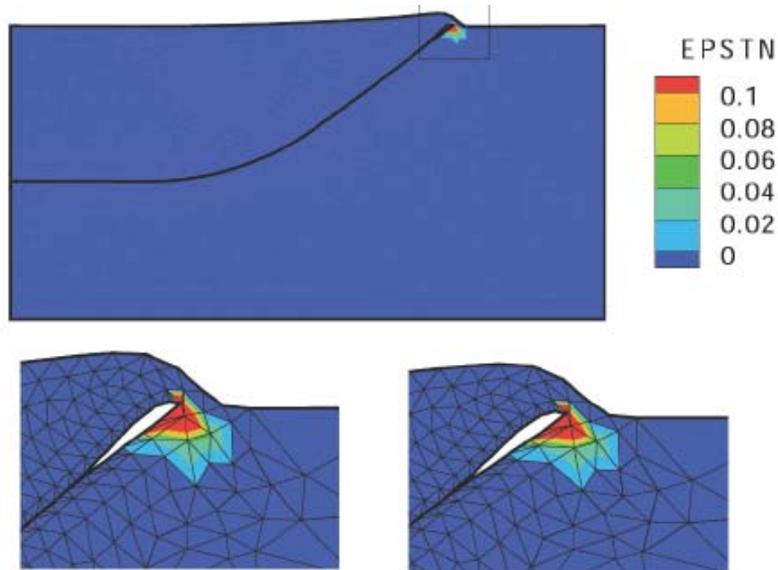


Figure 1. Simulation of thrust faulting on kilometer-scale fault and folding of rock layer above it: insets demonstrate two solutions of plastic strain contour generated by Bubnov-Galerkin (left) and Petrov-Galerkin (right) extended finite element approximations.

Figure 2 shows another application example in which we embedded a wavy (sine-wave) fault into a background finite element mesh and sheared it to very large deformation until the fault tip opens. We imposed the contact condition in the current configuration and employed the symmetric Galerkin approximation in the simulation. This example may be used to investigate the stress patterns near the contacting faces of the fault as well as in the surrounding fault tip region.

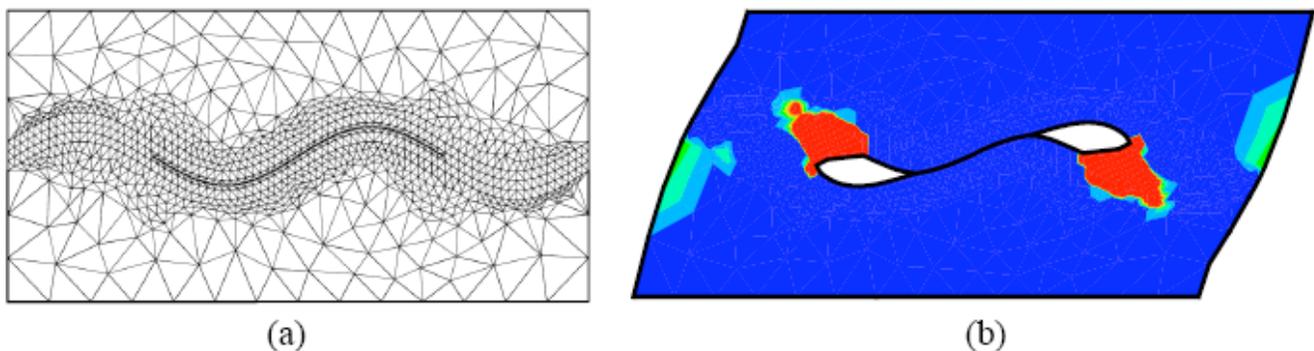


Figure 2. Simulation of large deformation shearing of a wavy frictional fault: (a) finite element mesh; and (b) deformed mesh and plastic strain contour after imposing a nominal engineering shear strain of 40%.

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

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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. One specific application of this work will be on sediment with unconventional pore-filling materials: gas hydrate and heavy oil (tar).

Results: By conducting a series of computational determination of experiments for permeability, electrical properties and conductivity on digital samples of oil sand, we have found that under certain circumstances, trends formed by pairs of datapoints obtained on an internally heterogeneous dataset form a trend that is valid in a range of scales (Figure 1). Such a trend is spatially- and scale-stationary (or homogeneous) and, as such, can be applied to a remotely-sensed quantity (e.g., porosity) to arrive at another desired property (e.g., permeability) at a much larger scale. This pattern of a trend is akin to ergodicity in theoretical physics and statistics, also called “statistical stationarity” and usually described in terms of objective properties of an ensemble of diverse objects. The ergodicity of natural-rock data, as explored in this project, means that we may be able in the future “to see a rock in a grain of sand.” This digital-rock-physics effort has been complemented by advances in our physical laboratory where are currently at the completion and testing stage of a setup that will allow us to measure the elastic properties of oil sands in a realistic *in-situ* range of temperature and pressure.

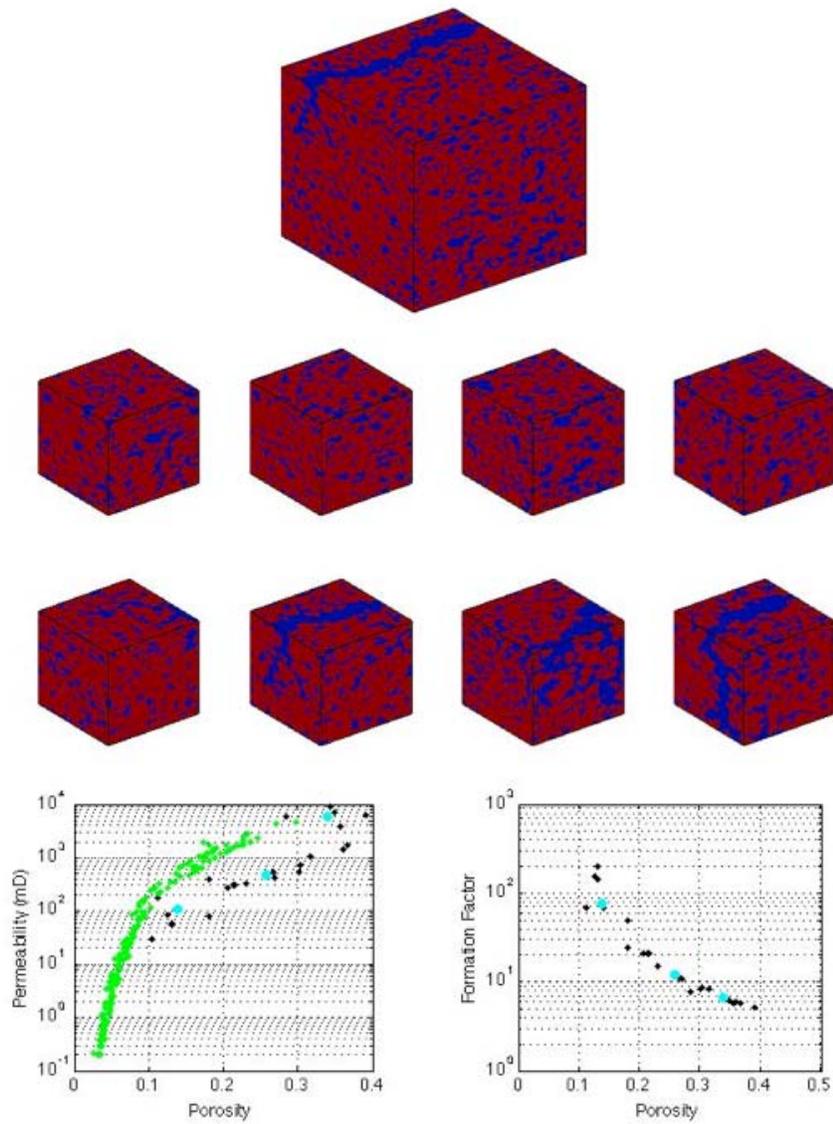


Figure 1. Top: a digital oil sand sample (about 3 mm on the side) and its 8 subsamples. Bottom: permeability-porosity and electrical formation factor-porosity digitally generated data for 3 sand samples (cyan) and their subsamples, 8 for each sample (black). The green symbols are physically generated data for Fontainebleau sandstone. The digital data form consistent trends.

STANFORD UNIVERSITY

Department of Geological and Environmental Sciences
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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 subsurface 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 three complementary sub-projects: (1) the origin of the joint system responsible for strike-slip faulting; (2) fault growth and related processes; and (3) modeling the two- and three-dimensional evolution of faults and deformation bands 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: Three sub-projects are summarized below.

(1) Origin of the joint system responsible for strike-slip faulting

This study expands on our earlier studies of the evolution of fracturing and faulting in the Jurassic Aeolian Aztec Sandstone in the Valley of Fire State Park, Nevada. Based on a three-dimensional analysis of the data collected from nearly vertical cliff-face exposures with as much as 200m relief, we find that a series of low angle normal faults and their splay fractures are precursors of strike-slip fault networks.

(2) Fault growth and related processes

Increases in the length, height, and width of faults including the thickness of fault rock and the surrounding damage zone collectively are quantitative measures of fault growth. A vast amount of field data shows that fault dimensions increase by some fashion as the slip across the fault zone increases. Using effective medium models, this paper address how and when fault dimensions increase. The calculated and extrapolated values of the Young's and Shear moduli for idealized fractured and

fragmented rock provide a set of criteria that may be helpful for a better understanding of the physical processes responsible for fault growth and the related fault scaling relationships.

(3) Modeling the evolution of faults and deformation bands

Inelastic deformation of brittle rock loaded in compression at the meter to kilometer scale typically involves localized frictional sliding along preexisting weak interfaces that are oblique to the principal stress directions. Associated local tensile stress concentrations can produce secondary opening fractures called wing cracks that emanate from the sides of faults or slipping interfaces such as pre-existing joints, sedimentary bedding planes, and deformation bands. A second and independent form of inelastic deformation involves the formation of compaction bands: thin, tabular, bounded features of localized porosity loss that form perpendicular to the direction of greatest compressive stress. Boundary element methods with the explicit incorporation of contact mechanics and a solution method based upon complementarity have proved particularly effective in studying the combination of sliding flaw and wing cracks. Preliminary results indicate that the extension of these methods to compaction band propagation in 2D and 3D will be very effective.

Because stress states and geometry change with sliding on flaws and wing crack propagation, one cannot specify the boundary conditions a priori for this problem in solid mechanics. Under these circumstances complementarity is superior to other well-known contact algorithms. We focus on meter scale phenomena where mineralogical heterogeneity (common to centimeter-scale laboratory samples) and 3D geometry (common to kilometer-scale crustal structures) reasonably can be ignored. We consider linearly varying friction and curved wing cracks, and we allow the sliding flaw to open when mechanical interaction with the wing crack dictates that it should. Opening displacement profiles of wing cracks from the numerical model results can be significantly different from approximate analytical solutions. These analytical solutions may produce significant errors in stable crack length for curved propagation paths. The smeared out stress concentration near the tip of the sliding flaw and the heterogeneity in strength of rock suggest that multiple wing cracks may form in one slip event. The mechanical interactions of these cracks leads to kink angles that increase with distance from the flaw tip, a relationship commonly observed in nature.

STANFORD UNIVERSITY

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Grant: DE-FG02-08ER15991

Multiscale Investigation and Modeling of Flow Mechanisms Related to CO₂ Sequestration in Geologic Formations

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Objectives: Our objective is 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 CO₂ 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 CO₂ sequestration and other geologic flows.

Results: This project began in Sept. 2008, and thus no results have been obtained to date.

TEMPLE UNIVERSITY

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Grant: DE-FG02-96ER14644

Complexities Affecting the Rate and Mechanism of Pyrite Oxidation: An Interdisciplinary Approach

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Objectives: The primary goal of this research program is to understand the microscopic aspects of pyrite oxidation. Our continuing research strategy is to understand macroscopic observations of pyrite reactivity with an atomic/molecular level view. The results of this research will lead to a better understanding how pyrite reacts in a range of chemical environments.

Project Description: The reactivity of pyrite in anoxic and oxic environments is being investigated by integrating aqueous geochemical and modern surface science techniques. An emphasis of the research is to develop *in-situ* techniques to study the mineral surface on a microscopic level in the presence of an aqueous or gaseous phase.

Results: Research progress in FY2008 focused on probe microscopy and batch reaction experiments that were used to study the effect of autotrophic and heterotrophic bacteria (those common to AMD environments) on pyrite with and without adsorbed phosphocholine lipid. A smaller set of studies investigated the oxidation of vaesite in the abiotic environment.

Suppression of Pyrite Oxidation under Biotic Conditions

Research has continued to address the solution of a significant environmental problem referred to as acid mine drainage (AMD), resulting from the oxidation of metal-sulfides, primarily pyrite. This environmental impact includes acidification of rivers and streams as well as leaching of toxic metals from the metal-sulfide material. Prior studies investigated the use of phospholipid layers on pyrite to suppress the oxidation of the mineral in abiotic and biotic conditions. Even in the presence of iron oxidizing *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) bacteria the lipid layer, which assembles into a bilayer structure, significantly suppresses the rate of pyrite oxidation (by 80% relative to pyrite without lipid). FY2008 studies have investigated the ability of the adsorbed lipid layers to suppress pyrite oxidation in the presence of heterotrophic bacteria that are also found in AMD environments. The figure exhibits aqueous iron versus time data for an experiment that investigated the batch oxidation kinetics of mixed microbial solutions containing both *Acidiphilium acidophilum* (*A. acidophilum*) and *A. ferrooxidans* on pyrite that was pre-exposed to the phosphocholine lipid, [1,2-bis(10,12-tricosadiynoyl)-sn-glycero-3-phosphocholine (23:2 PC Diyne)], with and without UV treatment. These data show that after 4 days the amount of aqueous iron is 2 times less in the *A. ferrooxidans*/*A. acidophilum*/lipid/pyrite solution than in the lipid-free *A. ferrooxidans*/*A. acidophilum*/pyrite sample solution. However, after 5 days there is an increasing rate of aqueous iron production (proportional to the slope of each plot) in this system and after 15 days *A. ferrooxidans*/*A. acidophilum*/lipid/pyrite has generated a similar amount of aqueous iron as lipid-free *A. ferrooxidans*/*A. Acidophilum*/pyrite. In the

15-30 day time period the behavior of the lipid-free and lipid-present pyrite systems behave similarly in the presence of *A. ferrooxidans* and *A. acidophilum* based on a comparison of their aqueous iron production rates. Hence, the heterotrophic bacteria disrupts the lipid bilayer structure.

We have recently shown that the irradiation of the 23:2 diyne results in the cross-linking of the organic tails via diacetylene groups in the organic chains of the lipid. Data plotted in the figure shows that the UV-pretreatment of the lipid/pyrite system prior to the introduction of bacteria leads to a significant suppression of pyrite oxidation in the mixed bacterial community for at least 30 days. Data in the figure allows us to conclude that the cross-linking process results in an 80% decrease in rate of aqueous iron production rate compared to the lipid free system in the presence of both autotrophic and heterotrophic bacteria.

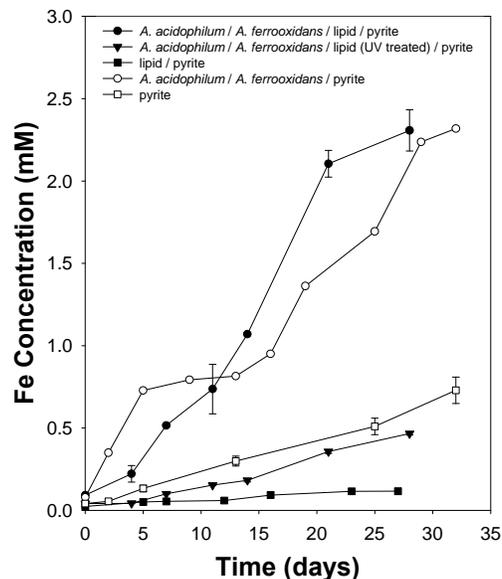


Figure: Batch reaction data associated with pyrite oxidation under various experimental conditions.

TEXAS A&M UNIVERSITY

Texas Engineering Experiment Station
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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 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 ($p\text{CO}_2$), 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 $p\text{CO}_2$;
- b) determination of how $p\text{CO}_2$, 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: *Calcite Dissolution Kinetics in Saline Waters* - The specific effect of ionic strength on the reaction kinetics of calcite dissolution in intermediate to high ionic strength ($0.5 \leq I \leq 6.0$) solutions applicable to natural waters has been investigated using classical free-drift methods where all other parameters ($m_{\text{Ca}^{2+}}$, P_{CO_2} , and T) have been held constant. Phosphate-free solutions of both potassium chloride (KCl) and sodium chloride (NaCl), as the dominant ionic strength determining salt, were investigated. Calcium concentrations were held close to constant in all solutions at approximately 10^{-2}

molal. Reaction rates were found to vary significantly as a function of ionic strength of the reacting solution, beyond its influence on activity coefficients. This is probably due to the lowering of the activity of water with increasing ionic strength resulting in a decrease in the rate of cation hydration. When modeled with the general rate equation, $R = k(1 - \Omega)^n$, first-order kinetics ($n=1$) are sufficient to fit the experimental data. Furthermore, the rate constant (k) is directly proportional to the ionic strength of the reacting solution. The influences of $p\text{CO}_2$ and T were also investigated. Dissolution rates increase with either an increase in $p\text{CO}_2$ or an increase in T , but are less sensitive to these parameters as ionic strength increases. These results provide a baseline for calcite dissolution in solutions of relatively simple composition from which the influences of other common constituents of natural waters may be evaluated in future studies. Results also have potential applications to the response of the ocean to acidification by fossil fuel CO_2 , as well as CO_2 sequestration in subsurface saline waters in calcium carbonate-hosted reservoirs.

Calcite Nucleation and Epitaxial Growth from High Ionic Strength NaCl Solutions - The concentration of NaCl was varied from 0.5 to 5 molal in solutions containing low Ca^{2+} concentrations ($\sim 10^{-2}$ m) and the supersaturation with respect to calcite was adjusted by varying carbonate alkalinity and $p\text{CO}_2$. Iceland spar calcite was used as the host substrate for epitaxial overgrowth experiments. Calcite did not nucleate directly from solution, but instead formed on the surface of homogeneously nucleated vaterite crystals. No aragonite was observed. Subsequently vaterite recrystallization initially produced euhedral, well-formed calcite rhombs up to tens of microns in size. Epitaxial calcite growth on Iceland spar calcite produced a variety of different surface structures that changed with time and degree of supersaturation. The most common overgrowth was submicron crystals that formed incomplete layers in a manner characteristic of surface instability. Overgrowth layers were often observed to inherit macroscopic surface patterns of the underlying host calcite substrate. Longer reaction times (months) produced extensive recrystallization and heterogeneous evolution of large surface features.

TEXAS A&M UNIVERSITY

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Grant: DE-FG02-00ER15034

Time-Lapse Seismic Monitoring and Performance Assessment of CO₂ 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 CO₂ 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 CO₂ sequestration including compressibility, compositional and geochemical effects. We performed comprehensive simulations of the gas injection process accounting for the phase behavior of CO₂-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 CO₂ injection enhanced oil recovery pilot project, we plan to develop a systematic workflow for the detection and location of CO₂ movement using fluid flow and seismic data.

Results: We have developed a compositional streamline formulation for fast modeling of CO₂ injection with rigorous treatment of compressibility effects (Osako and Datta-Gupta, 2007). Unlike previous works, our approach accounts for compressibility effects during both pressure calculations and 1D transport of overall composition/saturation along streamlines. This is made possible by introducing an ‘effective density’ that accounts for volume changes along streamline (Cheng et. al., 2006). To speed-up the solution of the 1D compositional equation along streamlines, we introduced an ‘optimal’ coarsening algorithm that minimizes the numbers of nodes for the 1D solution. We have also included detailed CO₂ phase behavior and precipitation-dissolution reactions to account for CO₂ sequestration through brine solubility and mineral precipitation.

We have utilized the compositional streamline simulator to visualize the movement of CO₂ and understand the sequestration mechanisms active in the reservoir. We show that the use of phase and component streamlines, in addition to the more commonly used total velocity streamlines, can provide important insights into the reservoir mechanisms. Unlike the total velocity streamlines, the phase and component streamlines can be discontinuous and display important information about the local appearance and disappearance of components or phases because of compositional or geochemical

effects. In particular, the compositional streamlines can be very useful in the tracking of CO₂ in the subsurface as illustrated in **Fig. 1**. Currently we are in the process of applying compositional streamline simulation to the Weyburn field, a large carbonate reservoir in Canada undergoing CO₂ injection. The streamline simulator is being used for determining the reservoir sweep pattern of the injected CO₂ and the long-term sequestration potential.

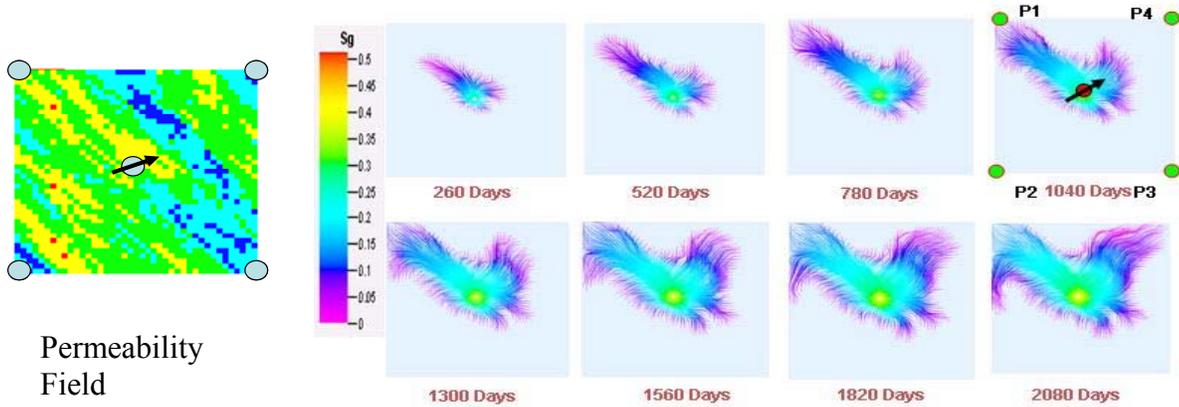


Fig.1 Illustration of the use of compositional streamlines to track the movement of CO₂

We also continue to examine the pressure dependence of seismic velocities of fractured rock for modeling of time-lapse seismic data acquired from reservoirs where the influence of fractures is important. Typical theoretical models for the effective properties of such materials allow for fluid substitution, but their analytic forms are complex and include many parameters that will be difficult to specify in typical field applications, quantities characterizing the fractures, the host medium, or the pore fluids. In contrast, the asperity deformation model (“bed of nails” model) provides a very simple analytic formula including only three parameters that can be estimated easily given a set of measurements of velocity as a function of pressure (Gangi, 1978, 1981; Carlson and Gangi, 1985, Gangi and Carlson, 1996). This phenomenological model reproduces the pressure dependence of velocity by representing a rough fracture as a set of asperities with a certain distribution of heights. Another important approach to modeling the pressure dependence of velocity, one that is not an explicit model of fractures, is based on differential effective medium approach. Here the behavior is modeled theoretically using a distribution of pores of varying aspect ratios (ratio of the minimum and maximum radii of the assumed ellipsoidal pores). In this approach, small aspect ratio pores close at small pressures, while more other pores close at higher pressure values. Though this solution relies on fairly complicated equations, it is widely used in industry, in part because it allows for consideration of the influence of different fluid types. For the first time, we directly compare the results of both models on the same velocity data, suggesting that the estimated distributions of pore aspect ratios and asperity heights can be compared in a way that shows they provide similar characterizations of the rock properties. This in turn suggests that the asperity deformation model, which is much simpler to utilize, offers strong potential for contributions to time-lapse seismic analysis.

UNIVERSITY OF TEXAS

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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 and vibrational sum frequency generation spectroscopies (XAS, VSFG), and molecular modeling to investigate the potential formation of ternary metal-anion complexes at mineral surfaces in different solution compositions over a range of surface coverages. XAS provides data on how the metal binds to the surface (monodentate, bidentate) and VSFG provides data on the anions adsorbed with the metals, polyatomic anion orientation in some cases, and water structure at the mineral surface. Molecular modeling supports data from both spectroscopic techniques by providing information on water structure at the surface, the surface sites for metal-binding and the orientation of any associated ions, and the relative energetics of different surface complexes. We initially focused on investigating water structure and Sr^{2+} , Co^{2+} , and Pb^{2+} adsorption from NaCl, NaNO_3 , and NaClO_4 solutions onto quartz, amorphous silica, corundum, and gibbsite.

Results: In this fiscal year, the Katz lab focused on studying the effect of temperature on alkaline earth metal ion adsorption onto gibbsite surfaces and evaluating different methods for describing sorption of surface complexation of metal ions to oxide surfaces in multicomponent systems. Three alkaline earth metals, Mg^{2+} , Sr^{2+} , and Ba^{2+} , were used in this study to investigate the temperature effects on metal ion adsorption. The results showed that outer-sphere adsorption is favored for ions with large hydration radii upon sorption onto gibbsite, while inner-sphere sorption is favored with increasing temperature and decreasing hydrated radii. The results are consistent with that derived from MD simulations. For modeling efforts, two approaches were adapted to count for the dependence of solid concentrations due to the use of bi-dentate reactions. The first approach was to utilize a mole fraction reference state for adsorbed species, and the second approach was to separate the mole balance and mass action expressions such that the mole balance equation accounts for the loss of two sites in the formation of a bi-dentate site. The results of this extensive modeling effort demonstrated that the mole fraction approach predicted sorption with greater success over the range of conditions examined. Overall, our model results showed that the DLM was able to describe single-solute adsorption of As(V), Ca^{2+} and Si(IV) onto iron oxides. The DLM was able to predict anion competition with As(V), but over predicted As removal in tri-solute systems, however, it qualitatively captured sorption behaviors of the other solutes.

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Grant: DE-FG02-03ER15430

Predicting Fracture Porosity Evolution in Sandstone

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Objectives: Our goal is to explain how fracture growth and diagenetic alteration interact to create and destroy fracture porosity. 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 duration and rates at which fractures open and rock properties change.

Project Description: We use SEM-based cathodoluminescence 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. We use the model along with cement textures to infer patterns, rates and durations of fracture opening. We take advantage of new automated image collection systems and protocols, and fluid inclusion and sandstone crystallography 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. Fracture patterns in both models and outcrops are rigorously described using our newly developed methods for quantifying fracture size and spatial patterning. Palinspastic reconstruction of natural fracture aperture and length profiles allows direct comparison with geomechanical models. 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. We take advantage of the large and diverse core data set from the Piceance and East Texas basins to investigate how carbonate cementation seals large fractures.

Results: Fluid inclusion assemblages (FIAs) hosted in fracture-bridging quartz cements record the PTX properties of fluids present during opening. Temperature decreases with the relative age of FIAs hosted in a synkinematic quartz cement bridge from the East Texas basin implies fracture widening from ~42 Ma to the near-present day. We collected Laser Raman spectroscopic analyses to estimate the methane concentration in FIAs of known relative age in synkinematic quartz bridges sampled from largely open fractures in core at a depth of 3 km. The methane concentrations decrease systematically with temperature (and by extension, time), from ~3300 ppm at 151°C to ~1900 ppm at 134°C, suggesting a PT path that traversed the two-phase field in the ternary H₂O-NaCl-CH₄ system. Calculated trapping pressures for these inclusions range from lithostatic pressure at maximum burial of 3.5 km when fracture formation initiated, down to hydrostatic pressure near the modern day burial depth of 3.0 km. We propose a model in which reservoir charge occurs near maximum burial conditions at ~42 Ma, increasing the pore fluid pressure to lithostatic conditions and providing an impetus for fractures to form. During uplift and cooling from ~42 Ma to the present, methane continuously leaks out of the system at a gas-water contact, maintaining methane saturation of pore fluids below the contact while fracture apertures repeatedly widen due to overpressure driven crack tip propagation. The pressure eventually decreases to hydrostatic conditions near to the present day, and fracture growth ceases.

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. The nature of preserved aperture distributions in fractures suggests that mineral precipitation and fracture growth often occur simultaneously. In addition to mineral precipitation in the fractures, there will also be concurrent mineral precipitation in the matrix rock around the fracture. This mineral precipitation, in both the fracture and the host rock around it, will act to preserve fracture opening. We used a fracture mechanics model to examine the feedback between these aperture propping mechanisms and fracture network growth. Field observations indicate that fractures often have power-law aperture distributions, probably a consequence of feedback processes, such as the mechanical interaction between fractures and interaction between fracture growth and cementation. Our work shows that only certain degrees of interactive feedback will generate a power-law distribution. Mechanical interaction without diagenetic propping of apertures does not result in a power-law aperture distribution, but power-laws do result from diagenesis active during fracture propagation.

TUFTS UNIVERSITY

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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 methane migration and chemical diagenetic effects within deforming faults in a transpressional setting that is seismically active. Most of the work deals with faulted basins of California, most recently in the Santa Barbara Basin (SBB) and the Los Angeles Basin (LAB).

Project Description: We have mainly targeted active faults and young petroleum fields in southern California for study including the Refugio and Elwood faults in the SBB, and the Newport-Inglewood fault (NIF) in the LAB. Subsurface core 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 degree of compartmentalization for these known fault networks. We are also investigating the geochemical signatures in carbonate that characterize rapid CO₂ degassing. These data provide constraints for mathematical models that are being developed to predict fluid pressures, multiphase CH₄/CO₂ flow patterns, rates and patterns of deformation, subsurface temperatures and heat flow, and geochemistry associated with large transpressive-related fault systems.

Results: Geochemical analysis of well-scale carbonate mineralization formed by rapid CO₂ degassing has shown some surprising results from Boles: oxygen and carbon isotopic composition of the scales are extremely enriched in light isotopes, which suggests that the CO₃⁼ molecule is sourced directly from CO₂ gas, rather than from dissolved carbonate ion in equilibrium with an aqueous fluid. These results are not predicted by conventional geochemical models and demonstrate the potential importance of meta-stable phases during CO₂ degassing. The importance of this finding is relevant to understanding the effects of injection of CO₂ gas into the formation and the possible effects of leakage of reservoir seals for carbon sequestration.

In related studies with Venoco Inc., Boles & Garven continue to study the South Ellwood Fault by examining and acquiring data from Platform Holly in the SBB. These include fluid composition, shut-in well pressure and temperature data, and submarine methane seepage along the fault. Our recent work indicates that surface seepage rates, which are quantitatively measured in steel tents on the seafloor, can be directly linked to the production history of individual wells at Platform Holly that directly underlie the seep collection area. The changes in flow rates are consistent enough that we are calculating permeability ($k \sim 10$ md) of the ~ 1 km flow path from the wells to the overlying sea bed. We are also in the process of sampling fluid for elemental and isotopic composition in key wells that have pressure data suggesting that seawater is being drawn down into the underpressured Monterey Formation reservoir at Platform Holly.

In the lab, Mike Ryan, a UCSB Master's student, has completed his sampling, petrographic, and stable-isotopic analyses of carbonate cements associated with the igneous intrusions associated with the north end of the Newport-Inglewood Fault Zone. The igneous body appears to be largely a series of surface flows intruded along the fault (see cross section below). We continue to plan the drilling and coring of the NIFZ near its southern end with monthly visits to Long Beach. Offset tubing strings and thermal anomalies indicate active fluid movement and aseismic creep along the fault in this area. Currently the Signal Hill Petroleum Corp., located in Long Beach, California is planning on funding the drilling and coring of the fault zone. Collaborators include the Southern California Earthquake Center and Cal State Long Beach. We anticipate that this project will provide a rich data set for analysis of coupled diagenesis-fluid-fault processes in 2009.

Garven's flow mathematical modeling in 2008 mostly focused on the development of both basin-scale and reservoir-scale geohydrologic models of the LAB (see shaded relief map below). In this work, Ph.D. student Byeongju Jung, has made excellent progress in building a 2-D two-phase flow model for deep groundwater flow and petroleum migration. The model also includes coupled effects of geothermal heating and poroelastic tectonic deformation—the first that we know of in the geosciences. We continue to refine the model with feedback from Boles, and prepare a sensitivity study related to effects of petroleum generation rates, fault permeability, and basin deformation. The collaboration between UCSB and Tufts continues to be strong and successful, and we continue to also interact with Prof. Juli Morgan (Rice University). She is sharing with us her expertise and numerical experience on strike-slip fault deformation processes. With her large-scale geomechanical model, we will be better prepared to characterize the transient geohydrologic properties and multiphase fluid dynamics and relate it to the Boles' petrologic observations and geochemical data and the reservoir scale model of fluid flow by Garven's group.

Figure 1: Digital elevation and Landsat map of the Los Angeles Basin.

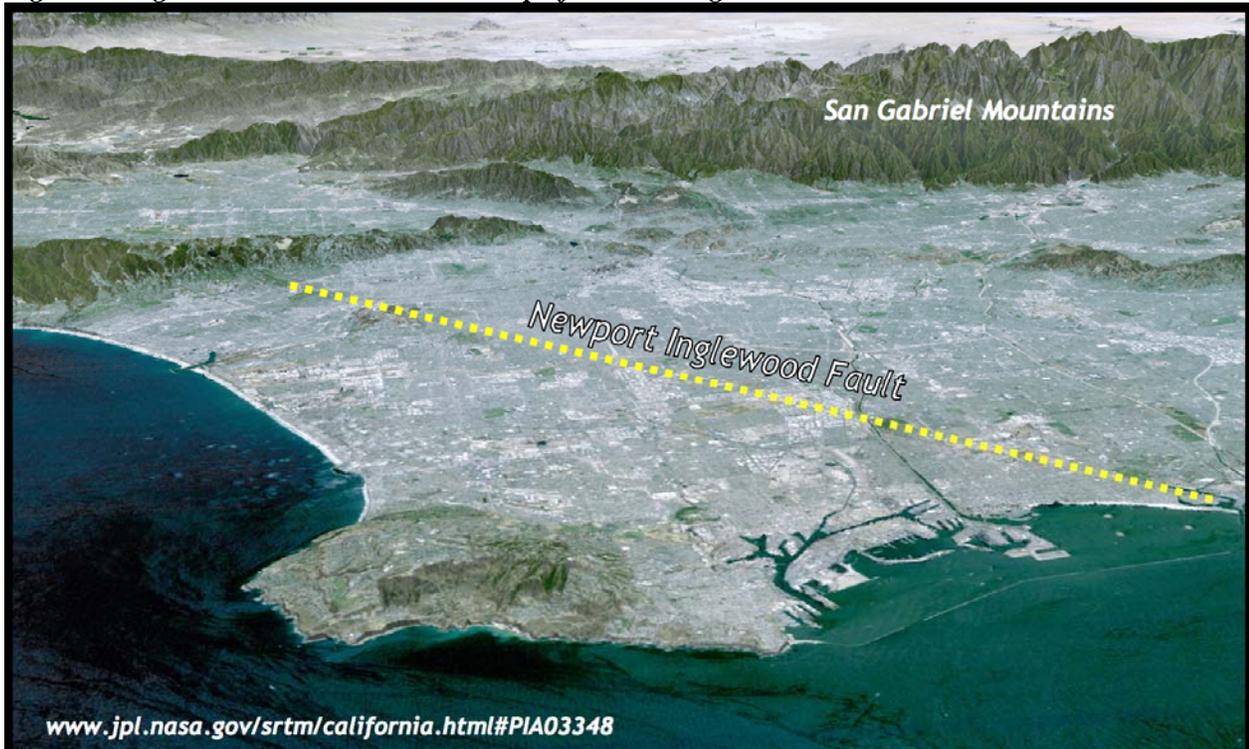
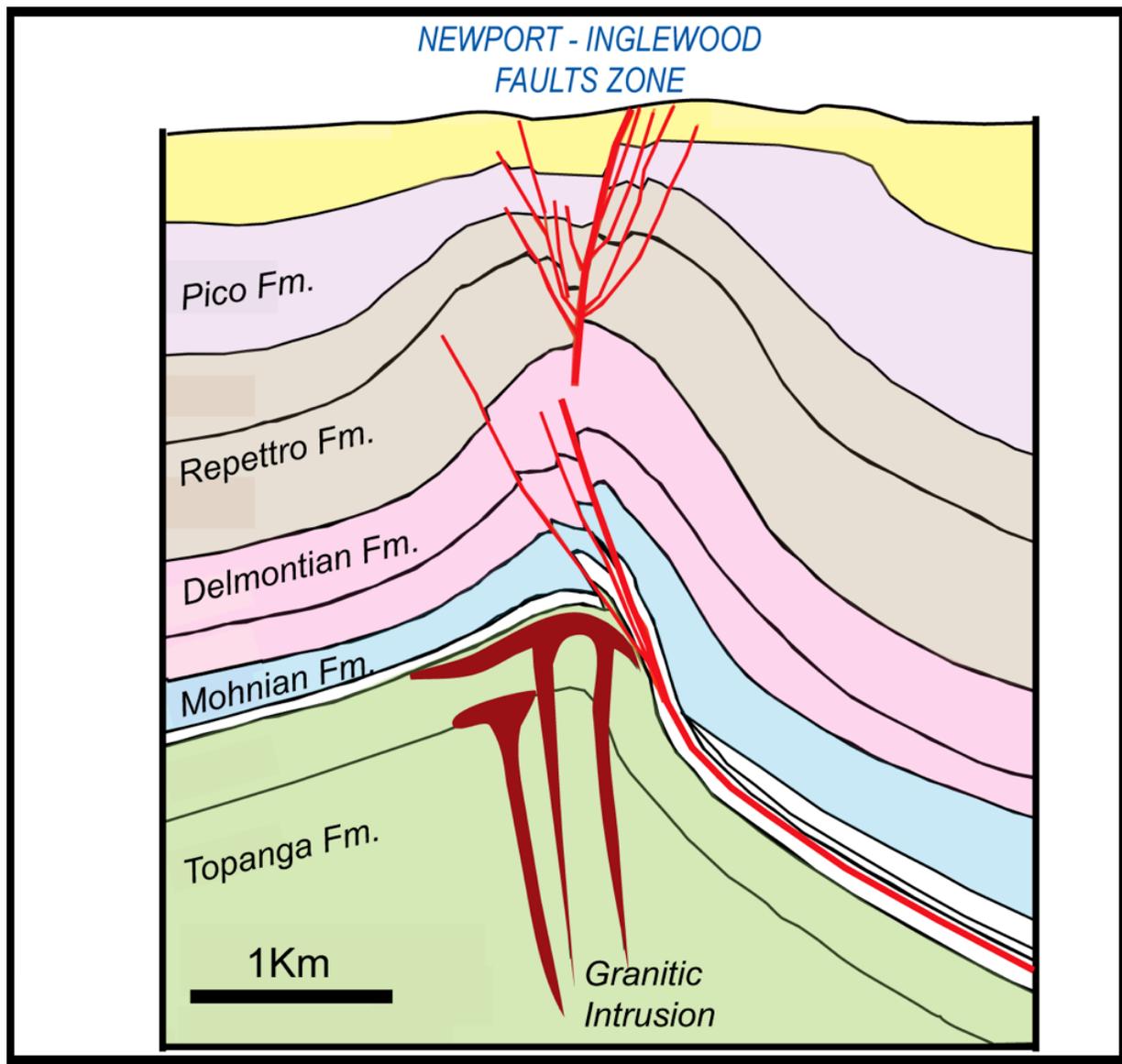


Figure 2. Cross section of the NIFZ (courtesy of Dalton Lockman, 2008, Plains Petroleum Exploration Company, unpublished).

SOUTHWEST

NORTHEAST



VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

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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 that form. A long-term goal is to establish the physical basis for biomineralization and accompanying roles of solutes in natural and engineered Earth systems.

Project Description: This work is focused on developing a mechanism-based picture of controls imposed by Asp-rich polypeptides and biomineralizing proteins on the elemental signatures in calcite. We are also probing the transient events and phase evolution during CaCO₃ nucleation at peptide-derivatized templates. In particular, we seek an understanding of the amorphous to crystalline transformation that we recently showed routinely occurs during nucleation at these templates. Growth studies include: AFM and time-of-flight 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 CaCO₃ nucleation and transformation on peptide derivatized 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 2008:

Peptides enhance magnesium signature in calcite: New insights into origins of vital effects. Studies relating the magnesium content of calcified skeletons to temperature often report unexplained deviations from the signature expected for inorganically precipitated calcite. These ‘vital effects’ are believed to have biological origins but mechanistic bases for measured offsets remain unclear. The composition of biologic molecules isolated from biominerals suggests that control of mineral growth must certainly be linked to biochemical features. Building on papers funded by this project that established relationship between the ability of biomolecules in solution to promote calcite growth and their and hydrophilicity, we hypothesize that because 1) cation incorporation is the rate-limiting step to growth and 2) 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 Mg content. In this study, we show that a simple hydrophilic peptide, sharing the same carboxyl-rich character as macromolecules isolated from sites of calcification, increases calcite magnesium content up to 3 mol%. Comparisons to previous studies correlating Mg content with temperature show that the Mg enhancement due to peptides results in offsets equivalent to 7-14°C. The insights also 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 in controlled materials synthesis.

We have commissioned our fluid cells and holder for in situ TEM studies of nucleation from solution. (R. Friddle, J. J. De Yoreo, P. M. Dove.). The system exhibits excellent temperature response between 0 and 60°C and has electrochemical control via a working electrode on the gold-coated SiN₄ window through which the electron beam passes. We have developed a sealing procedure that enables to form cells with a thickness between ~100 nm and ~1 mm. We have shown that, even in 10 mm thick cells, we can resolve nanoparticles that are less than 5 nm in size and follow their diffusion in fluid. We have also directly observed the growth of silicone-based colloids in real time. Most importantly, we have now shown that we can set the operating parameters to induce carbonate nucleation at will on the working electrode. The next step is to use the fluid stage to measure nucleation rates and follow the evolution of phases as a function of applied chemical potential. These will be the first measurements of their kind.

Kinetics of amorphous silica dissolution: Paradox of the silica polymorphs. Amorphous materials lack the structural order that allows them to be studied by classical terrace, ledge, kink models applied to crystal dissolution. This would seem to imply that the surfaces of amorphous phases are atomically rough so that transfer of SiO₂ to solution leaves the surface free energy of the solid unchanged. As a consequence, dissolution rates of amorphous phases should scale linearly with driving force (undersaturation) through the higher probability of detaching silica tetrahedra from surfaces. By examining rates for amorphous SiO₂ polymorphs— fused quartz glass, synthetic colloidal, and biological silicas— we find, instead, a paradox. Just as seen for their crystalline polymorph, quartz, dissolution rates of SiO₂(am) in electrolyte solutions have an exponential dependence on driving force. We analyze this enigma by considering silica polymorphs present common types of surface-bonded silica groups. In electrolyte solutions, nucleated detachment of higher coordinated groups increases surface free energy and the probability of doing so scales exponentially with driving force. The result is a plausible mechanism-based model that is formally identical with the polynuclear theory originally developed for crystal growth. The approach also quantitatively explains dissolution data reported for biogenic silica and growth/dissolution of synthetic colloidal silica. The insights should be applicable to materials with diverse compositions and structural order.

Kinetics of Mineral Dissolution and Growth as Reciprocal Microscopic Surface Processes Across Chemical Driving Force. Nanoscale in situ imaging technologies are leading a new understanding of the microscopic processes that underlie widely used empirical ‘rate laws’. We examine findings that the kinetics of mineral dissolution can be explained by equivalent, but inverse, microscopic processes that describe growth. Like growth, dissolution occurs by multiple microscopic processes— each with an empirical and mechanism-based rate law and a unique dependency on chemical driving force. As with increasing undersaturation, dissolution rates are first dominated by step propagation, followed by generation of steps at dislocation sources, and then nucleation of vacancy islands. Interplays between step edge energy, temperature and other parameters determine if/when minerals express all of these processes across driving force. Net rates that measured from reactor studies to give power law dependencies upon driving force describe the sum of these processes. Process-specific energy barriers control rates at different surface structures and defects of minerals and materials.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

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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.

Project Description: *Shewanella oneidensis* MR-1 is a potential candidate for bioremediation because of its ability to respire a variety of substances, such as oxygen, iron and manganese oxides, hexavalent chromium and uranium(VI). Since it has been unknown if *S. oneidensis* can utilize quorum sensing, our work is focused on understanding the role of a potential quorum sensing signal gene *luxS* in *S. oneidensis* and how this affects its ability to interact with the environment.

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.

Results: *Shewanella oneidensis* MR-1 LuxS involvement in biofilm development and sulfur metabolism. The role of LuxS in *Shewanella oneidensis* MR-1 has been examined by transcriptomic profiling, and biochemical and physiological experiments. Results indicate that a mutation in *luxS* alters biofilm development, not by altering quorum sensing abilities, but by disrupting the activated methyl cycle (AMC). *S. oneidensis* wild-type (WT) can produce a luminescence response in the AI-2 reporter strain, *Vibrio harveyi* MM32. This luminescence response is abolished upon deletion of *luxS*. Deletion of *luxS* also altered biofilm formations in static and flow-through conditions. Genetic complementation could restore the mutant biofilm defect, but the addition of synthetic AI-2 had no effect. These results led to the conclusion that AI-2 is not likely used as a quorum sensing signal to regulate biofilm development in *S. oneidensis*. Growth on various sulfur sources was examined because of the involvement of LuxS in the AMC. A mutation in *luxS* produced a reduced ability to grow with methionine as the sole sulfur source. Methionine is a key metabolite used in the AMC to produce a methyl source in the cell and to recycle homocysteine. The data suggests that LuxS is important to metabolizing methionine and the AMC in *S. oneidensis*.

The non-oxidative dissolution of galena nanocrystals: Insights into mineral dissolution rates as a function of grain size, shape, and aggregation state. Nearly monodisperse galena nanocrystals with

an average diameter of 14.4 nm were synthesized for this study, and samples were exposed to pH 3, deoxygenated HCl solutions for up to 3 hours at 25°C. Detailed XPS analysis showed the nanocrystals to be free of unwanted contamination, surface complexes, and oxidative artifacts, except for small amounts of PbO species in both pre- and post-dissolution samples which have been observed in fresh, natural bulk galena. Depending on the calculation methods used, galena nanocrystals, under the conditions of our experiments, dissolve at a surface area normalized rate of one to two orders of magnitude faster than bulk galena under similar conditions. We believe that this reflects the higher percentage of reactive surface area on nanocrystalline surfaces vs. surfaces on larger crystals. In addition, it was shown that {111} and {110} faces dissolve faster than {100} faces on nanocrystals, rationalized by the average coordination number of ions on each of these faces. Finally, dissolution was greatly inhibited for galena nanocrystal surfaces that were closely adjacent (1-2 nm, or less) to other nanocrystals (Figure 1), a direct indication of the properties of aqueous solutions and ion transport in extremely confined spaces and relevant to dissolution variations that have been suspected within aggregates.

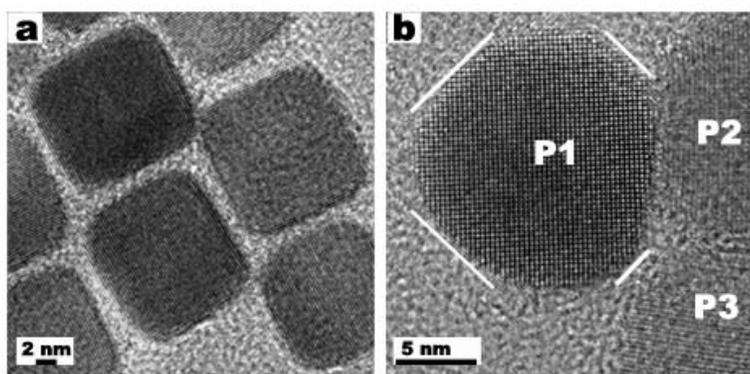


Figure 1. (a) HRTEM image of pre-dissolution PbS nanocrystal cluster. The inter-particle spacing is nano-scale. (b) HRTEM image of the post-dissolution PbS nanocrystal, P₁, adjacent to two nanocrystals, P₂ and P₃. {110} faces on the left side, open to bulk solution, are dissolved faster than the equivalent faces on the right side, close to other particles.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

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Fall 2007 American Geophysical Union Meeting: Student Travel Support for Environmental Nanomaterials Session #B35 (December 10-14, 2007)

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Objectives: In the first session of its kind at AGU, the “Environmental Nanomaterials” session presented a number of high-quality talks and posters, some by well-respected researchers from both pure and applied fields, and was very well attended. The session basically followed a subject thread from fundamental properties of nanoparticles to reactivity and mobility to environmental and biological interactions and processes. Funding for student travel scholarships allowed students to attend our session at greatly reduced personal expenses, as well as to develop both their CVs and professional associations, potentially leading to greater postdoctoral research opportunities and/or future long-term employment.

Project Description: Student presentations were particularly high in quality and were well-received. A number of talks included results from advanced techniques and instrumentation in the study of nanoparticles and nanoscale mineral-fluid interactions. Several talks showed the unique effects of microbes on the structure and properties of nanoparticulate metal-bearing phases and vice versa, the toxicity of nanophases towards microbial and ecosystem health. This session represented a first successful attempt to connect researchers across disciplines who study environmentally significant properties that inherently involve nanometer-scale reagents and reactions.

Results: This session was, to my knowledge, the first of its kind at AGU, bringing together researchers from geology, environmental science, physics, chemistry and biology. Presentations ranged in topic from the fundamental physical and chemical structure of natural analog (synthetic) nanomaterials to the effects of impurities on surface reactivity to the precipitation of contaminant metal-sequestering nanoparticles by bacteria to the transport of nanoparticulate radionuclides in contaminated aquifers. Highlights of the session included talks from high-profile researchers in nano(geo)science such as Paul Alivisatos (UC Berkeley), George Helz (U Maryland) and Udo Becker (U Michigan), as well as from rapidly rising younger scientists like Young-shin Jun (Washington University), Trevor Kendall (Harvard U) and Jay Nadeau (McGill U). Paul presented interesting new data showing the self-segregation of metals within mixed-phase metal-bearing nanoparticles (e.g., Ag and Cd in a synthetic AgCd-sulfide phase), with implications for the environmental behavior of such synthetic materials once they are, according to many researchers, inevitably released. Trevor Kendall and Udo Becker both presented visually stunning and easy-to-understand embedded videos of nanoparticulate surface mineralization on calcite associated with biopolymer templation and restructuring of iron-sulfide nanoparticles due to arsenic atom impurities, respectively. Jun presented new data elucidating geochemical and thermodynamic factors controlling the precipitation of iron-oxide phases in the environment. Nadeau

showed some incredible fluorescence microscopy data illustrating the use of biomolecule specific quantum dot probes in medical microbiology applications. Finally, Helz presented early results from a newly developed voltammetric technique designed to detect phase-specific nanoparticles in natural waters.

A number of high-quality poster presentations were also given, many by first-time AGU student presenters. Four of the DOE student travel scholarship winners presented in the poster session, while a senior student presenter from ETH in Zurich (graduating this Dec.) gave a talk. Student presentations ranged in topic from the reactive transport behavior of nanoparticulate fullerenes to the association of Cu nanoparticles in a contaminated natural environment with metalloproteins.

The oral sessions were well attended, generally keeping a solid audience of about 30-40 people, with a mid-morning increase to approximately 60-70. Several well-known researchers in environmental science and nanogeoscience were present for much of the oral session. The poster session was very well attended, with AGU attendees clustering at nearly every poster during the mid-afternoon. A late-afternoon verbal survey of students' poster presentations indicated that all had spoken with several interested researchers, including potential future collaborators or supervisors. Thus, the poster session seemed to afford students with ample opportunities for networking and career development.

UNIVERSITY OF WISCONSIN

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Mapping of Temporal and Spatial Phase Transitions of CaCO₃ 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 acquired extensive data on sea urchin spicules (**objective 1**) and sea urchin teeth (**objective 3**), and obtained exciting results, leading to two major publications, in collaboration with Steve Weiner, Lia Addadi, and their group at the Weizmann, where Gilbert spent 1 month in early 2008. All experiments were done at the SRC and ALS, using X-PEEM spectromicroscopy. **(1)** In sea urchin spicules we observed for the first time the mechanism of transformation from amorphous calcium carbonate (ACC, phase 1) to calcite (phase 3), which occurs via a newly discovered intermediate

amorphous phase 2. We did spectromicroscopy of transforming spicules, with pixel sizes down to 40 nm, and never observed a crystal propagation front. The transformation, instead, follows a random-walk pattern, akin to fractal network percolation of a liquid through a porous solid (PNAS, accepted for publication). (3) In sea urchin teeth we observed, unexpectedly, that the grinding tip of the tooth is not formed by a single crystal, but by alternating and repeating layers of two crystals, approximately 10-micron thick, misaligned by ~ 5 degrees. This novel result shows that the conventional wisdom, according to which each sea urchin tooth is a single-crystal, and several decades of literature, were inaccurate.

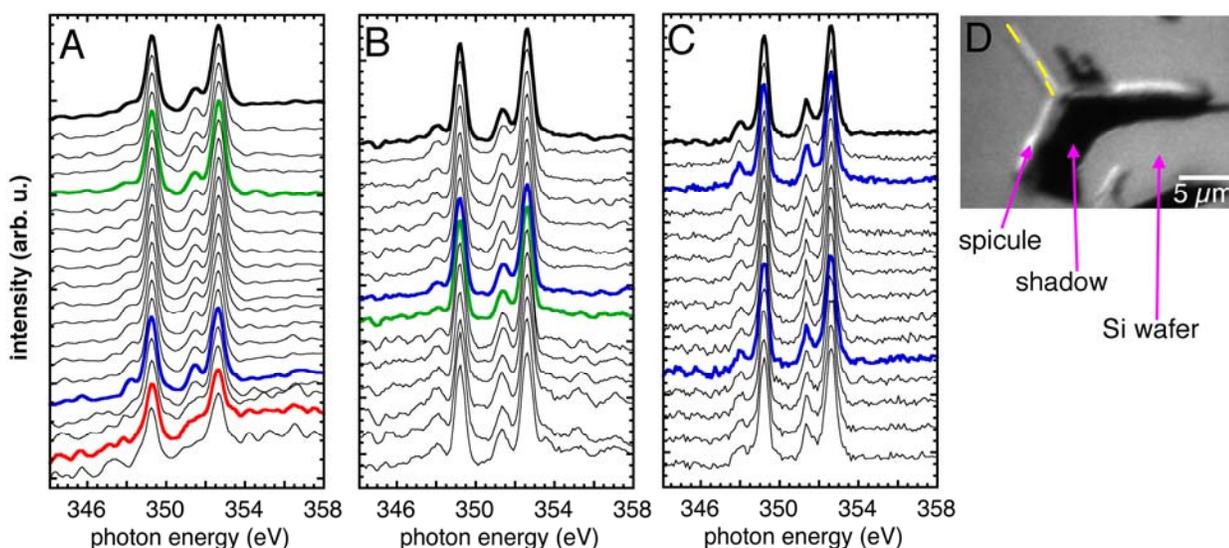


Figure 1: Ca *L*-edge spectromicroscopy of a triradiate sea urchin larval spicule. (A,B,C) Spectra extracted with X-PEEM from 100-nm pixels along the three yellow lines in D. (D) X-PEEM micrograph of the spicule. Red, present in A only (near the spicule tip), highlights spectra of ACC phase 1, green is the new ACC phase 2, blue is the calcite phase 3. Black thicker spectra in A, B and C are the averages of all spectra below. Note that in C, the spectra are relatively uniform and are similar to calcite.

UNIVERSITY OF WISCONSIN

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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 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 requires us to develop methods of appropriately small-scale experimental deformation and structural characterization of granular porous media. We chose to work with both *natural* and *synthetic* grain-cement systems using novel approaches that provide insight into grain-scale mechanics. We are:

- (1) Developing methods for fabrication and apparatus to test the mechanical properties of synthetic assemblages of soda-lime silicate beads and ice cement.
- (2) Integrating microstructural and experimental analyses to relate physical elements of progressively cemented natural and synthetic systems to their structural response to stress.
- (3) Developing quantitative relationships describing the stress-strain response of cemented granular systems and incorporate microscale material response into a DEM.

Results: 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. *We know of no natural system that exhibits this geometry.* Therefore, the UW group has designed and implemented an approach using detailed microstructural characterization and ultrasonic velocities to quantitatively characterize and determine the mechanical impact of progressive cementation and natural cement morphologies in the St. Peter Sandstone, a quartz-cemented quartz arenite.

Samples have a range of cement abundances, from < 2% to greater than 10%. Detailed back-scattered electron and cathodoluminescence images were used to distinguish and quantitatively characterize cement and pore distribution and geometry. Grains in low-cement (<2%) samples exhibit thin, encrusting layers of quartz with isolated facets and pore spaces are relatively equant and interconnected. In contrast, samples with > 10% cement exhibit an interconnected network of cement with well-defined facets, more crack-like pores, and diminished pore connectivity (and therefore permeability). With progressive cementation, 2D bond-to-grain (BGR) ratios and grain (BGR) ratios and grain contact

lengths increase, even where porosity remains high (Fig.1). Grain contact length is expressed as the mean ratio of contact length to grain diameter (d/D) of a given sample.

The mechanical effect of these geometric changes is being evaluated using ultrasonic velocity measurements. Shear wave velocity is a useful proxy for grain contact strength, and therefore allows us to evaluate the relative controls of porosity and grain contact strength on the elastic properties of variably cemented sandstone. Our data show that shear-wave velocity and shear modulus correlate most strongly with cement percent (and therefore grain contact length; Fig.1), whereas compressional-wave velocity shows a stronger correlation with decreasing porosity. The results agree with finite element models run by our colleague at Sandia National Labs: quartz precipitated at the grain boundaries has the largest effect on mechanical properties.

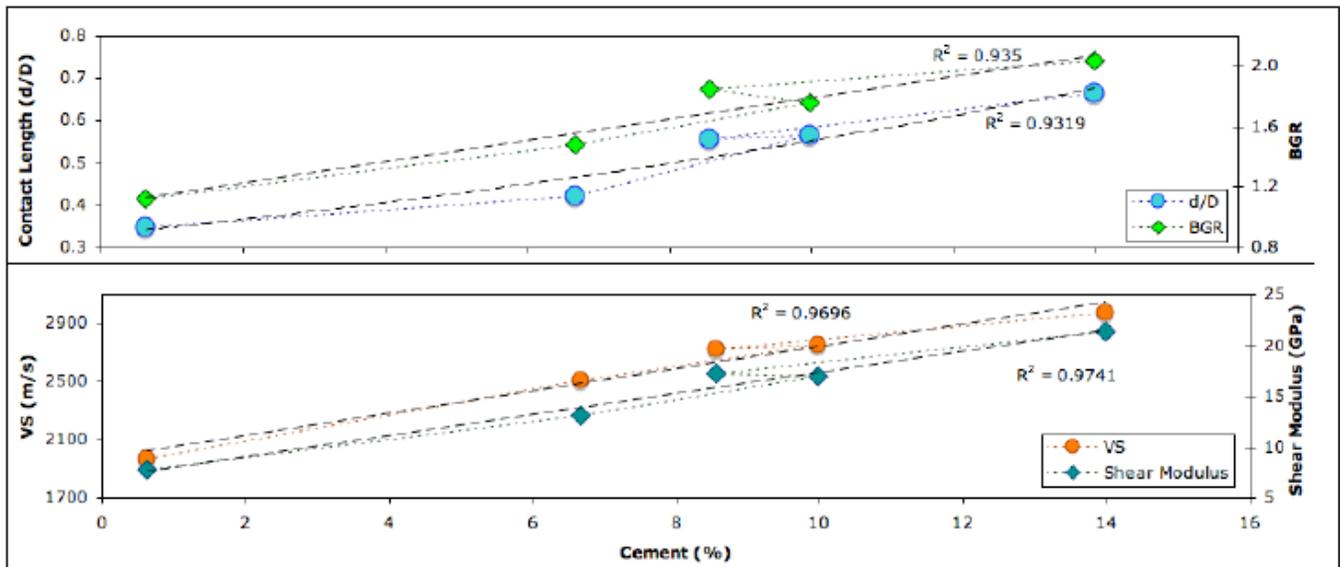


Figure 1: Comparison of contact length, BGR, shear wave velocity (V_s), and shear modulus versus cement (%) in St. Peter Sandstone samples. Data points are linked by dashed line in order of decreasing porosity. Note that two samples with similar contact lengths have similar V_s and shear moduli, in spite of the fact that one has both higher cement abundance **AND** higher porosity, emphasizing the importance of contact length.

Data obtained from the St. Peter Sandstone are being used to inform modeling efforts conducted by our collaborators at Sandia and UMass. The Sandia team is investigating the mechanical effects of quartz cement geometry, distribution, and abundance in quartz arenites with a series of 2D finite element simulations of two- and multi-grain arrangements with variable amounts of cement. Cement geometries are either grain-bridging bands or idealized overgrowths. Both sets of models demonstrate that as contact length increases, stress is more distributed and contact stiffness increases, regardless of geometry. In multi-grain assemblages, for a given contact length, stiffness is essentially the same for both geometries even though the overgrowth model has more than 3 times the cement and 25% less pore space than the grain-bridging model.

The UMass team has continued to explore the hydromechanical effect of cementation at the meso- and macro-scales in a series of discrete element models (DEMs) where deformation is driven by pore fluid volume changes (pumping). Realistic BGR values were used as a proxy for cementation in DEMs, from which elastic parameters for variable cement content were determined. The latter were used with

preliminary measurements of permeabilities of St. Peter Sandstone to parameterize 2D continuum poroelastic models. Model results indicate that that deformation behavior is strongly controlled by *both* the hydrologic and mechanical effects of cement. Research was ongoing as of September, 2008, and will continue into August, 2009.

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High Precision Ion Microprobe Analysis of Low Temperature Quartz Cements

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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 and fossil fuel reservoirs.

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 $\delta^{18}\text{O}$ across single crystals and within individual overgrowths at all scales down to sub-one-micron. Mineral zonation patterns provide new insights into timing and processes of water/rock interaction, and migration of fluids through sandstone aquifers.

We are investigating applications of the new analytical technology to paleoclimate studies, and groundwater and hydrothermal systems. We are applying experience gained in the past three year period by microanalysis of syntaxial quartz overgrowths in the St. Peter sandstone (Kelly et al. 2007) to quartz cements in the Mount Simon sandstone (Trzaskus et al. 2008); Potsdam sandstone, New York; 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 from Yucca Mtn.

Results: The CAMECA ims-1280 at Wisc-SIMS, University of Wisconsin- Madison is a large radius multicollector ion microprobe/ secondary ion mass spectrometer. This instrument has many new developments compared to earlier ims-1270's including: 10 electron multiplier and faraday detectors, improved focusing of primary and secondary beams, dedicated detection and monitoring of primary beam intensities, all digital electronics, PC control, and new operating and corrections software. Analytical results are excellent. *In situ* analyses of 10 micron spots in thin section attain precision of $\delta^{18}\text{O}$ (quartz, calcite, or zircon) as good as 0.1‰ (1 SD) for sample volumes that are 100 times smaller (~ng) than by single collector ion probe and 10^6 to 10^9 times smaller than possible by laser fluorination/mass-spectrometry. Procedures have also been developed for use of a sub-micron spot that yields precision of $\delta^{18}\text{O}$ better than 1‰ (Page et al. 2007) and analysis of Si and Li isotope ratios (Ushikubo et al. 2008).

We have completed a detailed oxygen isotope study of detrital quartz (DQ) and authigenic quartz overgrowths from shallowly buried St. Peter Sandstone (SW Wisconsin) to constrain temperature and fluid sources during diagenesis (Kelly et al. 2006, 2007). Quartz overgrowths in these cratonic supermature quartz arenites are syntaxial and show multiple growth generations by cathodoluminescence, but values of $\delta^{18}\text{O}$ are remarkably constant at $29.3 \pm 1.0\text{‰}$.

Following on our studies of silica cements in the Ordovician St. Peter sandstone, we have completed a pilot study of $\delta^{18}\text{O}$ in porosity occluding cements in the underlying Mount Simon sandstone from Wisconsin (Figure 1, Trzaskus et al. 2008). In contrast to the more shallow St. Peter sandstone, these new results are heterogeneous and suggest that some cements formed from hydrothermal brines. Analysis of silicon isotope ratios in quartz overgrowths is underway to evaluate the importance of groundwater silcrete cements.

The Mount Simon sandstone was identified as the likely reservoir for CO_2 sequestration from the \$1.5B FutureGen project in Illinois, which was proposed to be a prototype zero-emissions coal-burning power plant. In spite of the uncertain future of this project, we are investigating the availability of drill core samples from the Illinois basin. The comparison of shallowly buried samples from the Wisconsin dome to deeper samples of the Illinois basin will constrain the importance of pressure solution at different levels in the crust.

A homogeneous opal standard for $\delta^{18}\text{O}$ has been identified by detailed ion microprobe analysis and calibrated by laser fluorination/ gas-source mass-spectrometry. This new standard will allow studies of pedogenic opal from Yucca Mountain and vicinity.

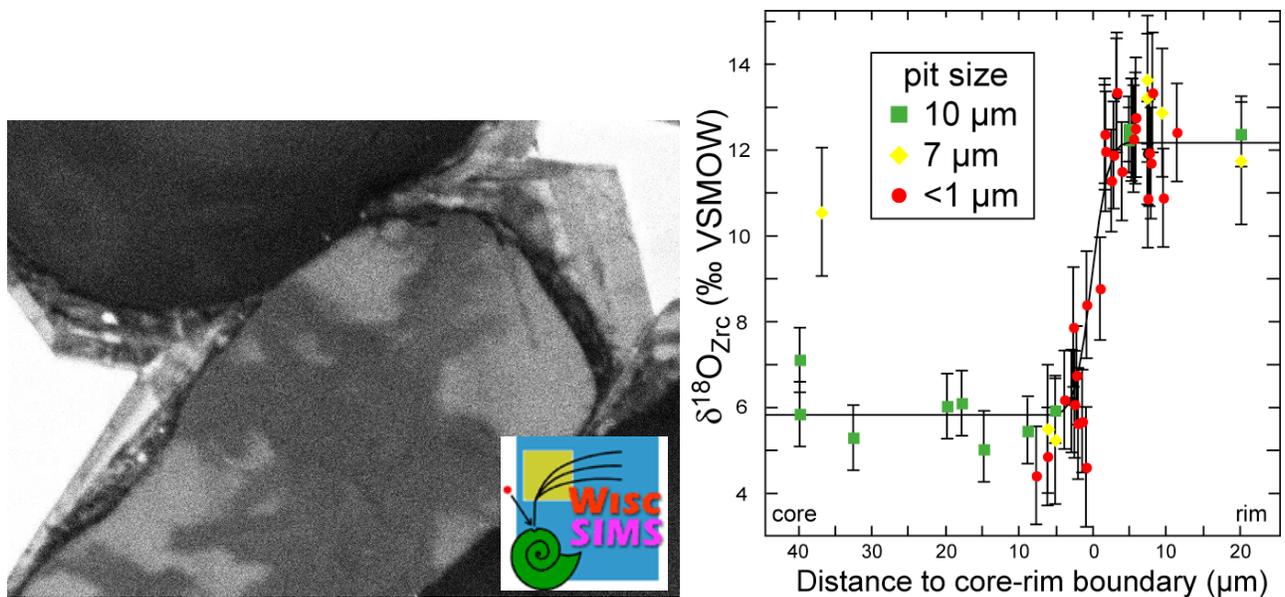


Figure 1. **Left:** CL image of thin syntaxial quartz overgrowths on detrital quartz in Mt. Simon sandstone from the Wisconsin dome (07WI-14, FOV = $250\mu\text{m}$, Trzaskus et al. 2008). **Right:** Analysis of oxygen isotope ratio at Wise-SIMS with spot sizes of 10, 7, and $<1\mu\text{m}$ reveals a sharp diffusion profile within zircon of $\sim 6\text{‰}/2\mu\text{m}$ (Page et al. 2007).

WOODS HOLE OCEANOGRAPHIC INSTITUTION

Department of Marine Chemistry and Geochemistry
Woods Hole MA 02543

Grant: DE-FG02-06ER15775

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

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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: To address the fate and behavior of oil seeping from the ocean bottom at Santa Barbara, we collected 15 sediment samples down current from the seeps. Each sediment sample was analyzed by GC × GC. The spatial distribution of oil forms a plume along the continental shelf that represents a chronic fallout pattern for heavy oil from the persistent surface slicks; average surface currents appear to modulate the distribution of the fallout over a period of 0.4 – 5 days. GC × GC data indicates that the extent of hydrocarbon loss is consistent for all sediments, indicating a common limit to oil weathering with contributions from evaporation, biodegradation, and dissolution compared to fresh seep oil (Figure 1). Compound classes lost to weathering include *n*-alkanes, isoprenoidal alkanes, alkylcyclopentanes, alkylcyclohexanes, alkylbenzenes, and many alkylated PAHs – leaving sediment oil dominated by recalcitrant biomarkers such as hopanes and diasteranes. Considering the amount of oil and quantity of sediment impacted, we estimate a sediment oil burden of $0.3 - 3 \times 10^{12}$ g in the study area, equivalent to 8-80 spills of the *Exxon Valdez* accident of 1989.

Overall, the project is progressing better than expected.

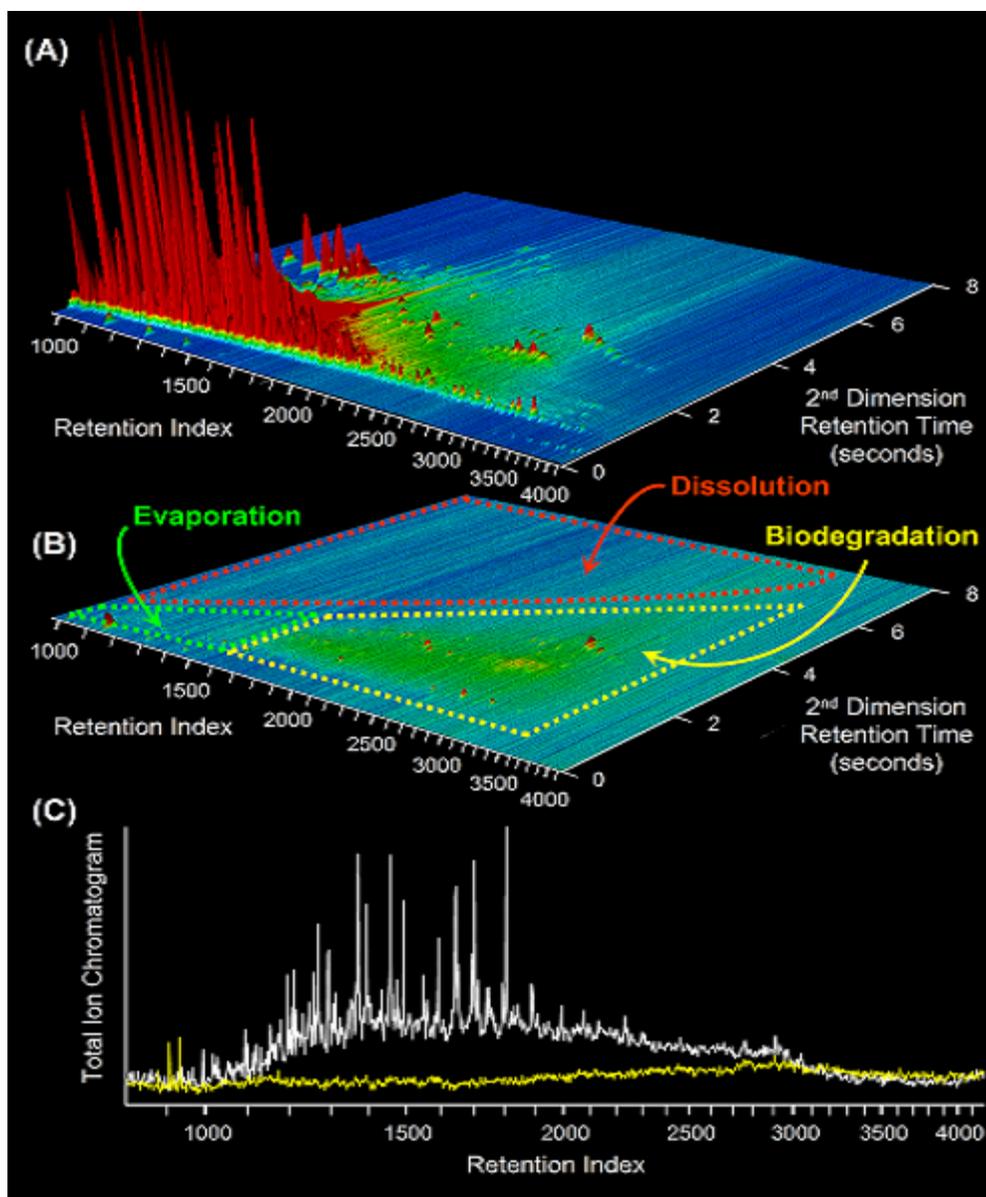


Figure 1. GC × GC chromatograms of A) “fresh” surface slick oil collected above an active oil seep; B) oil extracted from sediment collected down current from the seeps, with regions of the chromatogram marked corresponding to the likely associated forms of weathering; and C) comparison of the signal traces from panels A (white) and B (yellow) collapsed into one dimension. Retention indices in all three panels are consistent with carbon number, i.e. RI = 1000 is *n*-C10, RI = 1500 is *n*-C15, etc., and each chromatogram is scaled to the biomarker, bisnorhopane.

WRIGHT STATE UNIVERSITY

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Grant: DE-FG02-03ER15379

Fluid Chemistry, Surface Chemistry and Fracture Mechanics: An Investigation of the Connection at the Nanoscale

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Objectives: The project objectives center around two major hypotheses: (1) that the surface chemistry of minerals has a direct influence on fracture mechanics at the molecular scale and (2) that changes in the surface chemistry has a quantifiable influence on the sliding resistance between a scanning probe microscope tip and mineral surfaces. The former objective requires development of new capabilities for the Hydrothermal Atomic Force Microscope (HAFM).

Project Description: The project has two main thrusts toward understanding the principal influences on surface chemistry of carbonate minerals upon exposure to aqueous solutions. These areas include the elucidation of lateral force contrast mechanisms in mineral/water interface systems and of the coupling processes among fluid chemistry, surface chemistry, and applied stress and the resulting impacts on subcritical crack growth (SCG) and mineral growth/dissolution using *in-situ* scanning probe microscopy (SPM). Our approach is to quantify the friction forces between an atomic force microscope (AFM) probe tip and carbonate mineral surfaces of interest using frictional force microscopy (FFM). In addition, the surfaces are fully characterized using fluid cell AFM measurements of growth and dissolution kinetics and x-ray reflectivity measurements. These characterization methods allow us to describe both the thermodynamic properties of the surface layers as well as their atomic-scale structure and composition. The FFM measurements then enable us to relate the mechanical surface properties to the chemical and physical properties in a manner that could lead to future applications of the AFM as a surface chemistry-mapping tool with nanometer-scale resolution. In order to achieve the objective of developing improved models for the coupling of fluid chemistry, surface chemistry and mechanical stress at mineral-fluid interfaces, the project will develop a mini-bending jig for the HAFM and make extensive modifications (see Results below) to accommodate the jig and to greatly increase the HAFM scan range. The results from this project will improve our understanding of the surface chemistry of carbonate minerals relevant to surface and subsurface aquifer systems under mechanical stress and on a distance scale (nanometers) that can be computationally modeled at the semi-empirical level.

Results: In the last project period, we have continued to test proposed mechanisms for friction between the AFM probe and mineral surfaces through experimental work on divalent cation-doped surfaces of carbonate minerals. Addressing the mechanisms for lateral force contrast observed in the last project period, FFM was used to study monolayer film mechanics on calcite in aqueous solutions. The major findings in our study of (Cd,Ca)CO₃ and (Sr,Ca)CO₃ films deposited on calcite, based on FFM observations, demonstrated that two key physicochemical factors, previously ignored, must be

determined to correctly link friction forces to surface composition. These two factors are the work of adhesion (related to the force required to break the probe-surface contact) and the contact shear strength. The former property is governed primarily by the surface speciation as regards surface charge on the mineral. When the pH of the aqueous solution is such that the electrostatic forces between probe and sample surfaces are minimal (i.e., near the pH_{PZC} (pH at point of zero charge)), the friction signal goes to zero at zero load. However, oppositely charged probe and sample surfaces result in significant friction at zero applied load due to the resultant adhesion. At higher load however, where mechanical properties become more important in the friction signal, differences in shear strength become apparent. The current hypothesis related to shear strength is that the dehydration enthalpy largely determines the forces that must be overcome to maintain the dynamic sliding contact. For example, in studies of heterogeneously doped surfaces of calcite containing regions enriched in dopant among regions devoid of the dopant, the interplay of the electrostatic and hydration properties results in reversal of the friction differences on the two surface regions. $\text{Cd}^{2+}(\text{aq})$ has a larger hydration enthalpy than $\text{Ca}^{2+}(\text{aq})$, which, by hypothesis, will give Cd-rich regions higher friction than Ca-rich regions. Fig. 1 (top) shows friction-load data on Cd-rich and Ca-rich surfaces revealing that at low load, the Ca-rich regions have higher friction due to stronger adhesion between the probe and sample but at high load, Cd-rich surfaces display higher friction due to the larger shear strength of the probe-surface contact (evidenced by the larger slope in the Cd-rich friction-load plot). By applying similar reasoning to the $(\text{Sr,Ca})\text{CO}_3$ (rhombohedral) system, the hydration enthalpy hypothesis predicts that Sr-rich surfaces will have lower shear strength (lower friction-load slope) when compared with Ca-rich surfaces. The experimental data (Fig. 1 (bottom)) show negligible difference in the slopes of the two friction-load plots, suggesting that additional factors, in addition to adhesion strength, must be important to consider. One explanation for the lack of agreement with the hypothesis is that the relatively poor mismatch of Sr and Ca ion sizes produces a Sr-rich film that has significant strain, and therefore has mechanical properties (e.g., compressibility) that significantly depart from the properties of the Ca-rich regions. This work has demonstrated the sensitivity of FFM to surface chemistry, but several factors are important in determining friction forces under controlled conditions. These factors, including adhesion, shear strength and material compressibility are not entirely separable when considering the friction of molecularly-thin films but the foundation developed in this work will lead to new methods in determining spatially-resolved chemistry of mineral-water interfaces.

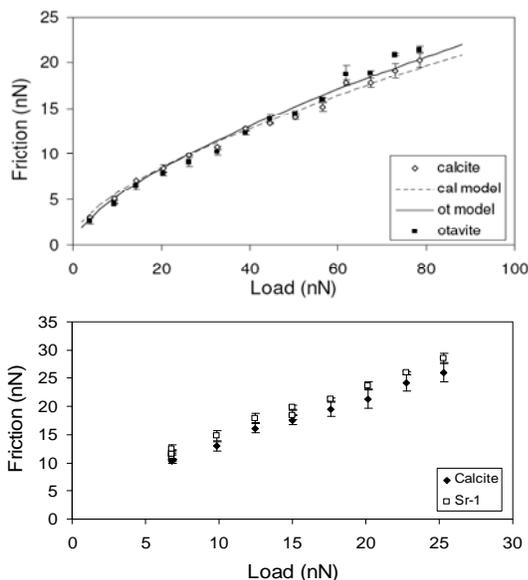


Figure 1. (top) In-situ FFM-acquired friction-load data from a calcite surface (open diamonds) and from a calcite surface covered by a Cd-rich monolayer film (black squares). The larger slope of the Cd-rich data trend correlates with the larger hydration enthalpy of the Cd ion. Due to the differences in pH_{PZC} for CdCO_3 vs. CaCO_3 , the friction force does not converge at zero load. Fit lines are based on the Johnson-Kendall-Roberts contact mechanical model. (bottom) *In-situ* FFM-acquired friction-load data from a calcite surface (black diamonds) and from a calcite surface covered by a Sr-rich monolayer film (open squares). The slopes of the two plots are identical, suggesting hydration enthalpy may not dominate the friction-load behavior.

UNIVERSITY OF WYOMING

Department of Geology and Geophysics
Laramie WY 82071

Grant: DE-FG02-06ER15825

Waveguide Scanning Photocurrent 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) nanocrystalline 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 WO₃ films by CVD as alternative approaches if the hematite films prove to be less efficient than ultimately needed at low light intensities.

Results: We have acquired the necessary waveguide apparatus, laser, and other equipment, refurbished an existing laser, and set up two new CVD systems in a lab using three fume hoods. We have now manufactured photosensitive tips for the proposed Waveguide Scanning Photocurrent Microscopy (WaSPM). We have successfully tested for light outscattering by these and other tips, and have detected outscattered light. The first full WaSPM apparatus has been constructed in our machine shop, and incorporates a commercial electrochemical STM system with the total-internal reflection laser configuration in order to attempt our first microscopic images. We have also included a waveguide holder for use of subwavelength waveguides in the microscope (~200 nm thick).

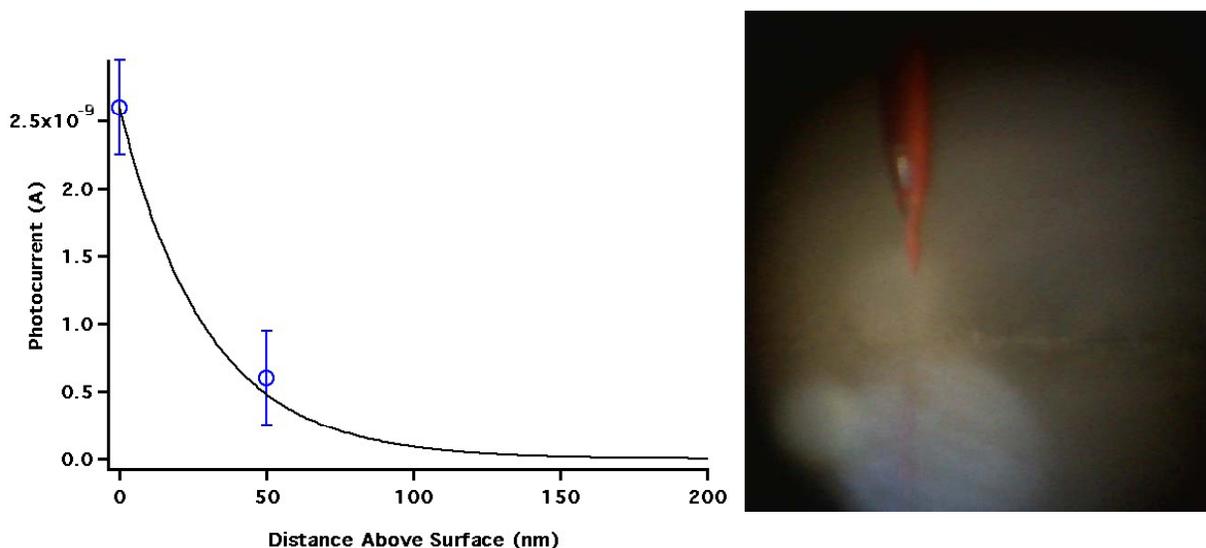
a) As stated in previous years, we have continued to study the anisotropy of photocurrent generation in hematite. This has resulted in a manuscript current in preparation in which we outline evidence that edges of hematite crystals have a less negative photocurrent onset potential than crystal basal faces.

b) Another problem in optimization is the limitation of photocurrent density by recombination mediated by an “intra-gap” state. One hypothesis is that water impurities, probably in the form of internal OH defects, are the origin of at least some of the intragap states. Hematite films made by atmospheric pressure chemical vapor deposition using water-saturated air as well as dry air indeed show a difference in photocurrent. We have examined this question in detail. The wet-preparation films are the same thickness as the dry-preparation films, but show photocurrent transient spikes in chopped light to much more positive potential than do the dry-preparation films. We conclude that the intragap states that limit

photocurrent in hematite extend over a wider portion of the bandgap in the wet films vs. the dry films. The dry films also have much higher charge carrier densities.

c) Our current “best” Si-doped hematite films rival the best that have been reported in the recent literature with regard to photocurrent generation. This development has implications for solar energy generation as well as the WaSPM microscope.

d) We have performed experiments in boosting tip photocurrent in the WaSPM by using electrolyte solutions containing oxalate. The result, as anticipated, is a significant increase in photocurrent for the photosensitive tips.



The figure at left shows measured photocurrents near a total internal reflection surface (zero recorded at large distances) compared to the expected evanescent wave decay for the laser wavelength. The image at right is of an iron oxide coated tip in the WaSPM.

UNIVERSITY OF WYOMING

Department of Geology and Geophysics
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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 change conformation in relation to redox reactions, adsorption, and interaction with other proteins. 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 have completed an electrochemical study of isolated and purified OmcA and MtrC (provided courtesy of Liang Shi and Brian Lower 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. Cyclic voltammetry of isolated proteins is similar to that of the whole organisms. The midpoint potentials of redox peaks are slightly more negative for isolated OmcA and for the MtrC-deficient mutant (which is presumably not deficient in OmcA) than for MtrC and the OmcA-deficient mutant. The double-deletion mutant show no electrochemical activity. This work has been submitted for publication.

2) Comparative Optical Waveguide Lightmode Spectroscopy (OWLS) and Quartz Crystal Microbalance with Dissipation (QCM-D) studies are providing a window on the different properties of outer-membrane vs. periplasmic cytochrome. We will concentrate, in this summary, on this comparative data. We have found some very substantial differences in the behavior of MtrC as compared to OmcA. Our findings include:

a) MtrC desorbs readily from oxide surfaces in response to dilution into protein-free buffer, whereas OmcA does not.

b) MtrC is a very low density protein in the adsorbed state – of the total adsorbed mass, only about 23% is polypeptide 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. This percentage is larger than those reported for most other proteins.

c) MtrC adsorbs to alumina in a different pH range from OmcA.

d) The periplasmic protein PpcA from *Geobacter sulfurreducens* is a compact protein that carries little solvent with it (18%), desorbs readily, and appears to contract slightly upon adsorption, whereas the outer-membrane cytochrome OmcB from the same organism is less dense than PpcA (37% solvent; Fig. c), though it desorbs upon dilution more than does OmcA from *Shewanella oneidensis* MR-1.

e) Results similar to those for PpcA (above) were found for ApcA from *Acidiphilium cryptum*.

f) The decaheme outer membrane cytochrome from *Shewanella oneidensis* MR-1 OmcA is the least dense protein we have measured so far – only 18% protein.

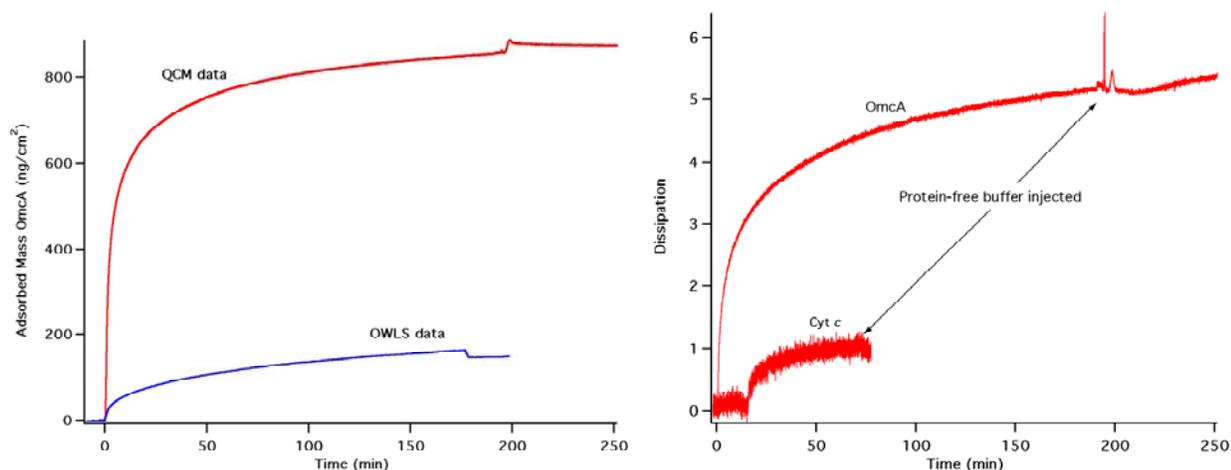
g) The density of Stc, a periplasmic tetraheme cytochrome from *S. oneidensis* MR-1, is 75% protein and desorbs almost completely upon dilution.

h) For comparison, we have run a set of experiments with cytochrome *c* (cyt *c*). The cyt *c* is 30% solvent in the adsorbed state, which is comparable to other periplasmic cytochromes measured in this study (cyt *c* occurs in mitochondria, but in a location analogous to the periplasmic space of bacteria).

i) A summary of results so far clearly shows that periplasmic cytochromes are relatively dense, with low solvent content, whereas outer-membrane cytochromes have very high solvent content and low density. This result is consistent with the possibility of greater conformational flexibility for outer-membrane cytochromes.

j) Energy dissipation results are consistent with the OWLS/QCM results, with relatively little dissipation for cyt *c* and other periplasmic cytochromes (indicating a more rigid and compact adsorbed molecule) and high dissipation for OmcA (indicating a “floppier” adsorbed molecule).

The figures below are two examples of our results. On the left is the comparison of QCM to OWLS data for adsorption of OmcA. On the right is comparison of the dissipation results for OmcA compared to those for the more dense cyt *c*.



YALE UNIVERSITY

Departments of Geology & Geophysics and Physics
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: When a premelted film forms around a foreign particle within a subfreezing solid, the particle can migrate under the influence of a temperature gradient, a phenomenon referred to as regelation or thermodynamic buoyancy. A principal goal of our work at the DoE's APS at Argonne is to understand this phenomenon quantitatively. We have focused on the role that directional temperature gradients may play in segregation of particles in our frozen colloidal suspensions. As noted last year, we have taken the approach that, while this may create important issues for our XPCS experiments, in the natural

environment there are very often persistent temperature gradients and hence segregation is a natural phenomenon. (1) Our proposed mechanism for the formation of ice lenses in colloidal clays is based on a generic instability of the ice-clay interface. We showed that a dilute clay suspension can be treated like a binary alloy with the particles playing the role of the solute. Because of its basic nature and broad applicability the work was published in Physical Review Letters. (2) From the XPCS data, our working hypothesis is that the particles cluster during freezing. This is supported by both static scattering data at APS and observations from video imagery in our Yale lab under conditions modeling those in the vacuum can at the APS. Specifically, we observe that dark regions appear upon freezing and a rapid sedimentation of visible clusters upon melting. This is also supported by the static scattering data that exhibits a very high intensity near the q -origin, consistent with a cluster model of the form factor. For example, our frozen solutions at $-25\text{ }^{\circ}\text{C}$ are fit with a fractal cluster form factor that incorporates the polydisperse sphere form factor and a monodisperse hard sphere structure factor. However, only a full analysis of the static scattering will tell us if there really are any systematic changes in the volume fraction or cluster size over time or temperature that are not discernible by video imagery. (3) Perhaps ironically, efforts to isolate and understand the magnitude of methane clathrate hydrate in marine sediments and to mitigate anthropogenic climate change through sequestration of greenhouse gases such as CO_2 in geologic formations rely on the same detailed knowledge of flow and phase change in a porous medium on small scales inaccessible in numerical reservoir simulations. Hence, the relevance of our approach to the small-scale fluid dynamic and thermodynamic processes underlying the formation of two-phase two-component systems such as ice on the polar oceans or the flow of CO_2 through porous rock. (a) We have uncovered the basic influence of an external shear flow on the buoyant instabilities inherent in the directional solidification of a dendritic mushy layer. Perturbations of the mush-liquid interface lead to perturbed flow in the bulk fluid that create pressure variations along the mush-liquid interface, thereby driving flow in the mushy layer. The conditions for instability have been identified theoretically and experimentally. (b) In the setting of viscous flow in a porous media, of relevance to the sequestration problem, we studied the axisymmetric propagation of a viscous gravity current over a deep porous medium into which it drains. We developed a theory for its propagation and drainage and solved it numerically in the case of constant input from a point source. We developed analytical expressions for the steady profile that compared well with our experiments, which used a bed of vertically aligned tubes. Importantly, we discovered that analogous experiments using glass beads as the porous medium exhibit a variety of unexpected behaviors; overshoot of the steady-state radius and subsequent retreat, thus highlighting the importance of the permeability structure in these systems of clear relevance to the natural environment.

DOE/OBES Geosciences Research: Historical Budget Summary
(Thousands of dollars)

ON-SITE INSTITUTION	FY04	FY05	FY06	FY07	FY08
Argonne National Laboratory	480	535	758	461	506
Idaho National Laboratory	50	50	50	60	
Los Alamos National Laboratory	1409	1320	963	1050	415
Lawrence Berkeley National Laboratory	2758	3240	2939	4063	4416
Lawrence Livermore National Laboratory	1598	1335	1141	1270	1172
Oak Ridge Institute for Science and Education			105	12	
Oak Ridge National Laboratory	1250	2075	1750	1750	1850
Pacific Northwest Laboratory	920	860	910	975	980
Sandia National Laboratory	1274	980	975	1130	1170
total, on-site	9739	10395	9591	10771	10509
total, off-site	10410	10492	9544	9869	9605
total, operating	20149	20887	19135	20640	20114
total, equipment					
Total GEOSCIENCES	20149	20877	19135	20640	20114
OFF-SITE INSTITUTION					
Alabama, Univ. of (Dixon)			47	48	48
Alabama, Univ. of (Dixon)				58	60
American Chemical Society (Brandes)	5				
American Chemical Society (Criscenti)					3
American Society for Microbiology (Colwell)		5			
Arizona, Univ. of (Roth)	25				
Arizona State Univ. (Shock)	239	101			

Arizona State Univ. (Hervig/Williams)	133	132	135		
Boston Univ. (Klein)	126	130	134		145
Caltech (Stolper)	162		167	172	177
Caltech (Wasserburg)	215	200			
Calif., Univ. of Berkeley (Banfield)		200	200	200	
Calif., Univ. of Berkeley (Banfield)	150	153	123		177
Calif., Univ. of Berkeley (Helgeson)	163	167		100	100
Calif., Univ. of Berkeley (Wenk)		150	150	150	
Calif., Univ. of Davis (Navrotsky)	202	194	197	215	221
Calif., Univ. of Davis (Rustad)	97	78	82	85	
Calif., Univ. of Davis (Rustad)		136	137	68	69
Calif., Univ. of Davis (Casey)	113	319		135	
Calif., Univ. of Davis (Rundle)	135	143	151		156
Calif., Univ. of Los Angeles (Harrison/McKeegan)	148	79			
Calif., Univ. of Santa Barbara (Boles)	86	79	95	95	83
Calif., Univ. of Santa Barbara (Gibou)					190
Calif., Univ. of Santa Cruz (Wu)	306	318	327		
Calif., Univ. of San Diego (Weare)	125		269		138
Chicago, Univ. of (Sutton/Rivers)	575	600	697	718	739
Chicago, Univ. of (Sutton)	143	125	148	139	138
Chicago, Univ. of (Richter)	102	138	143	148	174
Clark Univ. (Kudrolli)	47		59	54	55
Clay Minerals Society (Cygan)				10	
Clay Minerals Society (Ross)					5
Colorado School of Mines (Batzle)	117	114			
Colorado School of Mines (Tsvankin)	249	150		75	
Colorado School of Mines (Snieder)			97	101	106

Colorado School of Mines (Benson)				79	82
Colorado, Univ. of (Rajaram)	72				
Colorado, Univ. of (Spetzler)	155	55	58	60	62
Connecticut, Univ. of (Torgersen)	33		32	34	35
Delaware, Univ. of (Wood)	142				
Florida, Univ. of (Ladd)		155	108	111	
George Washington Univ. (Teng)		98		48	
George Washington Univ. (IPA Lesmes)	225	150	6	5	
Georgia State Univ. (Elliott)		22			
Georgia Tech (Stack)				210	
Gordon Res. Conf. (Kronenberg, Jessell)	10				
Gordon Res. Conf. (Hirth)			10		10
Harvard Univ. (Martin)	83	81	96	99	102
Houston, Univ. of (Weglein)		101		51	
Idaho, Univ. of (Wood)	10	10			
Idaho State Univ. (Magnuson)			88	90	93
Illinois, Univ. of (Kirkpatrick)	241	248	216		
Illinois, Univ. of (Bethke)	92	270		135	138
Illinois, Univ. of (Bass)					151
Illinois, Univ. of Chicago (Sturchio)	60	62	51	53	54
Illinois, Univ. of Chicago (Nagy)	148	145			
Indiana, Univ. of (Schimmelman)	112	119	141	133	128
Johns Hopkins Univ. (Garven)	80	88	124		
Johns Hopkins Univ. (Veblen)	289	205	205	250	250
Johns Hopkins Univ. (Sverjensky)	137	153	158	163	176
Johns Hopkins Univ. (Jahren)			101	105	
Louisiana State Univ. (White)	46				

Louisiana State Univ. (Dutrow)	9	9			
Maryland, Univ. of (Tossell)	99	99			
Maryland, Univ. of (Zhu)				130	
Mass. Inst. Tech. (Evans)	222	235	304	318	328
Mass. Inst. Tech. (Rothman)	160		160	168	172
Mass. Inst. Tech. (Durham)				40	42
Massachusetts, Univ. of (Boutt)		145		41	
Michigan State Univ. (Kirkpatrick)					230
Michigan Tech Univ. (Turpening)		144			
Mineralogical Society of America (Speer)	20		35	10	10
Mineralogical Society of America (Speer)			5		10
Minnesota, Univ. of (Kohlstedt)	38	39	176	185	192
Missouri, Univ. of (Appold)					107
NAS/NRC (Schiffries/DeSouza)	90	90	90	90	90
NAS (Linn)		200			
New England Res. (Brown)	206	100			
New Mexico Inst. Min. Tech. (Wilson)	108				
New Mexico, Univ. of (Weissmann)					15
NY, City Univ. of CC (Koplik)	102		107	109	110
NY, City Univ. of CC (Makse)	85		85	100	100
NY, State Univ. of Stony Brook (Schoonen)	66		87	83	85
NY, State Univ. of Stony Brook (Wong)	124	128	125	128	132
NY, State Univ. of Stony Brook (Lindquist)		64	87	66	
North Texas, Univ. of (Bagus)	35	35	35	50	50
Northwestern Univ. (Rudnicki)	118	123	113	114	119
Northwestern Univ. (Geiger)		3	49	50	52
Northwestern Univ. (Andrade)					304

Notre Dame, Univ. of (Maurice)	178				
Notre Dame, Univ. of (Maurice)	6				
Ohio State Univ. (Lower)	71				
Ohio State Univ. (Allen)	41	42	44	80	79
Oklahoma, Univ. of (Elmore)		47			
Oregon State Univ. (Haggerty)					
Oregon State Univ. (Egbert)	86		98	95	104
Penn State Univ. (Brantley)		174	176	223	261
Penn State Univ. (Brantley)	9				
Princeton Univ. (Peters)		114	160	169	
Purdue Univ. (Pyrak-Nolte)	109		288		117
Rensselaer Polytech. Inst. (Newell)	47				
Rensselaer Polytech. Inst. (Watson)	247	208	215		199
Society of Exploration Geophysics (Smith)			5		
South Carolina, Univ. of (Wilson)	50	54	54		
Stanford Univ. (Mavko)	150				
Stanford Univ. (Borja)		99	102	110	110
Stanford Univ (Knight)	139	146			
Stanford Univ. (Nur)	208	217		207	221
Stanford Univ. (Pollard/Aydin)	261	261		273	264
Stanford Univ. (Tchelepi)					208
Temple Univ. (Strongin)	91		91	83	87
Texas A&M Univ. (Morse)	133	135	157	149	153
Texas A&M Univ. (Datta-Gupta)	138	140	143	142	145
Texas, Univ. of (Katz)	71	75	78	75	78
Texas, Univ. of (Laubach)		227	197	241	264
Texas, Univ. of Dallas (McMechan/Bhattacharya)	96				

Tufts Univ. (Garvin)				227	
Virginia Tech (Rimstidt)	118	124			
Virginia Tech (Dove)		178	226	250	202
Virginia Tech (Hochella)	104	98	122	127	143
Virginia Tech (Hochella)					4
Wisconsin, Univ. of (Alumbaugh)	96				
Wisconsin, Univ. of (Goodwin)		108		73	
Wisconsin, Univ. of (Valley)	204	210	217	234	239
Wisconsin, Univ. of (Gilbert)				325	
Woods Hole OI (Whelan)	204				
Woods Hole OI (Zhu)	48	50	61		
Woods Hole OI (Seewald)	179	177	184		
Woods Hole OI (Reddy)			157	164	172
Wright State Univ. (Higgins)	71	73	98	110	115
Wyoming, Univ. of (Eggleston)	45	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	130		
Yale Univ. (Bolton)				77	
Other			1		
OFF-SITE TOTALS	10410	10492	9544	9869	9605