Summary of FY 2006 Geosciences Research

December 2007

U.S. Department of Energy

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

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FORWARD

The Department of Energy supports research in the geosciences in order to provide a sound foundation of fundamental knowledge in those areas of the geosciences that are germane to the Department of Energy's many missions, and those which provide stewardship for geosciences research capabilities at the DOE National Laboratories. Excellent fundamental science that can improve and support DOE's mission needs will also provide basic knowledge applicable to many other areas of Earth science beyond DOE's borders. 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 Department of Energy 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 in 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. 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 is directed by the Department of Energy's (DOE's) Office of Science (SC) through its Office of Basic Energy Sciences (OBES). 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 though 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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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 principle 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: (1) ion adsorption at mineral-water interfaces, (2) interfacial hydration structure, (3) advances in X-ray based interfacial techniques. Observations of mono- and divalent ions adsorbed at muscovite (001) revealed that monovalent ions adsorbed as expected in both coverage and position (i.e., as an inner-sphere ion in the ditrigonal site), while divalent ions were found to co-exist as both inner- and outer-sphere species, revealing new insight into the importance of outer-sphere species in ion adsorption. Se(IV) was found to bind as an inner-sphere species to hematite (100). Observations of the Al_2O_3(102)-water interface surface revealed a different surface termination than had been previously assumed and a multi-layer hydration structure extending ~5 Å. The hydration structure at a hydrophobic interface was also determined demonstrating an upper limit of ~3 Å to the purported interfacial "vapor" layers at these interfaces. We demonstrated, for the first time, the ability to image the lateral surface topography of a mineral surface using interfacial X-ray microscopy. This fully non-invasive approach images sub-nanometer high topography (e.g., steps) in a mineral surface through X-ray phase contrast. The use of area detectors for measuring X-ray reflectivity was demonstrated allowing for ~40-fold improvement in data acquisition rates.

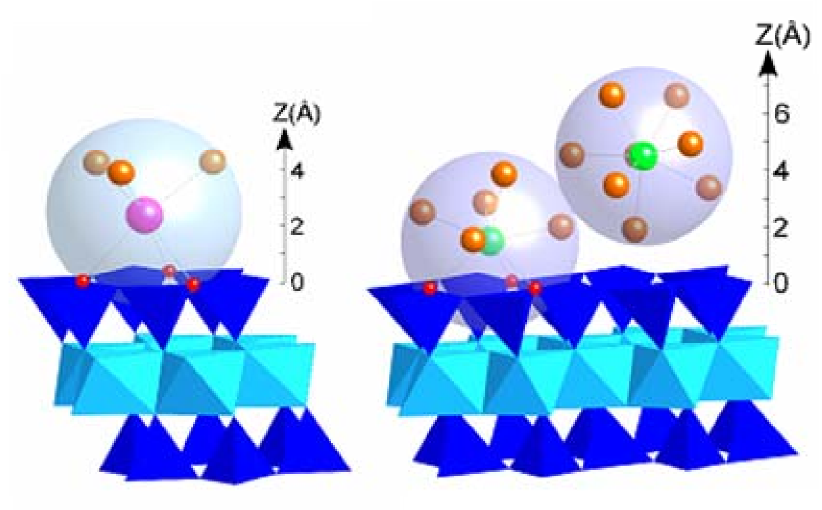

Figure: Schematic model depicting the vertical distribution of Rb^+ (left) and Sr^{2+} (right) at the muscovite-water interface along with the adsorbed ion's hydration shell. Note that while the height of the inner-sphere species is consistent with direct contact between the ion and the surface oxygen (i.e., displacing some of the ions waters of hydration), the outer-sphere Sr^{2+} species is separated from the surface by a water layer preserving its ion hydration shell.

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Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces

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Objectives: This project aims to: 1) Determine chemical mechanisms for dissolution of specific surfaces of major oxide minerals, 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 major 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: The solid-on-solid kinetic Monte Carlo model of Lasaga and Blum for dislocation-controlled etch pit growth was extended to the growth of etch pits under the control of multiple dislocations and point defects. This required the development of algorithms that are $O(10^3) - O(10^4)$ times faster than primitive kinetic Monte Carlo models for surfaces with areas in the range $1024\times1024 - 4096\times4096$ lattice sites. Simulations with multiple line defects indicated that the surface morphology coarsens with increasing time and that the coarsening is more pronounced for large bond-breaking activation energies. For small bond breaking activation energies, dissolution enhanced by line defects perpendicular to the dissolving surface resulted in pits with steep sides terminated by deep narrow hollow tubes (nanopipes). Larger bond breaking activation energies led to shallow pits without deep nanopipes, and if the bond breaking activation energy was set large enough, step flow was the primary dissolution mechanism, and pit formation was suppressed. Simplified models that neglected the far field strain energy density but included either a rapidly dissolving core or an initially empty core led to results that are qualitatively similar to those obtained using models that included the effects of the far field stress and strain. Simulations with a regular array of line defects showed that microscopic random thermal fluctuations play an important role in the coarsening process.

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Upgrade of the Geophysical Computational Cluster at LBNL

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Objectives: Provide advanced computational capability in geophysics to address needs in subsurface imaging using seismic and electromagnetic wavefields. 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: A new 256 processor DELL cluster has was installed at Lawrence Berkeley National Laboratory (LBNL) Earth Sciences Division. The new cluster was assembled through a joint collaborative effort between LBNL's Scientific Cluster Support (SCS) Division, Dell and the National Center for Supercomputing Applications (NCSA) University of Illinois Urbana. In all, only eleven days were required by the teams in assembling the cluster and passing of acceptance testing which allowed staying on time and under budget ($500k). Sustained performance of the new cluster on large-scale geophysical inverse modeling codes, using all 256 processors, is commensurate with other similar cluster platforms within the DOE complex, such as Pacific Northwest Laboratory (PNL) Molecular Science Computing Facility - MPP2. Its 1.5 Tflop performance places this computer well within the "top 500 list" in the world. Scaling tests on the new cluster also show excellent scaling, as time to solution decreases in direct proportion to the number of processors employed for a given problem. The scientific benefit of the new cluster will be employed in the advancement of subsurface science using new geophysical imaging technologies. With dedicated and sufficient computing power these imaging technologies will now offer a great benefit to understanding 3-D complex subsurface processes at an unparalleled level of resolution and accuracy and directly impact BES Geosciences missions in Energy and Environment, including its 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 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. Our aim is to advance the state of the art of the isotopic approaches, and to use these advances to investigate fundamental issues in geochemistry. Mathematical models are developed to help extend the application of isotopic measurements. Modeling and systematic measurements of simple natural systems are supplemented by efforts to improve sampling methodologies and measurement techniques.

Results: (1) *U-Th-He chronologies*: The U-Th-He method can theoretically be used to measure the ages of volcanic rocks as young as a few thousand years and as old as several million years, and hence could span the gaps often encountered with other geochronological methods. One limitation of the approach is that it has been applied mainly to minerals with high U concentrations, which are uncommon in volcanic rocks. We have demonstrated that U–Th/^{4}He ages can be obtained from relatively U-poor olivine phenocrysts from late Quaternary basalts. The approach employs abrasion to remove the outer rinds of olivine crystals, which addresses problems with ^{4}He implantation from U-rich groundmass, and a specially designed extraction system that allows U, Th and He concentrations and isotopic compositions to be measured on the same olivine grains. The U-Th/He approach was also combined with ^{3}He cosmogenic measurements, and constitutes a new U-Th-^{4}He-^{3}He method that allows uncertainties in both methods to be reduced.

(2) *U-Sr groundwater velocimeter*: The ^{87}Sr^{86}Sr ratio and (^{234}U/^{238}U) activity ratio of groundwater are sensitive indicators of water-rock interaction, and thus provide a means of quantifying both flow and reactivity. The ^{87}Sr^{86}Sr values in ground waters are controlled by the ratio of the dissolution rate to the flow rate. Similarly, the (^{234}U/^{238}U) ratio of natural ground waters is a balance between the flow rate and the dissolution of solids, and α-recoil loss of ^{234}U from the solids. We have been able to show that by coupling these two isotope systems, and taking advantage of their differing dependencies on flow and reaction, it is possible to constrain both the long-term (ca. 100’s to 1,000’s of years) flow rate and the bulk dissolution rate along groundwater flow paths. Estimates of long-term flow velocity, especially in vadose zone environments, is important for forecasting future migration distances and impacts of radionuclides.

(3) *U-series alpha-recoil as a nanoscale probe of natural systems*: Our studies of (^{234}U/^{238}U) of fine-grained marine sediments show systematic effects suggesting that α-recoil associated with the

decay of ^{238}U is primarily responsible for ^{234}U depletions in minerals. Because the rate of ^{234}U loss reflects the scale of recoil, which is 30-50 nm, and the shape and surface properties of mineral grains, the U-series characteristics of minerals constitutes a nanoscale probe of mineral surfaces. The rate of this process in natural systems also affects the interpretation of most U-series data from fluids. Models for quantifying the α-recoil loss fraction based on theoretical estimates of recoil range, mineral grain geometry, surface area constraints, and chemical methods have been developed. We also are building a data set for size –separated granitic sediment grains in the range of a few microns to ca. 50 μm. The U series effects complement other measurements of grain surface area and give additional information on surface roughness and dissolution rates.

(4) *U comminution age method for Quaternary sediments*: High precision uranium isotope measurements of marine clastic sediments have been shown to provide information on the transport time of continental sediment from its origin as glacial flour and soil, to its deposition on the seafloor. The ^{234}U/^{238}U ratios of the silicate portion of sediment from the North Atlantic sea floor, isolated by leaching with hydrochloric acid, are significantly less than the secular equilibrium value and show large and systematic variations that are correlated with glacial cycles and sediment provenance. The ^{234}U depletions are used to calculate "comminution ages" of the sediment - the time elapsed between the generation of the small ($\leq$ 50 μm) sediment grains in the source areas by comminution of bedrock, and the time of deposition on the seafloor. The comminution age approach could be used to date Quaternary non-marine sediments, soils, and atmospheric dust, and may be enhanced by concomitant measurement of ^{226}Ra/^{230}Th, ^{230}Th/^{234}U, and cosmogenic nuclides.

(5) *Ca isotope fractionation probe of mineral precipitation processes*: The precise mechanisms by which dissolved ions are attached to mineral surfaces to allow solid crystals to grow from solution are both complex and poorly characterized even for familiar minerals. We study the processes at mineral surfaces using isotopes, an approach based on chemical differences between isotopic species - their mobility in solution, rates of attachment and detachment from mineral surfaces, and thermodynamic affinity in different chemical bonding environments. We have shown that at equilibrium there is no Ca isotopic fractionation during precipitation of calcite. However, laboratory experiments and studies of natural calcite indicate that calcite precipitated from aqueous solution has Ca isotope ratios that are shifted relative to those of the Ca ions in solution. Because the equilibrium fractionation is near zero for Ca, the isotopic fractionations observed are entirely dependent on processes at the mineral-water interface. Recent results indicate that Ca isotope fractionation can be modeled assuming that isotope-dependent attachment kinetics are the primary cause.

(6) *Collaborative studies*: We also work 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 the 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 soils and fractured rocks is strongly dependent on the water content (saturation), with flow and transport rates at low saturation levels controlled by properties of water films. However, some basic properties of water films in unsaturated media remain poorly understood. Two environmentally important characteristics being investigated in this study are the film thicknesses dependence on capillary (matric) potential, and possible dependence on major ion chemistry.

Project Description: Capillary potentials of water films coating mineral surfaces (smooth as well as rough) are being controlled in a small suction plate chamber by equilibration with aqueous solutions under regulated sub-atmospheric pressures. The Kapton-windowed chamber is placed in front of an X-ray beam (National Synchrotron Light Source X26A, and Advanced Photon Source 13-IDC) used to determine film thicknesses through X-ray fluorescence of monovalent (Rb^+ and Br^-) and divalent (Ca^{2+} and SeO_4^{2-}) ion tracers in the water films. These hard X-ray synchrotron sources are necessary for efficient X-ray fluorescence monitoring of ionic tracers in water films within sealed environmental control chambers. The measurements on flat mineral surfaces are providing information on limiting conditions for unsaturated flow and transport, and also test various equilibrium models for adsorbed water film thickness. The experiments on microscopically rough surfaces, including natural fracture surfaces, are testing capillary film flow models.

Results: Using aqueous solutions of RbBr, $MgSeO_4$, and $CaSeO_4$ (up to 330 mM), film thickness standards were prepared by evaporating these salts on filter paper and tested at NSLS X26A. A linear X-ray fluorescence response was measured on calibration samples (Rb^+, Br^-, and SeO_4^{2-}) up to an equivalent film thickness of 500 nm, with a detection limit of about 20 nm. The lower detection limit relative to our earlier water film studies at X26A was largely from more efficient X-ray fluorescence detection (9-element Ge detector). Measurements of average film thicknesses and film transmissivities have been completed on several natural rough fracture surfaces. The most recent experiments have focused on basic measurements on flat quartz glass surfaces, at very near-zero matric potentials. We have successfully measured water films as thin as 90 nm using this method. The measured film thickness-potential trends (Figure 1) are qualitatively in agreement with an early model derived by Irving Langmuir, but the data are indicative of generally thicker films (consistent with other more recent studies done with less accurate control over water potentials). A predicted ion valence dependence of film thicknesses is being tested through comparisons of systems containing RbBr versus $CaSeO_4$ and $MgSeO_4$ solutions.

Water films in the range of tens to hundreds of nm thickness have been inferred to be common in unsaturated soils and rocks, yet have previously been inaccessible to direct measurements, even by synchrotron X-ray microtomography. This new approach is allowing direct quantification of unsaturated transport properties within water films under environmentally relevant conditions, including physicochemical influences on unsaturated hydraulic properties. It is particularly useful for measurements of area-averaged (nominally 1 mm^2) film hydraulic properties on natural, rough surfaces.

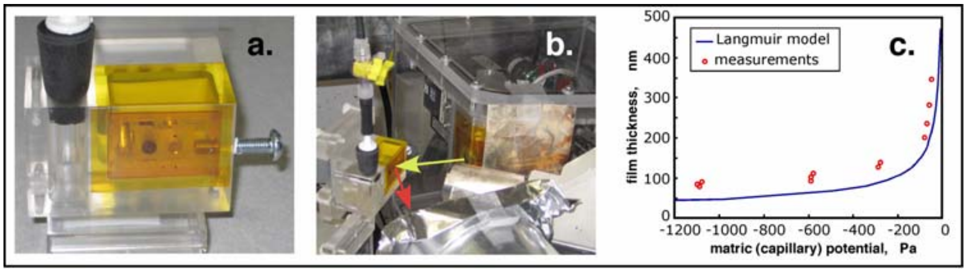

Figure 1. Water film thickness measurements on mineral grain surfaces. (**a.**) Chamber with quartz glass sample on fritted glass plate (behind Kapton film window). The tracer solution reservoir is on the left, and its potential is regulated by controlling the subatmospheric pressure in the reservoir headspace. (**b.**) Sample chamber in position at NSLS X26A. The monochromatic incident X-ray beam path is illustrated by the yellow arrow, and X-ray fluorescence returning to the detector is illustrated with the red arrow. (**c.**) Comparisons between measured RbBr water film thicknesses on quartz glass and predictions based on the Langmuir model (for a 1:1 solution).

Clay Mineral Surface Geochemistry

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Objectives: The overall objective of this project is to investigate the properties of clay mineral nanoparticles at molecular scales using computer simulation methods. Current research focused on the isotopic mass dependence of the diffusion coefficients of ionic solutes in liquid water, a topic of great importance in isotope geochemistry as applied to investigate fluid-rock interactions.

Project Description: Molecular dynamics simulations of one ion (Li$^+$, Cl$^-$ or Mg^{2+}) and 215 water molecules in a periodically-replicated, cubic simulation cell (see Fig. 1 inset) were carried out with the program MOLDY on supercomputers at the National Energy Research Scientific Computing Center. Configuration and velocity data were saved every 5 steps (every 2 steps for simulations with solutes masses smaller than 3 Da) during 8 ns simulations. Liquid water interactions were described by the extended simple point charge model, in which water molecules are rigid and non-polarizable. Coulomb interactions between water molecules result from discrete charges located on each atom, while short-range interactions between O atoms are described by a Lennard-Jones (LJ) 6-12 potential function. Besides coulomb interactions, short-range ion-water interactions were also described using a LJ 6-12 potential. Ion diffusion coefficients were calculated with output configuration and velocity data using a conventional quadrature. Simulations were performed at 348 K for each ion and for isotopic mass in the range 1-1000 Da. Diffusion coefficients were examined for mass dependence by making log-log plots for isotopic mass up to100 Da (Fig. 1).

Results: Our results showed that the diffusion coefficients of lithium, chloride, and magnesium isotopes in liquid water follow an inverse power-law dependence on isotopic mass ($D_i \propto m_i^{-\beta}$, where D_i is the diffusion coefficient of an ion with isotopic mass m_i). The power-law exponents we found were consistent with those deduced from the very recent experimental measurements published by our DOE-BES collaborators, Frank Richter and John Christensen: β-values equal to 0.01483 ± 0.00169, 0.0258 ±

0.0144 and – 0.000783 ± 0.001492, respectively, for Li^+, Cl^- and Mg^{2+} in liquid water at 348 K. Figure 1 shows an example of this agreement for Li^+ in the form of a log-log plot of D_i against m_i.

Further analysis of our simulation results showed that the β-values are inversely related to the residence times of water molecules in the first hydration shell of the diffusing ion. The underlying concept is that the mass dependence of the diffusion coefficient arises from correlations between the modes of motion of an ion and those of its neighboring water molecules (see Fig. 1 inset) on short timescales that are characteristic of binary collisions. For example, a water molecule may first collide with the ion, then be repulsed to collide with a second nearby water molecule, which in turn sends the first water molecule back to collide with the ion again. The average residence time of water molecules that are nearest neighbors of an ion ($\tau^S{}_i$) may be an indicator of the relative importance of these short-time correlations, with longer residence times allowing for more collisions of the ion with the same group of water molecules, resulting in less mass-dependence of the ion diffusion coefficient. If such an inverse relation between $\tau^S{}_i$ and β exists, the residence times of nearest-neighbor water molecules for Li^+, Cl^- and Mg^{2+} at 348 K should vary in the order $\tau^S{}_{Cl} < \tau^S{}_{Li} < \tau^S{}_{Mg}$, which is exactly what we found from direct calculation using our molecular dynamics results.

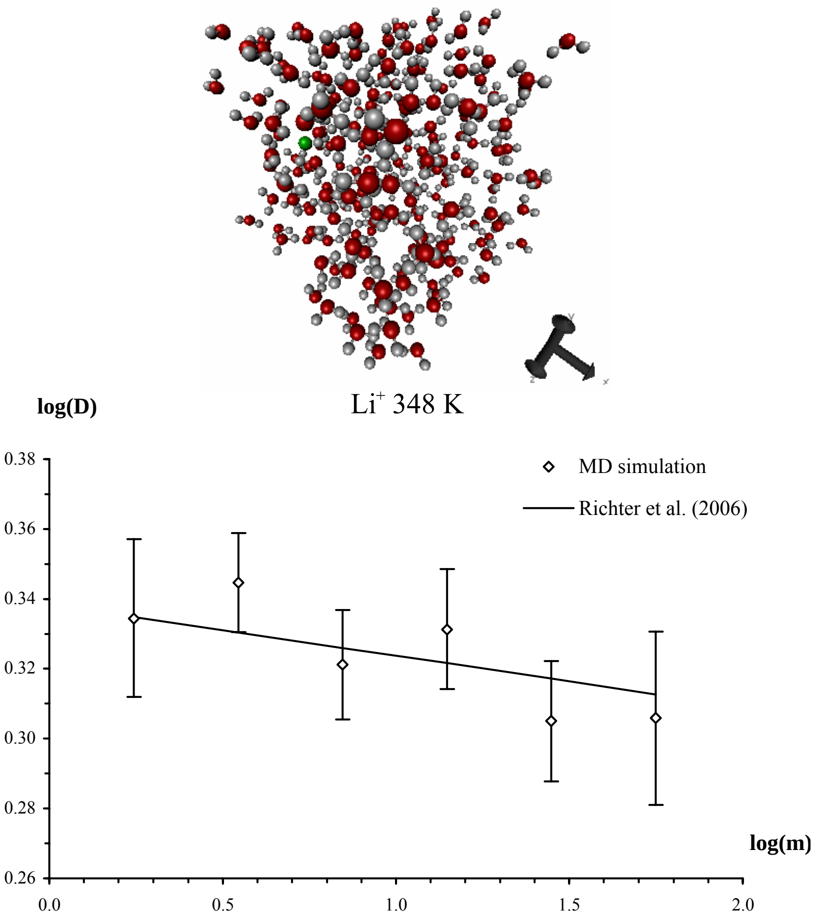

Figure 1. Log-log plot of the diffusion coefficient (D, 10^{-9} m^2s^{-1}) of Li^+ in liquid water at 348 K, obtained from our simulations, as a function of isotopic mass (m, Da). Confidence intervals around mean values of D (open diamonds) were calculated as $\pm 2\sigma(D)/(\ln 10)\, D$, where $\sigma(D)$ is the standard deviation of D. The solid line represents the isotopic mass dependence inferred from recent Li^+ diffusion data of Richter and his coworkers. The inset above shows a Li^+ ion (green sphere) among 215 water molecules in the periodic simulation cell used for our molecular dynamics simulations.

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 CO_2 sequestration in deep aquifers, and even to determine the fundamental controls on the rates of chemical weathering, an important long-term regulator of atmospheric CO_2 levels.

Project Description: The project consists of two principal parts: 1) an experimental study of kaolinite dissolution and precipitation rates at 22ºC conducted in well-mixed flowthrough reactors, and 2) a study of porosity and permeability change in basaltic rocks due to chemical weathering and its effect on the rate and mechanism of weathering rind growth.

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. Steady state dissolution experiments showed slightly incongruent dissolution, with a Si/Al ratio of about 1.12 that is attributed to the re-adsorption of Al on to the kaolinite surface. No inhibition of the kaolinite dissolution rate was apparent when dissolved aluminum was varied from 0 and 60 µM. The relationship between dissolution rates and the reaction affinity can be described well by a Transition State Theory (TST) rate formulation with a Temkin coefficient of 2

$$R_{diss}\left({}^{\mathrm{mol}}\!\big/_{\mathrm{m^2 s}}\right) = 1.15\times10^{-13}\left[1-\exp\left(\frac{-\Delta G}{2RT}\right)\right].$$

Stopping of flow in a close to equilibrium dissolution experiment yielded a solubility constant for kaolinite at 22°C of $10^{7.57}$.

Experiments on the precipitation kinetics of kaolinite showed a more complex behavior. One conducted using kaolinite seed that had previously undergone extensive dissolution under far from equilibrium conditions for 5 months showed a quasi-steady state precipitation rate for 105 hours that was compatible with the TST expression above. After this initial period, however, precipitation rates decreased by an order of magnitude, and like other precipitation experiments conducted at higher supersaturation and without kaolinite seed subjected to extensive prior dissolution, could not be described with the TST law. The initial quasi-steady state rate is interpreted as growth on activated sites created by the dissolution process, but this reversible growth mechanism could not be maintained once these sites were filled. 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

$$R_{ppt}\left({}^{\mathrm{mol}}\!\big/_{\mathrm{m^2 s}}\right) = 3.38\times10^{-14}\exp\left[-\frac{181776}{T^2\ln\Omega}\right].$$

Further analysis using Synchrotron Scanning Transmission X-ray Microscopy (STXM) in Total Electron Yield (TEY) mode of the material from the precipitation experiments showed spectra for newly precipitated material compatible with kaolinite.

For the purpose of understanding the rates of weathering rind advance in basaltic clasts from Costa Rica (Sak et al., 2004), we have undertaken X-ray microtomographic imaging of the reaction interface separating weathered from fresh rock. The microtomography carried out on Berkeley Laboratory Advanced Light Source Beamline 8.3.2 indicates that weathering results in the formation of sinuous dissolution channels or "micro-wormholes" that enhance both the porosity and its connectivity. This has been confirmed by analyzing the data with the code Percolate, which employs a "burning algorithm" to map pore connectivity in three dimensional samples. The data indicate that there is almost no pore connectivity in the porosity range of 3% to about 16% bulk porosity, while at about 16% porosity, a dramatic increase in pore connectivity occurs. 3D non-reactive diffusion simulations were carried out using the pore geometry determined with the X-ray microtomography—pixels that correspond to pores (fluid only) were given a tortuosity of 1, while pixels that correspond to matrix were given a tortuosity determined from tracer experiments in unweathered basalt. The simulations were then compared with diffusion experiments on the same sample using a bromide tracer imaged with μ-XRF at the Advanced Light Source. The good agreement between the position of the bromide front and the tracer front computed using the microtomographic data suggests that the latter may be useful in estimating effective diffusion coefficients where the pores are sufficiently large that they can be resolved with current X-ray synchrotron techniques.

Nanoparticle Aggregation in Natural Aqueous Systems

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Objectives: Mineral nanoparticles are common components of natural aqueous systems. Numerous natural inorganic and biologically mediated processes produce mineral nanoparticles such as metal sulfides and metal oxides that can be exceedingly small (< 10 nm). Nanoscale iron oxyhydroxide (FeOOH) phases are among the most common natural mineral nanoparticles, formed by precipitation from solution following oxidation of aqueous ferrous iron. Natural nanoparticles exhibit size dependent trends in structure and reactivity that are analogous to those found in synthetic materials. Because the chemistry of these materials involves surface processes, the dispersion behavior of nanoparticles is an important aspect of their effective reactivity in both environmental and technological settings. Moreover, aggregation is a major factor determining the transport of environmental particles, which can move material between redox zones and facilitate or inhibit contaminant transport. Although environmental colloidal particles frequently aggregate in circumneutral water, studies have indicated that certain nanoscale colloids have the ability to travel unexpectedly large distances in the environment. Despite numerous observations that nanoscale minerals are an important fraction of environmental colloids, the fundamental aggregation and transport properties of nanoparticles have not yet been established. We addressed these topics with a study of the colloidal properties of iron oxyhydroxide (FeOOH) nanoparticles with diameters of approximately 6 nm.

Project Description: We synthesized suspensions of ~6 nm iron oxyhydroxide nanoparticles and studied their tendency to aggregate or to remain suspended in solution under different aqueous chemical conditions. We acquired small-angle x-ray scattering (SAXS) and dynamic light scattering (DLS) data from solutions containing FeOOH nanoparticles as a function of pH from pH 4 - 10 and constant temperature. Independently, we determined how the nanoparticle surface charge density changes in this pH range using potentiomentric titrations.

Results: We found that the nanoparticles spontaneously formed suspended fractal nanoclusters between pH 5 – 6.6 with well-defined maximum diameters that can be varied from 25 nm to approximately 1000 nm. DLS observations of this phenomenon are given in Figure 1a. In addition, the SAXS data showed that the nanoclusters retain a very high surface area, and persist in suspension without settling for at least 10 weeks in solution. We are developing methods for visualizing representative aggregate structures based on SAXS data. In Figure 1b we show the SAXS acquired from FeOOH nanoparticle clusters formed under different aqueous conditions, and additionally present a cluster morphology that is consistent with one of the SAXS patterns. It is clear from this depiction that the surfaces of the aggregated particles remain highly accessible for the sorption of aqueous ions.

Because the cluster size is controlled predominantly by solution pH, we concluded that clusters form under conditions in which long-range Coulombic interactions between charged nanoparticle surfaces limit the maximum size of aggregates. We performed calculations of the particle-particle interaction energies using the surface charge measured by titration. The calculations showed that cluster formation is highly dependent on particle size, and FeOOH colloids that are five times larger would not exhibit this behavior. Our findings are highly relevant to the environmental transport of nanoparticles, because colloidal particles or aggregates in the micron size regime are significantly more mobile than either individual nanoparticles or macroscopic aggregates.

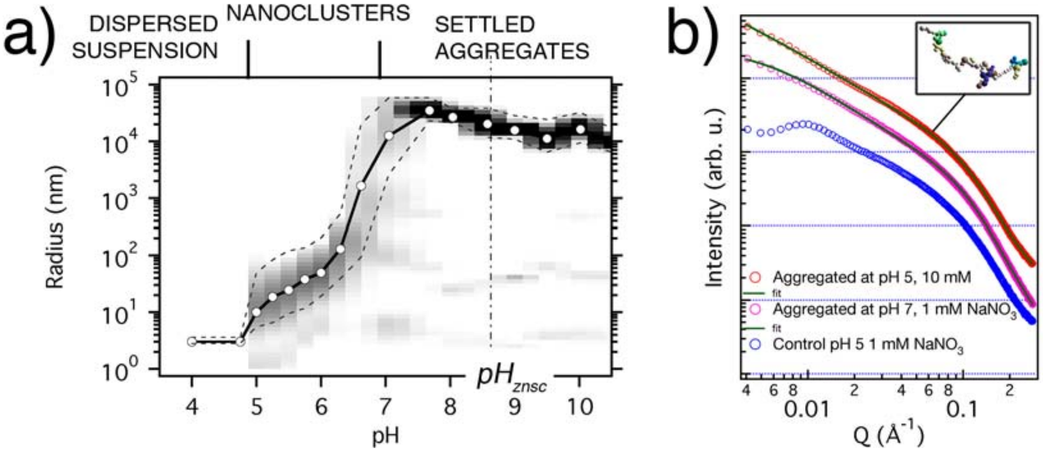


FIGURE 1: Iron oxyhydroxide (FeOOH) nanoparticles form suspended clusters in water within a range of aqueous conditions. (a) Dynamic light scattering data reveals three regimes of colloid behavior as the solution pH is varied. The measured pH of zero net surface charge (pH_{zpc}) is indicated. Between pH 5 – 7, the nanoparticles form suspended clusters with effective diameters that range from ~10 nm to more than one micron. (b) Small-angle x-ray scattering analysis of clusters reveals the characteristic scattering lineshape typical of fractal aggregates. [Inset: an example computer model of a fractal aggregate that was generated using geometric parameters derived from the SAXS pattern.]

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

Glenn Waychunas (email: gawaychunas@lbl.gov; phone: 510-495-2224), Y. Ron Shen (UC Berkeley), J. A. Davis (USGS, Menlo Park, CA)

Objectives: We wish to define the specific molecular geometries of mineral surfaces equilibrated with aqueous solutions, including the nature of surface relaxations or reorganizations, the 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.

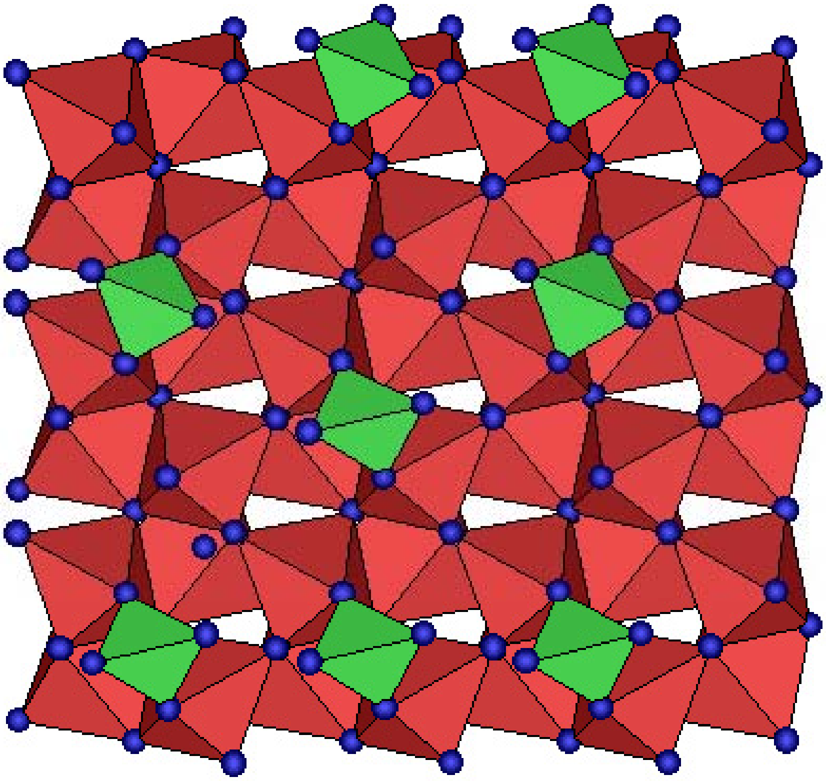


Figure 1. Geometry of sorbed silicate (green tetrahedral) on the R-plane (1-102) surface of hematite at 40% occupancy. At higher occupancy vertical silicate polymer chains are expected form.

Results: Our work during fiscal 2006 focused on the hematite, goethite and corundum surfaces. The wet surface structure for the R-plane of hematite was refined by surface diffraction and found to differ significantly from the analogous surface of corundum. As with the hematite C-plane, the surface is deficient in Fe, suggesting that hematite nanoparticles may have stoichiometry different from the bulk. We were also able to collect the first surface scattering data for a small cleaved goethite crystal sample, extending our techniques to samples less than 1 mm in diameter. For hematite we investigated the surface variations produced by acids or bases, as well as the geometry of sorbed species like arsenate, silicate or uranyl. Surface diffraction results have shown that the geometry of arsenate sorption on hematite is as a bidentate complex with strong surface attachment. Interestingly however, grazing-incidence x-ray absorption spectroscopy (GIXAS) measurements show both corner-sharing and edge-sharing bidentate complexes, with the latter seen only on the R-plane surface and assigned to step edge locations. Uranyl complexes differ between the R-plane surface of corundum and hematite, with a monodentate complex on corundum, but a bidentate complex on hematite. Silicate sorption also produces well-defined changes in the surface diffraction patterns, which indicate bidentate monomer attachment (Figure 1).

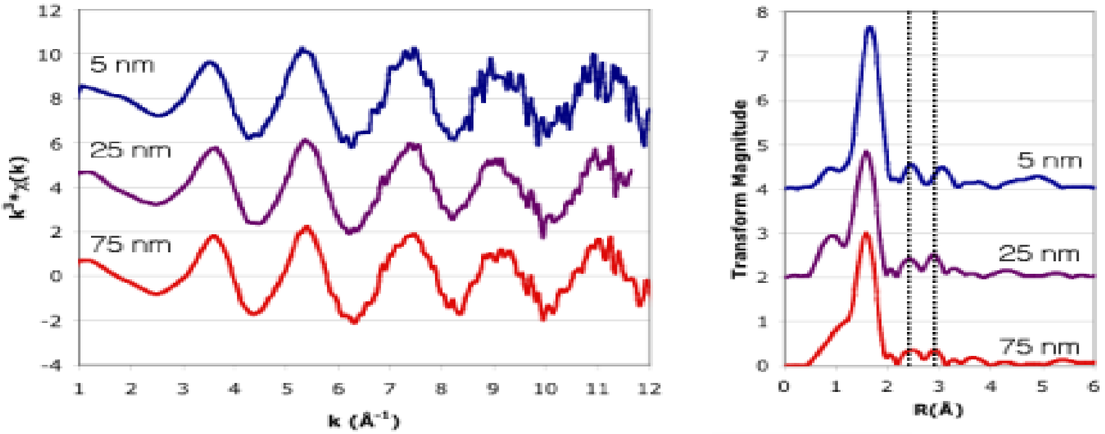
Our surface SFG water studies show that the pH point of zero charge (PZC) for clean corundum (0001) faces is ca. 5.5, rather than the ca. 9.0 measured for corundum powders. This points to a basic misunderstanding of the aluminate-water surface interaction, which we are addressing with our newly developed phase-sensitive sum frequency vibrational spectroscopy (PS-SFVS) technique. This method allows investigation of interfacial water structure beneath thick layers of surface water. Additional work has focused on characterization of silicate and phosphate sorption sites on hematite and other single crystals via GIXAS at soft x-ray energies, a potentially very useful application of soft x-ray synchrotron sources not previously accomplished.

How Does Nanoparticle Structure Control Interfacial Phenomena?

Glenn Waychunas (email: gawaychunas@lbl.gov; phone: 510-495-2224), James R. Rustad (UC Davis), Jillian F. Banfield (UC Berkeley)

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.



Left: Hg(II) L-edge EXAFS for goethite nanoparticles of varying mean sizes with similar surface coverages of sorbed Hg. **Right:** radial distribution functions from Fourier transform of the EXAFS. The small peaks indicate Hg-Fe interatomic distances for the sorbed Hg. These are constant from 25 to 75 nm mean particle diameter, but are lengthened in 5 nm particle samples, consistent with strained and/or distorted surface sites.

Results: Recent work shows that nanoparticle uptake of many types of sorbants is very high initially, reflecting the large surface to volume ratio. In general the numbers of active surface sites that sorb aqueous species does not seem to markedly increase in nanoparticles relative to larger particles, and in some cases are observed to decrease. This may be due to a high degree of surface strain, manifested by surface site distortion, and thus somewhat disfavored geometries for strong covalent binding of sorbates (see Figure 1 for Hg sorption). Growth of Fe oxyhydroxide nanoparticles is also affected by sorption, with effects proportional to the strength of the binding of the sorbate. Arsenate sorption, for example, quenches growth at high sorption densities, but most metal complexes have less effect. Nanoparticle growth mechanisms in iron oxyhydroxides appears to occur by both oriented attachment (OA) and ripening mechanisms, with the OA prevalent in the 20 nm size regime. These studies show that an important mechanism for the uptake of natural pollutants by nanoparticles is incorporation by growing surfaces or via aggregation mechanisms. We have shown that growth is highly sensitive to sorption of particular species, and hence that the fate and transport of environmental toxics is related in a complex manner to the size distribution of nanoparticles and the precise chemistry of sorbing species. For example, nanoparticles at smallest sizes may transport sorbed species for long distances without aggregation or growth if sorption densities are high. However the same particles would tend to aggregate or continue growth at low sorption densities, thus encapsulating the pollutants but with much limited transport.

Development of Isotope Techniques for Reservoir and Aquifer Characterization

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Objectives: This project is to develops geochemical and isotope techniques for reservoir and aquifer characterization in support of CO_2 geologic sequestration studies and measurement of groundwater ages. Two projects constitute the main focus of our research: (1) the development of noble gases as phase-partitioning tracers to study water-CO_2 interaction along a flow path as part of planned CO_2 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: *Phase-Partitioning Tracers and CO_2-Injection:*
The primary sites being considered for underground sequestration of anthropogenic CO_2 are active or depleted oil and gas reservoirs, deep aquifers, and underground coal beds. An important issue for gas transport in water-saturated zones is the amount of interstitial pore water and the extent of gas-water interaction. Preliminary modeling (Pruess et al., 2000, 25th Workshop on Geothermal Reservoir Engineering, Stanford University) suggests that gases of different solubility will exhibit chromatographic separation along a flow path with continued gas-water interaction. The model predicts that precisely measured details of a chromatographic separation profile for a suite of gases with different solubility would provide important information for modeling transport, the extent of gas-water interaction and an integrated gas/H_2O 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.

Results: *Phase-Partitioning Tracers and CO_2-Injection:*
A noble gas monitoring project was conducted as part of a CO_2 sequestration experiment in the Frio Formation in the Gulf Coast South Liberty Field, Texas. Preliminary results were presented at the Fourth Annual Conference on Carbon Capture and Sequestration (Pruess et al., 2005). The experiment called for the injection of CO_2 into a non-productive brine-bearing portion of the Frio sand formation at a rate of ~3 kg/s into an injection well ~30 meters down-dip from a second well reworked for monitoring fluid chemistry, among other things. Five days after the CO_2 injection began (and ~3 days after CO_2 arrival at the monitoring well), a noble gas cocktail [N_2 (61.827%), Ne (28.5%), Kr (8.461%) and Xe (1.212%)] was added to the CO_2 injection stream along with several other tracers. Despite the close proximity of the monitoring and injection wells, which would act to minimize the anticipated chromatographic effect, significant differences in peak arrival times of Kr and SF_6 were observed from which an inferred integrated aqueous phase saturations of ~32-45% was calculated. Although experimental difficulties in measuring Ne and Xe prevented us from taking full advantage of the wide disparity in solubility, the pilot test clearly demonstrated the utility of phase-partitioning tracers, such as noble gases, in defining reservoir environments and processes relevant to geologic sequestration of CO_2.

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, waste management, and paleoclimate studies and subsurface water-rock reaction and transport rates. To address these and similar issues, reliable techniques for determining aquifer recharge rates and water residence ages are required.

Results: *Groundwater ages:*
In collaboration with Neil Sturchio, University of Illinois, Chicago and Dr. Zheng-Tian Lu, Physics Division, Argonne National Laboratory, radio-chlorine (^{36}Cl) and radiogenic noble gases (^{4}He and ^{40}Ar) were measured to assess the residence time of old groundwater in the Nubian Aquifer of the Western Desert of Egypt (Patterson et al. 2005, Geochem., Geophys., Geosystems, v6, 1-19). A systematic increase in the amount of radiogenic ^{4}He that accumulated in the groundwater along the inferred flow path confirmed the age progression indicated by the $^{36}Cl/Cl$ ratios, but a flux of external radiogenic ^{4}He equivalent to ~3.5 times the in situ production rate of the aquifer is required to reconcile the ^{4}He

accumulation ages with those determined from ^{36}Cl. Furthermore, a divergence of the oldest sample (~650 kyr) from a linear trend between the ^{36}Cl age and the amount of accumulated ^{4}He suggests the external ^{4}He flux is not constant along the entire flow path. This clearly demonstrates that comparative dating provides useful constraints on the interpretations of each dating technique and on aquifer residence times. Presently, we are expanding this line of research to include other radio-chronometers, such as ^{81}Kr, by investigating old groundwater from aquifers of the mid-continental United States.

Kinetic Isotope Fractionation by Diffusion in Liquid

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Objectives: Our research seeks to document and quantify kinetic isotope fractionation during chemical diffusion, and most recently thermal diffusion, in a variety of liquids ranging from silicate melts to water.

Project Description: Our experiments regarding diffusion of dissolved salts in water and other liquids (e.g. methanol) involve 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 other methods as appropriate). The resultant data from the experiments provides determinations of the relative diffusivities of elements or isotopes. Other experiments involving diffusion in silicate melts are described by Frank Richter in a parallel contribution in this volume.

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. Molecular dynamics calculations by Ian Bourg and Garrison Sposito have reproduced our results. 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.

We have developed a new technique using MC-ICPMS to measure the isotopic composition of K (^{41}K/^{39}K) down to a precision of ±0.3 ‰ (2σ). Our measurements of experiments involving diffusion of K in water have demonstrated fractionation up to 7.5 ‰, indicating a greater fractionation effect for K than Li. In diffusion experiments using methanol (a less polar solvent than water), we have found that Li diffuses faster than K, the opposite of what is observed for their relative diffusivities in water. Comparing K diffusion in water to diffusion in methanol we have found a greater degree of K isotopic fractionation in methanol. These observations are consistent with the reduced dielectric drag associated with methanol compared to water.

Seismic Signature of Permeable and Impermeable Fractures and Faults

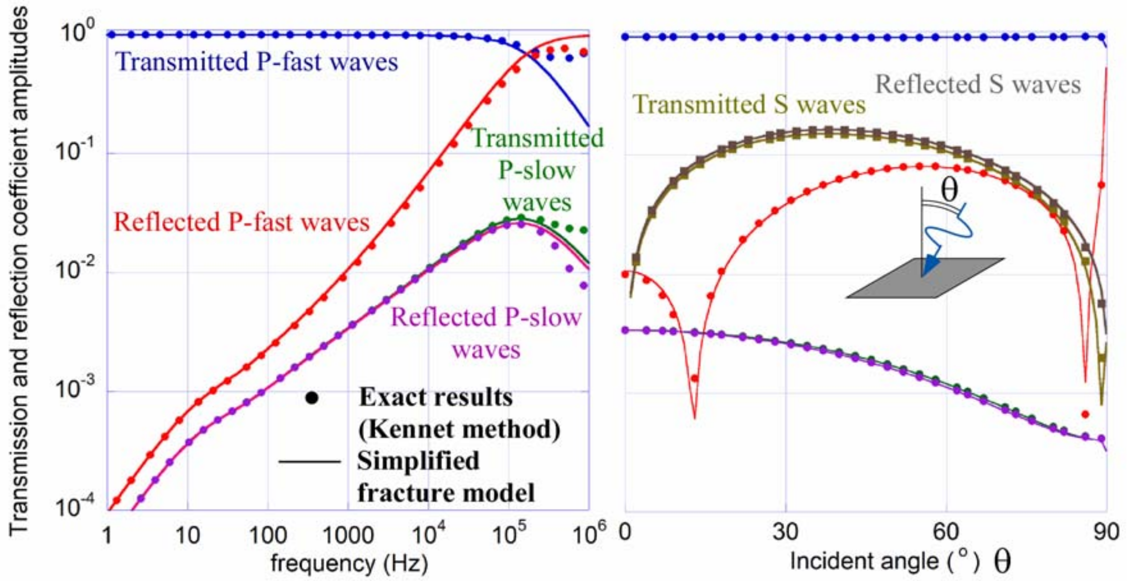
Seiji Nakagawa (510-486-7894, snakagawa@lbl.gov), Larry R. Myer

Objectives: Fractures and faults define important subsurface permeability boundaries (either sealing or conducting) which dominate subsurface fluid migration. The primary objectives of this research are to understand the dynamic (seismic) poroelastic behavior of single fractures and faults and to develop 'constitutive models' that can be used to delineate different permeability characteristics.

Project Description: The project consists of (1) laboratory experiments to measure dynamic poroelastic properties of a fracture and a fault, (2) theoretical model development to understand the fundamental physics, and (3) numerical simulations. The laboratory measurements are conducted using a modified resonant bar test device which allows us to measure small changes in fracture properties using wave frequencies near a kilohertz. The theoretical model is developed based upon a previously developed fracture model for non-poroelastic media by modeling a fracture as a thin layer of poroelastic medium. This approach provides a set of boundary conditions relating the velocity and stress across a fracture as a function of mechanical and hydraulic properties. The model is used to interpret the experimental results and to build numerical models to study wave propagation within and around heterogeneous, poroelastic fractures and faults.

Results: We derived new, poroelastic seismic boundary conditions for seismic wave scattering by fractures and faults. These are an extension of the conventional *seismic displacement-discontinuity* (or "linear-slip interface") model for viscoelastic fractures. For realistic fracture thickness and background rock properties, the models accurately predict frequency-dependent scattering of poroelastic seismic waves as a function of fracture compliance and permeability (Figure 1). These models were also used to derive velocity dispersion equations for poroelastic fracture interface waves with both symmetric and antisymmetric particle motions. Further, a simplified version of the models was used to identify and define characteristic parameters of a poroelastic fracture (corresponding to the fracture compliance [or stiffness] for a viscoelastic fracture).

We also conducted a numerical modeling and laboratory seismic measurements (using ultrasonic waves) on a sheared, fluid-saturated fracture. Shear stress on a fracture is known to convert a part of incoming, normally incident compressional waves into shear waves. These waves' particle motions indicate the shearing direction. When a low-permeability fracture is saturated with a fluid, however, we found that the particle motions can be reversed. Numerical experiments clearly demonstrated this effect, while the experimental results were somewhat obscured by an additional effect from the heterogeneity of a fracture.



(a) Normal incidence frequency response. $k_0=10^{-16}$ m (b) 1 kHz angle-of-incidence response. $k_0=10^{-16}$ m^2

FIGURE 1. Transmission and reflection coefficients of a thin (1mm), homogeneous fracture for incident Biot's fast P-waves. The coefficients were computed using both an exact method and the simplified version of the poroelastic fracture boundary conditions with five characteristic fracture parameters. (k_0 is the permeability of the fracture)

Scattering and Intrinsic Attenuation in Rock with Heterogeneous Multiphase Fluids

Lane R. Johnson (lrjohnson@lbl.gov, 510 486-4173), Kurt T. Nihei, Seiji Nakagawa

Objectives: The general objective was to perform fundamental research on seismic wave propagation and attenuation in rock containing heterogeneously distributed pore fluids. The primary focus was on the development of robust and efficient algorithms that could be used for both forward and inverse modeling of wave propagation in the types of heterogeneous materials encountered in the shallow crust.

Project Description: The primary task during FY06 was the completion of a new algorithm for computing the frequency response of seismic waves propagating in 2-D and 3-D earth models where the magnitude and phase are required at many locations. The basic idea of the approach is to run an explicit time domain finite difference code with a harmonic source out to steady state and then use a phase sensitive detection algorithm to extract the magnitude and phase.
Unlike frequency domain approaches, this method does not require storage of time series and this significantly reduces the storage requirements. For 3-D models this approach also requires a significantly lower arithmetic complexity than the frequency domain approach.

In a parallel effort the possibility of extending composite medium methods to materials containing non-spherical grains and pores was investigated.

Results: The time domain phase sensitive detection method was tested for accuracy by comparing its results with those of a finite difference boundary element method and the agreement was found to be very good. The method was also tested by applying it to the SEG/EAGE salt model.

The effects of changing the amount of attenuation in the model were also investigated. Extensions of the method were developed that allow the computation in a single run of multiple frequencies from a single source or of multiple sources each encoded with a different frequency.
More detailed results can be found in Nihei and Li (Geophys. J. Int., 169, 1069-1078, 2007).

The composite medium work concentrated on a feasibility study of a method for solving the boundary value problem for elastic waves in spheroidal coordinates. The choice of spheroidal coordinates has the advantages of being able to represent both elongated or flattened inclusions and it also allows separation of coordinates for the elastic wave equation. It requires that the problems of mode coupling be addressed, but this is true of all non-spherical geometries. The results of this study suggested that such an approach was viable and initial steps were taken toward obtaining a solution.

Faster and Better Solutions to 3D Electromagnetic Inverse Problems

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

Objectives: Provide an enabling technology in subsurface imaging using diffusive electromagnetic wavefields, addressing critical needs within the DOE mission, including waste legacy issues and energy and environmental security, which are difficult to address with existing 3D geophysical imaging technologies.

Project Description: This project seeks to develop robust, reliable and fast computational techniques to construct and appraise solutions to three-dimensional (3D) electromagnetic (EM) inverse problems using full wave equation modeling based upon finite difference approximations to the diffusive Maxwell equations. Our philosophy is to develop 3D inverse solutions with as much rigor as possible and to avoid approximations, which sacrifice solution accuracy for speed. Our work focuses on solving these types of inverse problems on massively parallel computing platforms using conjugate gradient type and Gauss-Newton solution techniques, including a variety of constraints to stabilize the inversion process. We have also come to realize that much more work remains in improving the convergence, accuracy and robustness of these solutions. Moreover the ability to incorporate better constraints to further alleviate solution non-uniqueness issues is warranted. Directly related to these issues are faster solution times for data inversion, which translates into fewer and faster non-linear inversion iterations as well as a substantial reduction in the computational burden required for the solution of the forward modeling problem, without sacrificing accuracy. Not only do significant improvements in solution speed translate into more reliable 3D images, it also advances the prospect of real-time 3D earth imaging in the not too distant future, given the anticipated improvements in algorithms and computer hardware.

Results: A grid used to simulate 3D electromagnetic fields need not conform to the underlying imaging grid. For a given transmitter, the EM field's resolving power will be dictated by the excitation frequency and effective volume of the subsurface interrogated by the field, sometimes called the source footprint. It therefore makes sense to impose an independent set of grids for simulation of the fields, which are a subset of the imaging gird. Grid-transfer operators have been developed to transfer predicted and observed data, cost functional and its gradients, from the forward modeling grids to the common inversion grid. Without grid separation the meshing required for EM field simulation would need to exactly match the fine level of meshing dictated by the basin-scale, thereby producing enormous and impractical meshes for 3D EM field simulation. The concept has been applied to field imaging examples leading to orders of magnitude speed up in the time to solution for large scale 3D imaging/inversion experiments.

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 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: After numerically verifying that the codes developed as part of this project are working as they should, the codes were used in FY2006 to demonstrate several findings about seismic attenuation that were published in two articles. First, for compressional attenuation in materials in which one porous material is embedded within another (a so-called "double porosity model"), the analytical theory developed by Pride and Berryman was demonstrated to give the same attenuation as that predicted numerically. The level of attenuation in samples containing mesoscopic-scale heterogeneity was both numerically and analytically demonstrated to be proportional to the square of the contrast in elastic moduli present. Stated differently, in random materials, the attenuation is proportional to the variance of the probability distribution used to randomly distribute the local elastic moduli. Further, it was demonstrated, both numerically and analytically, that when the heterogeneity is smoothly varying (i.e., not placed in the form of "patches" that are characterized by step function changes), the high frequency limit of seismic Q^{-1} is not the often assumed (and modeled) $f^{-1/2}$ dependence, but is instead f^{-1} where f is wave frequency. Further, when the poroelastic moduli are distributed as self-affine fractals having a Hurst exponent H, both numerical results and analytical arguments demonstrate the scaling law $Q(f) = f^{H}$. Last, in pure shear, it was demonstrated that contrasts in the bulk modulus can be responsible for local fluid pressure changes (some positive and some negative) that average to zero in pure shear, but that are responsible for a considerable amount of mesoscopic-scale flow and associated shear attenuation.

Imaging Permeability and Fluid Mobility Using Time-Lapse Measurements

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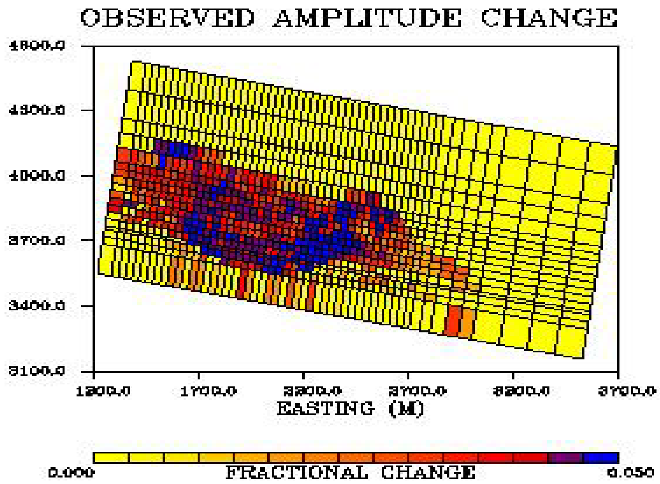
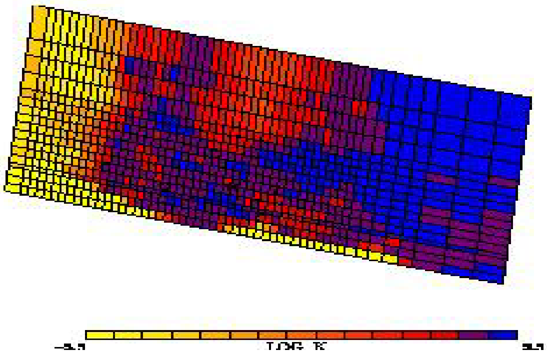
Objectives: I am investigating the fundamental relationships between changes in time-lapse geophysical attributes and sub-surface flow properties. A key feature of this work is the development of new ways to relate changes in geophysical observations directly to flow properties. The ultimate goal is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

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: I have explored two methods for inferring flow properties using time-lapse seismic and deformation data. The first technique is a trajectory-based methodology that was extended to account for capillary effects [Vasco 2004]. This method was applied to time-lapse seismic [Vasco et al. 2004]. The figure below shows the time-lapse amplitude changes from that study, based upon data from the Bay Marchand field in the Gulf of Mexico. A trajectory-based algorithm, a technique developed in the project, was used to map the time-lapse amplitude changes into estimates of reservoir permeability, shown in the lower panel of this figure. A variation of the technique, for transient pressure, was used to estimate permeability in a fracture zone, using tilt measurements [Vasco 2004].





An alternative methodology, based upon the pressure equation, was introduced in Vasco [2004] and applied to a set of time-lapse seismic and electromagnetic data to estimated permeability between two boreholes. The method was extended to treat deformation data and was applied to interferometric synthetic aperture (InSAR) data gathered over the Wilmington oil field [Vasco and Ferretti 2005].

A study of the resolution associated with the inversion of time-lapse seismic amplitude data was just concluded. The case in which water encroaches from below due to oil production from the reservoir was considered. It was found that, by using reflections from the top and base of a reservoir, and any internal reflections, one can image flow properties within the reservoir. The study examined time-lapse seismic amplitude data from the Norne field in the North Sea.

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

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Objectives: This project will isolate and identify noble gas components in sediments and address how noble gas elemental patterns are acquired and retained, how they are transferred to basin fluids in which they have been measured, and improve 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 hypotheses, 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: Following our theoretical analysis of diffusive filling and emptying as an initial explanation for the observed absolute and relative abundances in sedimentary rocks, laboratory work is currently underway to isolate and identify noble gas carrier phases and trapping mechanisms. We have found large Xe enrichments in organic silica: diatomites and sponge needles extracted from live sponges (*Calyxnicaeensis*). Step-wise degassing released light noble gases (He, Ne, and Ar) from these samples at low temperatures (T~400^{o}C), whereas Kr and Xe were retained up to temperatures in excess of ~1400^{o}C. We have yet to find excess noble gases in inorganic silica phases, such as diagenetic euhedral quartz and petrified wood. However, we have grown diatoms (Thalassionira weissflorii) under controlled conditions to determine if this is a biotic effect or a post-depositional effect. In order to investigate the post-depositional effect, we have acquired sediment samples from sapropels of the Black Sea and the Mediterranean as well as oceanic sediments from the Peru Trench (organic rich) and the Antarctic (Si-rich). We are currently building and testing sample handling protocols. We have also initiated a study of a variety of lab aggregated nanoparticles. We have found that aggregated FeOOH (goethite) is enriched in He and Ne up to 1000 and 40 times that expected for an equal mass of air saturated water, respectively. Step-wise degassing ruled out adsorption or diffusive acquisition of air-derived He and Ne. We will continue to focus on the processes by which these diverse phases acquire noble gases and why they are so well retained upon laboratory heating.

Nanoparticles in the Subsurface Environment: Abundance and Transport of the Mobile Fraction

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Objectives: The goals of this work were to conduct an inventory of natural nanoparticles in soils and to evaluate colloid formation and transport associated with moving waste plumes.

Project Description: We collected representative soils from different DOE sites. Sodium hexametaphosphate (HMP), a strong dispersing agent, was used to release aggregated clays and nanoparticles into suspension. Sedimentation by gravity followed by centrifugation was used to separate soil particles into the size ranges of < 2 µm, < 100 nm, 100-50 nm, and < 50 nm (defined as nanoparticles). Particle size distributions within individual fractions were initially measured using a disc centrifuge particle sizer. Morphology, chemical compositions, and mineralogy of the < 2 µm and < 100 nm particle size fractions were analyzed using HRTEM, EDS, and XRD.

To understand colloid behavior at reaction fronts during migration of waste solutions, we simulated the leakage process by infiltrating synthetic tank waste solutions into sediment columns at ambient and elevated temperatures. Nine different solution compositions were used to test ionic strength and pH effects. Both conventional flow-through and profiling column methods developed in our earlier studies were used. We also created a laboratory simulation of U migration for tank waste plume at the Hanford site.

Results: The results of our study of nanoparticles in soils indicated that the inventory (released by HMP) of < 50 nm size fraction was consistently at or below our detection limit (0.01 to 0.44 mass %). The quantities of potentially mobile particles are strongly pH-dependent, because higher pH systems are further removed from the characteristically acidic PZC range of soil clays, thus favoring greater suspension stability. Clay minerals such as illite and montmorillonite were the dominant crystalline phases in the two size fractions studied, and organic carbon was abundant in Oak Ridge and Savannah River sediments.

Our laboratory experiments revealed the striking phenomenon of pH neutralization of waste plumes. Starting with an original waste solution pH of 14, the pH dropped to values as low as 6.5 within the plume front region, more than 7 units lower than the initial value. This phenomenon was not predicted by geochemical modeling, nor detectable from batch equilibrium-based laboratory studies. We found massive colloid formation at the plume fronts. The measured size distributions of the plume front particles show that 90% of the mass is associated with colloids in the size range of 0.5-2.3 μm, with the highest contribution by 1.0 μm particles.

The controlling process responsible for the observed dramatic pH reduction and massive colloid formation at plume fronts is cation exchange. Sodium is the most abundant cation in many saline waste solutions. During infiltration of a waste solution, cation exchange of Na^+ replacing exchangeable Ca^{2+} and Mg^{2+} from the sediment occurs rapidly at the advancing plume front, leading to precipitation of calcium carbonate and pH reduction. Because of the large amounts of mobile particles generated and the large reduction in pH, this phenomenon could affect the fate and transport of contaminant trace elements contained within the waste plume. Synthesis of the Hanford metal waste plume using the column profiling method resulted in the formation of large quantities of U-bearing colloids at the plume front.

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Investigation of the Physical Basis for Biomineralization

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Objectives: The objectives of this project are to: 1) determine the impact of acidic polypeptides and proteins on Mg and Sr signatures in calcite. 2) map the pathways and kinetics of template-directed nucleation and growth of calcite on Asp-rich polypeptide and protein derivitized SAMs. 3) develop comprehensive models of kink-limited growth and mineral dissolution over the range of reasonable materials.

Project Description: The purpose of this project is to investigate biomolecular controls on crystal growth and dissolution. To achieve this purpose we are utilizing *in situ* force microscopy to investigate nucleation and growth of calcite surfaces under controlled conditions of temperature and supersaturation in the presence of acidic peptides, proteins, Sr and Mg. Concomitantly, we are performing molecular modeling to elucidate the stereochemical relationships between additives and crystal surfaces leading to growth modification, as well as ion-beam spectroscopy to determine distributions of incorporated additives. For all modifiers, our results to date have provided significant advances in our quantitative understanding of controls on calcite growth morphology, kinetics, and habit. Our methodology for investigating nucleation has also utilized *in situ* atomic force microscopy, but has focused on quantifying nucleation kinetics and phase transformations at self-assembled monolayers (SAMs). Concomitantly, we have used X-ray absorption spectroscopy to follow the structural evolution of the SAMs and Raman spectroscopy and *in situ* electron microscopy to follow the evolution of the mineral structure and phase during template-directed nucleation.

Results: In FY06, we reported two major findings and made a significant advance in development of measurement tools. Using *in situ* AFM, we showed that the introduction of peptides and proteins at low concentrations led to an *acceleration* of growth kinetics. Moreover, the magnitude of acceleration was found to scale with the degree of peptide hydrophilicity and a reduction in the energy barrier to solute incorporation was implicated as the source of the acceleration. The hypothesis to emerge from this discovery is that peptides and proteins alter the water structure of the solvation shell near the crystal surface and, thus, act like catalysts to enhance solute attachment rates. Using X-ray absorption spectroscopy and X-ray diffraction, we showed that exposure of OH-terminated mercaptophenol (MP) self assembled monolayers (SAMs) on gold to calcium-bearing solution leads to complete disorder of the film on the timescale required for mineralization. Moreover, mineralization proceeds via initial formation of an amorphous phase, which then converts to calcite. For the right combination of MP isomers and noble metal substrates, the final calcite crystal film exhibits a high degree of orientation control despite the initial disordering of the SAM. These results suggest that the crystal and film template one another. Finally, we designed and took delivery of a sample arm and a set of fluid cells for *in situ* TEM applications. This development will allow us to directly observe templated nucleation with near-molecular resolution at video rates, providing the first direct information on nucleation pathways and the role of templates.

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

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Objectives: The project objective at LLNL (see separate Wright State University input) is to study the coupling of chemistry and mechanics at the molecular scale. This objective requires development of new mechanical capabilities for the Hydrothermal Atomic Force Microscope (HAFM).

Project Description: We are studying the coupling 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). In order to achieve this objective, the project will develop a micro-bending jig for the HAFM and make extensive modifications (see Results below) to accommodate the jig and to greatly increase the scan range. Once we have developed these new capabilities we will address questions, such as: What is the impact of applied stress on the rate of surface step motion and density? What are the impacts of ionic species (dissolved salts) on SCG rates at near-neutral pH? What is the SCG rate and mechanism at temperatures greater than 80°C and, more generally, over what range in chemical, stress and temperature space does the Dove SCG rate model apply? Does it apply to minerals other than quartz? Is the pH dependency of SCG rate controlled by the reaction frequency (pre-exponential) term A_i or the activation energy? Is the b* term in the Dove model temperature independent?

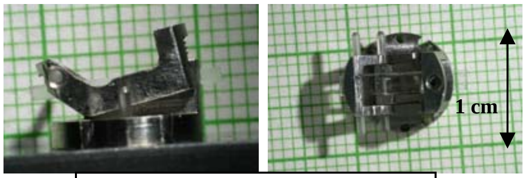

Fig. 1 Mini-bending jig for HAFM

Results: During this first year of the project we developed a mini-bending jig for the HAFM (Fig. 1). The bending jig that we designed and constructed permits us to achieve stress intensity factors ranging from 2.5×10^{-2} to 7.2×10^{-1} MPa*m$^{1/2}$. This covers the stress range pertinent to most materials of geologic significance. It is constructed entirely of non-reactive materials and fits within the flow cell of the modified HAFM. We redesigned the HAFM to use a longer piezo tube that extends the x-y scan range from 30 to 120 µm and the z-range from 1.2 to 2.3 µm. We extended the HAFM body to accommodate the new, longer piezo tube. 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. The new shape uses a pre-formed dimple that lowers stiffness and drag on the piezo. 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 an etched foil heater for the larger flow cell. Finally, we redesigned the HAFM to include a Picostage positioner for translating the piezo+sample over a ± 1mm range, increasing the effective scan range by 1000x. 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. In this experiment we initiated a small (20μm) crack using a Vickers indenter, stressed the sample and then imaged the crack in a pH 5.5 (equilibrated with the atmosphere) aqueous fluid for several hours. We then switched the incoming fluid to a pH 9 dilute buffer solution and watched the crack grow to over 120 μm length.

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

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Objectives: Dissolution of fracture surfaces leads to local transmissivity alterations that can develop into large-scale dissolution channels under certain conditions. We explore the influence of parameters including local reaction rates, flow rates, and normal stress applied to the fracture surfaces on the evolution of fracture transmissivities caused by reactive fluid flow.

Project Description: Local fracture dissolution rates are controlled by a combination of reaction-rate kinetics and advective/diffusive transport of dissolved minerals from the surfaces. The relative magnitude of these local mechanisms controls the evolution of large-scale dissolution patterns, and must be considered in large-scale models aimed at predicting permeability alteration due to reactive fluid flow. Additionally, stresses acting on fractures lead to changes in fracture aperture that may be influenced by dissolution-induced changes in the contacting fracture surfaces. We integrate laboratory experimentation and high-resolution computational modeling to explore the influence of dissolution on fracture transmissivities over a broad range of parameters and length scales.

Experiments carried out in10 x 15-cm transparent analog fractures fabricated by mating a rough glass surface with a smooth reactive surface (KH_2PO_4 crystal) allow reproducible experiments in fractures with well-characterized surface mineralogy. Light transmission techniques yield high-resolution (83 x 83 μm pixels at ±4 μm measurement resolution) measurements of fracture apertures over the entire fracture repeatedly during experiments. A newly designed experimental system allows application of a steady confining stress to the fracture surfaces to systematically investigate the coupled influence of surface dissolution and stress-induced closure. Experimental results are used to evaluate a depth-averaged model of fracture dissolution, which is in turn used to explore a much broader range of relevant parameters.

Results: Efforts in FY 2006 focused on three tasks: 1) depth-averaged dissolution model development and evaluation through detailed comparison to previous dissolution experiments; 2) computational simulations to investigate the dissolution process over a broad range of flow rates and reaction rates; and 3) dissolution experiments under constant normal stress.

1) We developed a model of local reaction rates that implicitly includes the transition from reaction-limited to transport-limited dissolution. Incorporating this local reaction-rate model into a high-resolution, depth-averaged fracture dissolution model resulted in a scalable model of fracture dissolution that can be used to efficiently explore a broader range of parameters and scales than is

experimentally feasible. Detailed comparison to previous experimental results demonstrated excellent agreement between the evolution of large-scale dissolution features.

2) Parametric simulations in which we varied Peclet number (Pe ~ advection / diffusion) and Damkohler number (Da ~ reaction / advection) over several orders of magnitude and fracture size over a factor of four demonstrate the relative influence of local reaction kinetics and transport of dissolved minerals on the development of dissolution patterns. Results ranged from relatively uniform dissolution over the entire fracture (high Pe, low Da) to the formation of a single dominant channel (low Pe, high Da).
3) Experiments conducted under constant normal stress demonstrate that dissolution of contacting asperities leads to closure of the fracture surfaces over time. Experiments at high Pe and low Da show an initial increase in transmissivity due to dissolution of the surfaces followed by transmissivity oscillations. The transmissivity oscillations appear to result from dissolution at contacting asperities, which leads to a gradual build-up of stress in contacts as transmissivity gradually increases. Subsequent failure of contacting asperities leads to small closures of the fracture and sudden transmissivity reductions.

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 a variety of alumino-silicate precipitates and mineral surfaces such as amorphous silica, quartz, and kaolinite that have reacted with dissolved aluminum from pH 4 to 8.

Results: Figures 1 and 2 show that Al(III) has a distinct coordination geometry and chemical environment on alumino-silicate precipitates and amorphous silica gels reacted with dissolved aluminum from pH 4 to 8. The ^{27}Al NMR data show that tetrahedral Al is the predominate species (Figure 1). Additionally, there is little cross-polarization from protons bound to oxygen atoms near Al(III) sites, indicating that the Al may reside near the surface. These data suggest that the primary mechanism responsible for enhanced silica precipitation rates and inhibited dissolution rates by dissolved aluminum is the formation of Al-O-Si framework bonds at the mineral surface. This behavior is different from the mixed octahedral and tetrahedral coordination observed in alumino-silicate precipitates formed in the absence of the solid substrate. In the alumino-silicate precipitates a large fraction of the Al has octahedral coordination and is probably gibbsite. As the pH increases, the percentage of Al with tetrahedral coordination increases, indicating that at pH 8, aqueous Al and Si concentrations are controlled by the solubility of an alumino-silicate with tetrahedral coordination even in the presence of amorphous silica. Future experiments will explore Al coordination geometry and chemical environment in the presence of quartz and kaolinite.

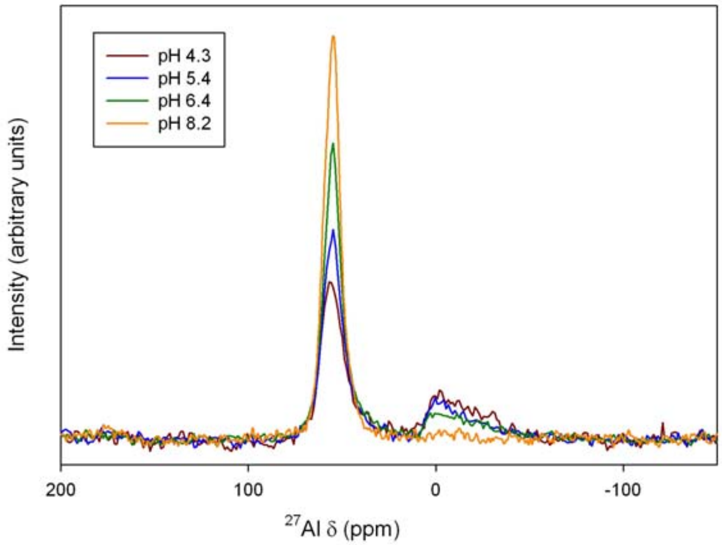

Figure 1. ^{27}Al NMR spectra from gels when 1 mM Al was reacted with dissolved silica in the presence of amorphous silica substrate. The bulk of the aluminum has tetrahedral coordination at the amorphous silica surface, and the extent of aluminum tetrahedral coordination increases with increasing pH.

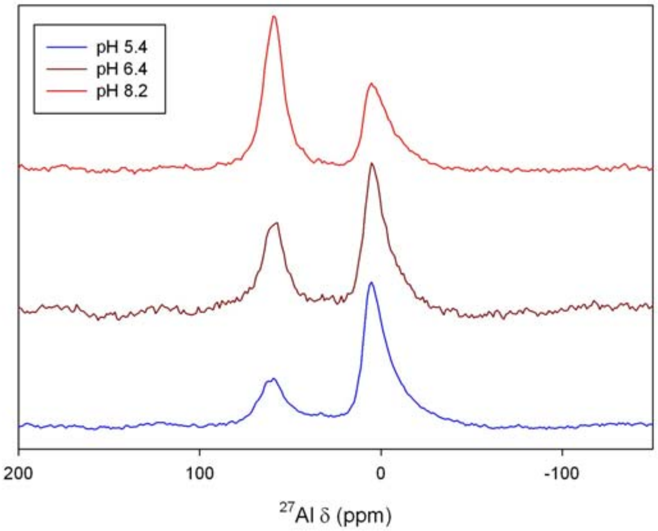

Figure 2. ^{27}Al NMR spectra from precipitates that formed when 1 mM Al was reacted with dissolved silica in the absence of amorphous silica substrate. Two phases are indicated by the spectra as tetrahedral Al in a Al-O-Si precipitate and octahedral Al in gibbsite or kaolinite structure. The relative ratio of tetrahedral to octahedral Al coordination increases with increasing pH.

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 IsoProbe multi-collector ICPMS. In FY06 we proposed to measure the Mg isotopic composition of a broad range of igneous rocks (including those used by Marshall and DePaolo (1989) to document the natural variability of Ca isotopes) to determine the natural variability of Mg isotopic compositions in crustal igneous rocks. We also proposed to measure the Mg isotopic composition as a function of age of bulk deep-sea carbonate and separated forams from DSDP Sites 590B and 575. Our work on the magnesium isotopic composition of carbonates and forams has focused on developing an isotopic fingerprint of dissolution. Ocean acidification and associated carbonate and aragonite dissolution have become a major environmental issue as more and more anthropogenic CO_2 dissolves in the ocean and developing isotopic monitors of carbonate dissolution could provide a new quantitative measure of ocean acidification rates.

Results: The Mg isotopic compositions of the Marshall and DePaolo (1989) samples were measured at Lawrence Livermore National Laboratory, along with additional samples measured at the Univ. of Chicago. Samples include the SUNY MORB, Columbia River Basalt standard BCR2 and a set of andesites from Ecuador. We found the magnesium isotopic composition to be constant across all the rock types so far studied at a level of ±0.2 ‰ in δ^{26}Mg. A preliminary report of this work by Teng et al. will be presented at the 2007 Goldschmidt Conference and a manuscript is being prepared for publication in Geochimica Cosmochimica Acta. We also measured a suite of Kilauea Iki lava lake olivine-rich cumulates and differentiated basalts with MgO contents ranging from 2.4 to 26.9 wt% (Teng et al., 2007) and showed that there is no measurable equilibrium Mg isotopic fractionation associated with crystal fractionation. The fact that igneous rocks have a very uniform magnesium isotopic composition means that magma mixing and/or equilibrium fractionations can be excluded as possible sources of magnesium isotopic variations that might compromise our ability to detect kinetic isotope fractionations. This task is now complete. Activities in FY07 will focus on measuring the Mg isotopic composition of forams to see if it correlates with commonly used dissolution proxies (e.g., Mg/Ca). We are looking for an isotopic fingerprint of the preferential loss of Mg relative to Ca during dissolution, potentially analogous to the isotopic fractionations associated with preferential loss of Mg by evaporation (Richter et al., 2003, 2007).

Pore Fluid Effects on Physical Properties of Rocks: Analysis and Computations

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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. Specific systems of interest are normally those containing fluids (oil, gas, water, CO_2) in rock pores. Seismic waves are used to image the earth, and thereby locate potential deposits of resources or contaminants, depending on the focus of the investigation. In addition, the waves can also be used in special cases 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 over the last several years.

Project Description: Prior work of the PI has focused on isotropic systems or finely layered systems, but recent work concentrates instead 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 can all have a very strong effect 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 as well as the seismic properties. The PI has recently been working with researchers in industry who have done extensive numerical simulations of fractured reservoirs, and 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 the PI takes special care to incorporate as much rigorous information (such as rigorous mathematical bounds and results from the best effective medium theories) and known-to-be-correct physical theories such as Gassmann's theory for mechanics of systems having fluids in pores into the overall analyses.

Results: The work in the last three years has stressed the differences between the results of classical Gassmann theory on shear behavior of isotropic poroelastic systems (which amounts to saying that fluids do *not* affect shear behavior), and more realistic situations involving anisotropic media (as mentioned previously) and some experimentally observed significant deviations caused by fluids both at seismic frequencies and in laboratory measurements at ultrasonic frequencies. Results are expected to help explain various discrepancies that have been noted both in well-logging data and in laboratory data by many workers. The most recent work has been able to show how to make use of various types of effective medium theories, including certain rigorous bounding methods, for both dry and saturated cracked/fractured systems. The Sayers and Kachanov (1991) approach of parametrizing the mechanical behavior of fractured systems has been generalized to permit rigorous analysis of fluid effects on these systems. It has also been shown in several different contexts how fluids do influence shear behavior in anisotropic systems, and in particular what modes of deformation are involved when these fluid-dependent shear effects are present. Results of these investigations have been published in a series of papers in the geophysics, geomechanics, mechanics, and physics literatures.

Laboratory Electrical Measurements of Fluid-Saturated Rocks for Geophysical Applications

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Objectives: The objectives of this project are to understand the physical mechanisms responsible for electrical conduction in porous rocks and sediments by performing carefully controlled laboratory experiments under a variety of conditions and to apply the results to field geophysical (EM) surveys for better interpretation of the sub-surface.

Project Description: The electrical properties of fluid-bearing materials are dependent on a number of factors of geophysical interest including temperature, porosity, mineralogy, and clay content, as well as fluid content. Because of this sensitivity careful laboratory measurements are needed to improve pore-scale physical and chemical understanding and to best extract information from field electrical surveys. This project focused on the electrical properties of rocks as a function of confining and pore pressure, temperature, and pore saturant. Samples were obtained from active regions of geophysical interest such as geothermal fields, enhanced oil recovery sites, and CO_2 sequestration sites. Dielectric constant and electrical resistivity, including complex impedance spectra from 10^{-3} to 10^6 Hz, were measured using a variety of saturating fluids, including water and CO_2. Laboratory results were used to improve petrophysical models used in the interpretation and inversion of field EM surveys.

Results: A specific result in 2006 was the quantification of how fluid salinity affects the conductive properties of swelling and non-swelling clays. Impedance measurements performed over the range of 1 Hz to 1 MHz on clay suspensions in NaCl solutions ranging from zero to 0.35 molar demonstrated that, for all suspensions, the DC conductivity was well-described by Archie's Law down to very low brine concentrations. At lower NaCl concentrations the conductivity of the mixture is constant at a level consistent with the relative cation exchange capacity of each specific clay (Figure 1).

A second important accomplishment was the application of developed techniques to highly porous materials and volcanic rocks with university collaborators. Electrical measurements of welded tuff samples suggest that pore pathways become increasingly dominated by crack-like geometries with increasing degree of welding. The permeability-porosity trend was modeled using a power-law fit with a percolation threshold to fit the data and it was observed that at low porosities, permeability drops rapidly, indicating a percolation threshold. This relationship can be used in models of compaction and cooling in pyroclastic flows and may assist in assessing volcanic hazards.

This project was completed in 2006. Over the course of the project numerous peer-reviewed papers were published. Several students were supported and university collaborations were developed.

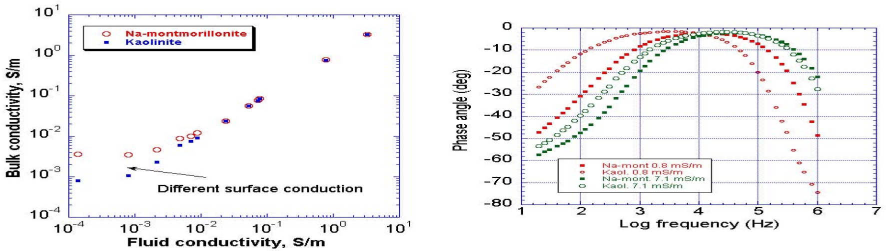

Figure 1. Examples of how clay type and fluid salinity affect electrical properties. (Left) Different surface conduction for Na-montmorillonite and kaolinite. (Right) Frequency-dependence of phase angle with clay type and salinity.

Rheology of the Earth's Interior

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Objectives: The objective of this work is to measure the flow properties of olivine-bearing rocks under upper mantle pressures and temperatures, which have been heretofore unachievable in deformation experiments, and to understand deformation processes sufficiently to extrapolate measurements to the geologic setting.

Project Description: Using a high-pressure deformation apparatus called the Deformation-DIA, we investigate the rheological properties of synthesized mantle rocks to pressures of 15 GPa. We study olivine-rich assemblages, since olivine is the most abundant mineral in the upper mantle, and we quantify the dependence of creep rate (viscosity) on deviatoric stress, pressure, temperature, and water fugacity. By avoiding the need for distant extrapolation from former laboratory pressure limits to mantle pressures, these measurements significantly reduce our uncertainty about the viscosity of materials at pressures approaching and surpassing that of the 410-km discontinuity and allow accurate modeling of the geodynamical behavior of Earth's interior. The key to measuring deviatoric stress under very high pressures is the use of high energy synchrotron x-rays, which can penetrate high-pressure seals and detect diffraction from lattice planes in the deforming sample.

Results: In close collaboration with David L. Kohlstedt and Shenghua Mei at the University of Minnesota, we have carried out several series of deformation experiments at synchrotron radiation facilities, mainly at the National Synchrotron Light Source, Brookhaven National Laboratory. Experiments cover a range of displacement rates of $\sim 1\times 10^{-5}$ to 4×10^{-4} s^{-1} over shortening strains of 10 – 40% at temperatures of 873 – 1573 K and pressures of 3-11 GPa. The most exciting results for us to date are machine developments that hold the promise scientific results in the very near future. A loose collaborative group of several institutions working on deformation and synchrotron x-rays now has a clear path forward to increasing stress resolution to a few tens of MPa and making the experimental process far more efficient that when this all began a few years ago. And we do have a few scientific results as well: we now resolve a positive pressure dependence of viscosity of olivine-rich rocks, which we look forward to quantifying soon with impressive precision. We also have measured and presented results on rheology of olivine under a state of very high deviatoric stress, above 1 GPa, with application to strength of the lithosphere.

LOS ALAMOS NATIONAL LABORATORY

CONTRACT: NA25396

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

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Objectives: The objectives of this project are to use 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 energy resource management (oil/gas exploration/production) and monitoring CO_2 sequestration. As oil/gas exploration is done in more complicated and difficult geological areas, more sophisticated imaging methods for complex structures are needed to pinpoint the targets. We propose to enhance the high-resolution/high fidelity multi-domain seismic imaging techniques that we have developed to date. We propose to exploit 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 propose to develop 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, CO_2 sequestration, and groundwater contamination monitoring and remediation.

Results: We studied the capability of our wave-equation migration methods for detection of faults in the cap rock. It is critical to characterize the integrity of the cap rock over very large areas to ensure safe geological carbon sequestration, because one of the primary possible CO_2 leakage paths is through the faults in the cap rock. We studied the effects of frequency of seismic data and velocity models on detection of faults, and demonstrated that high-resolution wave-equation migration has the potential to accurately detect faults. We conducted quantitative studies on migration imaging resolution. We defined and formulated the resolution of an imaging system based on the inverse theory and local angle domain decomposition of Green's functions. The resolution defined in this way included both the effects of an acquisition system and the migration imaging process. We improved the amplitude accuracy of one-way propagators. Using the beamlet propagator, we applied the WKBJ correction within localized windows to form a true amplitude one-way propagator in a generally heterogeneous medium. We developed an one-way propagator by a wavefront reconstruction method that combines and interpolates the two orthogonally propagated one-way wavefields. The method can be used to image steep subsalt reflectors and overhanging salt flanks.

Nonlinear Elasticity in Rocks

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

Objectives: We are studying the Nonlinear Nonequilibrium Dynamical (NND) properties of granular materials with the goal of understanding the physics of nonlinear response in these materials and their application to earthquake processes. NND is manifest by, with increasing wave amplitude modulus decreases simultaneous with wave distortion, and strong nonlinear wave dissipation. Another manifestation is the phenomenon of *slow dynamics* in which, after forcing, the ringing-frequency and dissipation characteristics recover to their original states, linearly with the logarithm of time, over hours to days.

Project Description: Currently we are attempting to understand the role of NND in dynamic earthquake triggering and strong ground motion. Both require understanding the NND behavior of granular media. For instance, the physical origin of dynamic triggering of earthquakes remains one of the least understood aspects of earthquake processes. We hypothesize that the dynamic, elastic-nonlinear behavior of fault gouge under disturbance by a seismic wave may be responsible for dynamic earthquake triggering. We base our hypothesis on recent laboratory dynamic-experiments of stick-slip conducted using granular media, a surrogate for fault gouge. Experiments indicate that, under relatively small effective pressures that one could expect in the fault zone, seismic waves with strain amplitudes known to trigger earthquakes cause triggering of laboratory earthquakes due, we think, to the nonlinear response of the material. In regards to strong ground motion, we are conducting field experiments showing that the nonlinear response of granular media dominates site response, and further, we can characterize it. Study of the *nonequilibrium dynamics* of granular media may have additional, unforeseen application to geophysical properties.

Results: A paper is currently in review in the journal *Nature* describing our recent work on earthquake processes. In addition, we just now undertaking studies aimed at supporting our renewal proposal, recently granted for funding starting FY08. In this work, we are studying the effects of pressure on the nonlinear response of rock. As pressures increase, the nonlinearly progressively diminishes. Currently, we have just finished equipping our INSTRON rock press with velocity sensors, so that wavespeed can be tracked along with strain, as stress is increased. We have also conducted a number of complex stress-strain histories on several reservoir rocks, to look for end point memory a physical property predicted from the P-M Theory of elasticity. No experimental proof yet exists in the literature. The following figure shows results for Berea sandstone showing experimentally, for the first time, End Point Memory.

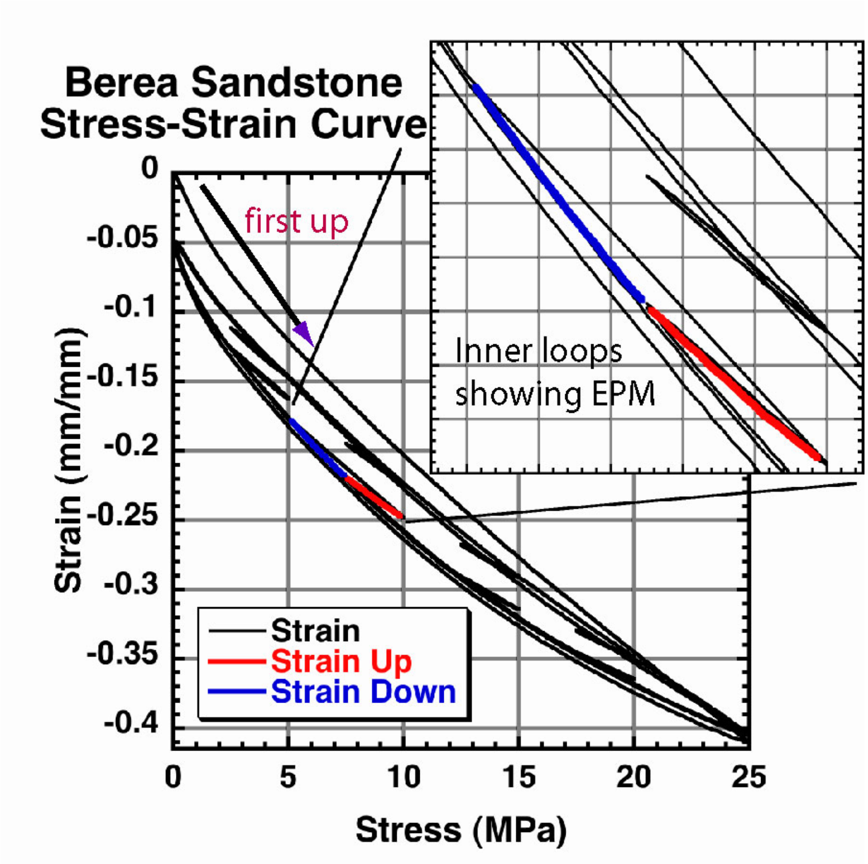

Figure 1. End point memory in Berea sandstone measured during quasistatic, uniaxial stress experiments. The main figure shows up-down curves repeated twice. Note the permanent deformation induced during the first up curve. The inset shows the behavior of the inner loops. They show that, when the stress level returns to the point of the original stress before small stress deviation, the outer stress-strain curve is maintained. This is End Point Memory (also known as Discrete Memory). This work will be submitted for publication soon by Claytor and TenCate to *Geophysical Research Letters*.

Elastic Wave Effects on Colloid Interactions and Porous Fluid Transport

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Objectives: Experimental approaches will be used to investigate the basic physics coupling stress waves to porous mass transport behavior. The major goals are to 1) quantify the physical and chemical conditions under which stress waves influence porous fluid flow and sub-pore size (colloidal) particle transport, and 2) obtain improved experimental data that will be used to validate and quantify proposed physical mechanisms.

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

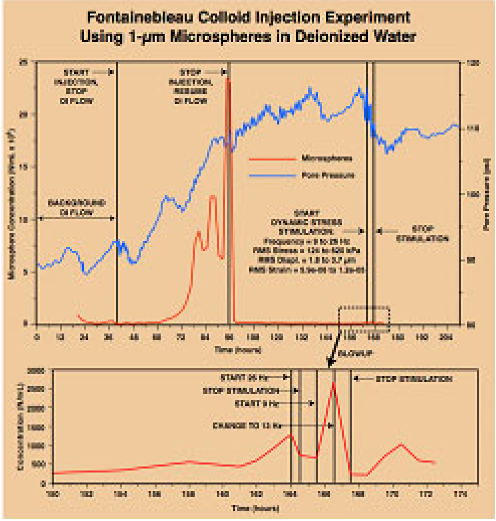
Our primary focus is on experimental laboratory studies of fluid flow and colloidal particle behavior under the influence of applied stress oscillations. Two LANL facilities are being used in these studies: The Dynamic Stress Stimulation Laboratory (DSSL) and the Automated Video Microscopic Imaging and Data Acquisition System (AVMIDAS). The DSSL is used to study low-frequency (1-1000 Hz) effects on core-scale fluid flow and particle behavior in porous material. AVMIDAS is used to visualize sub-pore size particle behavior in parallel-plate glass cells and porous micro-models under the influence of high-frequency (0.1-10 MHz) acoustic waves. Data from these two systems are compared to investigate possible scaling mechanisms that can be used to predict similar behavior in the Earth's crust.

Results: This 3-year renewal project is currently in the middle of its first year (FY06) of work. Following on experiments started in FY05 (under the original project), two additional experiments were performed in the DSSL, where 1) Fontainebleau sandstone was injected with a known suspension of 0.3-micron polystyrene micro-spheres in a solution of 0.1M NaCl, and 2) 1.0-micron microspheres were injected with deionized water. The effects of low-frequency stress oscillations on particle flux and transport were measured for all experiments. Background permeability during constant-rate flow through the core at 0.1 mL/min was measured from pressure-drop data, and production histories for microspheres released from the core were obtained by flow cytometer measurements of the effluent fluids collected.

During the first experiment, the high ionic strength of the suspending fluid caused virtually all of the injected 0.3-micron microspheres to become trapped in the core due to colloidal attachment to the pore walls. After the injection, during flow of the NaCl solution alone, effluent samples showed no microspheres were exiting the core, even during dynamic stress stimulation. The core was then flushed with deionized water, and flow was maintained at 0.1 mL/min. This caused an immediate release of a large amount of microspheres due to the sudden change to low ionic strength. After the effluent microsphere concentration stabilized at a constant low value, stress stimulation was applied at 26 Hz with an RMS strain level of 3.7e-05. This caused an increase in effluent microsphere production by a factor of 3. Thus, dynamic stress cannot release trapped colloids at extremely high ionic strength (0.1M NaCl), but is very effective at low ionic strength. No significant permeability changes were observed because the 0.3-micron microspheres were too small to cause pore throat fouling or to decrease the effective pore diameter by attachment to the pore walls.

The second experiment was performed to investigate the effects of microsphere size under the same ionic strength conditions used in the previous experiments. Results are shown in the figure below. A suspension of 1.0-micron microns in deionized water was injected into the core at 0.1 mL/min continuously for approximately 4 days, followed by flowing deionized water alone. The pore pressure in the rock near the fluid inlet end increased by 25% as a result of microspheres being trapped in the core.

This means the permeability decreased to 75% of its initial value. Because colloidal attachment to pore walls cannot occur at such low ionic strength, the microspheres were most likely fouling the smaller diameter pore throats by bridge formation (log jams). After the permeability stabilized, dynamic stress was applied over a range of frequencies and strain amplitudes (see figure). The net result was an increase in permeability to approximately 80% of its initial value (5% recovery). Effluent microsphere concentrations indicated that increased microsphere production occurred during stimulation, presumably due to hydrodynamic breakup of pore throat fouling.



Summer of Applied Geophysical Experience (SAGE)

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Objective: This project (1) provides unique, hands-on training and research experience in basic and applied geophysics for 25-30 selected undergraduate- and graduate students (admission is on a competitive basis), (2) helps develop a broad, community-wide expertise in geophysics, (3) conducts leading-edge research with students on a variety of important problems, and (4) introduce students to a range of career options in the geophysical sciences. Results are expected to be important to a range of interests related to national security, including energy sources, waste-disposal, environmental remediation, carbon sequestration, and basic research.

Project description: The main project undertaken by SAGE 2006 was the structure and stratigraphy of a complex region (an "accommodation zone") of the Rio Grande separating two major faulted basins. Questions included the number and location of buried faults, amount of offset along faults and changes in offset along strike, existence of relay ramps, plunge of relay ramps, timing of faulting, and the general kinematics of the accommodation zone. The major methods used included seismic reflection and refraction, gravity, time-domain electromagnetics, magnetics, and integration of 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. Secondary objectives were to characterize the depth to the regional water table in the main project area, and to study man-made structures and excavations using similar techniques (augmented by ground-penetrating radar and several EM methods) at an archaeological site. Due to the difficulty of obtaining approval to work at the Los Alamos National Laboratory, the archaeological site served as a proxy for a small-scale environmental-restoration waste disposal site.

Results: Twenty seven students from a wide range of large and small colleges and universities attended SAGE 2006. Participants successfully imaged strata on the downfaulted (west) side of a major north-trending, basin-bounding fault (La Bajada fault) separating the Espanola and Santo Domingo basins of the Rio Grande rift. The presence of the fault, partially buried beneath young sediments, was located during SAGE 2005. By correlating strata across the fault and by integrating SAGE data in conjunction with proprietary industry seismic data, students were able to estimate that the vertical component of offset on the fault exceeded 1 km. The horizontal component remains unknown but is probably minor. The field area was located on a northward dipping "relay ramp," probably with both vertical- and horizontal axis rotation. The La Bajada fault and adjacent, parallel faults constitute part of a northeast-trending "accommodation zone," transferring offset laterally from the Espanola to the Santo Domingo basins and ultimately to the very deep Albuquerque basin of the rift. Strata on the east side of the La Bajada fault dip away from the fault zone by isostatic uplift and flexure of the footwall. Results of this work have already been used by the U. S. Geological Survey and by Cochiti Pueblo.

Figure Caption. Under the supervision of Dr. Peter Annan of Sensors&Software (right), who regularly visits SAGE and leads teams of students in field work and data interpretation, a SAGE student uses a ground-penetrating radar unit to image foundations and partially subterranean (now filled and covered) rooms at a major archaeological site near Santa Fe. The participation of geophysicists from companies is very important in bringing the latest in expertise, equipment, and software, and in providing a "bridge" to career opportunities.

(230)Th-(238)U Disequilibrium Measurements

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Objectives: The goal of our work is to use improved U-series analytical capabilities to provide unique information on the behavior of U-series members in the 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 have typically been 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 current efforts combined with new efforts to provide in-situ spatial resolution to U-series studies for geologic materials. Our goal is to move from what is currently know about laser ablation MC-ICPS from studies of bone, minerals, metal particles, etc. into new areas such as U-series studies of young volcanics, fracture filling material, and deep sea corals.. Emphasis is on utilizing the multiple ion counting capabilities of the Isoprobe MC-ICPMS. This work provides information on the recent evolution of magmatic systems, human evolution, natural hazard risk assessment, climate change, and the carbon cycle.

Results: We collaborated with R. Miner and S. Nelson from BYU in a study of fossil spring deposits from the Death Valley region to evaluate paleoflow paths. This work explores the potential for using fossil spring deposits to infer water sources and paleo flow paths. This new approach to paleo hydrology can be widely applied and here led to a better understanding of the controls of regional groundwater flow in arid region where water is a scarce resource. The work represents the Master's thesis of Reed Miner who conducted the U-series age dating study while at LANL and was recently published in the Journal of Quaternary Research.

We collaborated with Ken Sims at WHOI to provide a U-series eruption age for the Bluewater flow of the Zuni-Bandera volcanic field in western New Mexico. The ^{238}U-^{230}Th disequilibria measured on separated groundmass phases produced an internal isochron age of 68 ka. Previously published cosmic ray exposure ages for this flow are significantly younger than this U-Th isochron age unless estimates of surface erosion based on flow morphology are considered. These new estimates indicate a minimum erosion rate of 1.7 mm/k.y. at this location. These new ages have local significance for the geochronology of the Zuni-Bandera volcanic field; however, their larger significance is in their applicability to dating Quaternary basalts and quantifying erosion rates. These results were recently published in Geology.

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

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Objectives: This research effort is focused on determination of the mechanisms of microbially enhanced iron dissolution from iron bearing minerals.

Project Description: Contrary to the current body of literature, the results of our experiments, discussed in this report, show that reductive dissolution is being used by an aerobic microorganism to acquire iron from hematite. We show that the growth of *Pseudomonas mendocina ymp* on insoluble ferrihydrate is enhanced by exogenous reductants (ascorbate and cysteine). This enhanced growth was concurrent to increased soluble iron concentrations. In vitro experiments performed with the metabolites pyridine-2,6-bis(thiocarboxylic acid) (PDTC) and its carboxylic analogue pyridine-2,6-bis(monothiocarboxylate) (DPA) to examine the ability of these microbial metabolites to enhance the dissolution of ferrihydrate revealed that these molecules dissolve iron oxide minerals by a mechanism that involves the reduction of Fe(III) to Fe(II) at the mineral surface. This work demonstrates the interplay between microbially produced reductants and siderophores in the dissolution of iron oxide minerals and the acquisition of Fe from Fe-bearing mineral phases.

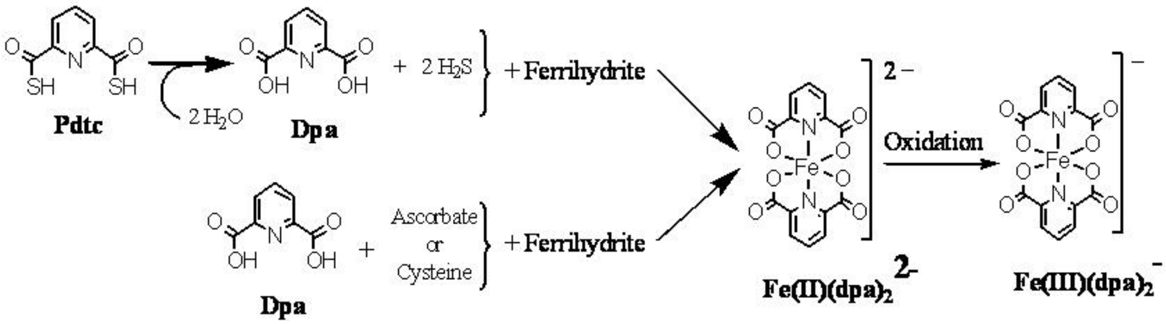
Results: We examined the effect of exogenous reductants on the on bacterial growth and iron mobilization from ferrihydrite. The bacterium used for this study, *Pseudomonas mendocina ymp*, was isolated as part of the Yucca Mountain Project from sediment in a surface holding pond of a drilling operation at the Nevada Test Site. Ferrihydrite used in these experiments was synthesized by precipitation with alkali according to methods described in the literature.

When ferrihydrite was the source of Fe, microbial growth was observed that slightly exceeded that of the control. The total dissolved Fe analysis indicated the presence of some dissolved Fe in the media when *P. mendocina* was grown in ferrihydrite compared to the control. This observation clearly suggested Fe mobilization from ferrihydrite by the *P. mendocina.*

When *P. mendocina* was grown on ferrihydrite supplemented with external reductant a significant increase in growth was observed. The growth in these reductant supplemented media were only slightly lower than that seen when *P. mendocina* was grown in chelated Fe (67 μM FeEDTA). The levels of total soluble Fe in the reductant supplemented growth media were greatly elevated, which in turn significantly facilitates bacterial growth. The data indicate that the presence of a reductant, whether produced by bacteria or external, significantly improves the ability of siderophore to supply the microbe with Fe. This synergistic relationship between siderophore and reductant appears to be crucial to meet the microbial demand for Fe. This is the first study that shows the involvement of a reductant in environmental Fe(III)(hydr)oxide dissolution and illustrates the significance of reductants in iron mineral dissolution.

We also examined the mechanism of ferrihydrite dissolution by pyridine-2,6-bis(monothiocarboxylic Acid) (PDTC) and its carboxylic acid analogue pyridine-2,6- dicarboxylic acid (DPA). Dissolution of ferrihydrite was followed as a function of time and PDTC and DPA concentrations. PDTC was found to be efficient at dissolving ferrihydrate and the dissolution rate followed a saturation profile indicating that the mechanism of the iron mineral dissolution was controlled by the ligand binding to the surface of the mineral phase. DPA alone was unable to dissolve ferrihydrite, but the addition of small amounts of exogenous reductants significantly enhanced the dissolution rate. In the presence of exogenous redutants the rate of ferrihydrite followed a saturation profile similar to that observed for PDTC. The concentration of the reducing agent showed very little influence on the dissolution of ferrihydrite by DPA. Doubling the concentration of ascorbate at a fixed concentration of DPA did not result in an increased amount dissolved Fe or acceleration in the rate of dissolution. This small change suggests the surface kinetics of ferrihydrite dissolution were strongly dominated by the interaction between the ferrihydrite surface and the ligand DPA, and not the reducing agent ascorbate.

MALDI-MS analysis of the final product of the dissolution experiments, showed a singly charged peak with a m/z = 386 in the negative ion mode. This peak corresponds to the mass of singly charged Fe complex of DPA. This interesting observation suggests that the final dissolution product for the PDTC and DPA facilitated dissolution are identical. This enabled us to confidently suggest a mechanism for ferrihydrite dissolution by pdtc, which is described in the scheme:



PDTC in an aqueous solution will hydrolyze to give DPA, a good Fe chelator and H_2S, a strong reducing agent. Fe(III) is reduced to Fe(II) on the ferrihydrite surface followed by subsequent chelation of Fe(II) by DPA in a manner identical to that seen in the ferrihydrite dissolution experiment that used DPA+ascorbate or DPA+cysteine, as ligand+reductant combination.

OAK RIDGE NATIONAL LABORATORY

CONTRACT: OR22725

PERSON IN CHARGE: D. Cole

Nanoscale Complexity at the Oxide/Water Interface

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Objectives: The objective of this project is to investigate the structure and dynamics of mineral-water interfaces. The observed phenomena span the subangstrom-micron length scales and femtosecond-millisecond time scales common to all nanophase processes. The relevance to earth sciences involves elemental migration in subsurface media, mineral dissolution/precipitation rates and mechanisms, transport and stability of colloids, and a wide range of energy technologies.

Project Description: A multidisciplinary, multi-institutional effort (ORNL, Argonne National Laboratory, Vanderbilt University, Pennsylvania State University, University of Illinois, Northwestern University) is focused on achieving a quantitative understanding of the structure and properties of the interface between aqueous solutions and metal oxide nanoparticle and macrocrystal surfaces, the electrical double layer (EDL), over a wide range of temperatures and solution chemistries. This research impacts a broad range of DOE mission areas, including catalysis, nanoscience, waste migration, energy production, and biological processes. The experimental studies are intended to quantify every aspect of the EDL, including degree of surface protonation and the total concentrations of counterions within the EDL, mineral surface structure and dynamics, detailed geometrical information on ions and water molecules, and local bonding environments using non-perturbing, *in situ* measurements wherever possible. These are coupled with advanced macroscopic multi-site sorption and protonation models, *ab initio* calculations and large-scale classical and *ab initio* molecular dynamics simulations.

Results: An extensive set of pH titrations and sampling studies of the surface charging and ion adsorption (Na^+, Sr^{2+}, Zn^{2+}) properties of tin oxide (cassiterite, α-SnO_2) were completed at ionic strengths of 0.03 and 0.3 molal and temperatures of 10, 25 and 50°C. This mineral, which is isostructural with rutile (α-TiO_2), exhibits weaker binding of all cations, in agreement with recent predictions by Dimitri Sverjensky (Johns Hopkins), based on consideration of the bulk dielectric properties of the two oxides. The pH of zero net proton charge (pH_{znpc}) of cassiterite, determined from pH titrations, is in general agreement with values obtained from microelectrophoresis measurements of the isoelectric point (pH_{iep}) at Penn State at temperatures of 25 to 200°C, though the latter are somewhat lower, suggesting that Na^+ and Cl^- exhibit asymmetrical binding constants on this surface. A classical molecular dynamics model of the cassiterite (110) surface has been developed based on an *ab initio* force field model developed previously in this program. X-ray standing wave and crystal truncation rod studies of water structure and the sorption of Sr^{2+} on cassiterite single crystal surfaces (the 110 crystal plane) have been initiated at Argonne's Advanced Photon Source, with preliminary indications that a.) water is fully-dissociated on this surface, forming a hydroxide-covered interface; and b.) Zn^{2+} and Sr^{2+} do not bind as strongly on the cassiterite surface as on the 110 surface of isostructural rutile, consistent with the powder pH titration results.

Site complexation models have been developed for the sorption of Rb^+, Na^+, K^+, Zn^{2+} and Y^{3+} on rutile surfaces over wide ranges of temperature and ionic strength. Sorption of Sr^{2+} and Zn^{2+} on rutile in a variety of 1:1 electrolyte media has been shown definitively to be predominantly inner-sphere, with sorption geometries and binding constants independent of the background electrolyte type or concentration. These models are greatly enhanced by input from our X-ray and computational studies of the rutile/water interface, making the models atomistically realistic. New X-ray absorption fine structure measurements were made on rutile powders in aqueous solutions containing Zn^{2+}. These results were combined with our previous X-ray standing wave, molecular dynamics, and new *ab initio* results, revealing the molecular level details of zinc adsorption on the rutile (110) surface, including a change in Zn^{2+} coordination from six- to four-fold upon adsorption, and sorption-enhanced hydrolysis of the solvated cation.

An *ab initio* molecular dynamics model of the rutile (110) surface in contact with many water molecules at liquid-densities is being developed and is shown to be largely consistent with our X-ray standing wave and crystal truncation results, and also with the MUSIC model calculation of surface oxygen proton affinities. Our recently-developed classical molecular dynamics model of the rutile-water interface is being used to investigate the viscosity distribution in the near-surface region, representing the first known computational representation of the spacial viscosity distribution for a molecular liquid at an interface. These simulations reveal a layer of strongly bound water molecules about 5 Å thick with essentially zero viscosity. From 5-15 Å a transition zone is observed in which the water structure is intermediate between the structure dictated by the crystal truncation and that of bulk water, and exhibiting a viscosity about 30-50% lower than that of bulk water. This observation of a region of high water mobility between the surface and the bulk phase will have major implications for hydrodynamics at the molecular level.

Neutron reflectivity studies of quartz single crystal surfaces in contact with water containing very large ions, such as poly(diallyldimethylammonium) and amphiphilic phospholipids, and hematite (α-Fe_2O_3) nanoparticles, in order to probe the long-range structure of the electrical double layer near the charged quartz surface. Small angle neutron scattering studies were also conducted on silica nanospheres in solutions containing the same phospholipids in order to determine the surfactant orientation and density at the solid/solution interface. Work continues on the properties of colloidal crystals formed by charged silica nanospheres in water, including manipulation of the particle hydrophobicity, which influences the colloidal crystal structures and photonic properties. We have also successfully synthesized rutile and cassiterite nanocrystals (5-6 nm average particle diameter), with the (110) crystal face predominant, for future studies of water dynamics at the oxide/solution interface using quasielastic neutron scattering techniques.

Fundamental Research in Isotope Geochemistry: Experimental, Molecular-Based Simulation, and Neutron-Scattering Studies of Fluids and Minerals

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Objectives: The objective of this project is to address macroscopic –, molecular –, and atomic – scale aspects of isotopic effects and associated isotope fractionations in fluids and minerals under conditions relevant to earth and planetary sciences in general. Recent findings of the pressure and fluid-composition dependencies of isotopic fractionations have dramatically changed a principal premise in isotope geochemistry.

Project Description: Accurate quantification of macroscopic isotope fractionation and better understanding of fundamental causes of isotopic effects in fluids and minerals are very important. We investigate these fundamental issues, using a synergistic approach of theoretical, computational, and experimental methods, including neutron scattering techniques. A model mineral – fluid system, brucite [$Mg(OH)_2$] – type minerals and simple molecular fluids (O_2, CO_2, and water, etc.), is investigated in depth, because these minerals and fluids serve as simple, yet useful analogs of more complex materials of geochemical interest. The specific goals are: (a) accurate laboratory determination of macroscopic isotopic fractionation between brucite – type minerals and water at high pressures (2 – 5 GPa), (b) molecular – based simulations and theoretical modeling for the isotopic effects of more complex molecular fluids, including water, and (c) advanced *in situ* neutron diffraction and scattering for D/H isotope effects on the structure and dynamics of brucite – type minerals at high pressures ($\leq$10 GPa).

Results: In order to understand high-pressure structure and hydrogen-bonding of brucite, we have conducted a first test of neutron powder diffraction at a recently upgraded Wide Angle Neutron Diffractometer (WAND) of the High Flux Isotope Reactor at Oak Ridge National Laboratory. Both hydrogenated and deuterated brucite, $Mg(OH)_2$ and $Mg(OD)_2$, were hydrothermally synthesized at 250ºC, by reacting high-purity powders of MgO, and normal and heavy waters, respectively. Sufficiently strong diffraction patters were obtained even from hydrogenated brucite. To determine the vapor-liquid equilibrium envelopes on O_2, N_2, CO, CO_2, and H_2O fluids, Gibbs Ensemble Monte Carlo simulations were performed on several molecular models, using realistic multi-site intermolecular potentials, including accurate intermolecular potential models. Canonical molecular dynamics simulations were also performed along the liquid-vapor coexistence curves of O_2, N_2, CO, CO_2, and H_2O, in order to assess the orthobaric temperature dependence of the vapor-liquid isotopic partitioning. Using these molecular-based simulation results and the Kirkwood-Wigner expansion approach, we have successfully predicted the vapor-liquid isotopic partitioning of $^{16}O_2/^{16}O\text{-}^{18}O$, $^{14}N_2/^{14}N\text{-}^{15}N$, and $^{12}CO_2/^{13}CO_2$. The simulation data for $^{12}CO/^{13}CO$ and $C^{16}O/C^{18}O$ are also being processed.

Multi-Scale Studies of Fluid-Rock Interaction

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Objectives: The objective of this research is to investigate how the microscale elemental and isotopic record, accessible using ion microprobe analysis, can be used to understand mass transfer processes occurring during fluid-rock interaction at low to moderate temperatures in the earth's crust, through interrogation of both natural and experimental samples.

Project Description: In this project, the ability of ORNL's Cameca 4f ion microprobe to obtain quantitative element and light (H, B, C, O, S) isotope ratio analyses with a 5-30 micron spatial resolution are being developed and applied to studies of fluid-rock interactions in a variety of settings, in both natural and experimental systems. The ion microprobe data is typically integrated with information obtained using a variety of other techniques, petrographic studies, conventional bulk gas source and thermal ionization isotope ratio analyses, electron microprobe, and fluid inclusion analysis. Primary areas of investigation include (1) use of the microscale isotope record to study mass transport during large-scale fluid-rock events, (2) determination of both diffusion rates and equilibrium water-mineral isotope partitioning factors in the O, H, and C systems, and (3) utilizing microscale isotopic and elemental disequilibrium in natural settings to study the duration of fluid-rock events.

Results: We have examined and compared the factors that control the behavior of water in glasses at both low- and high-temperatures. Surface concentrations, which equilibrate quickly at high temperature, change far more slowly as temperatures decrease, and may not equilibrate at room temperature for hundreds or thousands of years. Diffusion coefficients based on SIMS profiles are compositionally dependent under all known conditions, but at lower temperatures they appear to be time-dependent due to the build-up and relaxation of stress. Low-temperature FTIR data suggest that hydroxyl and molecular water are present, but represent a time-averaged bonding environment for hydrogen in the glass.

SIMS was coupled with high-resolution transmission electron microscopy (HRTEM) to quantify the relationship between nanotextures, oxygen isotope signatures and U-Pb ages in minerals. Minerals yielding the youngest ages have light $\delta^{18}O$ values, consistent with interaction with recent fluids. These minerals exhibit nano-size domains (5nm), allowing for fast diffusion of Pb (the daughter product of U) which results in young U-Pb ages. Phases retaining original U-Pb ages have also retained their original oxygen isotopic composition. Nanotextures in these phases which preserve original U-Pb and oxygen isotope compositions consist of micrometer-scale domains. These observations clearly demonstrate that nanoscale transport mechanisms (governed by nanotextural features) control the presence or resetting of both anion and cation isotope systems.

An experimental study was conducted to quantify the rate of breakdown of dolomite in rock cores as a function of both grain boundary diffusion and the rates of mineral reaction. Reaction products occur mainly along grain boundaries, fractures within grains, and along sample edges. Ion images and isotope-ratio analysis indicate that reaction products exchanged with infiltrating fluids. Isotopic enrichments in unreacted dolomite bordered by grain-boundary reactants suggest that diffusion continued beyond the reaction front. The extent of reaction was found to have a log-linear relationship with the square root of time, suggesting grain boundary diffusion controlled the rate. Initial reaction occurs relatively fast near the surface of dolomite grains, but continued diffusion through the reaction products ultimately controls the rate of dolomite breakdown.

Investigation of Mineral Reaction Zones and Associated Interfaces

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Objective: The purpose of this effort is to investigate the coupling of isotopic exchange with mineral replacement reactions. Mineral-fluid experiments provide the basis for quantitative insights into the isotopic, chemical and textural behavior in systems, where a reaction front moves into a single crystal (or monomineralic powder) that can be characterized with a variety of imaging and analytical methods.

Project Description: Microscale studies (high precision of small sample sizes or *in situ* spot analysis) of mineral-fluid interaction in natural systems indicate that isotopic heterogeneity and disequilibrium may be more widespread than previously realized. A number of key issues still remain poorly constrained: (a) the chemical, isotopic and textural features (e.g. porosity) associated with reaction zones and their rate of formation, (b) the nature of chemical and isotopic communication across the reaction zone as well as possible confinement effects on fluid properties and behavior, and (c) the molecular and atomistic details of the interface between the product and parent phases. Three chemical systems are currently being examined: the conversion of periclase to brucite, breakdown of dolomite, and cation exchange in alkali feldspars. In addition to traditional analytical approaches such as the ion microprobe and TEM, we are using neutron and x-ray scattering methods to interrogate the structural features of the reaction zone and interface, and fluid properties within the porous reaction layer.

Results: High resolution transmission electron microscopy (HRTEM) combined with secondary ion mass spectrometry (SIMS), and electron and X-ray back scatter spectrometry were used to document the mechanisms and rates of reaction rim formation on Na-K feldspars reacted with isotopically-labeled NaCl and KCl solutions at temperatures from 300-600°C and 200 MPa. These studies revealed fluids infiltrate the reaction rim through a finely divided set of nano-fractures that have been produced from the build-up of coherent stress during reaction. We also observed nanoscopic pores occurring at the reaction interface and within the rim itself. Ultra-small and small angle neutron scattering (USANS and SANS) experiments conducted at NIST documented the development of fractal-like features within the reaction zones.

The behavior of fluids under confinement was investigated using a number of techniques including gravimetric-based sorption, small-angle neutron scattering, and simulations. High temperature (100-200°C) sorption of water was quantified for phases such as zeolites, clay, porous silica and porous carbons. Water sorption in porous carbons (with slits or cylindrical pores) was simulated with Grand Canonical Monte Carlo and these results were compared to measured isotherms. CO_2 adsorption in silica aerogels near and above the critical temperature was investigated with SANS. These results revealed for the first time that SANS coupled with neutron transmission can be used to determine adsorption behavior of a confined supercritical fluid.

An experimental study was conducted to quantify the rate of breakdown of dolomite in rock cores as a function of both grain boundary diffusion and the rates of mineral reaction. Reaction products occur mainly along grain boundaries, fractures within grains, and along sample edges. Ion images and isotope-ratio analysis indicate that reaction products exchanged with infiltrating fluids. Isotopic enrichments in unreacted dolomite bordered by grain-boundary reactants suggest that diffusion continued beyond the reaction front. The extent of reaction was found to have a log-linear relationship with the square root of time, suggesting grain boundary diffusion controlled the rate. Initial reaction occurs relatively fast near the surface of dolomite grains, but continued diffusion through the reaction products ultimately controls the rate of dolomite breakdown.

Experimental and modeling support was provided to studies of water diffusion in obsidian glass for conditions below the glass transition. SIMS, FTIR and neutron reflectivity (NR) were used to interrogate the hydration layers in Obsidian exposed to water vapor at temperatures up to 150°C. The NR results are particularly noteworthy because we were able to effectively measure depth profiles below of about 1000Å.

Ultra-small and small angle scattering experiments were conducted at the Center for Neutron Research at NIST. Three types of materials were examined; natural recrystallized limestones from Marble Canyon, TX; limestone reacted at elevated temperatures with CO_2; and feldspars reacted with salt solutions at elevated temperature and pressure. In each case we observed interesting development of fractal-like behavior in the low Q range.

Experimental Studies of Hydrothermal Processes Employing In Situ pH Measurement

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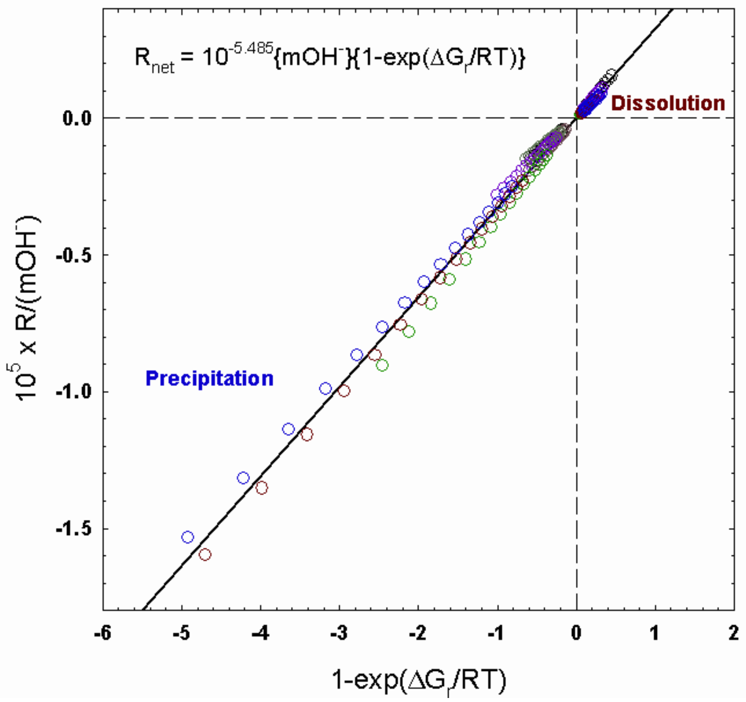
Objectives: The objective of this project is to utilize ORNL's unique, high temperature, hydrogen-electrode, pH-measurement cells and other potentiometric and hydrothermal approaches to study aqueous reactions and water/mineral interactions relevant to DOE's geoscience mission areas. The results have broad applications in the design of energy utilization and waste isolation schemes.

Project Description: The focus of this effort is to understand aqueous reactions of critical importance in modeling a variety of fluid-rock interactions and related hydrothermal processes which impact oil, gas, and geothermal resource formation and exploitation, contaminant migration and remediation, deep subsurface fluid/rock interactions, and a wide range of general geochemical and industrial processes. The effort is focused on experimental studies using the unique capabilities of ORNL's high temperature pH-measurement, flow-through and rocking-autoclave hydrothermal facilities. With these capabilities, we are investigating the speciation of metals (Al, Fe, Zn, Ni, Rare Earths, etc.) in low to high temperature brines, the dissociation constants, thermal stabilities, and complexing characteristics of naturally-occurring organic acids, and the thermodynamics of low to high temperature brine solutions in the system Na-K-Ca-Mg-Al-Si-Fe-O-C-H-Cl-S. Recent developments have enabled us to address the surface charge, sorptive properties, dissolution/precipitation kinetics, and solubilities of important minerals and energy-production materials.

Results: A series of experimental studies the redox-metastable transformation of magnetite (Fe_3O_4) to hematite (Fe_2O_3) at temperatures of 100 to 250°C in aqueous solutions saturated with high hydrogen (H_2) pressures was completed in collaboration with Ph.D. candidate Tsubasa Otake and Professor Hiroshi Ohmoto at Penn State University. This work demonstrates that the common assumption, that these abundant iron oxides reflect the oxidation state of the environment in which they formed, can be incorrect, since reaction of low-pH brines with magnetite readily produces highly-crystalline hematite, even under extremely-reducing conditions and elevated temperatures.

During this period, we also completed experimental studies of the stability and solubility of dawsonite, $NaAlCO_3(OH)_2$, at 50-200°C in aqueous solutions saturated with high CO_2 overpressures, representative of CO_2-sequestration environments. This phase is predicted for form by reaction of high-CO_2 brines with feldspars in subsurface aquifers and cap-rocks, thus potentially playing a role in the hydrodynamics of CO_2 injection as well as the integrity of the reservoir. Incongruent breakdown of dawsonite to bayerite or boehmite (aluminum oxyhydroxides) was observed at lower temperatures and/or CO_2 pressures.

Additional research included a.) exploratory studies of the rates of hydrogen gas (H_2) production from a wide range of naturally-occurring Fe(II) silicate minerals collected from sedimentary iron formations and ultramafic intrusions, with measurable hydrogen production rates (due to reduction of water) found for all rock types tested at temperatures of 200-350°C; and b.) completion of data analysis of experimental rate studies of gibbsite – α-$Al(OH)_3$ – and boehmite - α-$AlOOH$ – dissolution and precipitation in the 50-150°C range using a unique pH-perturbation method that enables rates to be determined at very near equilibrium conditions. Boehmite dissolution/precipitation rates in 0.1m NaCl at 100°C, over a wide range of pH (6-10), are plotted in the Figure, as a function of the deviation of the free-energy of reaction (ΔG_r) from the equilibrium state, where $\Delta G_r = 0$.



Thermodynamic Mixing Properties of C-O-H-N Fluids

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Objectives: Thermophysical data for CO_2-CH_4-N_2-H_2O-NaCl fluids at high temperatures and pressures are insufficient in quantity and quality to permit formulation of accurate equations of state (EOSs) for natural, deep-seated fluids in the Earth's crust (hydrothermal waters, natural gas, etc.) Such equations would have numerous applications in geochemistry, including geothermal- and hydrocarbon-reservoir hydrodynamics modeling, calculation of fluid-rock equilibria, predicting permeability changes in resource host rocks, quantifying contaminant transport, and characterizing global cycling of greenhouse gases.

Project Description: Experiments are performed with binary and multicomponent mixtures of CO_2, CH_4, N_2, H_2O and NaCl at temperature-pressure conditions similar to those encountered in deep aquifers, sedimentary basins, geothermal fields and many ore-forming environments. Volumetric properties and liquid-vapor phase relations are determined with high precision and accuracy using a unique vibrating-tube densimeter designed for operation at 50-500°C and 5-200 MPa. The activity-composition relations of the fluids are measured using another unique facility: a hydrogen-service internally heated pressure vessel capable of operation at high hydrogen fugacities, with an overall operating range of 100-1100°C and 5-800 MPa. Laboratory experiments and thermodynamic modeling are closely integrated to optimize the efficiency and effectiveness of data acquisition and EOS development.

Results: The most successful published equation of state (EOS) for CO_2-H_2O mixtures, developed by Duan et al. (1992), consists of a truncated virial series augmented by two terms possessing Gaussian exponential dependence on fluid density. While the expression performs reasonably well over wide ranges of state space, it also gives rise to physically unrealistic predictions of phase-equilibrium behavior, which are probably the result of deficiencies in the parameterization of the temperature-dependence of the virial coefficients. To rectify these problems, we developed a more robust model that uses a Helmholtz energy-based (pressure-explicit) EOS to represent density isotherms for the vapor, and a Gibbs energy-based (volume-explicit) EOS to represent the corresponding liquid-density isotherms as a function of pressure and composition. This modeling strategy gives rise to the pressure-explicit, four-term virial equation for the vapor, and the Krichevskii-Il'inskaya equation for the liquid.

Evaluations of the new EOS discussed above indicate that measured densities for CO_2-H_2O mixtures at 350°C are adequately represented, but the data are not quite numerous enough to permit estimation of all the mixture fourth virial coefficients to a high degree of statistical significance. The approach we have developed to obtain more reliable values of these coefficients involves estimating: (1) the first four *endmember* (pure CO_2 and H_2O) virial coefficients by fitting volumetric data suitable for constructing reference-quality EOSs for these fluids; and (2) the first three *mixture* (CO_2-H_2O) virial coefficients using published excess enthalpy measurements derived from flow calorimetry.

The four-term virial equation of state expresses the compressibility factor as a cubic function of the density, but determining virial coefficients from experimental data is more complicated than might be supposed. The values of the virial coefficients strongly depend on the multiplicative weights assigned to the data, and hence on the estimated precision of those results. Correct assignment of weights becomes particularly important when data from different sources are combined. In fitting EOSs to isothermal, polybaric density data, the fact that errors in values for density are almost never negligible in comparison with those for pressure requires use of Generalized Nonlinear Least Squares (GNLS), even though the the fitted EOS is linear with respect to its parameters.

Using isothermally derived virial coefficients to represent nonisothermal density data generally produces poor results. We have developed an improved procedure for the analysis of nonisothermal density data in which the least-squares calculation is embedded into a discrete optimization of the analytical form of the temperature dependence. GNLS is then used to estimate the parameters in the function that provides the lowest sum of squared residuals. Calculations to date have shown that volumetric data for supercritical CO_2 can be represented to within experimental error by EOSs designed in this way.

Isotopic Fractionation of Carbonate Systems Relevant to Subsurface CO_2-Sequestration

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Objectives: The objective of this project is to understand and quantify several key reactions controlling kinetic and equilibrium isotope partitioning during the precipitation, recrystallization, and transformation of carbonate minerals (calcite, dolomite, siderite) in CO_2-rich fluids at conditions encountered in various geologic settings (groundwater, deep aquifers, sedimentary basins, geothermal systems, etc.).

Project Description: This project is focused on: the mechanisms, rates, and isotope fractionation during three different reaction pathways leading to the formation of dolomite, the second most abundant carbonate mineral, as functions of several key variables (e.g., temperature, degree of supersaturation, ionic strength, microbial activity, inhibitor-promoter, etc.): (1) microbial and possible abiotic precipitation at low temperatures, (2) overgrowth of dolomite on seed crystals at intermediate temperatures, and (3) dolomitization of calcite and aragonite in Mg-rich solutions at intermediate to high temperatures. Microscopic- to macroscopic-scale measurement and characterization of solution chemistry and the solid phase will allow us to determine reaction mechanisms and rates as a function of time. Experimental results on oxygen and carbon isotope partitioning during the three different reaction pathways leading to the formation of dolomite will provide key information necessary for solving the "dolomite problem."

Results: We have successfully synthesized (proto)dolomite with the composition of $Ca_{0.51}Mg_{0.49}CO_3$ and an average grain size of 15 nm at 80°C. Also, a series of dolomitization experiments was conducted using powder calcite between 150 and 300°C. XRD shows that the products have a dolomite composition with peaks of cation-ordering, but no calcite or Mg-rich calcite. Our data of the oxygen isotope fractionation factor between these dolomite and water provide much-needed accurate information on this fractionation factor. We initiated a neutron pair-distribution-function (PDF) study of dolomite, both natural and experimental, in order to investigate the local structure and cation order-disorder of low-temperature dolomite. A set of natural and synthetic dolomite were characterized for their stoichiometry and purity. Holocene dolomite samples are in the excess of Ca with weak or no-ordering peak (protodolomite), while older dolomites are nearly stoichimometric with clear ordering peaks. We have conducted a first session of neutron PDF measurements for select dolomite samples discussed above at the Los Alamos Neutron Scattering Center (LANSCE) and the obtained data are currently being refined and modeled to investigate the local structure and Ca-Mg order and disorder of dolomite.

PACIFIC NORTHWEST NATIONAL LABORATORY

CONTRACT: RL01830

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

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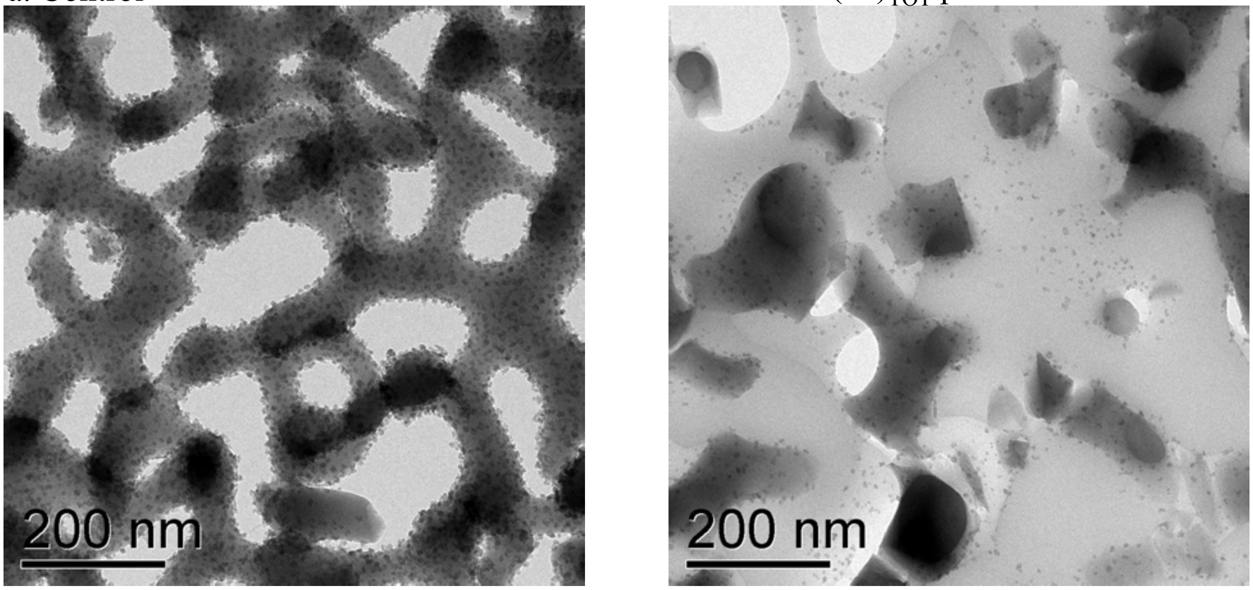
Objectives: Research is focused on the two following scientific questions. 1.) Can metal reducing bacteria induce the mineralogic transformation of nanometer-sized Fe(III) oxides that exhibit limited physical accessibility to whole cells, such as those that reside in microscopic fractures of lithic fragments or within the three dimensional matrix of a particle coating? 2.) Does the co-localization of nanoparticulate Fe(III) oxides in silicate micropores or particle coatings with Fe(II)-adsorbing accessory phases influence the nature of mineralogic products produced by chemical and biological reductants?

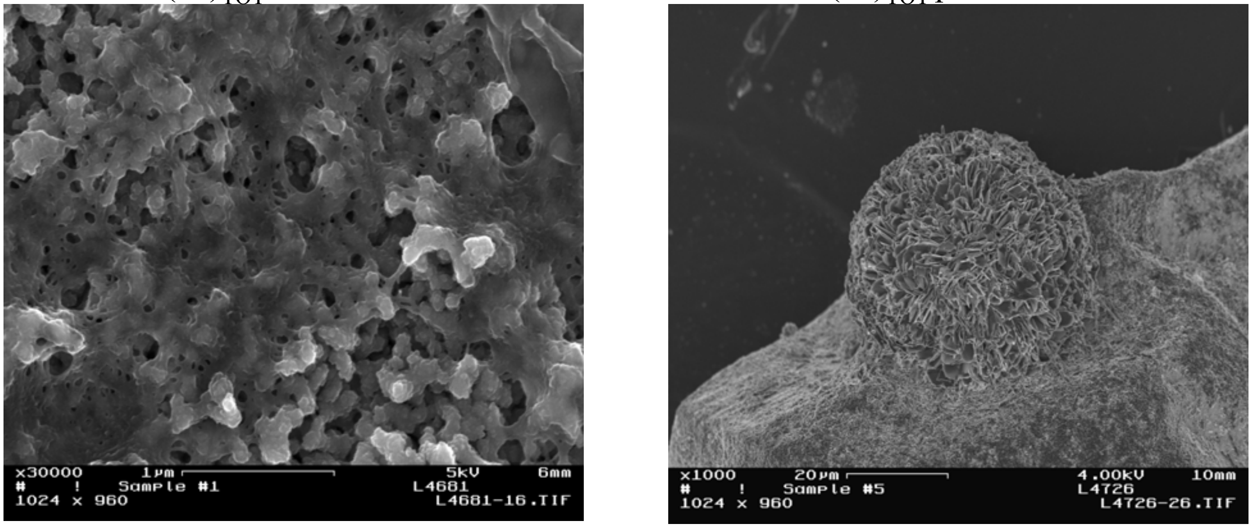
Project Description: The research project is using synthetic subsurface sediments with Fe(III) oxides in controlled distribution [e.g., Figure 1a, note nanoparticulate Fe(III) oxides present as small dark specks on internal channel surfaces of microporous silica] and natural materials containing particle coatings and intragrain precipitates of Fe(III) oxides to address the scientific questions stated above. The Fe(III) oxides being studied include 2- and 6-line ferrihydrite, nanoparticulate goethite, and lepidocrocite. Laboratory studies are being performed using static and dynamic-flow experimental systems with diffusible chemical reductants (bioreduced anthraquinone disulfonate) and chemotactic iron reducing bacteria to evaluate whether microorganisms can access iron oxide electron acceptors in pores and fractures that are smaller than the nominal size of the cell. Abiotic and biotic reduction kinetics are being monitored in response to changes in experimental variables, and variable temperature Mossbauer spectroscopy, conventional and synchrotron x-ray diffraction, micro-XANES spectroscopy, 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 target iron-reducing microorganisms (*Shewanella*, Anaeromyxobacter) were able to reduce intragrain Fe(III) oxides in the absence of direct contact with the outer cell envelope [note depletion of nanoparticulate Fe(III) oxides from intragrain surfaces, Figure 1b]. This finding was unexpected because the metalloproteins responsible for electron transfer are believed to be anchored to the outer cell membrane, requiring both continuity with the intracellular electron transport system of the bacteria and direct contact with the Fe(III) oxide surface to be functional. Intragrain reduction is facilitated by the production of exopolymeric substances by the organism [note surface coatings in Figure 1c], that invade intraparticle space and facilitate contact with inaccessible electron acceptors by as yet unidentified mechanisms. Bioreduced Fe(II) is held in internal pores of the solid phase if adsorbing phases are present, or diffuses to the grain surface a precipitates as a secondary solid as shown for biomineralization product vivianite [$Fe_3(PO_4)_2$; Figure 1d]. Correlations between intragrain/coating diffusivity and bioreduction rate are sought.



a. Control

b. 5 mM Fe(III)$_{TOT}$ plus P



c. 5 mM Fe(III)$_{TOT}$

d. 5 mM Fe(III)$_{TOT}$ plus P

Figure 1. A synthetic subsurface sediment was created by precipitating 6-line ferrihydrite in intragrain channels of porous silica. TEM analysis revealed that nanoparticulate ferrihydrite was uniformly distributed in intragrain pores with 100 nm diameters (a). The Fe(III) oxides were reduced when incubated with iron reducing bacteria and electron donor (b). During incubation, a thick layer of exopolymeric substance was deposited on the porous silica surface (c). Vivianite precipitated on the porous silica surface in distinct morphologies when P (at 0.4 mM) was present in the media (d). The distinct precipitate morphology was controlled by the rate of Fe(II) supply to the particle surface as influenced by the bioreduction rate and intragrain diffusivity.

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

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Objectives: The focus is a computational study to develop a fundamental molecular level description of the interactions of Gram-negative microbial membranes with subsurface materials.

Project Description: We are developing a better understanding of the molecular processes involved in 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. The project is focused on 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. A combination of molecular dynamics simulations and electronic structure calculations are providing new insights into the detailed molecular behavior of these membranes. The modeling capability allows the transfer of the necessary fundamental information across the needed series of spatial scales, and includes molecular level simulations of small molecular clusters, molecular dynamics investigations of large molecular systems, and predictions of macroscopic geochemical reactions using thermodynamic models.

Results: An important aspect of the structure of the LPS membrane as well as ion transport in the LPS is the ability of the sugar side groups such as the carboxylic acids and the phosphates to bind positively charged ions. Electronic structure calculations at the molecular orbital theory and density functional theory levels are being used to predict the free energies of solvation of ions in aqueous solution as well as in media with different dielectric constants, the acidity of the critical groups in the sugars in the LPS, and the binding of metal ions to the sugar anions, including the important environmental contaminant, UO_2^{2+}. The calculated values show that the phosphorylated sugar sidechains are much stronger acids in the gas phase than H_3PO_4, and in fact, the acidity of one is stronger than that of H_2SO_4 in the gas phase. The pK_a's of the phosphorylated sugars show that they are stronger acids in solution as compared to phosphoric acid, with the heptose being a very strong acid. The changes in acidities are correlated with hydrogen bonding in the sugars and with differential solvation effects. A component of the study is to predict the solvation properties of metal ions in aqueous solution. As part of this effort, we are predicting the solvation energies of ions in aqueous solution using a supermolecule-continuum solvation model developed in the group. We have used this model to study novel aspects of the solution chemistry of the uranyl cation. Our calculations are in agreement with the recent HEXS result that an equilibrium exists between four- and five-coordinate uranyl: $UO_2(H_2O)_4^{2+} + H_2O \leftrightarrow UO_2(H_2O)_5^{2+}$ and the latter is favored thermodynamically, counter to prevailing concepts of uranyl solvation.

In order to estimate the relative binding affinity of uranyl by the LPS membrane, the quantum-mechanical data was used in the development and validation of a parameter set for classical simulations of uranyl uptake by the LPS. Potentials of mean force molecular dynamics simulations were carried out to determine the free energy of the process. This profile was compared with free energy profiles for the uptake of sodium, calcium, chloride and a water molecule. As expected, due to the negatively charged surface of the LPS membrane, the uptake of negatively charged species, such as chlorine, by the membrane is found to be an unfavorable process. On the other hand, the uptake of cations is energetically favorable. The rough LPS of *P. aeruginosa* shows a relatively greater affinity for the uranyl ion as compared to the other cations. However, at neutral pH (our conditions) the nuclide remains partly solvated and binds to the outer core carboxyl and hydroxyl groups. Experimental studies in the low pH range (pH 3-5) describe also the participation of LPS phosphate-containing residues in uranyl complexation. Although *P. aeruginosa* does not tolerate low pH levels, the LPS of dead cells can still effectively be used for uranyl uptake as can live cells, widening the applicability of such biomaterial for environmental remediation.

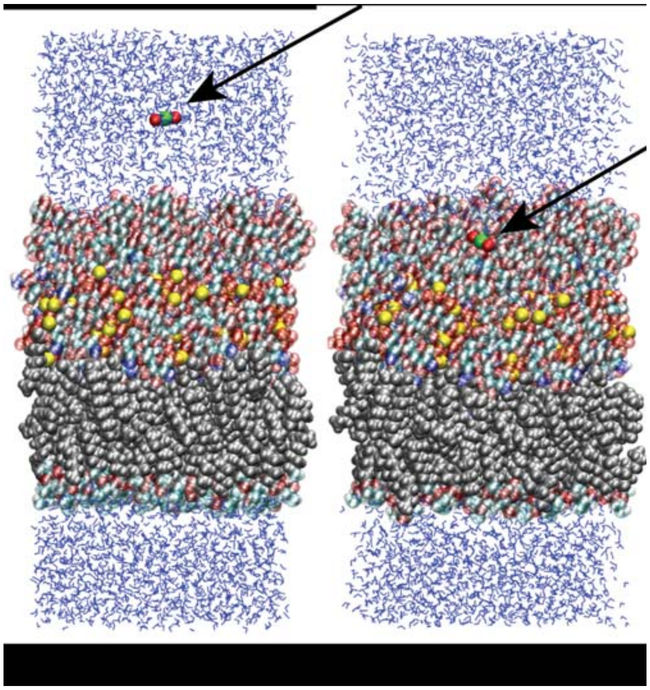

Figure 1. LPS-uranyl interactions. a) Initial and b) final configurations of the simulated uranyl uptake by the LPS membrane. (Uranyl is shown in solid CPK model).

Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces

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Objectives: This project aims to: 1) Determine chemical mechanisms for dissolution of specific surfaces of major oxide minerals, 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 major 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 FY06, microscopic examination of the dissolution of quartz (100) and (110) surfaces by KOH solutions led to identification three major categories of dissolution features (retreating steps, etch pits at crystal voids, and etch pits at dislocations) that dominated the release of material into solution. The rates of step retreat measured on both surfaces were similar, but the development of surface topography on the two surfaces is substantially different due to differences in defect populations. Despite the differences in the developing surface topographies of the prismatic and rhombohedral surfaces, we found that macroscopic dissolution rates could be rather well approximated by summing the separate rate contributions from the various dissolution features on the two different surfaces at the densities at which they occur. This result suggests that despite substantial overlap of the dissolution features during advanced stages of dissolution, their survival and therefore the overall dissolution rate can still be estimated simply by knowing the defect types that underlie them, in conjunction with the solution conditions. In current work, this finding is being contrasted with the behavior of electronically more complex oxide materials such as the Fe(III)-oxides during reductive dissolution.

Reaction and Transport of Toxic Metals in Rock-Forming Silicates at 25°C

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Objectives: To better understand electron transfer reactions between Fe(II) in silicates and sorbed 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 silicate 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: Important contributions in FY06 included a careful analysis of a series of U4f spectra that showed varying degrees of reduction. Using factor analysis and both constrained and unconstrained fitting of spectral features we were able to convincingly demonstrate that the satellite features normally associated with monovalent U(IV) and U(V) oxides are also robust indicators of U oxidation states in mixed valence U oxides. In other work we showed that even Fe(II) poor micas, under both oxidizing and reducing conditions, can reduce minor to trace amounts of U(VI) that have diffused into the interlayer region and that electron transfer must occur across the tetrahedral layer. Diffusion modeling coupled with XANES indicated that the reduced species was immobile and that only the oxidized species diffuses. Further, once reduced in the interlayer, reoxidation to U(VI) is kinetically hindered.

With respect to ab initio modeling of XPS and XANES spectra of actinides, much of the year was spent writing code and adapting codes for use on parallel computer systems in order to take into account environmental effects. The actinides pose a significant challenge due to the number of electrons in the system and the need to consider relativistic effects even for the valence level. We are now positioned to calculate the XANES and XPS of small embedded cluster models such as UO_8 to simulate the effect of covalency on the multiplet structure of UO_2 and to implement charge transfer configurations and higher order excitations.

Computational Investigation of Acid-Base, Surface Complexation and Oxidation/Reduction Mechanisms

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Objectives: The purpose of this project is to acquire a molecular-scale understanding of the chemical speciation at the surface and in the bulk of iron oxides by means of experimental techniques.

Project Description: This project consists of an experimental investigation of the reactivity of hydroxyl groups on goethite and hematite surfaces. It partially seeks to build upon previous funding cycles in which Molecular Dynamics calculations of the goethite surface have provided insight into the reactivity of individual goethite surface hydroxyls. Attenuated Total Reflectance (ATR) and Temperature Programmed Desorption (TPD) Fourier Transform Infrared (FTIR) measurements were used to study surface hydroxyls in the gas phase as a function of total acidity in the presence and absence of surface-bound carbonate and oxalate ions. The thermal-decomposition products of goethite were also monitored to study bulk-sequestered carbonate. Finally, hematite platelets exhibiting different edge-to-base ratios were investigated by cryogenic X-ray Photoelectron Spectroscopy (XPS) to provide insight into the reactivity of the neutrally-charged doubly-coordinated $\equiv Fe_2OH^0$ (μ-OH) group of the {001} basal plane towards Na^+ and Cl^- ions.

Results: The gas-phase O-H stretching vibrations of goethite nanoparticles dried under different total acid concentrations were correlated to different surface hydroxyls, also using the results of previous work by Rustad *et al.* (1996, *Geochim. Cosmochim. Acta*, vol. 60, 1553). These stretches were correlated to changes in total acidity resulting from the adsorption of carbonate and oxalate ions. TPD-FTIR measurements revealed that the singly-coordinated hydroxyls are expelled at lower temperatures than μ-OH and bulk hydroxyls. Carbonate TPD reactions are correlated to the loss of surface hydroxyls. Bulk-bound carbonate ions are expelled at larger temperatures than bulk dehydroxylation reactions. These results spun new efforts towards sequestered carbonate in the context of paleoclimatological studies. Finally, different mechanisms of oxalate TPD were correlated the molecular surface speciation (electrostatic-, hydrogen- and iron-bonded). The desorption of iron-bonded species notably proceeds through an electron transfer reaction to the surface, liberating $CO_2(g)$.

Cryogenic XPS measurements of fast-frozen wet pastes of hematite platelets revealed a strong correlation between the fraction of basal plane and multiple layers of hydrated Na^+ and Cl^- ions. These are proposed to have arisen from a structured array of Na^+ and Cl^- ions at the basal plane of hematite in aqueous solution.

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 CO_2, the storage of nuclear waste, and the transport of toxic materials. The 1st principles based simulation methods that are being used and developed allow the parameter free prediction of the properties of these chemically complex materials over the wide range of conditions encountered in geological applications.

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

Applications Results: See UCSD report (PI John Weare)

Methods Developments Results: An important problem with standard local density functional theory (DFT) methods is they fail to yield localized charge states such as polarons, excitons and solitons and to describe highly correlated bond formation by electrons in transition metals and actinide elements. These methods, which do not treat electron self-interaction correctly, tend to favor delocalized electronic states. Pragmatic approaches in which the exchange correlation functionals of local density functional theory (LDA, BLYP, PB96) are augmented with small amount of exact exchange (e.g. B3LYP and PBE0) have shown promise in localizing charge states and predicting accurate band gaps and reaction barriers for elements with highly correlated electrons (e.g., in actinides and transition metals). We have implemented exact exchange and self-interaction corrected DFT into pseudopotential plane-wave density functional theory. In FY06, several improvements were added to this code, including atomic forces, stresses, and Car-Parrinello *ab initio* molecular dynamics (now available in the NWChem program package). The hybrid DFT code has been applied to several systems for which standard DFT methods do not work well, including excitons in quartz and rutile, polarons in hematite and annite, and oxygen vacancies on the 110 rutile surface. As shown in Fig. 1 for the defected 110 rutile surface there is a significant degree of charge localization using hybrid DFT that would not be correctly described in standard DFT. Note that the qualitative change in the density of states of the rutile surface illustrated would have very important consequences to the reactive and electronic properties of the surface.

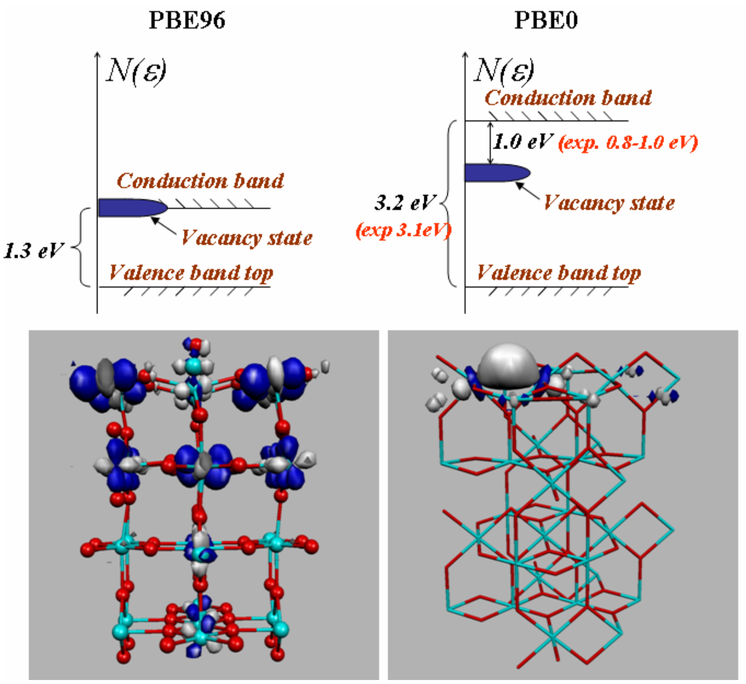

Figure 1. The density of states and the corresponding top most Wannier orbital of an oxygen vacancy on the 110 rutile. Left: vacancy state delocalized with DFT (not in agreement with observations); Right: vacancy state localized with hybrid DFT (in agreement with observations).

SANDIA NATIONAL LABORATORY/ALBUQUERQUE

CONTRACT: AL85000

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Models of Environmental Materials: Sorption, Intercalation, and Interfacial Behavior of Layered Minerals

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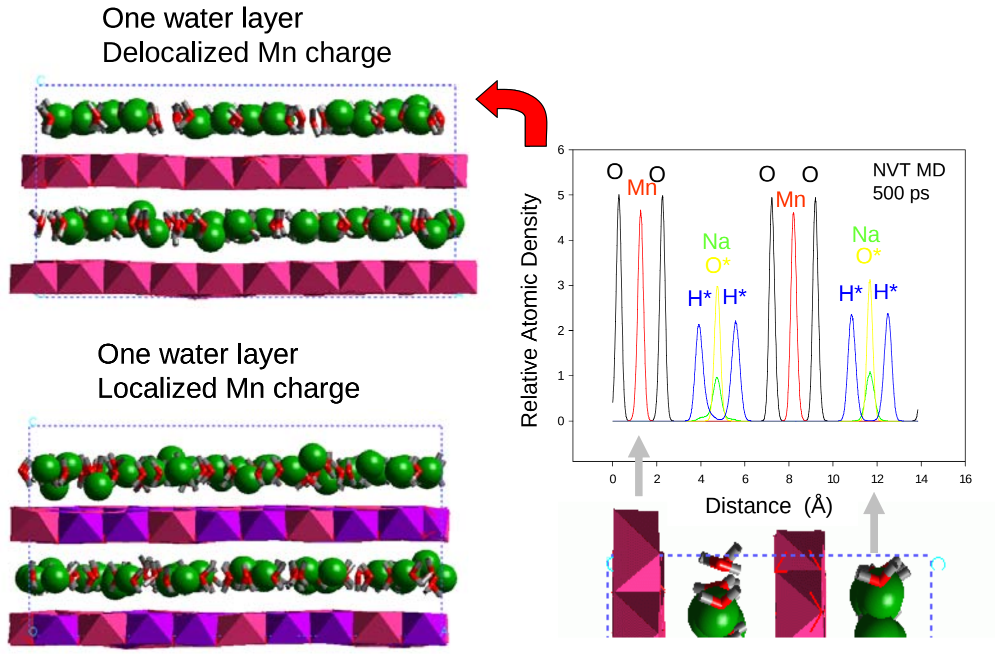
Objectives: Development of computational tools and forcefield parameters for the accurate simulation of environmental processes, especially those chemical mechanisms associated with layered nanomaterials and soil minerals that are difficult to evaluate using conventional analytical methods. Classical and quantum simulation methods are used to evaluate interfacial structure and dynamics of selected oxide, hydroxide, and aluminosilicate systems.

Project Description: An atomic level understanding of mineral-water interactions is important for the evaluation and prediction of numerous properties of clays and other related minerals, especially in the treatment of environmental waste. In particular, the behavior of water at the clay interface controls many processes including solvation, adsorption, precipitation, and growth. Our ability to understand these complex processes is provided by a few experimental and analytical methods. However, due to complexities in the structure, composition, and nano-size of clays it is important to apply theoretical molecular models to obtain a fundamental understanding and interpretation of these phenomena. We have developed a general forcefield CLAYFF suitable for the simulation of hydrated mineral systems, including several clay, layered manganese hydroxides, and layered double hydroxide (LDH) phases.

Results: Birnessite is one of the most enigmatic environmental materials to be investigated by geochemists and mineralogists. The unique exchange and adsorption properties of birnessite are structurally related to the charge layer structure and the coexistence of heterovalent manganese cations in the edge-sharing octahedral layer. Consequently, birnessite has the ability to efficiently adsorb and fix trace elements including heavy metals in marine and continental sediments. We have recently teamed with researchers from the Smithsonian Institution and Pennsylvania State University to combine experimental and spectroscopic methods with molecular simulations to investigate the atomic structure and behavior of monohydrate and two layer hydrate birnessite ($NaMn_3O_6 \cdot nH_2O$). The simulations were performed to test the hypothesis that the disorder valence state of manganese within the layer will influence the disposition and dynamics of the interlayer cations. The CLAYFF-based NVT molecular dynamics results for simulation cells of approximately 1200 atoms for 0.5 ns of simulation time indicates a birnessite interlayer with the hydration of the sodium in the central region based on the delocalization of manganese charge in the octahedral layer (see figure). In contrast, using the localized charge model where unique two manganese valence states occur, we observe the occurrence of inner sphere adsorption of sodium directly to the octahedral layer.



Comparison of simulated monohydrate birnessite structures based on different charge distributions for the manganese octahedra (left) and the corresponding atomic density profile for the upper delocalized charge model (right).

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 spectroscopies (XAS, VSGS), 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 VSGS will provide data on the anions adsorbed with the metals, polyatomic anion orientation in some cases, and water structure at the mineral surface. Molecular modeling will support 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: Molecular modeling results for alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) in chloride solutions successfully describe metal hydration shells as a function of ionic radii and M-O bond lengths, both in solution and adsorbed to the (001) gibbsite surface. Calculations suggest that the metal in different complexes (e.g., Sr^{2+}, $SrCl^{+}$, or $SrCl_2$) always adsorbs at the same height above the gibbsite surface, regardless of its association with chloride. This result suggests that no change in the distance between adsorbed metal ions and the gibbsite surface with increasing surface coverage, does not suggest the absence of ion-pairing at the surface.

The flexible SPC water model in combination with the ion-water potentials of Åqvist (1990) for the alkaline earth metals and Dang et al. (1990) for Cl^{-}, do not predict the experimentally-observed trend in aqueous metal-chloride complexation. Experimentally-derived association constants for $MgCl^{+}$, $CaCl^{+}$, $SrCl^{+}$, and $BaCl^{+}$ in aqueous solution (Majer and Stulik, 1982) decrease with increasing ion radius, suggesting that of these metals, Mg^{2+} binds with chloride most readily. Calculated metal-chloride potential energy minima and association constants suggest the reverse trend; that is, increasing association with increasing ion size. This result suggests that simulations for alkaline earth metal adsorption to the neutral basal surface may also provide only ambiguous information regarding the relative energetics of ternary complex formation at the gibbsite surface.

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

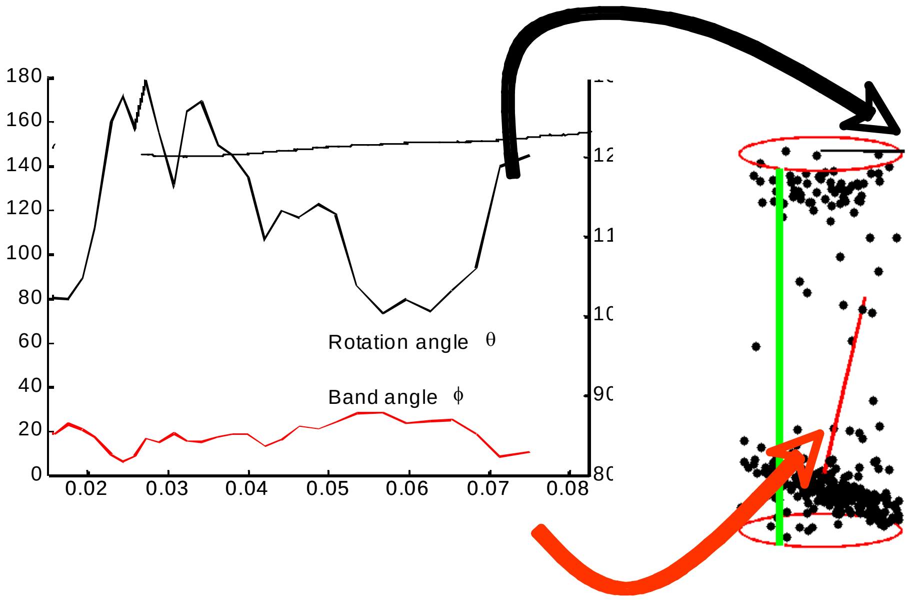
Objectives: Many porous materials, including some sandstones, exhibit compaction localization, a bifurcation from homogeneous compaction to localized compaction under non-hydrostatic stresses. Compaction localization in porous rock is potentially of importance to industries dependent on extraction or 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 FY06 concentrated on the use of acoustic emissions to verify the existence of low angle compaction bands. . Our initial work had considered compaction localization and the bands produced as forming perpendicular to the maximum compressive stress in conventional triaxial compression tests. Recent theoretical developments, using more realistic constitutive models, predict a wide range of possible angles between the normal to the localization plane relative to the maximum compressive stress, ranging from about 60 degrees for classical shear localization to 0 degrees for a compaction band. Acoustic emission (AE) data acquired in earlier experiments was reanalyzed to determine the actual orientation of the compaction bands as they formed and thickened. Individual AE events were analyzed to determine the focal mechanism of grain scale failures associated with compaction localization.

The figure shows the results for one experiment that measured the angle of the best-fit plane to the AE events associated with a thickening compaction band. The right side of the diagram shows the location of individual AE events (black dots) within the cylindrical outline of the sample. This is a snapshot of the activity just after localization occurred. The data plot shows the stress history (right axis, smooth black line) and the angle of the normal to a best-fit plane for the lower event cloud (red line) and its azimuth (black jagged line) relative to the reference line shown in green on the sample outline. All variables are plotted as a function of strain along the sample axis, with shortening considered as positive. The band angle was relatively constant, fluctuating around 20 degrees, indicating that localization was occurring at a low angle, but not at the 0 degrees predicted by a simple theory. It is significant that while the band angle remained roughly constant, the azimuth showed a large and systematic variation during the course of the test, varying from 80 degrees to 180 degrees and back during the course of the test. This variation indicates that the band angle is not just a reflection of bedding or other anisotropy. The observation of low-angle compaction localization is consistent with theory.

Band Angle and Rotation Angle



A related study of the focal mechanisms of individual AE events found that the micromechanisms for the grain scale failures shown in the figure indicated low angle slip, which is consistent with the macroscopic manifestation of the low angle planar cloud of AE events.

Microscale Processes and Microscopic Behavior in Porous Geomaterial

Joanne T. Fredrich (now at BP America)

Objectives: This project seeks to develop fundamental understanding of the microscale characteristics of natural earth materials, and to develop high-fidelity methods for predicting their macroscopic properties from high-resolution three-dimensional (3D) images acquired using modern imaging technologies, namely an in-house laser scanning confocal microscopy system, and synchrotron computed microtomographic experimental capabilities available at the GSE-CARS 13-BM beamline at the Advanced Photon Source. Specific efforts for the FY06 project period include: initial experiments to visualize and measure 3D multiphase flow in porous materials; high-resolution 3D imaging of porous media and geometric and topologic analysis of 3D image data; comparison of predicted fluid transport properties, including pore-scale velocity field, from physically representative network numerical modeling versus lattice Boltzmann numerical modeling techniques; and prediction of elastic properties from 3D image data.

Project Description: The project focuses on systematic investigation of the microscale characteristics of natural earth materials, and how these microscale characteristics control the macroscopic behavior. Emphasis is placed upon discoveries necessary to develop a robust capability to predict the macroscopic behavior from the microscopic structure, with a focus on physical, transport and mechanical properties. Central to our approach is the integration of experimental rock mechanics, three-dimensional quantitative microscopy, and theoretical and numerical analyses. The research program focuses on the porous earth materials that are central to geoscience applications of current societal concern and impact, including geologic sequestration of greenhouse gases, and hydrocarbon exploration and production.

Results: Full-physics numerical simulations using pore-scale models derived from microscopic image data (Figure 1) have been completed allowing us to probe a variety of issues in effective medium theory without relying on theoretical or empirical simplifications. Although the full-physics approach was initially adopted for fluid-flow simulations, it has recently been applied to studies of wave propagation.

Our method utilizes full-waveform, finite-difference modeling of wave propagation and is related to the resonant bar technique. During a full-waveform simulation, resonances, or standing waves, form along a single axis of a numerical model derived from microscopic image data. For example, the size of one of these models, based on Castlegate sandstone, is 424x424x460 samples in the xyz-directions. These microscopic image data are the result of X-ray CT at the GSECARS 13-BM beam line at the Advanced Photon Source. We take such a volume of microscopic image data and initiate a broadband planar source of energy on one of the two boundaries perpendicular to the z-axis, which are both stress-free. We set the other four boundaries to be periodic and allow the wave to bounce between the two free surfaces for a long period of time. By Fourier-transforming the mean displacement field at the stress-free boundary opposite of the source, we study resonances in the amplitude spectrum, in a way analogous to normal-mode seismology.

From the numerical simulations, we observe a transition in the wave propagation properties of the pore-scale models from an effective medium description to a regime of strong pore-scale scattering as a function of frequency. We are able to extend our initial results, obtained for acoustic wave propagation in the presence of a single fluid phase, to include elastic and anacoustic rheologies saturated by multiple fluid phases.

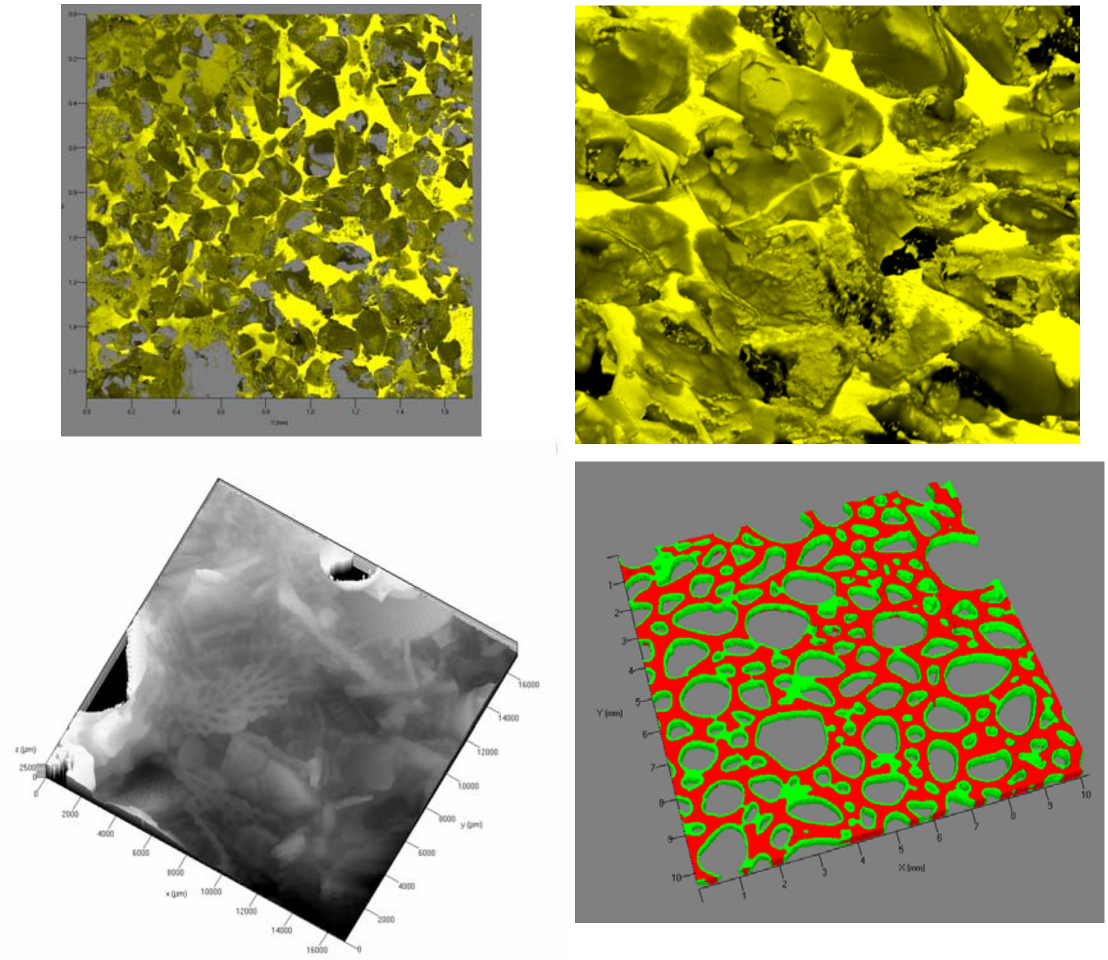


Figure 1. Scoping experiments performed with multi-channel laser scanning microscope. (Upper) The two images show 3D visualizations of the pore phase in Berea sandstone, at resolution of 1 micron. The right image is a blow-up of a small region of interest in the left image, shown to emphasize the resolution of the imaging system. (Lower left) Surface profilometry of a natural bedding plane parting in fossiliferous limestone. (Lower right) Two-phase immiscible flow experiment performed in a 2½D micromodel, with water phase shown in green and oil phase in red. The micromodel was originally water-wet, and flooded with oil to displace the water.

Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media

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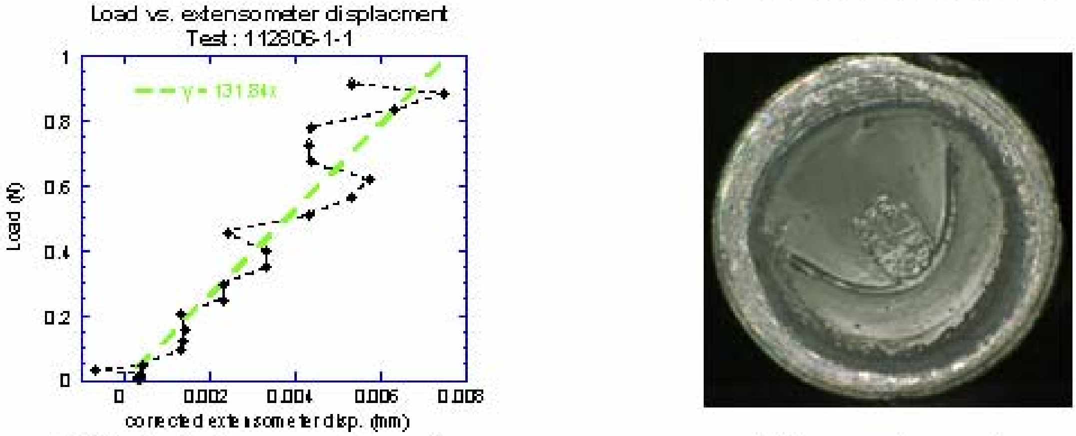
Objectives: (1) To quantify grain-scale physical effects of variable cement quantity, composition, and location on the elastic and inelastic deformation of granular porous media.
(2) To use the resulting understanding of the fundamental micromechanical processes that govern macroscopic deformation to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

Project Description: The project scope requires the development of methods of appropriately small-scale experimental deformation and structural characterization of granular porous media. We chose to work with both *synthetic* and *natural* grain-cement systems using novel approaches that provide insight into grain-scale mechanics. The project design includes:
(1) Development of methods for fabrication of synthetic assemblages of soda-lime silicate beads and both sodium silicate and calcium carbonate cements. Development of approaches to isolating similar elements from natural systems.
(2) Design of apparatus to test mechanical properties of synthetic grain-cement assemblages. Use of nanoindentation to probe properties such as elastic modulus, hardness, and plasticity of grains and cements in both natural and synthetic systems.
(3) Microstructural analysis of synthetic and natural systems to relate physical elements of system to their structural response to stress in both elastic and inelastic deformation.
(4) Development of quantitative relationships of stress-strain response of cemented granular systems and incorporation of microscale material response into a DEM.

Results: We cemented pairs of 1.0 and 1.5 mm diameter soda lime beads together at one contact point with various volumes of three sodium silicate cements (Figure 1). The formation of cracks and air bubbles as the sodium silicate cements cured was a major challenge, overcome by sonicating assemblages during initial curing.
Fixturing for shear and tensile testing of the bead assemblies was designed, fabricated and tested (Figure 1). Although bubbles and cracks within the cement certainly influenced the first tests, the experiments demonstrate that tensile and shear stiffness and strength of the bonded assemblies can be measured using both test configurations. *These initial tests show that, even with defects, the cement bonds are surprisingly strong*.
Using instrumented indentation, we measured variations in hardness, modulus, and fracture toughness within quartz grains in a natural sandstone. We had some success correlating inter- and intragranular variations in measured indentation response with crystallographic orientation and internal microstructure. However, we determined that we cannot easily test grain-cement boundaries. Relevant physical parameters therefore will be determined on selected sandstones and related to grain contact strength through measurement of P and S wave velocities. Ultrasonic velocities, and related elastic moduli, vary with grain contact strength.

(a) synthetic bonded sample

(b) tensile test experiment



(c) load-displacement trace from tensile test experiment

(d) fractured sample

Figure 1 – Images and plots associated with synthetic two particle grain-cement sample preparation and testing.

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

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Objectives: To determine the effects of fluid flow oscillation on dispersion in complex media, and to determine conditions where the Newhouse model of in-fracture precipitation is valid.

Project Description: This work continues a previous study of dispersion at fracture junctions and in Hele-Shaw cells, 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 experiments will involve growth from gypsum seeds in Hele-Shaw cells.

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Results: Initially, the study of oscillatory dispersion was designed to determine if experimental conditions would impose significant uncertainty on fracture-mixing experiments. Specifically, the concern was that out-of-phase oscillations in pumps or gravity fed water reservoirs would enhance mixing. It was found that relatively unusual conditions were required to produce significant uncertainties. However, the tools developed in that study were then applied to oscillatory dispersion in biomedical systems, resulting in two published papers for flow and dispersion in the human spinal canal, relevant to the distribution of drugs by spinal puncture. It was found that the fine structure of obstructions in the spinal canal greatly enhanced dispersion. This latter study allowed a fine-tuning of the LB codes, so it is now possible to handle oscillatory dispersion to high Peclet numbers (>1e4).

A second part of the project involves the testing of geochemical precipitation models postulated by Newhouse (1941) for in-vein precipitation. Newhouse suggested that precipitates tend to form on the "stoss" or upstream side of obstacles, when the primary source of solutes is also upstream. His argument, with some qualification, is simple: the solutions encounter the upstream side first, thus first precipitate material on the upstream side. Thus growing crystals will point into the flow. There have been no real tests of this hypothesis since Newhouse's original elegant experiments. Initial LB calculations suggest there is actually a fairly limited set of conditions where the proposed behavior actually occurs; the solubility of the solid must be high, yet the precipitation rate must be fast, and flow must be uncomplicated enough to prevent vortices from mixing the solutes. A set of simple experiments was designed to test the Newhouse models with growth of gypsum pillars in a Hele-Shaw cell.

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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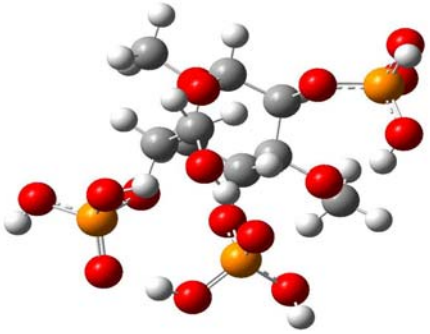
Objectives: The focus is a computational study to develop a fundamental molecular level description of the interactions of Gram-negative microbial membranes with subsurface materials.

Project Description: We are developing a better understanding of the molecular processes involved in 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. The project is focused on 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. A combination of molecular dynamics simulations and electronic structure calculations are providing new insights into the detailed molecular behavior of these membranes. The modeling capability allows the transfer of the necessary fundamental information across the needed series of spatial scales, and includes molecular level simulations of small molecular clusters, molecular dynamics investigations of large molecular systems, and predictions of macroscopic geochemical reactions using thermodynamic models. The experimental component has two objectives: (1) conduct electrochemical measurements on reconstituted outer membranes to determine transmembrane potentials across the LPS-membrane, and (2) quantify the adsorption of LPS-membranes to mineral surfaces using atomic force microscopy.

Results: An important aspect of the structure of the LPS membrane as well as ion transport in the LPS is the ability of the sugar side groups such as carboxylic acids and phosphates to bind positively charged ions. Electronic structure calculations at the molecular orbital theory and density functional theory levels are being used to predict the free energies of solvation of ions in aqueous solution as well as in media with different dielectric constants, the acidity of the critical groups in the sugars in the LPS, and the binding of metal ions to the sugar anions, including the important environmental contaminant, UO_2^{2+}. The calculated values show that the phosphorylated sugar sidechains are much stronger acids in the gas phase than H_3PO_4, and the acidity of the sugar shown to the right is stronger than that of H_2SO_4 in the gas phase. The pK_a's of the phosphorylated sugars show that they are stronger acids in solution as compared to phosphoric acid, with the sugar shown to the right being a very strong acid. The changes in acidities correlate with hydrogen bonding in the sugars and with differential solvation effects. A component of the study is to predict the solvation properties of metal ions in aqueous solution. We have predicted the solvation energies of ions in aqueous solution using a supermolecule-continuum solvation model developed in the group. We have used this model to study the solution chemistry of the uranyl cation. Our calculations are in agreement with recent HEXS experiments that an equilibrium exists between four- and five-coordinate uranyl: $UO_2(H_2O)_4^{2+} + H_2O \leftrightarrow UO_2(H_2O)_5^{2+}$ in water and that the penta-coordinated is favored thermodynamically, counter to prevailing concepts of uranyl solvation.



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Grant: DE-FG02-04ER15505

A SIMS Study of the Chemical Dynamics of Organic/Inorganic Interactions in Sedimentary Basins

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Objectives: Stable isotopes of trace elements (N, B, Li) in kerogen and diagenetic clays are being studied as a tool to monitor oil and gas migration through sedimentary basins. The goal is to determine the temperature of release of these elements from the organics and the fractionation between fluids and solids.

Project Description: Analyses of trace elements in kerogen and clays by secondary ion mass spectrometry (SIMS) can monitor organic/inorganic interactions. SIMS has the unique capability of analyzing trace elements in the solid state, without chemical extractions that may induce isotopic fractionation. Measured changes in B and Li isotopes in kerogen and diagenetic illite may be a more useful tracer of the hydrocarbon related fluids in sedimentary systems than major elements (C, O) because fewer minerals incorporate these elements at the reaction temperatures of oil and gas maturation, while major elements are involved in a variety of diagenetic reactions. This integrated trace element and isotopic study of kerogen and clays tests the hypothesis that diagenetic illite records the pulses of isotopically light fluids related to the movement of hydrocarbons through sedimentary basins. The results should lead to a better understanding of mass transfer between organic and inorganic phases during hydrocarbon migration.

Results: Evaluating equilibrium Li-isotope fractionation in illite-smectite (I-S) was the primary goal of this project period. The Green-Kelley test (Green-Kelley, 1952) for identifying montmorillonite by X-ray diffraction involves Li-saturation of a smectite and heating the sample to 300˚C for 12 hours. This causes irreversible collapse of montmorillonite via Li^+ substitution in the octahedral sites. We measured the isotope fractionation associated with the change from Li adsorbed on the surface of SWy-1 montmorillonite, to substitution in octahedral sites. Adsorbed Li retained the isotope ratio of the water (0‰) within error (-0.3±0.6‰), while the octahedral Li substituted at 300˚C showed δ^7Li of -10.4±0.7. This Li isotope fractionation is the same magnitude as that measured for illite formed from hydrothermal alteration of SWy-1 smectite over 5 months of reaction at 300˚C, 100MPa (Williams and Hervig, 2005). The result differs from earlier empirical studies of marine sediments containing a variety of clay minerals (Chan and Kastner, 2000) that gave lower absolute values and a smaller temperature-dependence for the isotope fractionation than we have observed for I-S. Our re-confirmation of the isotopic fractionation of Li between adsorbed and octahedral sites leads us to hypothesize that the fractionation of Li might be coordination-dependent. In 2:1 clay minerals Li may be adsorbed (II to IV coordinate), in pseudo-hexagonal cavities (VI coordinate) or in octahedral sites (VI coordinate) (Stackhouse and Coveney, 2002). We have tested the dependence of the bulk clay δ^7Li on coordination state. Chemical exchange allows removal of Li from adsorbed sites on the clay, leaving only Li (VI). Analysis of δ^7Li in these treated clays shows lighter ratios than untreated clays, suggesting that adsorbed lithium is isotopically heavy.

The Li isotope fractionation equation (Williams and Hervig, 2005) for I-S ($1000 \ln \alpha = 5.3 - 8.7 * (1000/T(K))$) was tested by measurements of δ^7Li in I-S samples from a metabentonite with a known temperature gradient (Walsenburg, Colorado) that induced illitization of smectite from 20% to 100% illite. No significant change in isotopic composition of the clay fraction (<2.0 µm I-S) was observed (-11.6 ± 1.6‰) across the entire temperature range (200-500°C). However, examination of different crystal size fractions of the clays from one sample at the edge of the metamorphic aureole revealed a range of δ^7Li values from +2.6 ± 0.3‰ for the <0.1µm fraction; –1.9 ± 0.7‰ for 0.1-0.5µm; –4.8 ± 0.6 for the 0.5-1.0µm; –10.6 ± 0.7 for the 1.0-2.0µm fraction. Using our Li-isotope fractionation equation for I-S (Williams and Hervig, 2005) these values may be interpreted to reflect the growth of clays from one fluid during cooling after intrusion. If δ^7Li of the fluid was +9‰, the δ^7Li values of different size fractions are consistent with the temperature range indicated by vitrinite reflectance. This field observation supports our experimental results (Williams and Hervig, 2006) indicating that different sized clay crystals retain the chemistry reflecting the fluid composition and temperature of precipitation. The smallest crystals represent nucleation and, as the bentonite cooled, the larger crystals continued to grow. The chemistry of each size fraction represents the average temperature of growth to a particular size, with the largest crystals reflecting growth from fluid at the temperature of the country rock when crystal growth stopped.

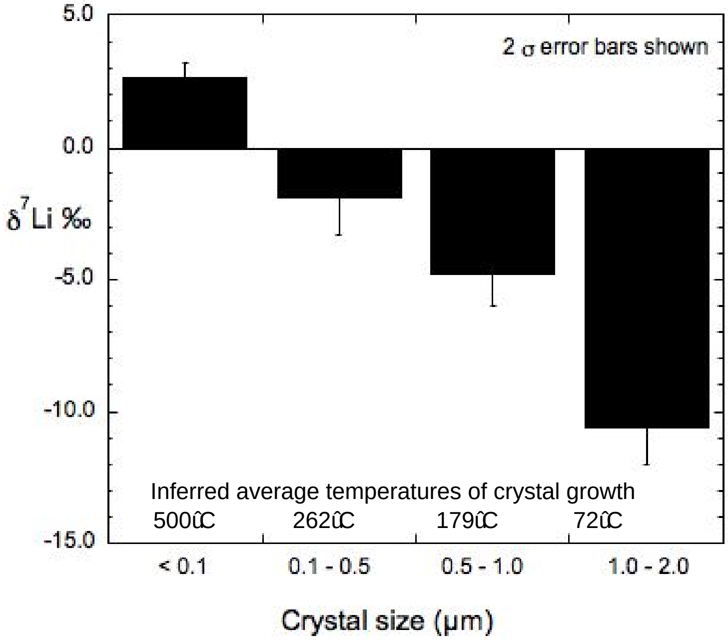

Figure 1.
Variation in δ^7Li among different crystal size fractions of the Walsenburg metamorphosed bentonite from a single sample collected near the outer edge of the metamorphic aureole. See text.

BOSTON UNIVERSITY

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Grant: DE-FG02-95ER14498

Collaborative Research: Understanding Multi-Scale Space-Time Patterns in Crustal Deformation Processes: Towards Ensemble Forecasting in Complex Tectonic Systems

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Objectives: To develop a physical understanding of the origins of space-time patterns and statistical correlations occurring in geomechanical and tectonic systems, and use these to forecast future activity that may produce disasters affecting a variety of critical energy facilities, such as nuclear power plants, oil refineries, and national laboratories.

Project Description: The complex earth system generates a variety of phenomena that are highly nonlinear and operate over a broad range of spatial and temporal scales. Signatures of these processes include scaling (fractal distributions), global and local self-organization, intermittancy, chaos and the emergence of coherent space-time structures and patterns. We are using massively parallel simulations to model geodynamical effects observed in earthquake systems in order to determine the origin of these phenomena. These investigations and the theoretical efforts done in parallel are particularly aimed at quantifying the limits of predictability for disasters such as earthquakes that occur within the earth system. We are currently continuing our development of the theoretical and computational tools that allow us to both obtain sufficient data on realistic models and to analyze the data we obtain. From these simulations we will then predict geodetic and other deformation associated with impending earthquakes to be tested against Global Positioning System, Synthetic Aperture Radar, seismicity and other field data.

Results: <u>Theoretical Models</u>: We developed methods for the computation and interpretation of gravity and height changes and gravity gradients produced by tectonic sources such as interacting earthquake faults in a layered elastic-gravitational medium. The results of these computations show spatial patterns very similar to those exhibited by Coulomb stress changes from natural active faults, and show that surface gravity changes can be used as a proxy for such stress changes.
<u>Pattern Analysis:</u> An algorithm that our group developed, pattern informatics ("pi"), was used to detect the locations where precursory activity occurred preceding the 1999 Chi-Chi, Taiwan, earthquake. The epicenter of the Chi-Chi mainshock was found to exhibit signatures of anomalous activity related to the seismic activation and quiescence in the Taiwan region over a time span of about 6 years before the mainshock.
<u>Numerical Simulations:</u> We have developed realistic numerical simulations, involving data-mining, pattern recognition, theoretical analyses and ensemble forecasting techniques, to understand how the observable space–time earthquake patterns are related to the fundamentally inaccessible and unobservable dynamics. Our simulations indicate that elastic interactions (stress transfer) combined with the nonlinearity in the frictional failure threshold law lead to the self-organization of the statistical dynamics and the observed earthquake scaling laws.

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Grant: DE-FG02-06ER15773

Experimental Petrology and Geochemistry of Volatile-Bearing Silicate Melts

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

Project Description: The goal of Part 1 is the definitive determination of the diffusion coefficient for water (D_{H_2O}) in basaltic, andesitic, and rhyolitic melts in order to understand its compositional dependence, 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_{H_2O} values were determined from FTIR profiles using both direct calculations (i.e., Boltzmann-Matano methods) and models assuming specific relationships between diffusivity and water content. Part 2 is the study of the zonation of phosphorus in olivines. Using electron microprobe, we have characterized the complex (and often oscillatory) phosphorus zoning in natural olivines from basalts, andesites, dacites, komatiites, and igneous meteorites. We have generated similar P, Al, and Cr zoning in olivines grown experimentally at 1 atm with cooling rates of 15-30°C/hr in a synthetic Hawaiian basalt. We have also begun measuring Al and P chemical diffusivities in olivine.

Results: *Part 1:* In the course of our FTIR analyses we developed a scheme for calculating the FTIR molar absorptivities for silicate glass compositions, for which FTIR calibration has not been determined, using the structural chemical parameter, 100NBO/T, for degree of polymerization. We have completed our pilot study of diffusion of water in silicate melts: 16 hydration and diffusion couple experiments with compositions of high-Al basalt, haplo-basalt, and haplo-andesite. Panels a and b in Figure 1 show how the various functional models for dependence of D_{H_2O} on water content fit profiles for hydration and couple experiments for the same high-Al basalt under the same experimental conditions. The relationships between D_{H_2O} and water content examined include constant D_{H_2O}, D_{H_2O} proportional to water content, D_{H_2O} proportional to the logarithm of water content, and D_{H_2O} of molecular water constant with immobile hydroxyl groups. Panels c and d show that the D_{H_2O} values derived from these profiles by the different models, especially those that vary with H_2O concentration, are quite consistent in the middle of the water content range of the experiments. The good agreement between results for hydration and couple experiments, which have very different boundary conditions, indicates the robustness of our results. Our data show that D_{H_2O} increases regularly with decreasing melt viscosity and increasing water content and degree of polymerization. This relationship between water content and viscosity can be used to estimate D_{H_2O} for compositions whose diffusivities have not been directly determined.

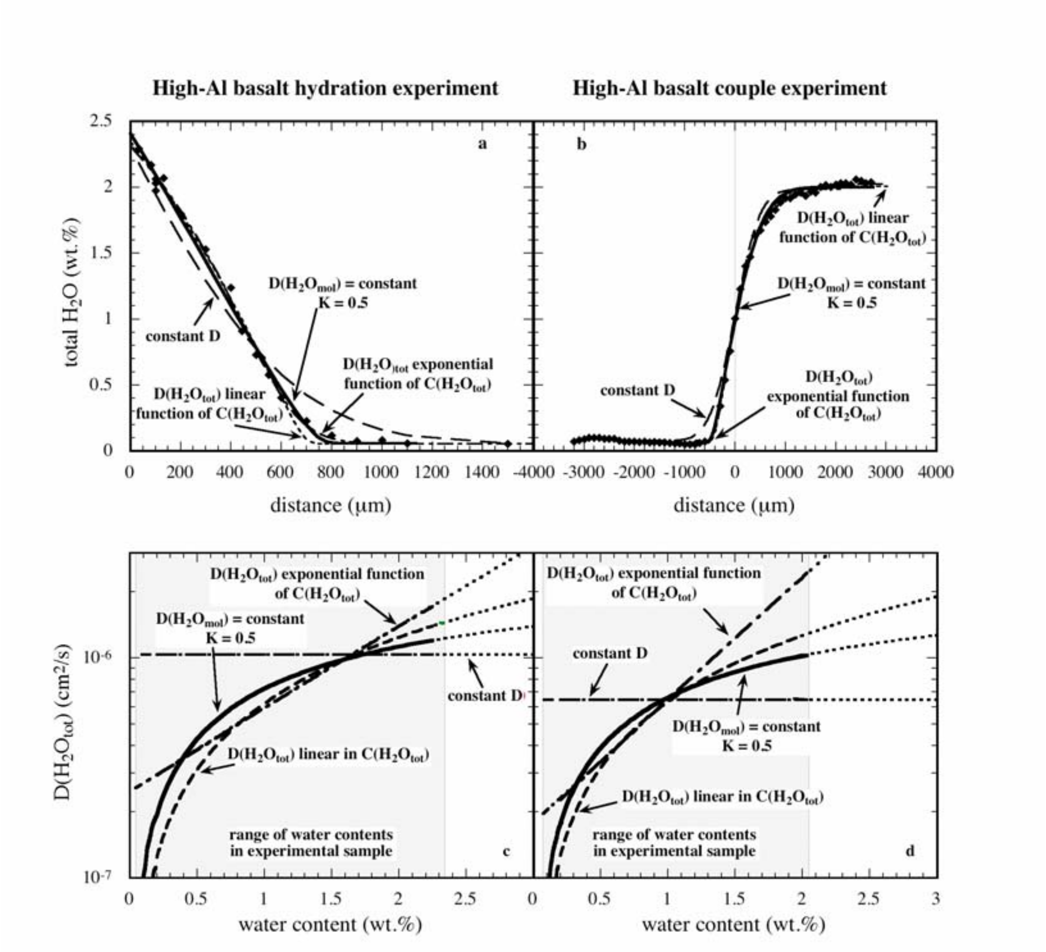

Figure 1. H_2O content profiles for the high-Al basalt (a) hydration and (b) couple experiments at P=0.5 kbar, T=1250°C, t=1200 s. Measured H_2O contents are shown as diamonds. Profiles calculated with various model relationships between D_{H_2O} and H_2O content are shown for comparison. Relationship between D_{H_2O} and H_2O content for various functional models for the (c) hydration and (d) couple experiments.

Part 2: Based on our initial survey, phosphorus zoning appears to be a widespread feature, being absent only in the single metal-saturated sample studied (Benham pallasite). In the majority of olivines, the P zoning is present in regions of the crystals that are homogeneous with respect to Fe-Mg and other divalent cations and frequently correlates with Al and Cr zoning. The width of P-enriched bands varies from 3 to 20 μm. The spatial correlations between enriched zones of P, Al, and Cr are very strong in these experimentally grown olivines. This suggests that, at least in the case of the Hawaiian phenocrysts, these grains may initially have had correlated P, Al, and Cr enrichments, but that the Cr- and Al-enriched zones either partially or completely diffused away due to a protracted high temperature thermal history in a magma chamber. Although chemical diffusion rates (D) of P and Al in olivine are unknown, and limited data exists for Cr (Ito and Ganguly, 2006, GCA 70, 799-809), the relative intensities of P, Al, and Cr zoning suggests that D_P is substantially slower than D_{Cr} which in turn is slower than D_{Al}. Using a standard expression for diffusion in a plane sheet, we have begun to develop equations for the evolution of oscillatory zoning as a function of time. Assuming the relative peak height of an enriched band to be a function of Dt (where t is time) and width, we have shown that for widths between 3 and 20 microns, time information can be extracted for log(Dt) values between -1 and 3 (for < -1 there has been no change in the relative peak height; for > 3 the relative peak height is essentially zero).

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Isotope Tracer Studies of Diffusion in Silicates and of Geological Transport Processes Using Actinide Elements

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Objectives: This project addresses understanding the transport of chemical species in nature by focusing on three general areas of study: actinide transport, platinum group elements and Re in deep sea sediments, and B and Ca isotopes in corals.

Project Description: The major efforts of this phase of the project have been directed toward the high precision measurement of Ca isotopic abundances in both terrestrial materials and in meteorites and lunar samples. The purpose of this study was to measure the evolution of ^{40}Ca as recorded in carbonate deposits due to the input of Ca from the continental crust and from mantle sources.

Results: This report covers the research activities during a period of no cost extension. The effects being investigated were the increase of ^{40}Ca due to the decay of ^{40}K. A base line would be the ^{40}Ca/^{42}Ca in early formed meteorite samples which have almost no K, lunar samples of very high age with no K, mantle samples with very low K/Ca and carbonates from marine deposits with ages ranging from 3.5 Gyr to recent marine deposits. The experimental difficulties have proven quite great. The effects are at the 1 epsilon level in ^{40}Ca, which is also the major Ca isotope.

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Grant: DE-FG02-01ER15218

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 or organics can influence their structure and surface reactivity. The approach taken in this is to combine nanoparticle synthesis with experimentation, characterization using a suite of methods, and molecular simulation and prediction tools. Our work includes analysis of how specific classes of molecules at nanoparticle surface influence particle behavior and has made use of high-pressure experimental methods to perturb nanoparticles and learn about how they respond to changes in their physical and chemical environments.

Results: ZnS nanoparticles are less crystalline when they interact with molecule via weak dipole interactions (methanol and chlorobenzene), more crystalline when they interact with ions via electrostatic interactions (sodium sulfate, calcium chloride and sodium chloride), and are most crystalline when they interact with molecules via strong chemical binding (water and thiophenol). The interaction strength increases in the sequence: dipole interaction, electrostatic interaction, and chemical binding. Temperature-programmed desorption (TPD) studies demonstrated that the extent of water binding and binding energy of water to ZnS nanoparticles increases with decreasing particle size. We have examined the compressibility of nanoparticles as a function of their size and determined that there is a particle size that corresponds to a maximum compressibility. These results have been analyzed in terms of a size-dependent pressure response to microstructure development. High-pressure studies reveal novel structural behavior in nanoparticles with disordered stacking and show a dependence of behavior on the chemical surroundings.

Surface interactions at nanoparticle surfaces: We used synchrotron-based wide-angle x-ray scattering (WAXS) to investigate the strengths and consequences of surface molecule-nanoparticle interactions. ZnS nanoparticles (~3 nm) were synthesized in anhydrous methanol and then were examined by WAXS in methanol, as well as in methanol with addition of water, thiophenol (C_6H_6S), chlorobenzene (C_6H_5Cl), sodium sulfate (Na_2SO_4), calcium chloride ($CaCl_2$) and sodium chloride (NaCl), respectively. Data were analyzed using atomic pair distribution functions (PDF) derived from the WAXS data. The interaction strength increases in the sequence: dipole interaction, electrostatic interaction, and chemical binding.

We have investigated the bonding of water to the surfaces of ZnS nanoparticles (~ 2-3 nm sphalerite) using TPD. The activation energy for water desorption was derived as a function of the surface coverage through kinetic modeling of the experimental TPD curves. The binding energy of water equals the activation energy of desorption, assuming that the activation energy for adsorption is nearly zero. Water binds with ZnS nanoparticle surface mainly via formation of Zn-O bonds. Compared with bulk ZnS crystals, ZnS nanoparticles can adsorb more water molecules per unit surface area primarily due to higher surface curvature, and water binding energy decreases with increasing the water surface coverage. MD supports the deduction that water binding energy increases with decreasing particle size.

We have also investigated how other aspects of nanoparticle surface chemistry control ZnS nanoparticle crystallinity. Combined small-angle X-ray scattering (SAXS) and WAXS measurements permitted interior strain and disorder to be observed directly in ZnS nanoparticles of known size through PDF analysis. Results showed that nanoparticles with similar mean diameters (3.2 - 3.6 nm), but synthesized and treated with different low-temperature procedures, have highly variable degrees of internal disorder.

The structural response of wurtzite nanoparticles to reaction with oxygen was studied by in-situ extended x-ray absorption fine structure (EXAFS). With reaction progress, the local environment of Zn gradually changed from S to O dominated, accompanied by shortening of the 1st shell distance.

In-situ small-angle x-ray scattering (SAXS) was used to study the dissolution of ZnS nanoparticles in dilute EDTA solutions. Both the population and the aggregate size of ZnS nanoparticles were derived as a function of time, reagent concentration and solution pH. Kinetic rate constants were obtained through kinetic modeling.

High pressure study of ZnS and TiO_2 nanoparticles with and without ligands: For TiO_2 nanoparticles, we find that compressibility decreases until a critical size is reached, below which the compressibility of nanoparticles decreases with decreasing size. We infer a role for dislocations in the compressibility response, thus draw a link between the elastic and plastic behavior in nanoparticles. Analysis of results includes insights from computer simulations and prediction of dislocation behavior as a function of pressure.

We have studied nano-sphalerite, wurtzite, and mixed layer nanoparticle behavior during high-pressure experiments. High pressure IR spectroscopy (up to ~ 27 GPa) revealed novel behavior in the mixed stacking structure. Adsorption of ethylene glycol adds more Raman modes and results into mode shifts, further illustrating that the surface environment can alter the internal structures of nanoparticles.

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Grant: DE-FG02-04ER15507

Microbial Metabolism and the Nature of Metal Sulfide Biomineralization Products

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Objectives: The primary question investigated in our work is "How does the activity of sulfate reducing microbial consortia impact the size, aggregation state, and behavior of metal sulfide nanoparticles, including their mobility in the environment".

Project Description: Microbial activity can strongly influence the form and distribution of metals in the environment. In this project we are studying the ways in which microbial sulfate reduction removes metals from solution by inducing the precipitation of metal sulfide nanoparticles. We have experimentally evaluated the ways in which solution chemistry impacts the rate of sulfide production, quantifying the effect in terms of thermodynamic controls on microbial activity levels. Using the ability to control sulfate reduction rates, we have investigated how microbial activity impacts aggregate size and aggregation rate and conducted experiments to study particle transport in microfluidic systems. We used nanoSIMS to show that natural metal sulfide nanoparticle aggregates contain substantial concentrations of protein and conducted experiments to test the ability of a suite of amino acids to promote nanoparticle aggregate development.

Results: In FY 2006, we completed research on natural microbial biofilms that contain micron-scale aggregates of biogenic metal sulfide nanoparticles (John Moreau, Ph.D. 2006). Results describing the abundance and distribution of proteins within the aggregates, and experimental work implicating the importance of an ~ 45 kDa protein and showing the role of cystine in nanoparticle aggregation were published (Science, 2007). Research on isotopic the isotopic composition of metal sulfide nanoparticle aggregates continued, with further validation of results showing isotopic gradients. We determined that microbial proteins drive rapid nanoparticle aggregation, preserving a concentric isotopic record of microbial activity that is just discernable via nanoSIMS methods. We infer that rapid aggregation will limit the dispersal of nanoparticles in the environment. In related experimental work in a model system, we described the influence of surface potential on aggregation and transport of nanoparticles in porous two-dimensional structures. We established both pure cultures and mixed communities of sulfate-reducing bacteria in the laboratory and verified that that mixed communities simulate natural consortia. Microbial communities dominated by sulfate-reducing bacteria will be used to investigate nanoparticle production, transport, and to seek evidence for a role of proteins in promoting aggregation.

Research results: In collaboration with Peter Webber (LLNL) and Michael Martin (LBNL) and others, John Moreau conducted *in situ* isotopic and biochemical analyses of natural nanoparticle aggregates formed by sulfate-reducing bacteria. Experiments utilized a secondary ion mass spectrometry (NanoSIMS, ~50 nm probe spatial resolution) at Lawrence Livermore National Laboratory and synchrotron Fourier transform infra-red spectroscopy (SR-FTIR, ~10 μm spatial resolution) at the Advanced Light Source of Lawrence Berkeley National Laboratory. The focus of the later part of the research was to establish the validity of apparent fine-scale sulfur isotopic variations ($\delta^{34}S$ variations in the 10-20‰ range across micron diameter spheres). Results appear indicative of locally varying biogeochemical conditions, and probably record information about the rate of microbial sulfate reduction. Significant organic nitrogen concentrations within aggregates were attributed to polypeptides on the basis of SR-FTIR data. Based on experimental results, it was estimated that approximately 14% of the aggregate volume is occupied by proteins. We completed an experimental study of the role of proteins and amino acids in generating dense (non-fractal) aggregates of metal-sulfide nanoparticles. Specifically, we tested the efficacy of individual amino acids (alanine, aspartate, cysteine, lysine, phenylalanine, proline, and serine, with chemically distinct side-chain functional groups) to promote the aggregation of synthetic 3 nm ZnS particles. Aggregation was monitored with dynamic light scattering. Results showed rapid inorganic aggregation to form ~100-nm-diameter structures. Aggregation slowed greatly or ceased after 1 week. Cysteine promoted more extensive and prolonged aggregation. Other amino acids had little (e.g., serine) to no (e.g., proline) detectable effect on nanoparticle aggregation, relative to controls. Proteins, peptides, and amino acids may have been deliberately produced or released after cell death and scavenged by hydrophobic ZnS surfaces. Regardless of whether they were deliberately produced or incidentally scavenged, aggregation of metal-sulfide nanoparticles prevented incidental uptake by cells and their entombment. The resulting dense aggregation state of nanoparticles may have a strong impact on metal mobility and water quality.

Laboratory experiments: Subsurface microbial sulfate reduction (~ 9 mM sulfate) was studied in column experiments packed with fresh sediments and exposed to complex anaerobic, metal-bearing (Zn, Cu, U, Se, V) containing 3 mM acetate. Sulfide detected after ~50 days (following the period of Fe(III) reduction) resulted in precipitation of iron sulfides. Molecular 16S rRNA gene analysis of the microbial community during the onset of sulfate reduction identified a number of clones that were closely related to acetate-oxidizing SRB (e.g. *Desulfotomaculum acetoxidans*). Interestingly, sequences that were close matches to Fe(III)-reducing species (e.g. *Ferribacterium limneticum, Rhodoferax ferrireducens*) were also detected, suggesting that iron reduction may occur in micro-sites within the column, even when the geochemistry is dominated by sulfate reduction. The cultivation of field-relevant consortia provides the basis for ongoing studies of the links between protein production and nanoparticle aggregation

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Grant: DE-FG02-03ER15418

Diffusion/Dispersion Transport of Chemically Reacting Species

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Website: http://affinity.berkeley.edu

Objectives: The principal aims of research were (1) calculation of the thermodynamic consequences of incongruent melting of kerogens in hydrocarbon source rocks and (2) calculation of the thermodynamic properties of biochemical reactions coupled to organic and inorganic oxidation/reduction reactions at high pressures and temperatures.

Description: Thermodynamic models of incongruent melting of kerogens to produce hydrocarbons can be used to predict the composition and quantity of petroleum generated from hydrocarbon source rocks. The results of thermodynamic calculations are consistent with known quantities of oil in the Los Angeles and North Paris basins and in other reservoirs. Although the formation of hydrocarbons may be found initially in water-absent regions, interactions between hydrocarbons and aqueous solutions are likely during expulsion and transport to reservoirs. The consequences of biochemical reactions coupled to organic/inorganic reactions at the oil/water interface can be assessed using thermodynamic models that take into account temperature, pressure, oxidation state and other chemical properties of the system.

Results: Using Gibbs energy minimization computer experiments, the consequences of incongruent melting of kerogens and of metastable equilibrium among kerogens, liquid hydrocarbon mixtures, $CO_{2(g)}$, and optionally aqueous solutions were documented at different temperatures and at pressures along a generalized U.S. Gulf Coast geothermal gradient. Results of the computer experiments and thermodynamic analysis of phase relationships in the system C-H-O suggest that incongruent melting of kerogens in source rocks to produce predominantly aliphatic hydrocarbons is favored at temperatures at or above ~140°C. With increasing temperature, the metastable speciation of liquid hydrocarbon mixtures in equilibrium with kerogens becomes increasingly aromatic. By combining volumes of hydrocarbons and of pore space produced by the chemical reactions with kerogen richness (H/C) and source rock thicknesses, the quantity of petroleum expelled during incongruent melting of kerogen in a particular source rock can be assessed. The calculations can be used to account for the quantity of petroleum in proven reserves worldwide (Helgeson et al., A chemical and thermodynamic model of oil generation in hydrocarbon source rocks, *Geochim. Cosmochim. Acta*, in review, 2007).

To characterize thermodynamically the interactions of biochemical species with inorganic and organic species, experimental calorimetric and volumetric data for biomolecules available in the literature were combined with equations of state to compute the standard molal thermodynamic properties and parameters of reference model compounds for proteins (Dick et al., Temperature, pressure, and electrochemical constraints on protein speciation: Group additivity calculation of the standard molal thermodynamic properties of ionized unfolded proteins, *Biogeosciences* **3**, 311-336, 2006) and nucleic acid bases and nucleotides (LaRowe and Helgeson, Biomolecules in hydrothermal systems: Calculation of the standard molal thermodynamic properties of nucleic-acid bases, nucleosides, and nucleotides at elevated temperatures and pressures, *Geochim. Cosmochim. Acta* **70**, 4680-4724, 2006; LaRowe and Helgeson, The energetics of metabolism in hydrothermal systems: Calculation of the standard molal thermodynamic properties of magnesium-complexed adenosine nucleotides and NAD and NADP at elevated temperatures and pressures, *Thermochim. Acta* **448**, 82-106, 2006) as a function of temperature and pressure. Calculations of the relative stabilities of biomolecules at high temperatures and pressures indicate that coupling of biochemical reactions to organic or inorganic reactions is a strong function of the oxidation state of the system. A model for production of ATP coupled to oxidation of acetic acid had been produced and is being used to quantify the energy yield of potential metabolic reactions at high temperatures. Quantifying these energies is essential to prediction of the limits of microbial metabolism and hence of the potential for biodegredation of petroleum.

Website/Thermodynamic Data: In March 2006 the website for the Laboratory for Theoretical Geochemistry (*aka* Prediction Central) was launched (http://affinity.berkeley.edu). The site contains thermodynamic data files generated from data produced in this laboratory for inorganic and organic species including liquid hydrocarbons and aqueous biomolecules. In addition, the SUPCRT software package for calculating standard molal thermodynamic properties of species and reactions is freely available for download from the site, as is its counterpart for Windows systems, OBIGT.

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Grant: DE-FG02-05ER15637

Extracting Geological Stresses and Anisotropy from Rocks by Means of Neutron Diffraction

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Objectives: The goal is to develop reliable methodologies to determine the influence of stress on anisotropy in polycrystalline materials. Emphasis is on sedimentary rocks, such as chert and shales where seismic anisotropy is crucial. Initially we concentrated on neutron diffraction but have since have broadened the approach to include synchrotron X-ray scattering.

Project description: Understanding geological stresses and anisotropy in sedimentary rocks is of great concern in structural geology, geophysics and, particularly, seismic exploration. Information is very limited because of the complexities and poor crystallinity of these polyphase materials. New tools such as time-of-flight neutron and synchrotron X-ray diffraction offer the possibility for probing the internal structure of geomaterials and to quantify micro-to-nano scale stress-induced changes in rocks. Research relies on advanced experiments at National laboratories and sophisticated data analysis. Based on observations on natural and experimental samples a comprehensive model can be derived that links macroscopic physical properties to the internal structure and the formation process.

Results: The general approach is to irradiate bulk rock samples with neutron and hard X-rays, record diffraction patterns and analyze these for phase, composition and preferred orientation with the crystallographic Rietveld method developed specifically for this investigation (e.g. Wenk, 2006 *Reviews in Mineralogy and Geochemistry* **63**).

Quartz emerged as a fascinating material where the mechanical twinning can be used to elucidate paleostresses. New experiments explored the influence of temperature and stress on the twinning activity (Wenk et al. 2006, *Phys. Chem. Mineral.* **33**, 667). New *in situ* neutron experiments with strain diffractometers allow following internal changes in structure as a material is deformed at stresses ranging from 100 to 500 MPa (Wenk et al. 2007). Currently the behavior during the trigonal-hexagonal phase transformation under stress is being investigated. The LANL SMARTS diffractometer proved invaluable for this study. With this new information we can now calibrate the quartz twinning pattern in its use as a paleopiezometer in natural situations such as tectonic deformation (Pehl and Wenk 2005, *J. Struct. Geol.* **33**, 273) and meteorite impacts (Wenk et al. 2005, *Geol.* **27**, 1741).

Preferred orientation of clays is a primary ingredient for anisotropy in *shales* that has never been quantitatively characterized. A most exciting result of the research was the fact that, after developing the hard synchrotron X-ray technique (Wenk et al. 2007, *Geoph.* **72**, E69), we can now investigate very complex shales such as those from European nuclear waste repositories with 6 major phases (Fig. 1). Preferred orientation of illite-smectite, kaolinite, chlorite and calcite produce strong anisotropy. Quartz is largely isotropic. Preferred orientation varies with geological setting, mineralogical composition and depth.

The new observations add constraints and also open a whole range of new questions. In looking forward, priorities are to concentrate on understanding the mechanisms of mechanical twinning and texture memory in quartz-bearing rocks by further neutron diffraction experiments at LANSCE, involving also analog materials such as low symmetry metals with twinning such as titanium (Lonardelli et al. 2007, *Acta Mater*, in press) and uranium. Experiments are complemented by finite element modeling (collaboration with N. Barton, LLNL). A systematic investigation of twinning patterns in naturally deformed quartz rocks is underway and preliminary results are very revealing. On shales we are now studying experimental material formed under well-defined conditions (illite-kaolinite-quartz mixtures). This collaboration with the University of Oslo relates experimental acoustic velocities with those predicted from crystallite orientation. Here uncertainties about single crystal elastic properties are a major limitation and we are working with L. Stixrude (now UCL) to obtain properties of clay minerals from first principles. We are applying the analysis to samples from the San Andreas fault drilling project (SAFOD) to quantify anisotropy in this shear zone.

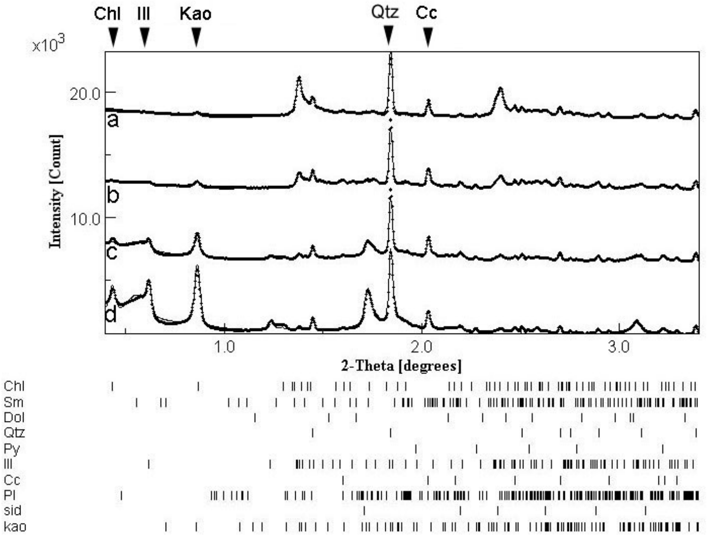

Figure 1. X-ray diffraction spectra of Opalinus clay composed of ten minerals. Line is experiment and dots are Rietveld fit. Peak intensity variations are indicative of preferred orientation. Diffraction peaks are indicated by lines at bottom. Measurements were done at APS.

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Grant: DE-FG02-97ER14749

Thermodynamics of Minerals Stable Near the Earth's Surface

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

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

Results: An extensive calorimetric study of iron oxides and oxyhydroxides is almost complete. It shows that maghemite, γ-Fe_2O_3, although metastable with respect to hematite, α-Fe_2O_3, when coarsely crystalline, becomes thermodynamically stable at the nanoscale because of lower surface energy. This energy crossover is similar to that seen in Al_2O_3. Furthermore, iron oxyhydroxides have lower surface energies than anhydrous oxides, leading to thermodynamic stabilization of the hydrated nanophases to higher temperatures than for the equilibrium dehydration of coarse goethite to hematite. The ferric oxyhydroxide polymorphs show a complex set of energy crossovers, see Fig. 1. At particle sizes <50nm, goethite, akaganeite, lepidocrocite, and ferrihydrite become very similar in enthalpy (and probably free energy), explaining their common occurrence. The Fe_2O_3 and FeOOH data support previous systematics found for Al_2O_3. TiO_2, and ZrO_2. Polymorphs having higher enthalpies as bulk phases have lower surface energies. Hydrous phases have lower surface energies than anhydrous phases. Hydrated surfaces have lower surface energies than anhydrous surfaces. As part of this work, we have developed an accurate method that simultaneously measures the adsorption isotherm and heat of adsorption of water on oxide powder surfaces.

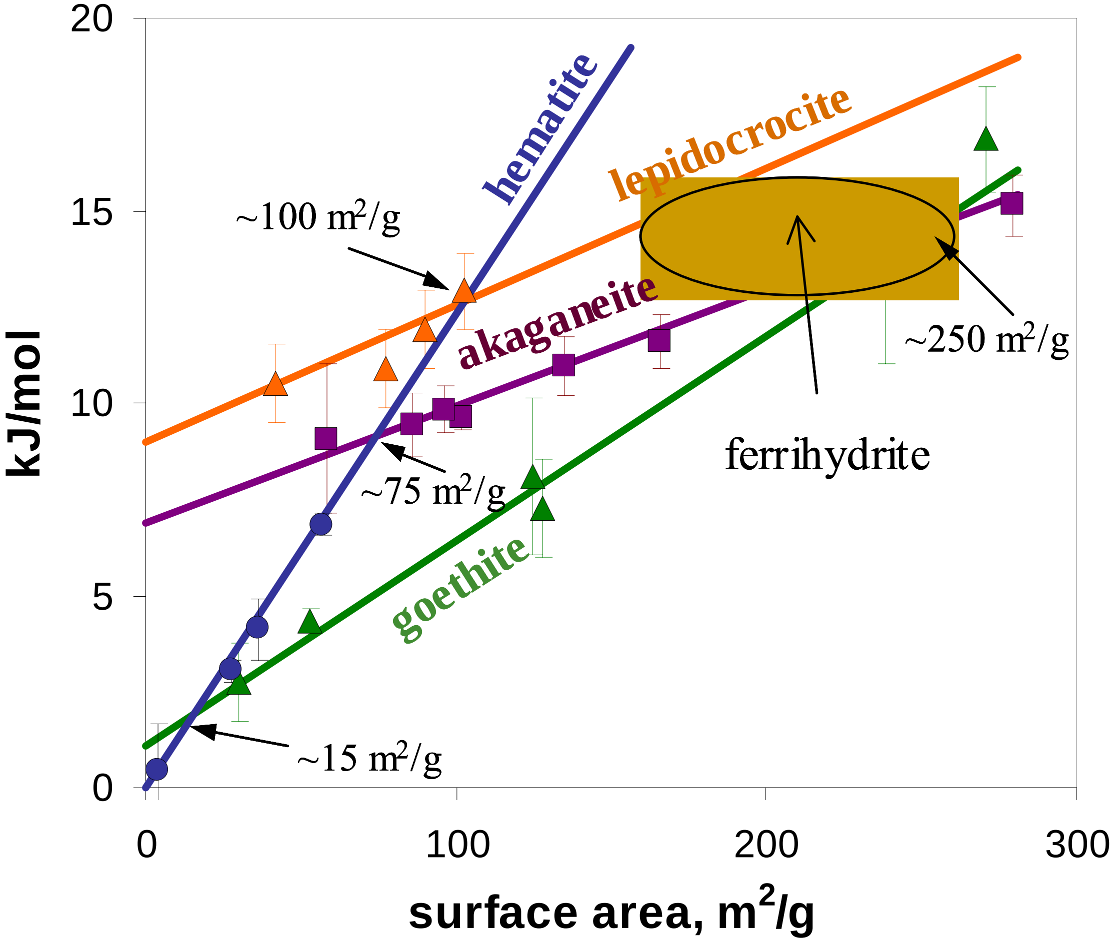

Fig. 1. Calorimetrically measured enthalpies relative to coarse hematite plus liquid water ½($Fe_2O_3 + H_2O$) for oxyhydroxides and fine grained hematite versus surface area (m^2/g) . The points are experimental data and the ellipse indicates the range for various ferrihydrite samples studied.

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Grant: DE-FG02-04ER15498

Size and Shape Effects on Surface Charging and Energetics of Goethite Nanoparticles

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Objectives: It is generally thought that surface reactivity at mineral-water interfaces is determined by variations in local coordination structures in stable terminations of protonated oxide surfaces. Solvent accessibility, global minimization of electrostatic potential, and edge effects also make some contribution to surface reactivity. Computational investigations of structurally well-defined aqueous polynuclear systems can be used to determine the relative importance of these effects in determining reactivity at geochemically important interfaces.

Project Description: During previous funding cycles, we have developed computational chemical models that allow direct investigation of complex reaction mechanisms at protonated oxide-water interfaces. The basis of these models is a polarizable, dissociating water model that is transferable from the gas-phase to condensed phases. These models have been extensively tested and benchmarked in aqueous and ultra-high vacuum environments. In this project, these models are used to study acid-base, ligand-exchange, and electron transfer reactions in heterogeneous aqueous environments. To check the model predictions, we use experimental studies conducted on polynuclear systems whose structure is known from x-ray studies on hydrated salts of the polynuclear ions.

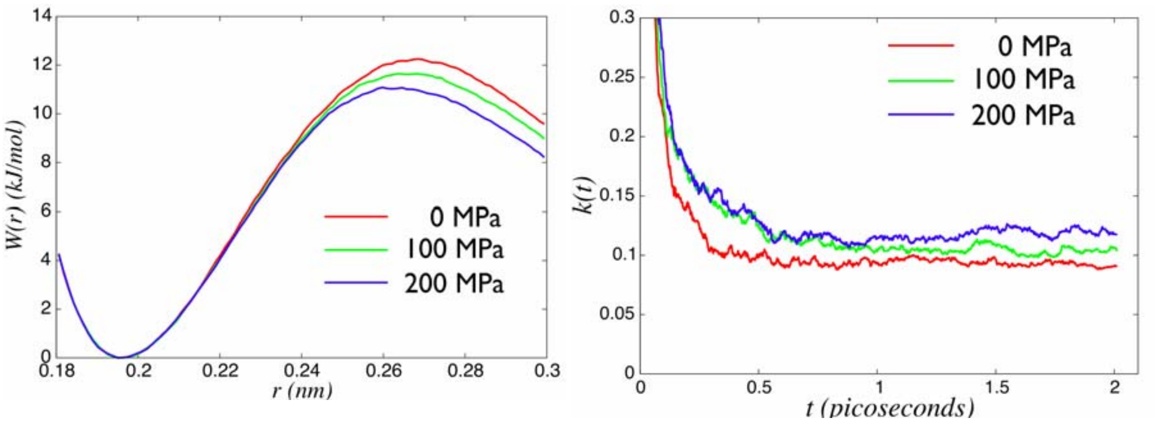

Figure: Pressure dependence of (a) free energy barrier and (b) transmission coefficient for water exchange around Li^+(aq)

Results: Studies over 2005-2006 have focused on developing techniques for predicting reaction kinetics for use in geochemical systems. The main connection with experiment is often not the rate itself, but the activation enthalpy, entropy and volume, derived from the temperature and pressure dependence of the rates. These activation parameters are believed to have important implications in the determination of reaction mechanism. Earlier work on this project indicated that mechanistic criteria developed for aqueous systems could be unreliable when used in interfacial systems. However, this was based on visual inspection of the reaction mechanism. Confirmation requires direct computation of the activation parameters. Very few studies have attempted this, and these have been far removed from the aqueous environments we are interested in.

Computational determination of a rate involves both the free energy barrier and the transmission coefficient across the barrier. Both of these could in principle depend on pressure or temperature. The activation volume of water exchange around Li^+ (aq) was determined from reactive flux calculations using molecular dynamics simulations with a classical force field. The $\Delta G^\ddagger$ for exchange decreases with pressure, giving a negative contribution to the activation volume, in agreement with the current paradigm for inferring exchange mechanism from activation volume. However, it is also demonstrated that pressure-dependent transmission effects make a significant contribution to the overall activation volume. These calculations indicate that small activation volumes should not be regarded as mechanistically indicative because of the potential contributions from transmission effects.

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Grant: DE-FG02-04ER15639

How Do Interfacial Phenomena Control Nanoparticle Structure?

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Objectives: Nanomaterials may have particularly heterogeneous surface structures owing to their high interfacial curvatures. Crystal structures of the hydrated salts of Al and Fe oxide nanoparticles exhibit a wide variety of structural environments with different accessibility of solvent and counterions at various regions on the particle surface. It is important to know how much variation this causes in site reactivity and what factors most strongly influence reactivity in nanoparticle environments.

Project Description: Water exchange rates are the most fundamental measure of the kinetics of water-mineral interaction. This project uses molecular dynamics methods to simulate chemical reactions on nanoparticle surfaces. The predictions can be compared to rate measurements in the literature, often at a site-specific level. These include the $Al(H_2O)_6^{3+}$ monomer; the ε-Keggin ion $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+/8+}$ (**Al_{13}**); the $[Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ (**Al_{30}**) aqueous polyoxocation; the surfaces of Al-oxyhydroxide minerals boehmite (AlOOH) and gibbsite ($Al(OH)_3$); and the aluminosilicate mineral kaolinite ($Al_2Si_2O_5(OH)_4$) **[**see Figure**].** Calculations use rare events molecular dynamics methods to calculate both the free energy barrier in the potential of mean force and the transmission coefficient. These are combined to generate the overall rate of reaction.

Results: Water exchange rates around aqueous **Al^{3+}** are accurately known. Water exchange data on the **Al_{13}** and **Al_{30}** nanoparticles form an important bridge between the ion and the surfaces. As evident in the Figure, the Al_{30} particle has six different site types; there is strong experimental evidence that water exchange rates vary by at least three orders of magnitude on the **Al_{30}** surface. The calculations show that there is a strong correlation between particle size and water exchange rate, with the slowest exchange rate calculated for the **Al^{3+}** ion with characteristic water residence times of ~100 seconds, and the fastest rates were calculated for the mineral surfaces, with characteristic residence times in the subnanosecond range. This variation is exhibited in the **Al_{30}** particle; with the fastest sites exchanging on microsecond timescales, and slow sites exchanging on timescales of seconds. On the **Al_{30}** particle, solvent accessibility plays a major role; the slowest sites are poorly hydrated while the fastest sites are well-hydrated. We observe an inverse relationship between exchange rate and bond length. Our results suggest that mineral surfaces have very fast rates of water exchange, approaching those of the most labile monovalent ions in solution. One important geochemical implication is that, for example, redox-based contaminant mitigation strategies would be expected to be much more effective in interfacial environments than in aqueous solutions because the higher rates of water exchange in interfacial environments should facilitate more frequent $=Fe^{2+}$-contaminant encounters than would be the case for $Fe^{2+}(aq)$.

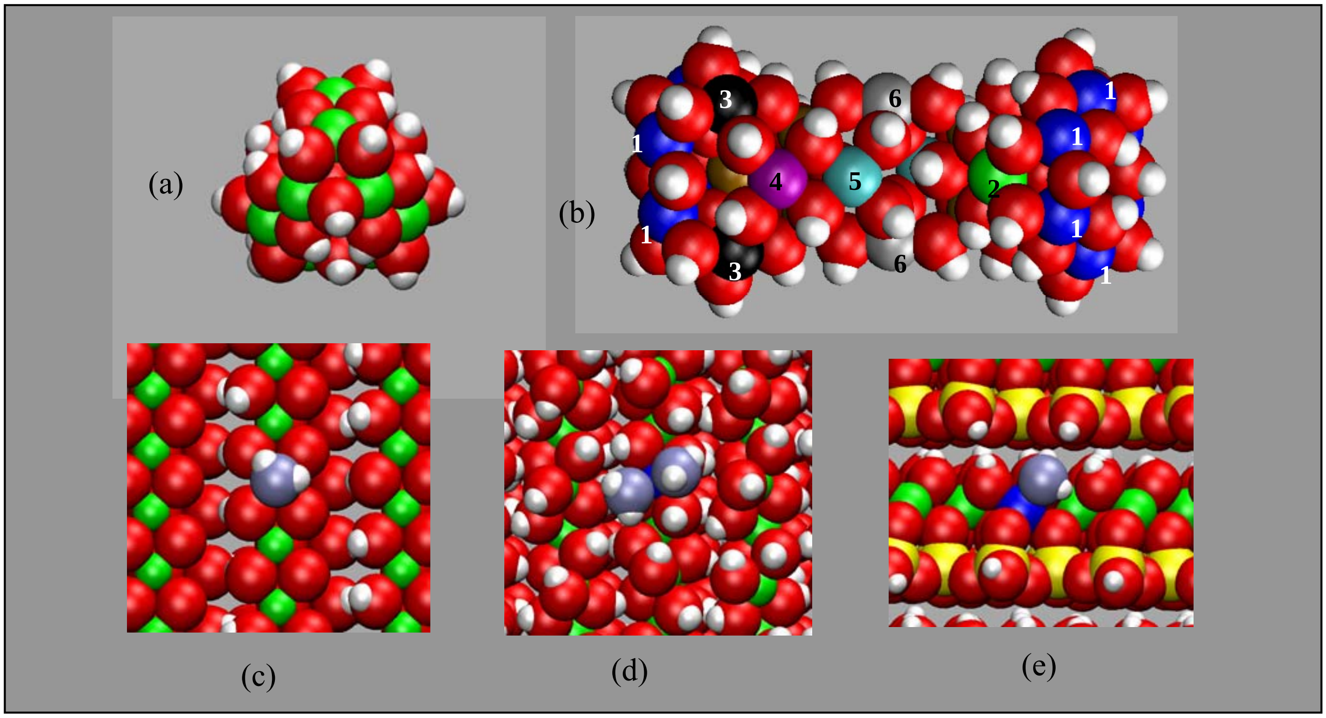

Figure : The Al(III) cationic clusters and mineral fragments used in these calculations. **(a)** The **Al_{13}** molecule is part of a class with stoichiometry: $[MO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7/8+}$ (M=Al(III), Ga(III), Ge(IV)) and similar rates of solvent exchanges from the twelve equivalent bound-waters.; **(b)** the **Al_{30}** $[Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ cation has six structurally distinct bound-water sites identified identified as **S_1** through **S_6**. **(c)** boehmite [γ-AlOOH] (001) **(d)** gibbsite [α-$Al(OH)_3$] (100) (1(1bar)0); **(e)** Kaolinite $[Al_2Si_2O_5(OH)_4]$

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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 establish reactivity trends for isotope-exchange reactions for oxide materials at the molecular scale using spectroscopy. The experiments are closely coupled to molecular simulation to uncover actual reaction pathways.

Project Description: The central thrust is to couple kinetic results on nanometer-size oxide ions, and proton lifetimes in particular, to sophisticated methods of simulation in order to predict rate parameters for oxide colloids and minerals, for which experimentation is virtually impossible. We succeeded in these experiments using a set of Al(III)-Keggin ions and have branched out to other Nb(V) and Ta(V) oxide nanometer-size clusters. The methods that we used to follow these elementary or near-elementary reactions are ^{17}O-NMR spectroscopy and electrospray-ionization mass spectrometry. These tools allow us to follow oxygen-isotope-exchange reactions at specific structural sites in nanometer-sized ions in aqueous solution, and yielded close correlation between cluster structure and reactivity.

Results: We reported residence times for protons on the bound waters and two sets of μ-OH bridges for the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}{}_{aq}$ ion nanocluster. Because of the similarity of this molecule to clays, the results provide a constraint for proton residence times for mineral surfaces. We since extended the work to other nanometer-size clusters. The Lindqvist ions are a superoctahedron of $M(O)_6$ octahedra that are all linked at a single inert μ_6-oxo. They have a central μ_6-O site, twelve μ_2-O bridges, and six terminal η=O sites, all of which are observable in ^{17}O-NMR. The structures of Nb(V) and Ta(V) Lindqvist ions are virtually identical because of the Lanthanide contraction that nearly equalizes the <M-O> bond lengths. Metals in the two structures have a closed-shell electronic configuration and primarily differ by the full shell of $4f^{14}$ electrons in the Ta(V) version of the Lindqvist ion. The relative rates of isotopic exchange of the η=O and μ_2-O sites *invert* as one goes from Period 5 [Nb(V)] to Period 6 [Ta(V)], although these molecules are virtually isostructural and nearly isoelectronic. These observations challenge our understanding of reaction pathways in aqueous solutions and provide key test cases for computer simulations of reaction dynamics in aqueous solutions.

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Grant: DE-FG02-04ER15568

Collaborative Research: Understanding Multi-Scale Space-Time Patterns in Crustal Deformation Processes: Towards Ensemble Forecasting in Complex Tectonic Systems

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Objectives: To develop a physical understanding of the origins of space-time patterns and statistical correlations occurring in geomechanical and tectonic systems, and use these to forecast future activity that may produce disasters affecting a variety of critical energy facilities, such as nuclear power plants, oil refineries, and national laboratories.

Project Description: The complex earth system generates a variety of phenomena that are highly nonlinear and operate over a broad range of spatial and temporal scales. Signatures of these processes include scaling (fractal distributions), global and local self-organization, intermittancy, chaos and the emergence of coherent space-time structures and patterns. We are using massively parallel simulations to model geodynamical effects observed in earthquake systems in order to determine the origin of these phenomena. These investigations and the theoretical efforts done in parallel are particularly aimed at quantifying the limits of predictability for disasters such as earthquakes that occur within the earth system. We are currently continuing our development of the theoretical and computational tools that allow us to both obtain sufficient data on realistic models and to analyze the data we obtain. From these simulations we will then predict geodetic and other deformation associated with impending earthquakes to be tested against Global Positioning System, Synthetic Aperture Radar, seismicity and other field data.

Results: Theoretical Models: We developed methods for the computation and interpretation of gravity and height changes and gravity gradients produced by tectonic sources such as interacting earthquake faults in a layered elastic-gravitational medium. The results of these computations show spatial patterns very similar to those exhibited by Coulomb stress changes from natural active faults, and show that surface gravity changes can be used as a proxy for such stress changes.

Pattern Analysis: An algorithm that our group developed, pattern informatics ("pi"), was used to detect the locations where precursory activity occurred preceding the 1999 Chi-Chi, Taiwan, earthquake. The epicenter of the Chi-Chi mainshock was found to exhibit signatures of anomalous activity related to the seismic activation and quiescence in the Taiwan region over a time span of about 6 years before the mainshock.

Numerical Simulations: We have developed realistic numerical simulations, involving data-mining, pattern recognition, theoretical analyses and ensemble forecasting techniques, to understand how the observable space–time earthquake patterns are related to the fundamentally inaccessible and unobservable dynamics. Our simulations indicate that elastic interactions (stress transfer) combined with the nonlinearity in the frictional failure threshold law lead to the self-organization of the statistical dynamics and the observed earthquake scaling laws.

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Grant: DE-FG02-89ER14049

Application of ^{40}Ar/^{39}Ar Thermochronometry and Ion Microprobe Stable Isotope Geochemistry to the Evolution of Petroleum Reservoirs and Hydrothermal Systems

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Objectives: Our goal is to measure high resolution oxygen isotope ratios from both modern and Pleistocene spelothems to test their use as reliable climate proxies. Determining the timing, duration and structure of rapid climate events requires annual to sub-decadal resolution that is not achievable in the poorly resolved chronologies of the deep sea cores which preserve Heinrich events, but may be obtained using this approach.

Project Description: Seasonal and inter-annual oxygen (δ^{18}O) isotope ratios from an 81-year-old stalagmite from Moondyne Cave, southwest Australia, provides an excellent test of speleothem climate proxies because the regional climate is strongly seasonal (wet winter/dry summer) and has experienced a 200 mm (20%) reduction of mean rainfall since the mid-1960's, and a 0.8°C temperature rise since ~1953. The growth history of stalagmite MND-S1 is known since it grew on a cave boardwalk that was installed in 1911 and removed in 1992. Seasonal variations in calcite δ^{18}O were measured *in situ* by high spatial resolution ion microprobe, whilst inter-annual variations of δ^{18}O and δ^{13}C were measured by conventional gas-source mass spectrometry. We are also critically examining the suitability of the SIMS technique for speleothem O isotope analyses by applying it to a portion of the well-known Hulu Cave record over the most recent Heinrich event: H1 or Termination I at 16.1 ka.

Results: Comparison of the speleothem stable isotopes and instrumental temperature records for Moondyne Cave reveals that δ^{18}O variations are too large to be driven by temperature alone, and are in the opposite sense. However, daily rainfall δ^{18}O measurements show that the mean seasonal range in δ^{18}O of rainfall in southwest Australia is large (2×) and inversely correlated with rainfall amount. A rainfall driver for the speleothem δ^{18}O is confirmed by the detection of seasonal shifts of 0.7-1.5× in speleothem δ^{18}O that track rainfall δ^{18}O, smoothed by storage in the overlying limestone. The seasonal range in speleothem δ^{18}O is larger than any interannual and decadal variation observed in the record. The prominent annual cycles in speleothem δ^{18}O revealed by ion microprobe analysis indicate that subtle changes in the frequency of intense winter rainfall events, or possibly also moisture sources, could produce significant changes in mean speleothem δ^{18}O. The ion microprobe results also raise the possibility that the masses of speleothem calcite deposited in winter and summer could vary as a function of the seasonal drip rate and carbonate saturation state of these waters. If this is the case, then small changes in the relative masses of calcite deposited in winter and summer could produce significant shifts in mean δ^{18}O and δ^{13}C that have a complex relation to climate. This finding should be generally applicable to the interpretation of long-term trends in speleothem geochemical records for shallow caves.

We also compared the SIMS $\delta^{18}O$ analyses to previously published $\delta^{18}O$ analyses obtained by micro-shaving and conventional methods and also considered *in situ* LA-ICPMS trace element data in the interpretation of the Hulu Cave results.

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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 deep fluid flow, submarine petroleum migration and diagenetic effects within deforming faults in a transpressional setting that is seismically active. Most of the work deals with faulted basins of southern California, as outlined in the 2005 proposal, and provides important data and modeling relevant to carbon sequestration.

Project Description: We have targeted active faults and young petroleum fields in southern California for study. Our most recent studies have been along the Newport-Inglewood (N-I) fault in the Los Angeles Basin including the Inglewood and Long Beach oil fields. These data provide constraints for finite element models that are being developed to predict fluid pressures, flow patterns, rates of deformation, temperatures, and diagenetic patterns associated with large fault systems. We are also seeking to identify isotopic and trace element geochemical signatures that result from rapid CO_2 degassing. Our samples include calcites from a variety of settings including oil field well tubing scales, fault zone precipitates, and speleothems in man-made tunnels.

Results: Well tubing scales and speleothems show co-varying carbon-oxygen isotopic values with slopes up to + 5. Scales are enriched in heavy carbon up to 28 per mil, due to CO_2 degassing. Scales show increasing departure from equilibrium down hole, presumably due to increasing precipitation rates at the deeper levels. Some scales have up to 16 wt. % Mg substitution and are out of isotopic equilibrium with formation waters, which is attributed to rapid calcite crystallization. We are checking this finding in other fields where rapid growth has occurred. Growth rate-related Mg-substitution in calcite may have important implications for interpreting Mg/Ca ratios in calcite used for temperature interpretations in paleoclimate studies. Graduate student Grace Giles has completed a Master's degree on this topic and is currently employed at Exxon-Mobil. Graduate student Mike Ryan is working on core samples, sidewall samples, electric (including image) well logs from 40 newly drilled deep wells associated with the N-I fault. These wells have penetrated an igneous body, previously unknown anywhere in the LA basin (Ryan et al., 2007). The igneous rock is associated with the termination of the N-I fault and appears to have caused significant diagenetic effects on the reservoir sands. We are also involved in the planning stages of an oil company sponsored well designed to core the N-I fault zone. On the hydrogeologic modeling front, Appold and others have a manuscript in press that numerically models the observations on the Refugio fault with different assumptions from the previous published work (Boles et al., 2004). This model considers the scenario that the hydrocarbons are derived from the deep Eocene strata north of the Refugio fault rather than from the offshore Miocene section in the Santa Barbara channel. This finite element model links evolving fluid chemistry during mass transport to calcite precipitation. An illustration of the modeling location and the 2-D domain is displayed below, as Figure 1.

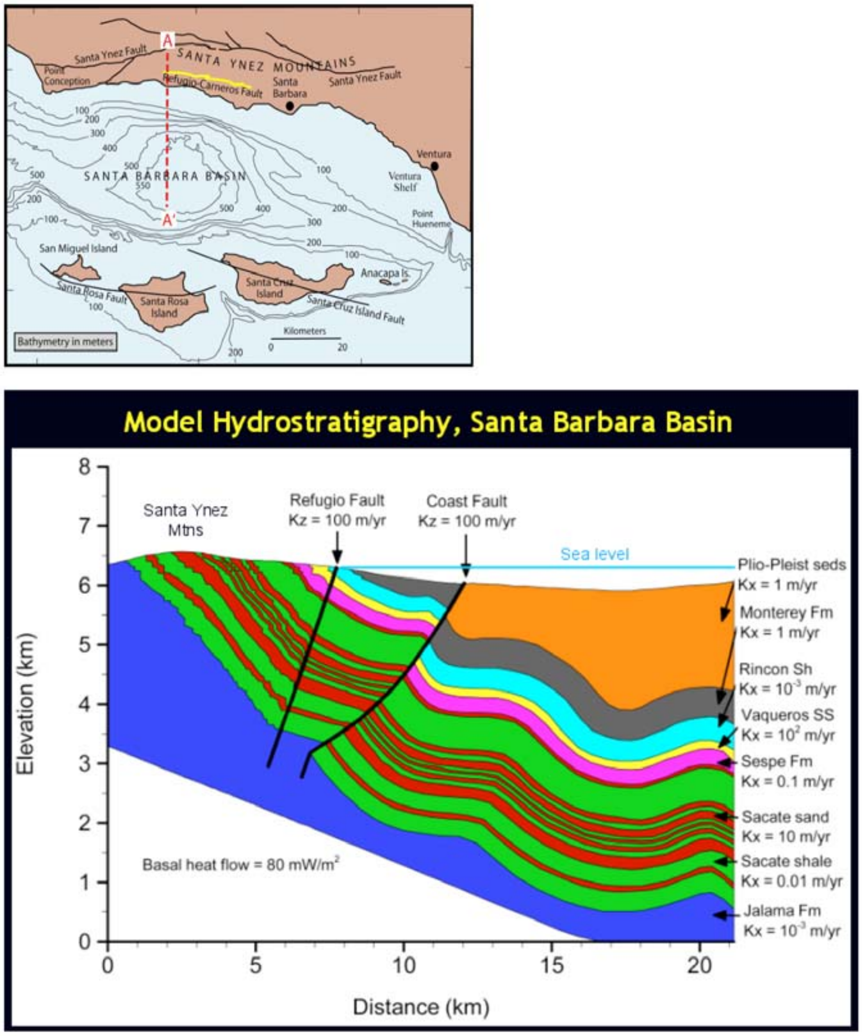

Figure 1. Location map and RST2D model hydrostratigaphy assumed for the Refugio Fault simulation (from Appold et al., 2005). The model assumes an initially overpressure basin section, which suddenly ruptures along the Refugio and Coast faults to allow mixing of shallow groundwater water with methane-bearing basinal fluids.

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Grant: DE-FG02-04ER15530

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

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Objectives: Develop new, improved methods for wave equation migration-imaging and extend these methods for estimating impedance contrasts and material properties at boundaries. The work focuses on three general areas: (1) development of new, more efficient, more accurate, wave-equation-based propagators and imaging conditions for migration imaging; (2) developments toward true amplitude imaging that allows estimation of the reflection as a function of angle at an interface; and (3) study of wave propagation in heterogeneous, elastic media. These efforts are all focused on obtaining more reliable quantitative information about rock properties from seismic data and images resulting from seismic data.

Project Description: High-resolution/high fidelity seismic imaging is critically important for both energy resource management (oil/gas exploration/production) and monitoring CO_2 sequestration. We propose to exploit 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 propose to develop imaging methods using multi-component elastic data. Conventional Amplitude vs. Offset (AVO) analysis to obtain material properties has had limited success in geologically complex regions. Thus, new methods of obtaining material property information are needed. Wave-equation based approaches have shown some promise for providing information about material properties but additional effort is needed to develop and fully exploit the capabilities of such methods.

Results:
(1) *Optimizations in true-amplitude one-way propagators:* To achieve better wavefield accuracy for the large-angle wave propagations, optimizations were applied to the True Amplitude One-way Propagator (TAOP). We investigated three types of implementations (one-step finite-difference method, two-step dual domain method and target-oriented flux transparent method) for the amplitude correction. Theoretical analysis and numerical results in a smoothly varying heterogeneous model showed that these implementations are different in accuracy, efficiency and compatibility when comparing with traditional one-way extrapolators. This enabled us to choose among different implementations according to different requirements and purposes.

(2) *One-return boundary element method and salt internal multiples:* Standard one-way and one-return method cannot handle rough boundaries with strong velocity contrast, such as the interfaces between sediments and salt inclusions. We proposed a one-way and one-return boundary element method (BEM) to calculate the primary transmission/reflection arrivals for layered or inclusion models with strong velocity contrast. The primaries were obtained by decoupling the interactions between the top and bottom of the inclusions defined for a given source-receivers configuration. Then the primaries were subtracted from the whole seismic records to obtain the internal multiples generated by the inclusion such as salt bodies. This method was applied to a modified 2D SEG-EAGE model to predict the internal multiples of acoustic wave. The results demonstrate that the proposed method was effective to obtain the primary transmission/reflections generated by internal interfaces with strong velocity contrast. The pre-stack depth image from these pure multiples was compatible with those artifacts in the conventional pre-stack image, thus demonstrating the potential applications of this method in multiple modeling and removal.

(3) *Super-wide angle one-way method:* We used a wavefront reconstruction technique to develop a super-wide angle one-way method which extended the capability of traditional one-way propagators beyond 90 degrees. This technique combines and interpolates the two orthogonally propagated one-way wavefields to accurately reconstruct the distorted wavefront. In this year, a more complex reconstruction scheme was developed to improve the accuracy and reduce the artifacts. The new scheme employed the wavefield gradients to determine the weighting function for combining the two orthogonally propagated wavefields. Numerical examples demonstrated the good accuracy of the weighting scheme. We also showed the advantage of this method in imaging the overhanging salt flanks in the BP 2D model (see figure below) by accurately modeling turning waves.

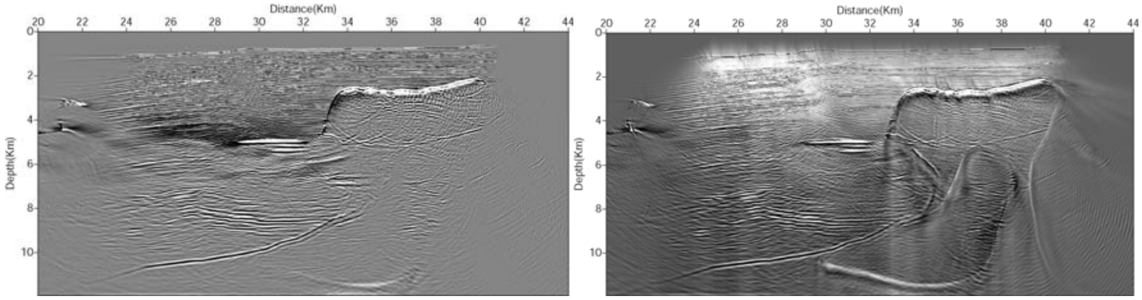

Figure: Comparison of salt flank images obtained by conventional one-way method (left panel) and our super-wide angle one-way method (right panel).

(4) *A migration velocity updating method based on the finite-frequency sensitivity kernel:* We developed a new tomography method for migration velocity updating. The method was based on the sensitivity analysis of finite-frequency signals. We derived the finite-frequency sensitivity kernels particularly for the migration residual moveout in shot-domain common image gathers. We validated these sensitivity kernels by comparing them with the residual moveout directly measured from the migrated image. Based on these sensitivity kernels, we built an inversion system for velocity updating. The new method was wave equation based and was naturally formulated for the shot-domain common image gathers. Using synthetic data sets, we successfully inverted velocity perturbations from the residual moveout. The results showed that the inversion has very good resolution on small scale velocity perturbations.

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Contract: 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 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.

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

Applications Results: Highly charged ions in aqueous solutions interact strongly with neighboring water molecules forming very stable 1st and 2nd hydration shells. The structure and dynamics of species in these shells are strong functions of properties of the ions such as charge, effective size and valence electronic structure. The rate of exchange of ligands and chemistry within the 1st and 2nd hydration shell are strongly affected by the structure and dynamics in this region. For example exchange rates vary over a very large range as a function of the properties of the ions (e.g. $t_{1/2}$, in the 1st solvation shell for Al^{3+} is ≈1 sec and `10^{-7} for Fe^{2+}) and cannot be rationalized on the basis of our present understanding of ion solvation. We used 1st principles dynamical simulations to investigate this behavior. In these simulations the interactions between ions were calculated directly from the electronic Schrödinger equation. This was required because the ion causes major changes in the solute-solvent and solvent-solvent interactions in the 1st and 2nd coordination shell. In FY06 we completed calculations for the Al^{3+} ion. These simulations included 128 waters and a total simulation time of 8 ps. In the Al^{3+} system there was a very well structured 1st and a trigonally coordinated 2nd hydration shell. For this ion the 1st hydration shell was very stable ($t_{1/2}$≈1sec). However, we observed transitions between the structured 2nd hydration shell and the bulk region with a time scale of 10's of picoseconds. As shown in Fig. 1, the exchange follows rare event dynamics using an intermediate exchange mechanism. The replacement of the 2nd shell water with a water molecule from the bulk was highly correlated with the departure of the water in the 2nd shell. The transition state appears to be symmetrical with similar bond lengths for both the departing and entering waters. The ability to simulate dynamical exchange processes in the hydration shells of these strongly perturbed systems represents an important advance in our ability to simulate the chemistry of complex systems.

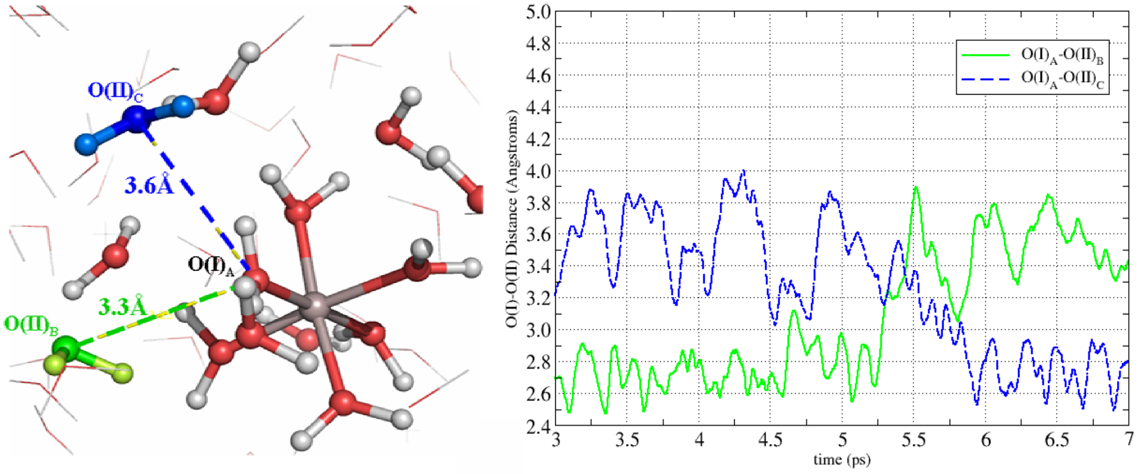

Figure 1. Ligand exchange mechanism seen between the second and third shells in 300K Al^{3+}+128H_2O simulation, (left) intermediate structure and (right) relevant O_I-O_{II} trajectories.

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

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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 fifty five (255) beam time proposals were received, 221 unique users conducted experiments, and 74 papers were published. Published research included the following (key collaborators in parentheses): (1) Metal Binding Mechanisms in Biosolids (G. M. Hettiarachchi et al.), (2) Pore-Scale Dissolution of Organic Immiscible Liquid in Natural Porous Media (G. Schnaar and M. L. Brusseau), (3) Chemical Speciation and Bioaccessibility of Arsenic and Chromium in Chromated Copper Arsenate-Treated Wood and Soils (P. S. Nico et al.), (4) Contrasting Effects of Dissimilatory Iron(III) and Arsenic(V) Reduction on Arsenic Retention and Transport (B. D. Kocar et al.), (5) Structure and Reactivity of Environmental Interfaces (T. P. Trainor et al.), (6) *In Situ* Bioremediation of Uranium in a Highly Contaminated Aquifer (M. W. Ginder-Vogel et al.), (7) Plutonium Oxidation and Subsequent Reduction by Mn(IV) Minerals in Yucca Mountain Tuff (B. A. Powell et al.), (8) Strontium Speciation during Reaction of Kaolinite with Simulated Tank-Waste Leachate (S. Choi et al.), (9) Copper Speciation in High-temperature Brines (A. J. Berry et al.), (10) Solid-phases and Desorption Processes of Arsenic within Bangladesh Sediments (M. L. Polizzotto et al.), (11) Uranium Speciation through a Depth Sequence of Contaminated Hanford Sediments (J. Catalano et al.), (12) Predicting Macroscopic Transport Properties using Microscopic Image Data (J. T. Friedrich et al.).

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Grant: DE-FG02-92ER14244

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

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Website: http://www.bnl.gov/x26a/

Objectives: The objectives are to apply a synchrotron-based x-ray microprobe for determinations of the compositions, structures, oxidation states, and bonding characteristics of earth materials with trace element sensitivity and micrometer spatial resolution.

Project Description: The project focuses on applications of the x-ray fluorescence microprobe on Beamline X26A at the National Synchrotron Light Source (Brookhaven National Laboratory) for determinations of the compositions, structures, oxidation states, and bonding characteristics of earth and environmental materials with trace element sensitivity and micrometer spatial resolution. In 2006, more than 25 publications in peer-reviewed journals were published from research conducted at the beamline. Research focused on actinide and metal incorporation in minerals and sediments, biogeochemistry of actinide and metal contaminants, and iron oxidation states in igneous petrogenesis.

Results: Sixty-two unique users conducted experiments within the past year and 25 papers were published. Published research included the following (key collaborators in parentheses): (1) long-term stability of organic carbon-stimulated chromate reduction in contaminated soils (T. Tokunaga et al.); (2) form, distribution and mobility of arsenic in soils contaminated by arsenic trioxide, at sites in southeast U.S.A. (L. Yang and R. Donahoe); (3) spatial and temporal variability of arsenic solid-state speciation in historically lead arsenate contaminated soils (Y. Arai et al.); (3) fate and speciation of gasoline-derived lead in organic horizons of the northeastern U.S.A. (J. Kaste et al.); (4) quantitative determination of absolute organohalogen concentrations in environmental samples; (5) evaluation of zinc coordination to multiple ligand atoms in organic-rich surface soils (C. Martinez et al.); (6) batch experiments and X-ray absorption spectroscopy studies of the coprecipitation of chromate with calcite (Y. Tang et al.); (7) crystal chemical and x-ray absorption near edge studies of Fe-bearing olenite with tetrahedrally-coordinated Al from abyssal pegmatites at Kutná Hora, Czech Republic (J. Cempirek et al.); and (8) characterization of arsenic-bearing near-surface and airborne particulates from gold-mine tailings in Nova Scotia, Canada (M. Corriveau and H. Jamieson).

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Grant: DE-FG02-01ER15254

Kinetic Isotope Fractionation by Diffusion in Liquids

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Objectives: Our research seeks to document and quantify kinetic isotope fractionations during chemical diffusion, and most recently thermal diffusion, in a variety of liquids ranging from silicate melts to water. A significant part of the effort involves developing and validating high-precision isotope measurements of Ca, Fe, K, Li, Mg, and Si of both experimental and natural samples.

Project Description: Diffusion couples juxtaposing rhyolite and basalt are run in a piston cylinder assembly for various lengths of time at a pressure of about 1GPa to avoid problems with gas bubble migration. The thermal diffusion experiment are also run in a piston cylinder but in this case the assembly contains only basalt and is offset from the hot spot so as to produce a 100 – 150 ˚C temperature difference across the molten sample. The experiments for diffusion of dissolved salts in water involve diffusion from a small spherical container into a much larger volume of water producing a system that we have shown to be a Rayleigh fractionator from which the relative diffusivity of elements or isotopes can be determined. The run products are measured by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) or with the CAMECA IMS-1280 ion microprobe at the University of Wisconsin.

Results:
(I) Diffusion in Silicate Liquids: A new series of diffusion couples juxtaposing mid-Ocean ridge basalt and natural rhyolite glass have been run for measuring the isotopic fractionation of Ca, Fe, Mg and Si during diffusion. The diffusion couples were annealed in a piston cylinder apparatus at 1.2 GPa, and held at temperatures in the range 1350˚C-1450˚C for times ranging from 10-15 hours. Profiles of the major element concentrations have been measured along the length of the diffusion couples using a JEOL JSM-5800LV scanning electron microscope equipped with an Oxford Link ISIS-300 energy dispersive microanalytical system. The profiles show very well developed diffusion profiles, which we use to guide the isotopic measurements by MC-ICPMS. We have now documented diffusive isotope fractionations of calcium (~ 6 ‰ in ^{44}Ca/^{40}Ca), magnesium (~ 8 ‰ in ^{26}Mg/^{24}Mg), and iron (~ 1 ‰ ^{56}Fe/^{54}Fe).

(II) Diffusion in Water: We recently published the results on the diffusion of Mg, Li, and Cl in water. We found no measurable diffusive isotope fractionation of magnesium, and small but well-resolved fractionations of both Li and Cl. Ian Bourg and Garrison Sposito have used molecular dynamics calculations to reproduce our results and suggest that the explanation for why there is so much less isotopic fractionation in water compared to what we found in silicate liquids has to do with both the number of waters in hydration spheres around the dissolved ions and the residence time of waters in the inner hydration shell.

(III) Isotope Fractionation by Thermal Diffusion: We have recently been running a set of experiments with mid-ocean ridge basalt as the starting material and intentionally displaced the sample from the hot spot of a piston cylinder assembly so that there would be about 100˚C temperature difference from one end to the other of the molten basalt. What we found is unexpected and quite extraordinary. A temperature difference of about 150˚C across molten basalt produces a relatively mild ~1 wt% change in the MgO (also CaO, FeO, and SiO_2) concentration but a whooping 10‰ change in $^{26}Mg/^{24}Mg$. This is an extraordinarily large isotopic fractionation, larger even than any previously reported thermal isotopic fractionation of gases as measured in terms of fractionations per atomic mass difference and per degree centigrade. We now have a complete set of data on the thermal fractionation of iron isotopes and found these to be 2 ‰ in $^{56}Fe/^{54}Fe$ per 100˚C and perfectly correlated with the magnesium fractionations. We also have preliminary data on the thermal fractionation of silicon isotopes (~ 2 ‰ per amu per 100˚C measured with the IMS-1280 ion microprobe).

(IV) Development of Analytical Techniques: We continue to develop new analytical capabilities for making high-precision isotope measurements on both natural and laboratory samples. The recent emphasis has been on developing methods using the CAMECA 1280 ion microprobe at the University of Wisconsin.

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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: As of September, 2006, our progress was in two areas: a field study of "steephead channels" near Bristol, Florida, and construction of a new laboratory apparatus that provides insight into the microscopic basis of erosive dynamics.

Our investigation of the Florida channels confirmed that the erosion of this channel network is dominantly driven by subsurface seepage flows. Measurements included sediment granulometry throughout the network; estimates of the apparent erosion rate; attempts to map the height of the water table using ground-penetrating radar; and GPS-aided mapping of the precise location of emerging springs. The latter two measurements provided preliminary data indicating that the unusual planform geometry of the channel network can be quantitatively related to the water-table geometry.

The initiation of erosion in systems such as the Florida channels is usually associated with the critical Shields number, i.e., the dimensionless shear stress that is just sufficient to mobilize grains. To study this condition in the laboratory, we have constructed a new apparatus that allows visualization of the grain-scale motions that occur near the onset of erosion. The apparatus allows us to not only visualize surficial motions, but also motions 10–20 grains deep within the bed.

COLORADO SCHOOL OF MINES
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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: Since 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 traveltime 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 are devising 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 will be used for evaluating the physical properties of heterogeneous, fractured reservoirs.

Results:

1. Moveout-based geometrical-spreading correction for wide-azimuth P-wave data.

Compensation for the geometrical spreading along the raypath is a key step in reconstructing the reflection coefficient at the target level. We developed an efficient methodology to correct long-spread, wide-azimuth reflection data for geometrical spreading in stratified azimuthally anisotropic media. The P-wave geometrical-spreading factor is expressed through the reflection traveltime described by a nonhyperbolic moveout equation. This moveout-based anisotropic spreading correction (abbreviated as "MASC") was successfully tested on both synthetic data (Figure 1) and wide-azimuth P-wave reflections recorded at Weyburn field in Canada. In particular, MASC helped to remove the amplitude distortions in the overburden and accurately estimate the azimuthally varying reflection coefficient for the fractured reservoir at Weyburn.

2. Seismic signatures of two orthogonal sets of vertical microcorrugated fractures.

Conventional fracture-characterization techniques operate with the idealized model of penny-shaped (rotationally invariant) cracks and ignore the roughness (microcorrugation) of fracture surfaces. We applied the linear-slip theory to examine wave propagation through an effective anisotropic medium that contains two microcorrugated, vertical, orthogonal fracture sets in isotropic background rock. The corrugation of fracture surfaces causes the deviation of the polarization vectors of the vertically traveling S-waves from the horizontal plane and makes the shear-wave splitting coefficient sensitive to fluid saturation. These results can be used to identify the underlying physical model and, potentially, to estimate the effective fracture parameters for reservoirs with multiple fracture sets.

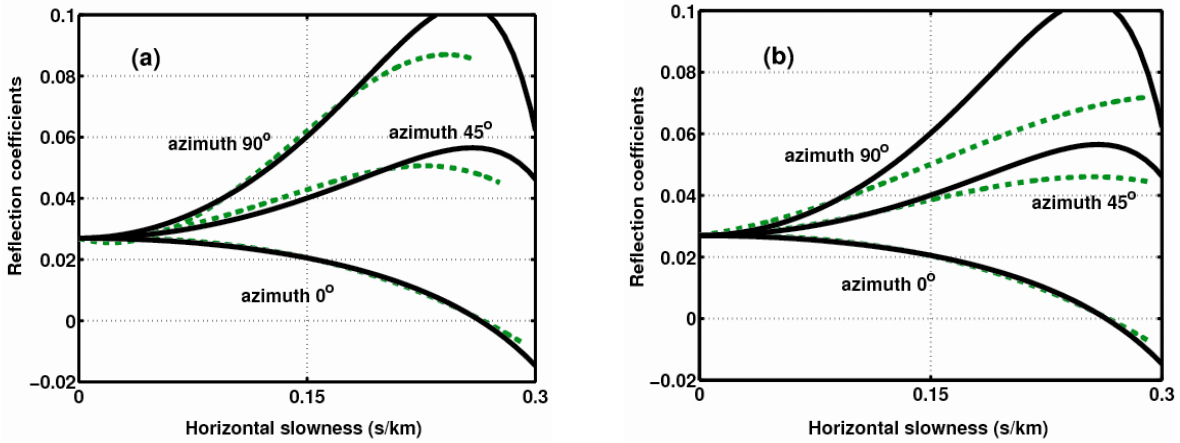

Figure 1: Performance of MASC on synthetic P-wave data reflected from the bottom of a fractured layer with orthorhombic symmetry. The dashed lines mark the reflection coefficient estimated from measured amplitudes using (a) MASC; (b) the conventional amplitude-gain function. The exact plane-wave reflection coefficient needed for AVO analysis is marked by the solid lines. MASC gives much more accurate results than the conventional method for the full range of azimuths (the azimuth is measured with respect to one of the vertical symmetry planes. The errors at large slownesses are caused by interference with PS-waves.

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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 in FY 2006 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 to above 200 degrees C within one year, and allowed to cool. An array of single component geophones was operated around the tunnel to detect microseisms, and their calibration shot-records have been processed for seismic interferometry and physical modeling. Our goal is to gain insight into changes in the velocity structure of the surrounding rock that will allow us to determine how thermal effects and changes in ground water affect the tunnel during extreme heating and cooling.

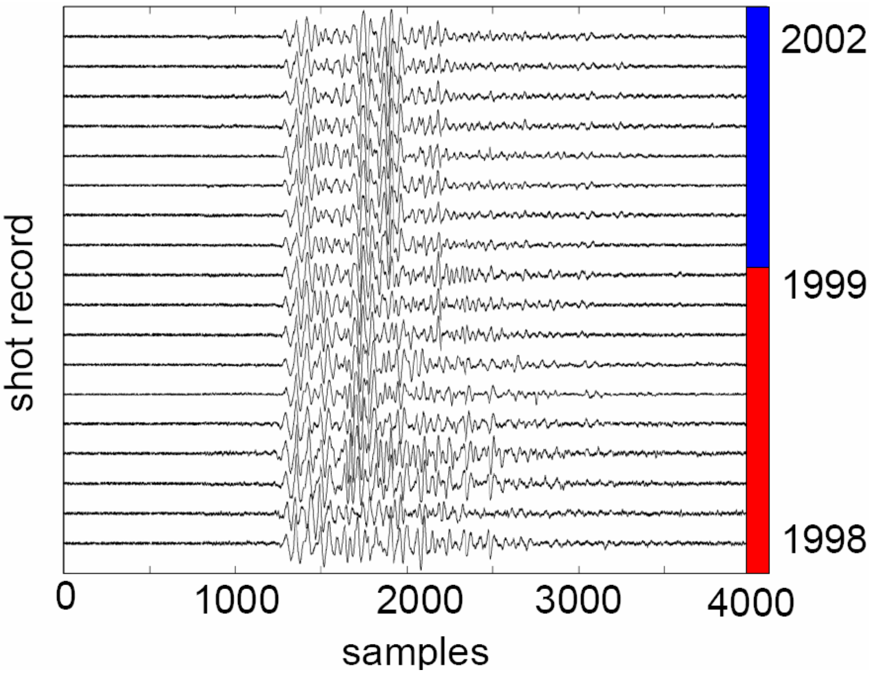

Figure 1. Data recorded at channel 14 after filtering and stacking as a function of shot time (indicated on the right). The red bar denotes the heating phase, the blue bar the cooling phase.

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 cleaned data recorded on channel 14 are shown in Figure 1. There are two things to note. First, the noise level before the first-arriving wave is low, this indicates an excellent signal to noise ratio. Second, the wave-forms show systematic changes from trace to trace. 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.

We first tested the potential for using coda wave interferometry with these data. The tail end of the wave-trains does not decay in the characteristic way of multiply scattered waves. For this reason we are hesitant to apply coda wave interferometry to these data. Instead, we performed numerical modeling of elastic waves in the vicinity of the tunnel, and found that some waves interact intensely with the region around the tunnel. Notable are the so-called Franz waves that behave like guided waves and that propagate around the drift tunnel while they are radiating body waves. We expect that these waves are a sensitive diagnostic for changes in temperature near the tunnel.

We found most numerical modeling techniques inadequate for dealing with the free surface at the tunnel wall, and finally opted for a spectral element modeling technique. The advantage of this method is that the free surface boundary condition at the tunnel wall is hard-wired into the modeling code.

The plan is to carry out waveform inversions and match the observed seismic waveforms with synthetics by changing the velocity near the tunnel using nonlinear optimization techniques. I order to match the data to the synthetics, one needs to account for the spectral characteristics of the hammer source and the receiver. We are currently in the process of designing a filter, based on recorded first arrivals and their numerical counterparts, that accounts for the spectral properties of the source and receivers.

Once this filter is designed we plan to use a genetic algorithm to do the nonlinear waveform inversion. A genetic algorithm is a pretty intelligent design that mimics evolution by breeding populations of models that have offspring, and whose "survival" depends on their ability to fit the data. The advantage of this method is that it produces numerous models that fit the data, which makes it possible to assess what model features can be trusted, and which ones cannot. We will apply the genetic algorithm to waveforms recorded at progressively later dates as a way of monitoring the temperature changes during the heating test.

An interesting aspect of this project is that the waves are sensitive to seismic velocity. This quantity depends both on temperature and fluid saturation. Because of the high temperature attained in the test (about 200 degrees C), boiling occurs and a severe hydro-thermal circulation occurs. Given the known dependence of seismic velocity of temperature, the measured seismic velocity can potentially be used as a constraint on the fluid migration.

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Grant: DE-FG02-04ER15589

Seismic Absorption and Modulus Measurements in Porous Rocks in Lab and Field: Physical, Chemical, and Biological Effects of Fluids

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Objectives: To investigate the use of quasi static deformation (tidal and microseism strains) in the detection of changes in the subsurface caused by the infiltration of fluid contaminants.

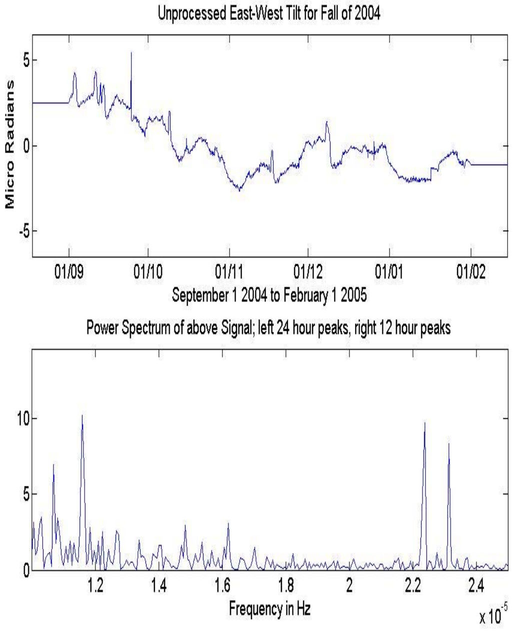
Project Description: We are exploring a new technology that is based on using low-frequency strain data to monitor changes in fluid saturation conditions in two-fluid phase porous materials. Strain data can reveal changes in complex moduli, which are caused by hysteresis in meniscus movement (changes 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.

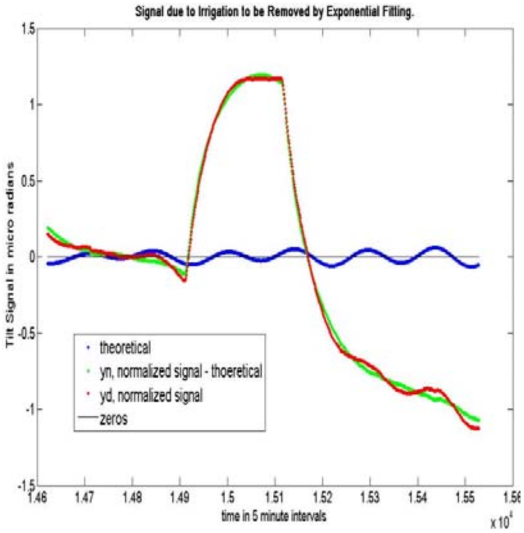
Results: A three year field study at the Maricopa Agricultural Center site of the University of Arizona has been concluded. Three sets of instruments were installed along an East-West line perpendicular to a 50m by 50m irrigation site. Each set of instruments consisted of one three component seismometer and one tiltmeter. Microseisms and solid Earth-tides served as strain sources. The former have a power peak at a period of about 6 seconds and the tides have about two cycles per day. During the past year the analysis of the tilt data has advanced considerably. The following shows the approach (see figures).

In addition to the tidal signal, which is barely visible and appears as a low level persistent noise, there are large signals from nearby irrigation (e.g. three events near the middle of September), spikes of unknown origin (e.g. beginning of last third in September) and earthquakes (e.g. latter part of December) as well as noise from construction and other agricultural activities.

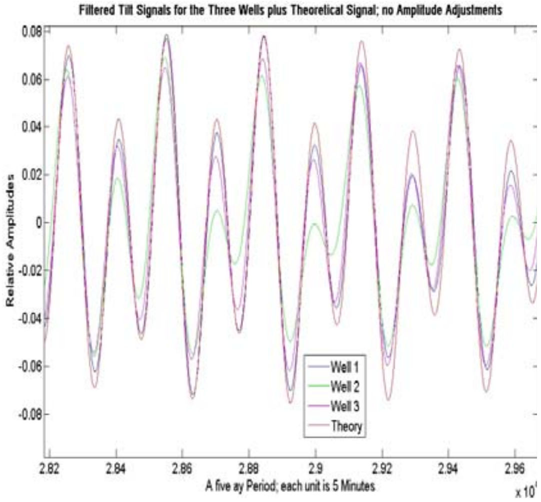
Conventional filtering is inappropriate at this stage since the large noise signals contain much energy in the frequencies of interest. In order to detect the effect of the irrigation, if any, we must detect subtle changes between the signals as a function of time; i.e. we must slide a time-window across the data set. We have therefore taken an approach where we remove the large signals wherever possible before we embark on conventional techniques of signal comparisons. Initially we apply a median filter to remove the large spikes. This is followed by removing sudden offsets (e.g. the offset in the middle of January 2005). Irrigation events and similar drifts are removed by curve fitting and subsequent subtraction. The middle figure shows an irrigation event that is fit with an exponential curve.

Once all major large features are removed the signals are filtered with a 4th order zero phase-shift Butterworth filter with a bandwidth from 9 hours to 26 hours. A representative section for all 4 signals (well-1, well-2, well-3 and the theoretical signal) is also shown. There have been no amplitude or phase adjustments of the signals. It is satisfying that the calculated (theoretical) signal agrees so well with the measured signals. We are now developing methods for comparing the signals with each other, and especially the measured ones with the theoretical signal, to find subtle effects on the signals that may be caused by the surfactant irrigation.





The top left figure shows the 153 day long signal for the East-West measured tilt for well 1 for the period from 1 September 2004 to 31 January 2005. This period includes the time during which the field was irrigated (October 15 to December 4) with a biosurfactant. It is clear from the bottom left figure that in the unreduced data there is considerable power in the tidal peaks near 12 hours (near 2.3 * 10^{-5} Hz) as well as near 24 hours (near $1*10^{-5}$ Hz). This section of the signal is selected (right figure) and vertically shifted (normalized) in preparation for the exponential fit. The vertical signal scale is in micro radians. The green signal, i.e., the measured minus the theoretical signal, is fit. Whenever possible the fit is between zero crossings of the theoretical signal to avoid large tilt components at the end points of the fits.



Only a small part (approximately 5 days) is shown of the 153 day period over which we compare the signals. Over this range the signal from well-2 is generally smaller than those from the other wells or the theoretical signal.

We are exploring various windowing techniques (e.g. Blackman Harris, Hamming, Tukey (tapered cosine) and Gaussian) and widths of sliding windows with which to sample the data. We are developing spectral, amplitude and phase comparison techniques to investigate the differences between the signals in the windows.

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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 will isolate and identify noble gas components in sediments and address how noble gas elemental patterns are acquired and retained, how they are transferred to basin fluids in which they have been measured, and improve 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 hypotheses, 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; (3) many sedimentary rocks (~half) and some oil field gases contain excess Ne in conjunction with excess Xe.

Results: Following our theoretical analysis of diffusive filling and emptying as an initial explanation for the observed absolute and relative abundances in sedimentary rocks, laboratory work is currently underway to isolate and identify noble gas carrier phases and trapping mechanisms. We have found large Xe enrichments in organic silica: diatomites and sponge needles extracted from live sponges (*Calyxnicaeensis*). Step-wise degassing released light noble gases (He, Ne, and Ar) from these samples at low temperatures (T~400°C), whereas Kr and Xe were retained up to temperatures in excess of ~1400°C. We have yet to find excess noble gases in inorganic silica phases, such as diagenetic euhedral quartz and petrified wood. However, we have grown diatoms (*Thalassionira weissflorii*) under controlled conditions to determine if this is a biotic effect or a post-depositional effect. In order to investigate the post-depositional effect, we have acquired sediment samples from sapropels of the Black Sea and the Mediterranean as well as oceanic sediments from the Peru Trench (organic rich) and the Antarctic (Si-rich). We are currently building and testing sample handling protocols. We have also initiated a study of a variety of lab aggregated nanoparticles. We have found that aggregated FeOOH (goethite) is enriched in He and Ne up to 1000 and 40 times that expected for an equal mass of air saturated water, respectively. Step-wise degassing ruled out adsorption or diffusive acquisition of air-derived He and Ne. We will continue to focus on the processes by which these diverse phases acquire noble gases and why they are so well retained upon laboratory heating.

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Grant: DE-FG02-98ER14853

Pore-Scale Simulations of Dissolution Breakthrough in Rough Fractures

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Objectives: To use numerical simulations to gain a better understanding of the role of roughness in controlling the time for dissolution breakthrough in fractured rocks.

Project Description: A fundamental understanding of the role of fractures, and the effects they have on fluid flow, solute transport and mechanical properties, is an essential component of theoretical models of geological systems. In particular, CO_2 sequestration will require predictive models for the effects of fracture on the overall permeability of rock-fluid systems, and more importantly, how this fracture permeability evolves with time. In fractured rocks, naturally occurring variations in aperture can, under the right flow conditions, cause highly localized erosion. There is a feedback mechanism, which tends to amplify initially small variations in permeability leading to the formation of channels through which almost all the fluid flows. We have confirmed that such mechanisms exist independent of order of the erosion kinetics. The goal of this work is to better understand how aperture variation can promote dissolution breakthrough via flow focusing. To accomplish this we are developing pore-scale numerical simulations of chemical erosion in fractured rocks and validating the methods by comparison with laboratory experiments on model fracture systems.

Results: The foundation of our investigation is a very efficient numerical simulation of fluid flow in irregular geometries. Since the evolving surface morphology modifies the fluid flow, it is necessary to run the flow solver many times over during a single calculation of the dissolution or deposition process. The flow solver was developed under our previous DOE grant, and is more than two orders of magnitude faster than conventional lattice-Boltzmann methods.

We have also implemented and tested a stochastic model for the transport of reactants in porous media, and used it to model chemical erosion in a rough fracture. Our microscopic numerical model was 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. This work reported last year in *Geophysical Research Letters* (31:L23606, 2004).

We have followed up on this work by developing a network model of the interaction between channels. We have tested the model by comparing predictions of channel length with numerical simulations. We obtained almost identical exponents for the number of channels of a given length, suggesting that the network model captures the key features of the interaction and competition between growing channels. This work was recently published in *Geophysical Research Letters*. It was also selected as a highlight by the editors of GRL.

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Grant: DE-FG02-02ER15366

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

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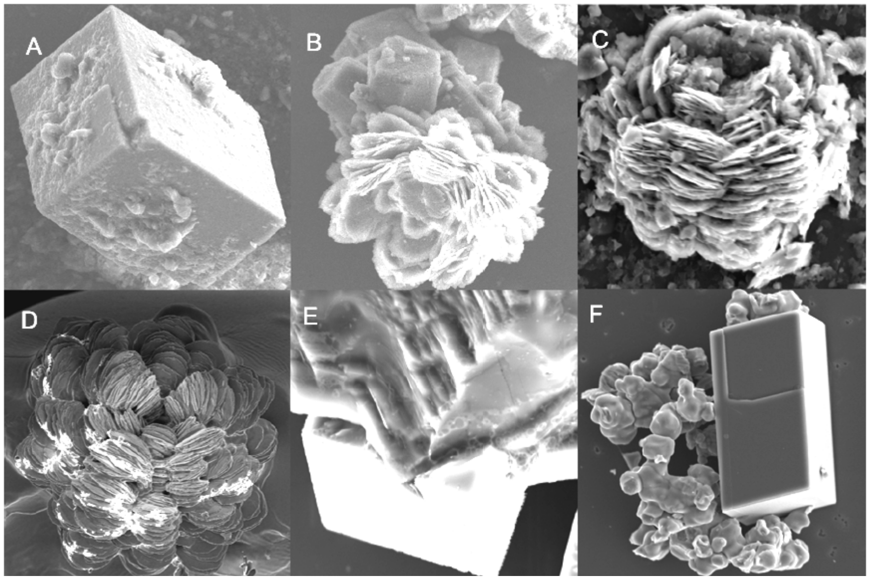
Objectives: To test the hypothesis that mineral surfaces, due to the presence of surface functional groups and associated surface charges, can direct the crystallization of carbonate polymorphs in a mode analogous to the way organic functional groups work

Project Description: The polymorphism of $CaCO_3$ (calcite, aragonite, and vaterite) attracts wide scientific interests due to its importance to a number of fields crossing geosciences and biology. A set of conditions has been reported capable of selectively crystallizing carbonate polymorphs. Of them, the presence of organic additives or templates is the most commonly observed and intensively studied. It is suggested that the templates and additives promote the formation of individual $CaCO_3$ polymorphs through interactions of specific organic functional groups with mineral surfaces or growth units. Inspired by such understanding and the prediction of surface complexation theory in the occurrence of mineral surface functional groups, we conduct carbonate crystallization experiments in the presence of minerals to explore the possibility of mineral surface functional groups to direct $CaCO_3$ polymorphism. We anticipate a systematic variation in the quantity of $CaCO_3$ polymorphs formed in reference to the different point-of-zero-charges (pH_{pzc}) of minerals.

Results: Three types of minerals, phyllosilicate, simple oxide, and framework aluminosilicate, are used in this study. Experimental results demonstrate that minerals indeed have the ability to control carbonate polymorphism (see Figure). For phyllosilicates, it seems that the presence structural charge favors the crystallization of non-calcite polymorphs, particularly vaterite; for simple oxide, it appears that the polymorphic selectivity is related to the minerals' pH_{pzc}, i.e., negatively charged surfaces prefer non-calcite phases, while positively charged ones favor calcite. For framework aluminosilicate feldspar, similar pH_{pzc} effect of is still at work but becomes less prominent, suggesting surface composition may play a more significant role. A comparison of results from pristine and acid-leached orthoclase lands support to this viewpoint.

To a first degree approximation, these results seem to indicate that the occurrence and sign of mineral surface charge are strongly relevant to predicting the selective formation of $CaCO_3$ polymorphs. An exception is observed in SiO_2 where calcite dominates in both cases of crystalline and amorphous SiO_2 despite the negatively charged mineral surfaces. This could be due to the active dissolution of SiO_2 at the high pH (8.5~9) required by $CaCO_3$ crystallization.



Carbonate polymorphs grown in the presence of kaolinite (A), montmorillonite (B), illite (C), orthoclase (D), quartz (E), and hausmannite (F).

GORDON RESEARCH CONFERENCES

West Kingston RI 02892

Grant: DE-FG02-06ER15812

2006 Gordon Research Conference on Rock Deformation

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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 assesses our understanding of the nature and controls on 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 coupling between chemical and mechanical forces in minerals, rocks and the fluids they contain, and the structures that result from these interactions.

Project Description: The 2006 GRC on Rock Deformation was held in Big Sky, Montana, Sept 3-8, 2006, organized by Mark Jessell (Chair) and Greg Hirth (Vice-Chair). The theme of the conference was to explore the relationship among processes of rock deformation (from the nano-scale diffusion of atoms up to the lithospheric-scale) and the spatial and temporal patterns that result. These issues were discussed in terms of their use as predictors of future tectonic activity, indicators of the current state of the Earth, and markers of past behavior. 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 a wide range of tectonic and geophysical settings, for which a broad range of scientific techniques were employed. The temporal periodicity of geological events was discussed from the viewpoint of earthquakes prediction and numerical simulation of complex systems, as well as results from new high-resolution dating techniques that enable us to resolve past behavior in ever greater detail. Particular focus was placed on input from new observations from natural systems, in situ experimental observations, and numerical simulations. In addition we discussed the nature of the coupling between evolving microstructures and rheology. Finally, we held an important discussion on the nature of single crystalline versus polycrystalline behavior in rocks to help define future research trends.

Results: To encompass the elements of this topic, speakers and discussion leaders with backgrounds in rock mechanics, geodynamics, metamorphic petrology, materials science, and mineral physics were invited to the conference. Following GRC guidelines we, organized 9 formal sessions, including 2 poster sessions open to presentations from all attendees. We invited 18 speakers to address topical issues in the relationships between processes and patterns, as well as 7 discussion leaders whose role was to encourage participation by all conference attendees, 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, receiving very strong reviews from the seriously monitored GRC review process. The agenda is outlined below and posted at:
http://www.grc.org/programs.aspx?year=2006&program=rockdef

TEMPORAL PERIODICITY OF GEOLOGICAL PROCESSES Discussion Leader: **Bruce Hobbs** (CSIRO, Perth); **Tom Jordan** (USC), "Predicting Earthquakes"; **David Bercovici** (Yale), "Geodynamic Prediction in a non-linear world".

SEEING IS BELIEVING: RESULTS FROM NEW IN SITU EXPERIMENTS Discussion Leader: **Renée Heilbronner** (University of Basel); **Don Weidner** (SUNY Stonybrook), "In situ measurements under mantle conditions"; **David Prior** (University of Liverpool), "EBSD observation of static and dynamic recrystallization"; **Henning Friis Poulsen** (Risø National Laboratory), "Microstructures in 4D"

COMPLEX RHEOLOGIES Discussion Leader: **Ernie Rutter** (University of Manchester); **Laurent Montesi,** (Woods Hole Oceanographic Institution)"Localization in the Earth"; **Marco Herwegh** (University of Bern), "Flow Laws in Real Materials" ; **Peter Vrojlik** (Exxon), "Mechanical response of sedimentary rocks in the upper crust and implications for subsurface fluid flow"

DATING DEFORMATION Discussion Leader: **Gordon Lister** (Australian National University); **Christian Teyssier** (University of Minnesota), "Precise dating of high-temperature deformation"; **Olivier Vidal** (LGCA Grenoble), "Quantification of continuous pressure-temperature-deformation maps"

GEO-MATERIALS SIMULATION Discussion Leader: **John Wheeler** (University of Liverpool); **Paul Bons** (University of Tübingen), "Dynamic Evolution of Partial Melts"; **Einat Aharonov** (The Weizmann Institute of Science), "Modeling pressure solution and stylolites in porous rocks"; **Andrea Tommasi** (ISTEEM Montpellier), "Multi-scale materials modeling"

NATURAL LABORATORIES Discussion Leader: **Dani Schmid** (PGP, Oslo); **Janos Urai** (RWTH Aachen), "Paleo-rheology of the middle crust"; **Marian Holness** (University of Cambridge), "Petrographic evidence for the microstructural evolution of solidifying magmas"; **Steve Hickman** (USGS), "Anatomy of a Fault Zone"

SINGLE CRYSTAL VS. AGGREGATE BEHAVIOUR Discussion Leader: **Mervyn Paterson** (ANU); **Jean-Pierre Gratier** (LGIT Grenoble), "Single vs poly-crystal mineral dissolution"; **Brian Evans** (MIT), "From Mineral Physics to Rock Mechanics"

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Grant: DE-FG02-03ER15384

Growth and Dissolution of Iron and Manganese Oxide Films

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Objectives: The first objective of the supported work 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: Over the past year, we have characterized the surface charge heterogeneities that Mn-oxide (MnO_x) nanostructures induce on the parent substrate. We grew the nanostructure films on rhodochrosite ($MnCO_3$) substrates in the presence of dissolved oxygen at pH 6.3. The nanostructures were identified by their morphology and height using atomic force microscopy. Their electrostatic properties, including surface potential, ion mobility, and interfacial adhesive forces, were characterized using Kelvin probe force microscopy, scanning polarization force microscopy, and force-volume microscopy, respectively. Surface potential and ion mobility were studied under increasing relative humidity to examine the effect of surface dissolution. The interfacial adhesive forces were measured in aqueous solution in equilibrium with $MnCO_3$. Results obtained with MnO_x films were then compared with the same properties of the parent $MnCO_3$ surface.

Results: The observations, which are highlighted in Figure 1, show that MnO_x nanostructures induce significant electrostatic heterogeneities on the parent substrate. Kelvin probe force microscopy is sensitive to differences in surface potential but filters out differences in height. The MnO_x nanostructures of 1.3(±0.7) nm thickness have a surface potential that is 271(±14) mV higher than that of $MnCO_3$. The excess surface potential decreases with increasing RH due to the screening effect of $MnCO_3$ ions dissolved on substrate surface. The presence of these dissolved ions and their mobility were probed by polarization force microscopy. The results show that the MnO_x nanostructures reduce the lateral movement of surface ions by acting act as transport barriers. Force-volume microscopy further shows that MnO_x nanostructures exert repulsion forces of approximately 20 pN (referenced to the AFM tip), indicative of the presence of net surface charge and a resulting electrical double layer. When the MnO_x nanostructures contact the AFM tip, the tip adheres to the surface and a pulling force as much as 400 pN is required to overcome the adhesion.

These results demonstrate that the nanostructures greatly alter the surface physics and chemistry, even though they contain a nearly negligible amount of mass compared to the parent carbonate surface. The electrostatic heterogeneities arising from these changes influence the interactions of Mn oxide surface coatings with charged contaminants and microorganisms in the environment.

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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 imaging, portions of the full 2D inverse scattering series have been identified as addressing multi-dimensional imaging objectives that have a 1D analog, and isolated. This subset of the full ISS capability has been successfully applied to synthetic data from salt model provided by Exxon-Mobil. This algorithm has further been extended to be applicable angle-by-angle, such that common image gathers are flattened without a determination of subsurface velocity, nor with any amplitude damage in the resulting common-image gather. The amplitude damage in conventional common-image gather methods is a major drawback to the use of amplitude analysis to identify potential hydrocarbon targets.

In the use of multiples to extract medium information, the amplitude discrepancy between an actual first-order internal multiple and the output of the inverse scattering series internal multiple attenuation algorithm, has been shown to be a direct expression of plane wave amplitude loss down to a particular reflector. We have now suggested that this be exploited to address the problem of estimating and removing overburden effects for amplitude analysis at depth. We have presented a simple, early stage study and example of such information extraction applied to a problem of an imaging overburden dominated by the effects of wave field attenuation.

In forward modeling, the theory of Pade approximants has been applied in an extension of forward scattering expressions, and it has been shown and reported that their approximation of the partial sums of the forward series is convergent for any contrast and any incidence angle. Further, we have developed fully multi-dimensional approximations of reflected primaries and transmitted direct waves based on non-linear scattering theory, that strongly emphasize wave-theoretic completeness, math-physics interpretability, and its support of medium heterogeneity. The latter provides the strengths of ray methods for isolated event modeling and the wave theory completeness of methods (e.g., finite difference) that do not allow modeling of specific isolated events.

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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 thus far have already made impacts in the fields of environmental microbiology and biogeochemistry. Among the key findings from the first year are 1) Successful large-scale production of biomass for protein isolation; 2) Purification of several c-type cytochromes for biochemical study; 3) Partial characterization of these proteins using spectrophotometric techniques; 4) A Proof-of-principle regarding protein conformational change and redox activity towards metal oxides using a small mass cytochrome c from *Acidiphilium cryptum*; 5) Training of an undergraduate research assistant; 6) Publications and several meeting presentations.

Results: Progress so far includes:

1) Development of large-scale (10 L) cultivation methods for several representative Fe(III)-reducing bacteria. These include *Acidiphilium cryptum*, *Geobacter sulfurreducens* (wild-type), and 2 mutant strains of *G. sulfurreducens*. Cell yields are on the order of 20g/L biomass, and large quantities have been produced for protein purtification.
2) Purification of several mono- and polyheme cytochromes c from *A. cryptum* and *G. sulfurreducens*. These include the 10.1 kDa monoheme periplasmic cytochrome c and 42kDa monoheme outer membrane cytochrome c from *A. cryptum*, and OmcB and OmcS from *G. sulfurreducens*.
3) Spectrophotometric analyses of the redox properties of purified cytochromes. We have demonstrated interesting redox properties, in that for *A. cryptum*, electron transfer to a soluble Fe(III) chelate is preferred at low pH (3.0), and reactions do not proceed at pH 7.0. This is consistent with the acidic environments (periplasm pH 6.0, outside pH 2-3) that the proteins occupy.
4) Antibody development for c-type cytochromes. We have developed polyclonal antidera for the periplasmic cytochrome c from *A. cryptum*. We are current purifying the antisera and are performing specificity experiments.
5) Training of undergraduate researchers (Andy Fielding, Sean Clark), and support of a Research Associate (Mike Swenson).

6) Development of new collaborations with Oak Ridge National Laboratory on the use of Neutron Reflectivity in the determination of protein structure in mono- and polyheme cytochromes.
7) Arrangement of a Sabbatical Leave for the PI to travel to University of Wyoming for conducting experiments and working directly with collaborators.

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Grant: DE-FG02-00ER15028

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

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

Project Description: Molecular scale knowledge of the structure and dynamics of aqueous fluids, how these fluids are affected by mineral surfaces and molecular-scale (nano-) confinement, and how water molecules and dissolved species interact with surfaces is essential to understanding the fundamental chemistry of a wide range of geochemical processes relevant to energy geoscience. These processes include sorption; mineral dissolution, precipitation and reactivity; 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 2006, we significantly advanced new, highly promising research directions leading to the modeling of proton exchange reactions in aqueous systems. These reactions are critical in controlling reactivity of many species in solution and at mineral-water interfaces. We used computational *ab initio* molecular dynamics (AIMD) and metadynamics (MTD) techniques to determine the free energy landscape and reaction paths of proton exchange reactions in the carbonate system: H_2CO_3 - HCO_3^- - CO_3^{2-} - CO_2 - H_2O. Understanding the molecular scale reactivity in this system is central to the solution chemistry and mineral-fluid reactions relevant to carbon sequestration, and this set of approaches shows great promise in addressing these issues. Development of force fields that effectively model proton exchange is important to allow the use of this approach for large scale simulations for water-mineral systems using molecular dynamics (MD) methods. We are using the recent empirical valence bond (EVB) approach to develop quantitatively accurate, force-field-based molecular models of protonated mineral surfaces that can overcome the system size and simulation time limitations of the more rigorous *ab initio* approaches. In 2006 we initiated this work by undertaking EVB MD simulations of proton transfer in the simplest system that exhibits water-hydroxide proton transfer: a single OH^- ion in liquid water. The results provide important new insight into the structure and dynamics of the solvated OH^- ion, the solvating water molecules, and the pathway of H-exchange among these species.

Other computational work has looked at the 10Å phase, a dense hydrous magnesium silicate with a talc-like structure, where the most recent NMR spectroscopic data indicate that the tetrahedral silicate sheets can contain about 10% of Q^2-type Si tetrahedra that are terminated by silanol groups that are hydrogen bonded to interlayer H_2O. These defect (Q^2) Si sites are important models for the broken edges of clays and other layer silicates and are especially important here for developing the EVB approach to simulating proton exchange reactions involving the critical Si-OH sites.

Our MD simulations of metal binding to natural organic matter (NOM) were significantly extended to include a broader range of alkali and alkaline earth cations and are demonstrating the importance of cation binding in controlling the structure of NOM molecules. The simulations suggest that Ca^{2+} has the strongest association with NOM, forms inner-sphere complexes with NOM carboxylate groups, and is likely to play a significant role in NOM binding in natural and technological situations. In contrast, Na^+ forms only very weak outer-sphere complexes with NOM, and Mg^{2+} interacts little with it due to its strongly held hydration shell.

Experimentally, we initiated significant new NMR studies examining the structural environments and dynamics of $^{39}K^+$ on muscovite surfaces and $^{23}Na^+$ and $^{35}Cl^-$ on quartz surfaces. In addition, we began development of ^{75}As NMR as an effective tool to study the chemical behavior of this environmentally important element. The work on muscovite and quartz is designed to test predictions from our MD studies of these surfaces. The ^{75}As work is based on recent technical developments in experimental NMR methods that allow for investigation of nuclides with very large quadrupole moments. We expect our work to lead to hypotheses concerning the behavior of As that can be tested by computational modeling

2006 also saw the final publication of research on the effects of mineral substrate structure and composition on near-surface water structure, dynamics and energetics; the structure and energetics of layered double hydroxides containing organic- and bio-molecules; and the complexation of cations and anions with natural organic matter.

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Grant: DE-FG02-02ER15317

Field-Constrained Quantitative Model of the Origin of Microbial and Geochemical Zoning in a Confined Fresh-Water Aquifer

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Objective: The goal of this project is to demonstrate the role of the subsurface microbial community in controlling the chemistry of groundwater, especially the content of metals and semi-metals. We are (1) extending our sampling of the Mahomet to a regional scale, to consider how microbial life affects the concentrations of a suite of heavy metals and semi-metals, (2) performing downhole experiments to directly observe microbial activity and measure its rate, and (3) using numerical modeling techniques to interpret those results quantitatively, and to extract parameters for kinetic models of microbial metabolism.

Project Description: The regional Mahomet Aquifer System is a widespread Pleistocene deposit that supplies drinking water to much of central Illinois. The aquifer system is composed of glacial sediments that infill a bedrock river valley that extends from West Virginia to the Illinois River Valley in western Illinois. Our study combines field, lab and numerical modeling tasks to obtain an integrative synthesis of aquifer biogeochemistry. This has led us to focus on relationships between microbial community composition, microbial activity and water geochemistry.

For field and lab studies we have developed a close working relationship with scientists at the Illinois State Water Survey, who allowed us unlimited access to dozens of their monitoring wells across the Mahomet Aquifer. We focused our study on 21 wells, located mainly in the eastern part of the aquifer. From these wells we obtained water samples for chemical and microbiological analysis. We use modern molecular microbiological tools for these analyses and this represents the first time such an extensive study has been done on a large regional aquifer. To investigate the attached microbial community we have developed an in situ microbial sampler using natural Mahomet sediments. Unattached microbes are obtained by filtering the groundwater. This allows us to evaluate the relative importance of attached verses unattached bacteria in the aquifer setting and is of fundamental importance to reactive transport modeling.

Our modeling focuses on developing the first theoretical analysis of the relationship between thermodynamic drive and the rate of microbial metabolism, and demonstrating the usefulness of these results in understanding natural systems. We are also using reactive transport modeling combined with the theoretical results just mentioned to develop a dynamic understanding of the origin of zoned microbial communities.

Results: In the last year we have developed a new DNA extraction protocol that is considerably more efficient than the method most people use, allowing us to extract high quality genomic DNA from only two liters of water.

We performed the first comprehensive comparison of the attached and planktonic microbial communities in an aquifer. We analyzed the bacterial communities of all samples using the PCR-based method, terminal restriction fragment length polymorphism (T-RFLP) analysis, which yields a fingerprint diagnostic of the community composition. A statistical comparison of these community profiles show systematic similarities and differences between attached and unattached bacterial communities. Both groups share populations, but some communities are exclusively planktonic or attached to aquifer sediments. Our data suggest that there are benefits to sampling both types of communites when investigating aquifer biogeochemistry.

To test if any geochemical parameter measured was associated with community changes based on TRFLP analysis, we looked for correlations between the geochemical data and the similarity between microbial communities in different wells. We observed an apparent relationship between the community profiles and the sulfate concentration. Our statistical analysis showed that microbial communities in areas with high (>100 mg/L) sulfate are distinctly different from those with low (0.9-20 mg/L) or no detectable sulfate. This result may indicate a switch from communities dominated by active sulfate reduction to a community where methanogenesis is most important.

We have made significant progress developing a quantitative understanding of the factors that influence the distribution of microbial populations in the subsurface, and the origin of microbial zoning in pristine aquifers. The numerical models show that current theories of the origin of zoning based on thermodynamics or simple kinetics do not explain the mechanism by which some microbial populations exclude others from a zone. Instead, populations appear capable of excluding others by maintained conditions at which growth is insufficient to replace cell decay and predation. The models also show that communities long assumed to be dominated by one 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.

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Grant: DE-FG0203ER15381

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

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

Project Description: The principle 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, dissolution/precipitation and nucleation/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.

Recent Progress: We have continued to explore the adsorption-reaction properties of various mineral surfaces in collaboration with Paul Fenter (ANL) and others. In a collaborative experiment with Prof. Steve Higgins (Chemistry Dept., Wright State University), the surface structure of dolomite and the epitaxial overgrowth of Mg-calcite on dolomite was investigated using synchrotron X-ray scattering. Interpretations based on AFM observations were confirmed. A paper describing these results was published in GCA (Fenter et al., 2006). Also, in our ongoing collaboration with Prof. Kathryn Nagy (University of Illinois at Chicago), we have made significant progress towards understanding the adsorption of mono- and divalent ions and natural organic matter on muscovite basal planes. Two manuscripts describing these results were published this year (Schelegel et al., 2006; Park et al., 2006) and others are in preparation. A progress report was presented by UIC graduate student Sang Soo Lee at the International Mineralogical Association Meeting in Kobe, Japan, during July 2006 (Lee et al., 2006). The paper by Park et al. (2006) used the new method of resonant anomalous x-ray reflectivity to help resolve fundamental questions pertaining to the contrasting behavior of monovalent and divalent ions at the mica surface; this technique has made a significant breakthrough in characterization of the hydration and distribution of ions at mineral-water-interfaces. Experiments are in progress to examine the mechanisms of ion exchange and mineral replacement at alkali feldspar-water interfaces at elevated temperatures.

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Grant: DE-FG02-02ER15364

Nanoscale Reactivity of Clays, Clay Analogues (Micas), and Clay Minerals

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Objectives: Our objectives are to determine the nanoscale/molecular scale structure of the interface between mica and aqueous solutions containing various sorbates and the systematics controlling the incorporation of inorganic and organic chemical components during aging of nanoparticles of iron-oxides and aluminosilicate clays.

Project Description: The basal surface of phyllosilicates is a primary sorbent of environmental contaminants, natural organic matter, and nutrients. Micas are also superb atomically-flat substrates used in materials science and surface physics applications. We are applying X-ray scattering techniques using high brilliance synchrotron radiation coupled with atomic force microscopy (AFM) to investigate molecular-scale details of mica's interface structure in solutions containing common and toxic cations, anions, and natural organic molecules. Nanoparticles are ubiquitous in the environment and have a high capacity for sorbing contaminants through the combined effects of their high surface areas and pH-dependent surface charge. Aging of nanoparticles from metastable to stable phases can be inhibited by sorption of nonstructural components, but exact mechanisms are unknown. We are precipitating Fe-oxides and phyllosilicate clays in the presence of selected anions, and organic molecules, and quantifying the effects of surface area, morphology, and phase proportions on the aging process.

Results: X-ray reflectivity and resonant anomalous X-ray reflectivity were used to determine the mica-solution interface structure in fulvic acid solutions as a function of pH and time, and in the presence of Sr, Hg, Pb, Cu, and Zn at selected pHs. Sorption of fulvic acid shows systematic changes that indicate a decrease in the amount of uptake as pH increases from 2 to 12, and an increase in the amount of uptake from 2 to 500 hours. Changes in the internal structure of the fulvic acid film also occur. Positions of cations in the films are determined with sub-Ångström-scale resolution and are correlated with pH, binding strength to functional groups on the fulvic acid, competition with the fulvic acid for mica sorption sites, and order of addition of cations to the fulvic acid (before or after addition of the mica).

Perrhenate uptake in Fe-oxide minerals aged at 90°C was quantified as a function of perrhenate concentration, pH (3 to 10), and presence of dissolved chromate. EXAFS spectroscopic measurements were made to determine the perrhenate binding environment. Uptake of natural organic matter was quantified in precipitated metastable aluminosilicate clays as a function of solution saturation state and composition.

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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 the geochemical conditions and mechanisms that contribute to changes in the D/H stable isotope ratio 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. The chemical interaction between hydrogen-limited but carbon-rich kerogen and abundant inorganic hydrogen in formation water may in fact extend the generation of hydrocarbon fluids beyond the limitations of pre-existing organic hydrogen in kerogen. Controlled isotopic equilibration of isotopically labile organic hydrogen with isotopically distinct water vapor hydrogen is used to quantify the amount of exchangeable organic hydrogen. Chemically bonded hydrogen in our samples is thermally converted to elemental hydrogen, followed by mass-spectrometric determination of D/H ratios.

Results: D/H stable isotope ratios of isotopically non-exchangeable hydrogen were measured in type-II kerogens from two suites of Late Devonian to Early Mississippian black shales from the New Albany Shale and the Exshaw Formation (see Figure 1 below). D/H ratios increase with maturation and suggest former isotopic exchange of organic hydrogen with water-derived deuterium and/or preferential loss of ^{1}H-enriched chemical moieties from kerogen during maturation. Formation water in the New Albany Shale is relatively enriched in deuterium and exchanged with some of the hydrogen in kerogen, leading to increased D/H ratios of kerogen. The resulting changes in D/H ratios are obscuring the original hydrogen isotopic paleoenvironmental signal in kerogen, albeit in a systematic fashion that still can be traced to the original organic matter (*Organic Geochemistry*, 2006, vol. 37(3), pp. 342-353; DOI: http://dx.doi.org/10.1016/j.orggeochem.2005.10.006).

We successfully explored the utility of hydrogen stable isotopes for exploration targeting Indiana's coalbed gases. Some of our novel geochemical gas sampling and analytical methods were published in 2006 in *Organic Geochemistry*, vol. 37: 152-164; DOI: http://dx.doi.org/10.1016/j.orggeochem.2005.10.002).

Our invited review article about "Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation" for the *Annual Review of Earth and Planetary Sciences* was published in 2006, vol. 34: 501-533 (DOI: http://dx.doi.org/10.1146/annurev.earth.34.031405.125011).

We completed an accessory study where we related D/H ratios in modern beetle fauna to D/H of modern meteoric water (published in 2006 in *Quaternary Science Reviews*, vol. 25: 1850-1864; DOI:

http://dx.doi.org/10.1016/j.quascirev.2006.01.021). Our results pave the way to use fossil beetle remains for D/H isotopic paleoclimatic reconstructions.

Finally, we finished the labor-intensive preparation of *ca.* 30 gram aliquots of high-quality, low-ash kerogen type-II and type-III samples for our ongoing work to probe the intra-molecular D/H isotopic composition. A new PhD student will join our group in August 2007 to adopt aspects of our project for her PhD research.

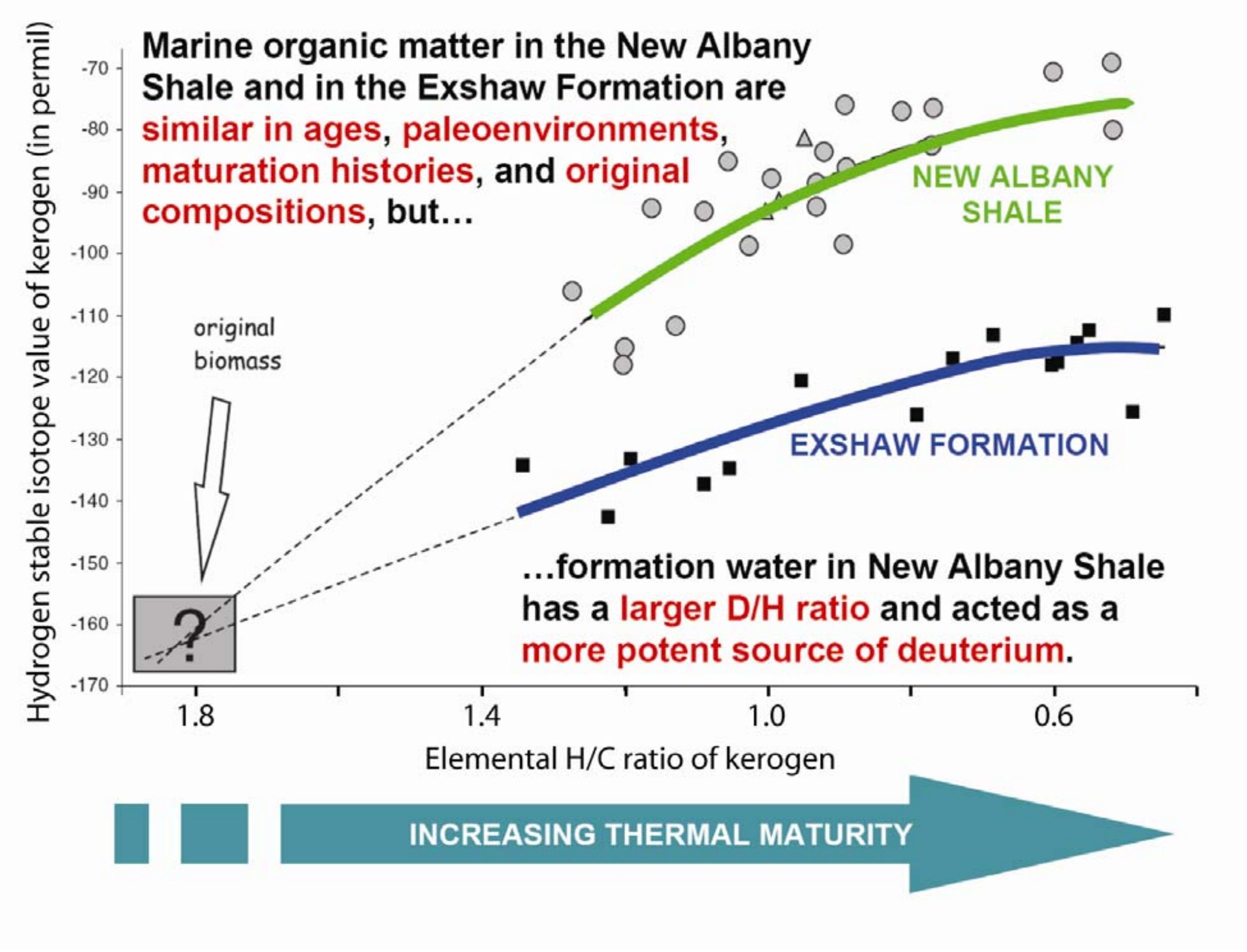

Figure 1: D/H stable isotope ratios of non-exchangeable hydrogen in type-II kerogens from two suites of black shales are expressed as δD values in permil. D/H ratios increase with maturation (expressed in terms of decreasing elemental H/C ratios), especially in the New Albany Shale where formation water is relatively enriched in deuterium (adapted from Lis et al., *Organic Geochemistry*, 2006, vol. 37(3), 342-353; DOI: http://dx.doi.org/10.1016/j.orggeochem.2005.10.006).

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Grant: DE-FG02-96ER14619

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 deep fluid flow, submarine petroleum migration and diagenetic effects within deforming faults in a transpressional setting that is seismically active. Most of the work deals with faulted basins of southern California, as outlined in the 2005 proposal, and provides important data and modeling relevant to carbon sequestration.

Project Description: We have targeted active faults and young petroleum fields in southern California for study. These data provide constraints for finite element models that are being developed to predict fluid pressures, flow patterns, rates of deformation, temperatures, and diagenetic patterns associated with large fault systems. We are also seeking to identify isotopic and trace element geochemical signatures that result from rapid CO_2 degassing. Our samples include calcites from a variety of settings including oil field well tubing scales, fault zone precipitates, and speleothems in man-made tunnels.

Results: Our most recent studies have been along the Newport-Inglewood (N-I) fault in the Los Angeles Basin including the Inglewood and Long Beach oil fields. Graduate student Mike Ryan is working on core samples, sidewall samples, electric (including image) well logs from 40 newly drilled deep wells associated with the N-I fault. These wells have penetrated an igneous body, previously unknown anywhere in the LA basin (Ryan et al., 2007). The igneous rock appears to have intruded along the termination of the N-I fault and caused significant diagenetic effects on the reservoir sands. We are also involved in the planning stages of an oil company sponsored well designed to core the N-I fault zone near the southern end. Graduate student Grace Giles has completed a Master's degree on the geochemistry of carbonate scales in well tubing. Well tubing scales and speleothems show co-varying carbon-oxygen isotopic values with slopes up to + 5. Scales are enriched in heavy carbon up to 28 per mil, due to CO_2 degassing. Scales show increasing departure from equilibrium down hole, presumably due to increasing precipitation rates at the deeper levels. Some scales have up to 16 wt. % Mg substitution and are out of isotopic equilibrium with formation waters, which is attributed to rapid calcite crystallization. We are checking this finding in other fields where rapid growth has occurred. Growth rate-related Mg-substitution in calcite may have important implications for interpreting Mg/Ca ratios in calcite used for temperature interpretations in paleoclimate studies. Ms Giles has recently taken a job with Exxon-Mobil.

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Grant: DE-FG02-89ER0614074

Reactions and Transport of Toxic Metals in Rock-Forming Silicates at 25°C

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Objectives: For FY06, specific objectives center on development of focused ion-beam milling (FIB) techniques, monochromated electron energy-loss spectroscopy (EELS) methods, and applications to U contaminated soils.

Project Description: The project centers on the crystal chemistry of mineral hosts and their interactions with toxic metal-bearing aqueous fluids. 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 first year of the project cycle, we have successfully developed focused ion-beam milling (FIB) for the sensitive uranyl-phosphate minerals of the autunite group. This work is a critical step in fully utilizing the TEM's spatial resolution to establish the uranium budget of contaminated sites. Our work includes museum samples as well as natural samples from contaminated soils at Hanford and Oak Ridge. Our protocol allows production of electron transparent, crystalline samples of the phosphates with nanometer scale precision. Specifically, we have established that we can maintain the basal spacing of metatorbernite despite ion- and electron-bombardment during milling and imaging. Meta-autunite is more beam-sensitive and shows some reduction in basal spacing in the TEM. This reduction is, however, reproducible and less than that shown by earlier workers. Aspects of the work were presented at the Frontiers in Mineral Sciences meeting in Cambridge, UK, in June.

We have also begun TEM based electron energy-loss spectroscopy (EELS) using the uranium $O_{4,5}$, $N_{4,5}$, $N_{6,7}$, and $M_{4,5}$ and oxygen K absorption edges to probe details of bonding and valence states or uranium. This work includes EELS with the monochromated instruments at Lawrence Livermore National Laboratory. To date, we have spectra on uranyl phosphates and UO_2 with ~0.4 eV resolution. We anticipate ~0.1 eV resolution with the improved instrumentation that will be available to us this fall.

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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 the chemical evolution of shallow and deep groundwaters and the fate of contaminants in groundwaters.

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. The model is being developed to integrate all the available experimental information on adsorption with spectroscopic results for the nature of surface species. By so doing, it will facilitate the comparison of experimental data from different investigators and enable interpolation and extrapolation to conditions not yet studied experimentally. This provides a basis for analyzing the role of surface complexation in natural and contaminated environments. It will help lead to predictive models of the behavior of nuclear waste in the subsurface, the migration of subsurface carbon dioxide, and the behavior of nanoparticles interacting with contaminants.

Results: Our predictive model for proton surface charge and electrolyte ion adsorption on oxides was extended with the publication of results for alkaline earths. These results add an internally consistent expansion to our previous work for the alkalis on mineral surfaces. In this way, the all major cations of natural waters are now covered. Our work has also focused on adding sulfate, carbonate and other anionic species critical to metal speciation in natural waters. In this effort, a new dipole-extension of the current adsorption model was published. This new development enables us to bridge the previously existing gap between models and experimental spectroscopic results. It enables prediction of oxyanion surface speciation as a function of environmental variables. An application of this new approach for As(III) has been published. Additional applications to sulfate, selenate, and As(V) are underway. These results move us much closer to the goal of simulating the interactions of the more complex natural waters and the migration of toxic species.

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Grant: DE-FG02-06ER15831

Development of New Biomarkers for Surficial Earth Processes

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Objectives: I.) An examination of isolated DNA as both an isotopic substrate and a source of genetic information, and **II.)** an emphasis on fungal microorganisms, with isotopic characterization of fractionation due to different carbon metabolic pathways.

Extended Description (this is the first year of this project):
I.) The first project will include an examination of isolated DNA as both an isotopic substrate, and a source of genetic information. I have included DNA ligation, plasmid introduction, and cloning techniques to better address resolve the phylogeny of soil microorganisms, in order to test my assumptions about community make-up. I am also prepared to engineer specific PCR primers to use for this approach, using a trial and error approach in order to focus primers on particular regions of DNA.
II.) The second project places emphasis on fungal microorganisms, and will isotopically characterize fractionation due to different carbon metabolic pathways (also as found within lipid biomarkers), while simultaneously monitoring the biochemistry of the substrate. Plans to pursue the isolation and analysis of PFLA 18:2ω6,9 are included, and will follow the method of Klamer and Baath (2004, Estimation of conversion factors for fungal biomass determination in compost using ergosterol and PLFA 18:2ω6,9: Soil Biology and Biochemistry, v. 36, p. 57-65); I will complement these analyses with ^{14}C studies on organic matter in particularly organic rich soils in order to confirm preservation. Finally, the lipid content (relative to other components of the cells) will be assessed for each species studied. Finally, in addition to oxygen fugacity and ethanol concentration, CO_2 concentration as well as $\delta^{13}C$ value will be monitored in order to quantify the variability of each microbial growth environment.

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Grant: DE-FG02-94ER14467

Theoretical Studies on Heavy Metal Species in Solution

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Objectives: This study utilizes the techniques of computational quantum chemistry to determine the structures, energetics and properties of various metal species in both gas-phase and aqueous solution, as components of mineral glasses, or absorbed on mineral surfaces. One focus in the past year has been on calculating accurate free energies in aqueous solution for reactions of borates, carbonates and As oxides and sulfides. We have also performed calculations of isotopic fractionation equilibrium constants for various borates, starting with the $B(OH)_3$ - $B(OH)_4^-$ pair used as a proxy for determination of oceanic paleo-pH values.. We have continued our collaboration with Prof. Robert Byrne (U. of South Florida) to experimentally measure this fractionation constant using the difference of pKa's of pure ^{11}B and ^{10}B forms of $B(OH)_3$ for several different temperatures, concentrations and solution compositions

Project Description: To understand the mechanisms of dissolution and formation of minerals one must understand the structures and properties of precursor species in aqueous solution. We are developing quantum methodologies which will allow us to accurately calculate the energetics for the formation of both light element and heavy metal complexes in solution and evaluate species properties, such as IR/Raman spectra and UV-vis spectra which will help in their identification. On several of the topics under study we are collaborating with Prof. George Helz (UMCP), who either made the initial experimental observations suggesting the theoretical study or is engaged in experimental work in response to our calculations. Much of the work involves the speciation of metalloids such as As and Sb or metals such as Mo and Re in both oxic and sulfidic solutions.

Results: We have established experimentally that the 11,10 fractionation equilibrium constant for the $B(OH)_3$, $B(OH)_4^-$ pair has a value of about 1.028 – 1.030, regardless of T, total B concentration or solution conditions, significantly different than the long used experimental value of 1.019. We have used quantum methods to evaluate stabilities, spectra and isotopic fractionations for the species formed when boric acid and borates are adsorbed on humic acids. State of the art quantum mechanical methods have also been applied to study the properties of carbonic acid, both as monomer and oligomers and their structure, energetics and vibrational and NMR spectra in both gas-phase and solution. We conclusively demonstrated that the species existing in solid or film-like H_2CO_3 cannot be the monomer but must be a dimer or higher oligomer. We have initiated a collaboration with Dr. George Cody at the Geophysical Lab to measure ^{11}B NMR spectra of both synthetic and natural corals and forminifera to establish the environments of B in these materials. Our initial results indicate that three- and four-coordinate B are found in roughly equal amounts in all the samples, in substantial disagreement with previous NMR studies.

We are in the process of assigning Raman spectra obtained by reacting aqueous $As(OH)_3$ with aqueous bisulfide by Wood et al. To interpret these spectra we have carried out an extensive series of calculations. By employing state of the art quantum chemical techniques to determine gas-phase harmonic and anharmonic frequencies and solution phase corrections we can accurately match features in the experimental spectrum. For the free solute species $AsS(SH)_2^-$ we have carried out a whole series of calculations, evaluating harmonic and anharmonic vibrational frequencies at a number of different quantum mechanical levels. Taking the highest level harmonic results, obtained from a CCSD calculation, and adding anharmonic and PCM corrections at the B3LYP level (as shown in Table 1) we obtain a frequency for the intense As=S stretch within 15 cm^{-1} of experiment.

Table 1. Calculated and experimental As-S and As-SH vibrational frequencies (cm^{-1}) for $AsS(SH)_2^{-1}$ (with relative Raman intensities given in parentheses for CBSB7 B3LYP harmonic frequencies)

model	method	ν
free	CBSB7 B3LYP Harmonic	448 270 256 (20.9 24.4 19.1)
free	CBSB7 B3LYP anharmonic	448 258 228
free	6-311+G(2d,p) CCSD	452 303 299
in PCM	CBSB7 B3LYP harmonic	430 284 261
in PCM	CBSB7 B3LYP anharmonic	426 281 250
in $(H_2O)_{22}$	CBSB7 B3LYP extrapolated	av. As=S 425
(3) + (5) – (1)		430 314 293
exp.(aq)		415 330

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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: First, we 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). Measurements of axial and volumetric strain, strength, and permeability were made using isostatic loading ($\sigma_1=\sigma_3=P_c>P_f$) and conventional triaxial loading ($\sigma_1>\sigma_3=P_c>P_f$). Second, using the oscillating pore pressure method, we determined the uncertainty of permeability and storativity measurements, assessed transient effects, and derived approximate solutions for cases of very small or large sample storage. In typical conditions, storativity is poorly determined, but permeability can be measured accurately. Third, we 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. Yield stresses map a failure envelope similar to that characteristic of intact silicate rocks, but here, the yield curve is temperature dependent. Fourth, we modeled the behavior of a single pair of asperities pressed against each other in presence of fluid, concentrating on the kinetics of intergranular contact processes. This analysis incorporates an initial elastic stress distribution at the contact. Finally, we constructed a flow-wave propagation model for a single, elastically deforming pipe.

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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: As of September, 2006, our progress was in two areas: a field study of “steephead channels” near Bristol, Florida, and construction of a new laboratory apparatus that provides insight into the microscopic basis of erosive dynamics.

Our investigation of the Florida channels confirmed that the erosion of this channel network is dominantly driven by subsurface seepage flows. Measurements included sediment granulometry throughout the network; estimates of the apparent erosion rate; attempts to map the height of the water table using ground-penetrating radar; and GPS-aided mapping of the precise location of emerging springs. The latter two measurements provided preliminary data indicating that the unusual planform geometry of the channel network can be quantitatively related to the water-table geometry.

The initiation of erosion in systems such as the Florida channels is usually associated with the critical Shields number, i.e., the dimensionless shear stress that is just sufficient to mobilize grains. To study this condition in the laboratory, we have constructed a new apparatus that allows visualization of the grain-scale motions that occur near the onset of erosion. The apparatus allows us to not only visualize surficial motions, but also motions 10–20 grains deep within the bed.

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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, composition, and location 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 *synthetic* and *natural* grain-cement systems using novel approaches that provide insight into grain-scale mechanics. We will:

1) Develop methods for fabrication of synthetic assemblages of soda-lime silicate beads and both sodium silicate and calcium carbonate cements, and approaches to isolating similar elements from natural systems.

2) Design apparatus to test mechanical properties of synthetic grain-cement assemblages. Use nanoindentation to probe properties such as elastic modulus, hardness, and plasticity of grains and cements in both natural and synthetic systems.

3) Conduct microstructural analysis to relate physical elements of synthetic and natural systems to their structural response to stress in both elastic and inelastic deformation.

4) Develop quantitative relationships describing the stress-strain response of cemented granular systems and incorporation of microscale material response into a DEM.

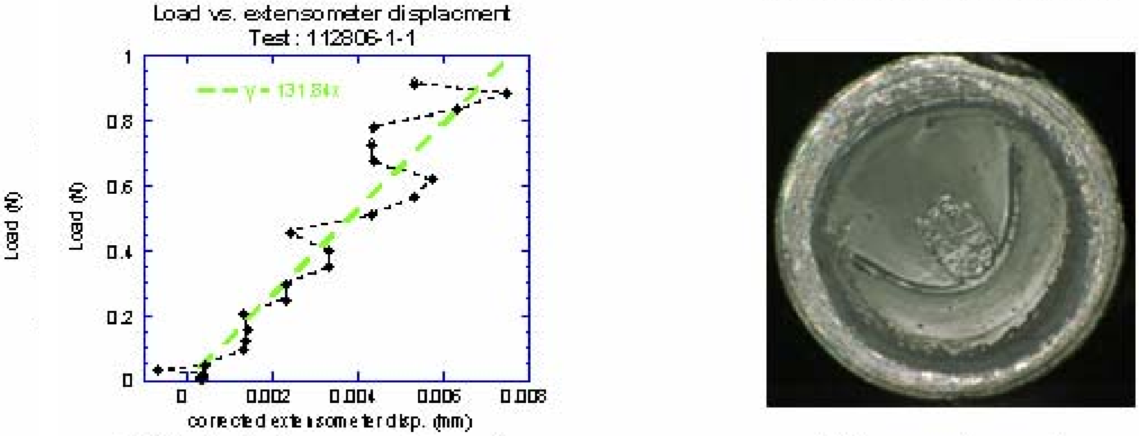
Results: We cemented pairs of 1.0 and 1.5 mm diameter soda lime beads together at one contact point with various volumes of three sodium silicate cements (Figure 1a). The formation of cracks and air bubbles as the sodium silicate cements cured was a major challenge, overcome by sonicating assemblages during initial curing.
Fixturing for shear and tensile testing of the bead assemblies was designed, fabricated and tested (Figure 1). Although bubbles and cracks within the cement certainly influenced the first tests, the experiments demonstrate that tensile and shear stiffness and strength of the bonded assemblies can be measured using

both test configurations. *These initial tests show that, even with defects, the cement bonds are surprisingly strong*.

Using instrumented indentation, we measured variations in hardness, modulus, and fracture toughness within quartz grains in a natural sandstone. We had some success correlating inter- and intragranular variations in measured indentation response with crystallographic orientation and internal microstructure. However, we determined that we cannot easily test grain-cement boundaries. Relevant physical parameters therefore will be determined on selected sandstones and related to grain contact strength through measurement of P and S wave velocities. Ultrasonic velocities, and related elastic moduli, vary with grain contact strength.

(a) synthetic bonded sample

(b) tensile test experiment



(c) load-displacement trace from tensile test experiment

(d) fractured sample

Figure 1 – Images and plots associated with synthetic two particle grain-cement sample preparation and testing.

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Grant: DE-FG02-01ER15127

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

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Objectives: The project is the support of short course 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.

Project Description: 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 were two short courses during FY2006, each with a companion Reviews volume:

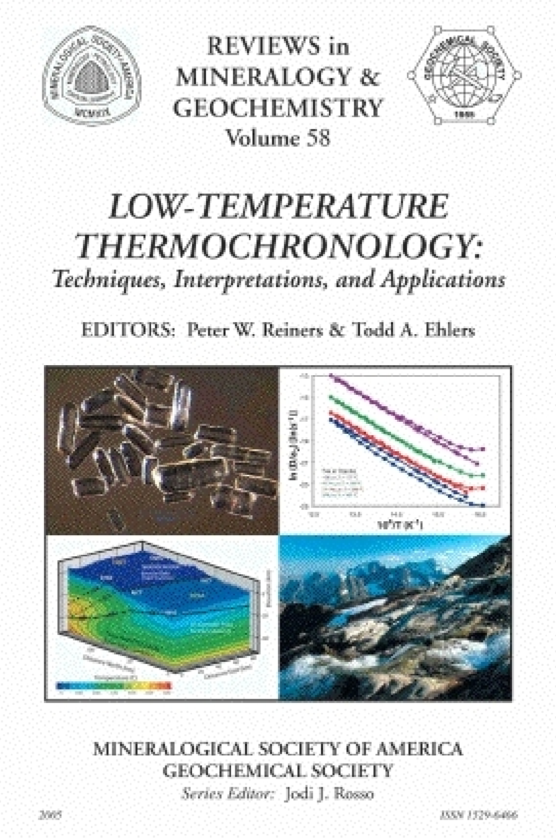
[1] **Low-Temperature Thermochronology: Techniques, Interpretations, and Applications,** October 13-15, 2005, Snowbird Resort, Snowbird, Utah just prior to the 2005 Geological Society of America Meeting in Salt Lake City, Utah. Organizers were Peter Reiners (Yale University) and Todd Ehlers (University of Michigan). The course had 82 participants (53 students and 18 professionals, 11 speakers).

Reviews in Mineralogy and Geochemistry volume 58: **Low-Temperature Thermochronology: Techniques, Interpretations, and Applications** i-xxii and 620 pp. ISBN 093995070-7 ($40 non-members, $30 MSA, GS, and CMS members) - 2500 copies printed on 10/06/2005.

[2] **Molecular Geomicrobiology**, December 2, 3 and 4, 2005, University of California Lawrence Hall of Science and in meeting rooms at the International House, Berkeley, California. Organizers were Jillian F. Banfield, Javiera Cervini-Silva, and Kenneth H. Nealson. The course had 137 participants (82 students and 39 professionals, 13 speakers).

Reviews in Mineralogy and Geochemistry volume 59: **Molecular Geomicrobiology** i-xiv and 294 pp. ISBN 093995071-5. ($40 non-members, $30 MSA, GS, and CMS members) - 2500 copies printed on 11/28/2005.

2,652 copies have been distributed of these 2 volumes as of 04/30/2007. Copies were distributed to all short course participants, 777 library subscribers to *American Mineralogist* (who are thought to include all library subscribers to *Geochemica et Cosmochimica Acta*), book reviewers, and by mail and meeting sales.



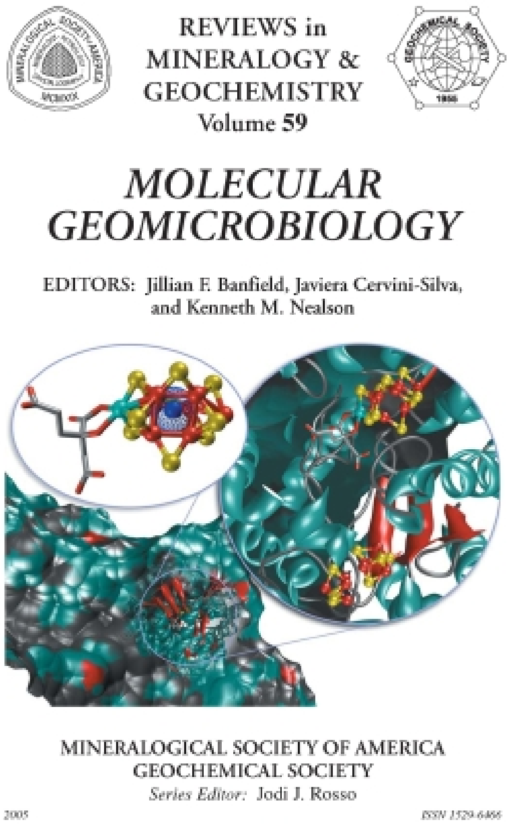
REVIEWS in
MINERALOGY &
GEOCHEMISTRY
Volume 58

LOW-TEMPERATURE
THERMOCHRONOLOGY:
Techniques, Interpretations, and Applications

EDITORS: Peter W. Reiners & Todd A. Ehlers

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

2005 ISSN 1529-6466



REVIEWS in
MINERALOGY &
GEOCHEMISTRY
Volume 59

MOLECULAR
GEOMICROBIOLOGY

EDITORS: Jillian F. Banfield, Javiera Cervini-Silva,
and Kenneth M. Nealson

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

2005 ISSN 1529-6466

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Grant: DE-FG02-06ER15766

Special Issue by the magazine Elements on "User Facilities in the Earth Sciences"

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Objectives: The grant was for partial support of a special issue of the magazine *Elements* on "User Facilities in the Earth Sciences", the first (February) issue of 2006.

Project Description: The theme of "User Facilities in the Earth Sciences" grew out of a DOE-Geosciences workshop held in May 2004 entitled "Geosciences User Facilities - Enhancing Instrumentation Access". It was organized by Prof. Rich Reeder of Stony Brook University, Prof. Marc Caffee of Purdue University and Dr. Stephen R. Sutton of University of Chicago and Argonne National Laboratory. Support was requested because the issue was to have eight additional pages, from 24 pages normally allotted for the thematic articles to 32 pages. This would enlarge the page coverage on user facilities.

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. This format is supported by news from each member society, as well as book reviews, conference reports, a calendar of upcoming events, news from the editors, and advertisements. During FY2006 *Elements* (ISSN 1811-5209) was a publication of eight societies:

Mineralogical Society of America
Mineralogical Society of Great Britain and Ireland
Geochemical Society
Mineralogical Society of Canada
Clay Minerals Society
International Association of Geochemistry
European Association for Geochemistry
Société Française de Mineralogie et Cristallographie

It is now a publication of 13 societies.

Results: The publication supported by the grant is *Elements* volume 2 number 1 (February issue of 2006). It contained 64 pages, 33 pages devoted to the topic of *User Facilities in Earth Science Research*. 8,902 copies were distributed to individuals, libraries, and societies - 46 % to US addresses, the remainder overseas. The issue will also available on line through GeoScienceWorld.org (http://www.geoscienceworld.org/) by the end of 2007.

The guest editor for the issues was *Stephen R. Sutton,* and articles with their authors:

- *User Research Facilities in the Earth Sciences*, Stephen R. Sutton
- *User Facilities around the World*, Gordon E. Brown Jr., Stephen R. Sutton, and Georges Calas
- *Synchrotron Radiation, Neutron, and Mass Spectrometry Techniques at User Facilities*, Stephen R. Sutton, Marc W. Caffee, and Martin T. Dove
- *Scientific Advances Made Possible by User Facilities*, Gordon E. Brown Jr., Georges Calas, and Russell J. Hemley
- *Accessing User Facilities and Making your Research Experience Successful*, Richard J. Reeder and Antonio Lanzirotti
- *New Opportunities at Emerging Facilities*, John B. Parise and Gordon E. Brown Jr.

Elements

February 2006
Volume 2, Number 1

ISSN 1811-5209

An International Magazine of Mineralogy, Geochemistry, and Petrology

User Research Facilities
in the Earth Sciences

User Facilities around the World

X-ray, Neutron, and Mass Spectrometry Techniques

Scientific Advances Made Possible by User Facilities

Accessing User Facilities

New Opportunities at Emerging Facilities

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Grant: DE-FG02-04ER15500

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

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Objectives: To provide a better understanding of rheological properties of mantle rocks under lithospheric conditions, we have undertaken deformation experiments on polycrystalline olivine samples under both anhydrous and hydrous conditions in a high-pressure deformation testing apparatus at low temperatures and high differential stresses. This study builds on our experience in carrying out high-pressure, high-temperature experiments under controlled thermodynamic conditions and takes advantage of our experience with large-volume, high-pressure deformation experiments at synchrotron x-ray beam lines. The objective of this study is to determine constitutive equations appropriate to low-temperature plastic flow in order to permit modeling of properties and processes in Earth's interior. Additionally, we perform microstructural and spectral analyses to improve the physical basis for those constitutive relationships.

Project Description: This project owes its existence to the recent development of the deformation-DIA (D-DIA), a solid-medium, multi-anvil type of apparatus. It differs from conventional deformation instruments in that synchrotron x-rays are used to measure stress and plastic strain directly within the material of the test sample. Experiments were carried out at temperatures in the range 673 to 1173 K and pressures from 6 to 12 GPa. First, we have focused on quantifying low-T plasticity of olivine under anhydrous conditions. Second, we are extending this research to hydrous conditions. Third, we are expanding our research to include not only dunitic but also hartzburgitic and lherzolitic rocks, that is, rocks with significant fractions of ortho- and clinopyroxene. Our primary goal is to produce low-temperature flow laws for olivine-rich rocks.

Results: Experiments have been performed to explore the rheological properties of olivine at pressures up to ~10 GPa and temperatures ranging from 673 to 1173K under anhydrous conditions. In experiments, small cylindrical samples are cored from materials that have been hot-pressed from powders of San Carlos olivine. A sample is assembled with Al_2O_3 pistons, a boron nitride sleeve, and graphite resistance heater into a 6-mm edge length cubic pressure medium. During an experiment, the cell is first pressurized isotropically to the desired level, heated to run temperature, and then deformed in compression at constant pressure.
Using x-ray diffraction, we determine pressure (i.e., mean stress) and differential stress from the elastic strain of various lattice planes measured as a function of orientation with respect to the stress field. Sample strain is computed from the length change of deforming samples measured from a series of x-

radiographic images. A typical plot of differential stresses vs sample strain for a run is shown in Figure 1. As illustrated in Figure 2, differential stress decrease substantially with increasing temperature. Our latest efforts are focused on experiments that further delineate the rheological behavior of olivine at low temperatures and high differential stresses in establishing a robust flow law at those conditions.

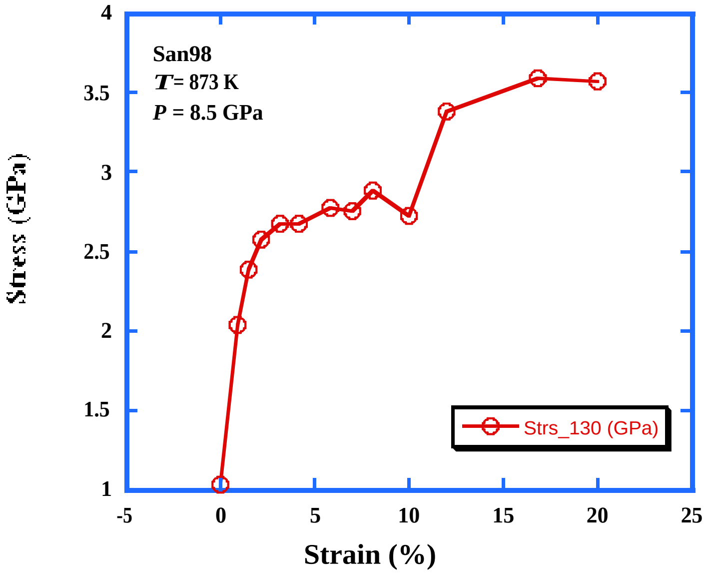

Figure 1. Typical stress-strain curve for a run conducted at high pressure and elevated temperature. Differential stress in the sample is computed from its (130) reflection based on x-ray diffraction pattern taken during deformation.

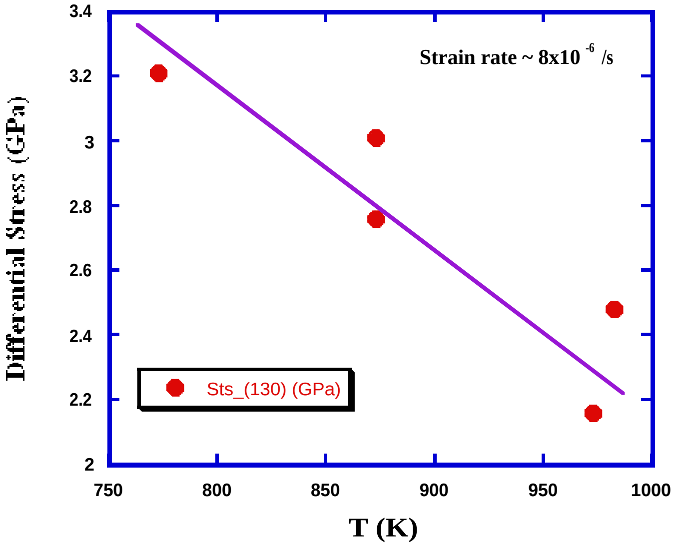

Figure 2. Differential stress decreases with increasing temperature. Each data point is obtained from a run conducted at constant deformation rate, pressure and temperature.

NATIONAL ACADEMY OF SCIENCES

Board on Earth Sciences and Resources
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Grant: DE-AT01-04ER15569

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 six standing committees (Committee on Earth Resources; Geographical Sciences Committee; Committee on Geological and Geotechnical Engineering; Committee on Geophysical and Environmental Data; Committee on Seismology and Geodynamics; and Mapping Science Committee) hold approximately two meetings each per year. At these meetings, potential studies are discussed and developed. Many of these activities are in response to requests from agencies of the federal government for advice on specific technical or policy issues. Other activities are federally mandated, or initiated by the Board in accordance with its efforts to support the continued health of the 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 2006, the Board oversaw 14 studies. Examples of studies underway in FY 2006 are Grand Research Questions in Solid-Earth Sciences, and Coal Research, Technology, and Resource Assessments to Inform Energy Policy. BESR completed 5 studies in FY 2006. The results of BESR's studies are published in its peer-reviewed reports. Examples of completed studies include Managing Coal Combustion Residues in Mines, and Geological and Geotechnical Engineering in the New Millennium: Opportunities for Research and Technological Innovation.

During this reporting period, the Board held two meetings. At its November 2005 meeting two reports published by the Board were discussed: (1) Learning to Think Spatially: GIS as a Support System in the K–12 Curriculum, and (2) Improved Seismic Monitoring—Improved Decision Making: Assessing the Value of Reduced Uncertainty. Most of the meeting was devoted to a roundtable on "Monitoring the State of Complex Earth Systems Services—Strategies and Problems." Presentations were held on the monitoring of the deep earth, shallow earth, ecology, hydrology, atmosphere, and land cover change/land use. At the May 2006 meeting, the results of the external review of the Board were discussed. The Board reviewed the work of two standing committees in detail—Committee on Geological and Geotechnical Engineering and the Committee on Geophysical and Environmental Data.

Proposals were developed as a result of the roundtable at the November 2005 meeting: Strategic Planning for Earth Science Infrastructure; Data Interoperability; Current and Future Research Efforts Involving “Environmental Observatories.” The most likely result of the November 2005 roundtable is a study of Earth science research facilities. Most of the Board meeting was devoted to a roundtable, “Life in the Material World.” This roundtable dealt with microbes, minerals, and the environment.

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Grand Research Questions in Solid-Earth Sciences

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Objectives: A National Academies committee will formulate a short list of grand research questions driving progress in the Earth sciences. The questions will cover a variety of spatial and temporal scales, from sub-atomic to planetary, and from the past (billions of years) to the present and beyond. The questions will be written in a clear, compelling way and will be supported by text and figures that summarize research progress to date and outline future challenges.

Project Description: Over the past three decades, Earth scientists have made great strides in understanding our planet's workings and history. We understand as never before how plate tectonics shapes our planet's surface, how life can be sustained over billions of years, and how geological, biological, atmospheric, and oceanic processes interact to produce climate-and climatic change. Yet, at the most basic level, 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 National Academies Committee on Grand Research Questions in the Solid-Earth Sciences was established to frame some of the great intellectual challenges inherent in the study of the Earth and planets. Although many reports have identified research priorities in Earth science, few have cast them as fundamental science questions. Such "big picture" questions may require decades to answer and research support from many agencies and organizations.

Results: The committee began by drafting "strawman" questions and publishing them for comment in *Eos, Transactions of the American Geophysical Union* (v. 87[9], p. 98); on the National Academies website; and in electronic newsletters of the American Geological Institute and Association of Women Geoscientists. The questions posted for comment were:

1. How did the Earth and planets form?
2. What happened during Earth's dark age? (the half billion years before the oldest known rock formed)
3. How did life begin on Earth?
4. Why plate tectonics?
5. How has Earth's interior evolved and how has it affected the surface?
6. Why does Earth have a magnetic field?
7. How do life and Earth co-evolve?
8. How has Earth's climate changed and why?

9. Can we understand and predict catastrophic natural events?
10. How do material properties control planetary processes?
11. How do air, water, land, and life processes interact to shape our environment?

The committee met three times in the reporting period to discuss community feedback, gather additional input, and write its report. The report is currently being peer reviewed and is expected to be released in September 2007.

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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 renders their analysis difficult. In the first case, the velocity variation within a heterogeneous fracture leads to an inhomogeneous shear stress pattern, which in a shear-thinning liquid causes spatial variations in viscosity, which enhances the velocity variation. In the second problem, deposition processes alter the fracture geometry which in turn alters the velocity and stress fields, which can then promote or discourage deposition in different regions of the fracture. We will employ numerical simulations based on the lattice-Boltzmann method, based on our newly developed codes for shear-thinning liquids and solid particle transport, complemented by effective medium and other averaging techniques. The proposed analytical and numerical work at CCNY will be complemented by a continuing collaboration with an experimental group led by J.-P. Hulin at the Universitè de Paris - Orsay.

Results: We have combined experiments and simulations to develop an improved understanding of the permeability anisotropy resulting from lateral shifts in opposing self-affine fracture surfaces. Shifts produce visible channeling effects in the fracture aperture in the orthogonal direction, and suggest a model analogous to electrical current flow where fluid flow perpendicular to the shift follows the channels and corresponds to current flow through resistors in parallel, while flow parallel to the shift runs across the channels and corresponds to resistors in series. This analogy explains the origin of the effect, and more quantitatively can be used to obtain upper and lower bounds on the permeability in the respective directions. In the particulate problem, as a preliminary to full scale simulations of particle laden-flows in fractures, and as a test of the numerical code, we have studied the interaction of cylinders in confined, periodic, non-zero Reynolds number linear shear flow. In addition to stable fixed points on the channel axis for well-separated particles, new types of particle trajectories were observed, including both open and closed limit cycles. We have obtained a phase diagram for the type of trajectory resulting from various initial conditions in the two-particle case, and we will be testing for traces of limit cycle dynamics in many-particle suspensions.

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Contract: DE-FG02-03ER15458

Stress-Dependent Acoustic Propagation and Dissipation in Granular Materials

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Objectives: The goal of this project is to combine experimental characterization, continuum and micromechanical modeling and computer simulations to develop (i) an understanding of the elastic and viscoelastic properties of cohesionless granular materials, (ii) a fundamental understanding of the damping properties of granular materials on acoustic modes.

Project Description: This project is motivated by a desire to understand acoustic propagation and dissipation in earth formations. Specifically, we study unconsolidated sediments, as those are the ones with the largest nonlinearity.

(i) The stress response and relaxation properties of granular materials confined by an external stress are enormously nonlinear and show slow relaxation dynamics in comparison with the microscopic motion of the constitutive particles. Acoustics and nonlinear elastic methods are at the forefront of the evolving technology to help plan and optimize well location. In order to position a well correctly, the knowledge of the stress distribution around the borehole is essential. Acoustic measurements in granular materials provide the natural way to understand such stress distributions.
Our experiments on the isotropic compression of a granular materials show that the shear and bulk moduli vary with the confining pressure faster than the 1/3 power-law predicted by Hertz-Mindlin effective medium theories (EMT) of contact elasticity. Moreover, the ratio between the moduli is found to be larger than the prediction of the elastic theory by a constant value. The understanding of these discrepancies has been a longstanding question in the field of granular matter.

(ii) Furthermore, the understanding of the mechanisms of energy dissipation via friction or contact dissipative forces between grains is of fundamental interest to unravel the unique dynamical behavior of granular matter. Despite the importance of this problem, an understanding of the origins of damping and dissipation in granular materials is still lacking. 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 acoustic borehole tools, in e.g., logging applications for oil exploration.

Results: (i) We have performed a complete test of the applicability of elasticity theory to granular materials and developed new theories of elasticity. We show that the elasticity theory partially describes the experimental and numerical results for a system under compressional loads. However, it drastically fails for systems under shear perturbations, particularly for unconsolidated packings with small friction near the jamming transition at the random close packing limit. Our work indicates that a correct treatment should include not only the purely elastic response but also collective relaxation mechanisms related to structural disorder and non-affine motion of grains. We have therefore developed theories of pair-fluctuation analysis going beyond the uniform strain approximations of the EMT which provide far better estimates for the elastic moduli of the system.

(ii) We also perform an experimental investigation of the frequency dependent effective mass of a rigid cavity filled with loose granular particles, and investigate the attenuation and the shift in resonance frequency of flexural modes in a resonance bar with a cavity filled with grains. The experimental results determine unequivocally the signatures of damping effects of acoustic modes in granular materials and allow the understanding of the dissipation mechanisms in earth materials.

The dominant features of the effective mass are a sharp resonance and a broad background, which we interpret within the context of continuum models as well as with molecular dynamic simulations. The resonance peak is understood in terms of a height-dependent effective sound speed (130 m/s) and an effective viscosity. On a fundamental level, we show that dissipation is dominated by that at grain-grain contacts, not by global viscous damping. Our results are further confirmed by experiments varying the degree of humidity in the system. These features are taken to understand the effects of the vast parameter space contributing to acoustic damping such as compaction, temperature tests, effects of humidity, and surrounding fluids, filling fractions, friction and coefficients of restitution and different particle characteristics.

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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 progress in FY2006 was into three areas: (A) micro- and macroscopic studies of the effect of bacteria (those common to AMD environments) on pyrite with and without adsorbed phosphocholine lipid; (B) spectroscopic studies of the pyrite (and isostructural disulfides) oxidation in both the abiotic and biotic environments; and (C) pyrite oxidation when commingled with other common sulfides.

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 research from our laboratory has shown that the adsorption of two-tail lipids of phosphocholine lipids, such as L-α-Phosphatidylcholine, Hydrogenated lipid and 1,2-bis(10,12-tricosadiynoyl)-*sn*-Glycero-3-Phosphocholine on pyrite resulted in a marked decrease in oxidation rate.

All of our prior studies were done in an abiotic environment. We have initiated research to investigate the behavior of these organic overlayers in the presence of bacteria common to AMD environments. Experiments are showing that the organic layers are not only stable in the biotic environment (using both autotrophic and heterotrophic bacteria) and supress pyrite oxidation, but in addition the adsorbates modify the binding of the bacteria on the pyrite surface. In particular, recent results are suggesting that the application of lipid to a pyrite surface with attached bacteria, results in the displacement of the microbe. These results suggest that the application of phosphocholine lipid to pyrite in the environment may prove to be a future remediation technique. Atomic force microscopy and attenuated total reflection Fourier transform infrared spectroscopy are the primary techniques in this research area.

Vibrational spectroscopic study of the oxidation of pyrite and vaesite in oxidizing gaseous and aqueous environments

The reaction of FeS_2 (pyrite) and NiS_2 (vaesite) gaseous and aqueous oxidizing condition was investigated using Horizontal Attenuated Total Reflection Fourier-Transform Infrared spectroscopy (HATR-FTIR). Vaesite adopts the pyrite structure and a comparison of the oxidation mechanism and reactivity of these isostructural minerals is allowing us to develop a relationship between reactivity and disulfide electronic structure. Isotopic labeling experiments were used to compare the reaction mechanism of pyrite and vaesite oxidation. These experiments have shown for example that while sulfate product is largely derived from water reactant, but the microscopic controls of the reactivity of the two minerals are quite different. Differences in the influence of defects (dominated by the presence of Fe^{III} on pyrite) and in electrical conductivity are being investigated as reasons for these differences.

Study of the Nature and Reactivity of Defects on the Pyrite Surface

A question that is being asked in the present research, is how does the commingling of pyrite with other metal sulfides affect oxidation rates and mechanism? This has profound implications on the rate of pyrite under real environmental conditions. Mine waste and natural occurrences of pyrite often contain an assemblage of sulfide minerals, non-sulfide minerals, and organic material (e.g., coal). To address the influence of the complexity of the waste or natural material, we are investigating the interaction between coexisting sulfide minerals. Few studies have addressed the interaction and possible synergistic interplay that may occur as two or more sulfides are present in the same system. Our working hypothesis is twofold. (1) Hydrogen peroxide and hydroxyl radical formed in the oxidation of pyrite may accelerate the oxidation of other sulfides. (2) Electron transfer between pyrite and other metal sulfides (i.e., galvanic contact) will alter the oxidation rate of the two phases, when compared to the individual and electrically separated phases. Recent experiments have shown that having galena (PbS) in contact with pyrite in a oxidizing aqueous environment, there is a significant reduction in the pyrite oxidation rate. Scanning electron microscopy images show that when galena is present the dissolution pits that characterize pyrite oxidization are reduced. Aqueous batch reaction data shows that the amount of Fe released into solution also is reduced under these same conditions consistent with the SEM observation. The galena however oxidizes readily (Pb secondary phases resulting from this process appear on the pyrite). Galena does not oxidize readily under these conditions if it appears alone. Hence, there is a synergistic effect when pyrite and galena are present together. Understanding this process will have great implications on understanding the oxidation of sulfides in important environmental processes, such as acid mine drainage.

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Grant: DE-FG02-99ER14996

Microscale Processes and Macroscopic Behavior of Porous Geomaterials

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Objectives: This project aims to provide a fundamental understanding of microscale basis for the macroscopic deformation and transport properties of porous earth materials in relation to energy-related problems, 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 chalks, 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 CO_2 sequestration, or during production of hydrocarbons) is necessary. Likewise, an increased understanding of how the pore structure and its evolution with deformation affect fluid transport processes (during underground injection of greenhouses gases to mitigate climate change, or during primary and enhanced oil recovery) is required. Systematic experimental investigation provides a detailed understanding of the microstructure of porous earth materials and how those microscale characteristics affect the deformation and fluid transport properties at the macroscale. The laboratory data together with quantitative microscopy will be used to formulate and evaluate theoretical and numerical models of rock deformation and fluid flow. The overall goal of the research program is to enhance the fundamental understanding of deformation and transport processes in geologic materials, and thereby strengthen the theoretical basis for the application of laboratory results to technological applications including carbon management, oil field geosciences, and other geotechnical engineering problems.

Results: (1) Constitutive modeling of mechanical compaction and strain localization. In geomechanics the phenomenon of mechanical compaction is conventionally simulated using either the critical state or cap model, which have been incorporated into various numerical codes even though there have been limited constraints from a paucity of high-quality data. On the basis of our relatively complete data set on mechanical compaction in porous sandstone, we mapped out the conditions under which some of the conventional models are valid and clarified the predictions on the inception of strain localization. In parallel we continue our comprehensive investigation of compaction in porous carbonate rock.

(2) Development of new experimental methodology and 3-D imaging technique to characterize the evolution of compaction and localization. A new experimental technique for mapping out the compactive yield envelope under undrained conditions was developed. The technique allows one to characterize the initial yield envelope and its evolution with strain hardening, which typically require several conventional triaxial tests to acquire. Furthermore the new technique circumvents variability

from sample to sample. Digital image correlation (DIR) is a technique that is widely used in experimental mechanics to map out the spatial distribution of strain, but seldom in geomaterials. We have developed a technique whereby X-ray radiographs of undeformed and deformed samples can be used to delineate the spatial distribution of relatively small inelastic strain and to characterize the influence of bedding on the development of strain localization.

(3) Discrete element and probabilistic modeling of compactive failure and permeability evolution. We have used the discrete element modeling for analyzing the complex micromechanics of brittle failure and compaction localization in clastic rocks. In particular we focus on the influence of grain-scale pore heterogeneity. Our simulations highlight how discrete compaction bands are promoted by grain-scale homogeneity. Compactive failure is accompanied by permeability reduction of up to several orders of magnitude, possibly with strong stress-induced anisotropy. We have formulated a probabilistic damage model that can realistically capture key attributes of the permeability evolution.

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Grant: DE-FG02-05ER15635

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

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

Project Description: This study focuses on reaction rate laws describing acid-driven mineral dissolution. 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 come from the Viking Formation in the Alberta Sedimentary Basin, provided by the Alberta Geological Survey. Imaging methods include X-ray computed microtomography and subsequent analysis for 3D void space characterization. We also employ a combination of backscatter electron microscopy (BSE) and energy dispersive X-ray (EDX) spectroscopy for statistical characterization of reactive mineral patterns. One important goal of the spectroscopic imaging and interpretation is to characterize pore contact with individual minerals thereby quantifying meaningful surface areas for use in reactive transport models.

Results: Analysis of the void space of nine rock specimens has provided a wealth of data on connectivity of pore networks as well as distributions of pore volumes, surface areas, and throat areas. All the specimens are sandstones of comparable porosity, and yet order of magnitude variation is found in pore properties across them. Furthermore, there is order of magnitude variation of pore properties within specimens. To characterize the mineralogy and its relation to pore space, we developed an innovative procedure which combines EDX spectroscopy and BSE imagery of 2D thin sections (see figure). Multiple element maps from EDX are interpreted to generate a single mineral map. The EDX map is combined with a BSE map, which has high resolution plus some information that cannot be obtained from EDX. Then the amount of each mineral present and adjacent to the pore space is calculated. As an example, in the image shown below, only 9% of the mineral matter is kaolinite, but it coats as much as 80% of the pore perimeter, obscuring the minerals that would be reactive under acidic conditions. The EDX/BSE image analysis method shows great potential for determining reactive mineral availability and better surface area estimations. Incorporation of these results into reactive transport models will allow for more accurate representation of formation reactivity with injected CO_2. New pore-network models were developed based on these void-space and mineralogical characterizations, and we have begun to develop models for reactive flow simulations. These simulations are designed to examine up-scaling of reaction rates, thereby quantifying the extent to which reactions rates measured in laboratory settings are applicable for larger-scale modeling. Simulation conditions represent inflow of acidic CO_2-rich brine under high-pressure conditions relevant to carbon geosequestration. We have found that approximating the distributed pore-scale network with a "bulk" continuum model becomes progressively inaccurate as the acidity of the system is increased. Simple corrections to reactive surface areas may work, but require generalization to other flow regimes and pH conditions.

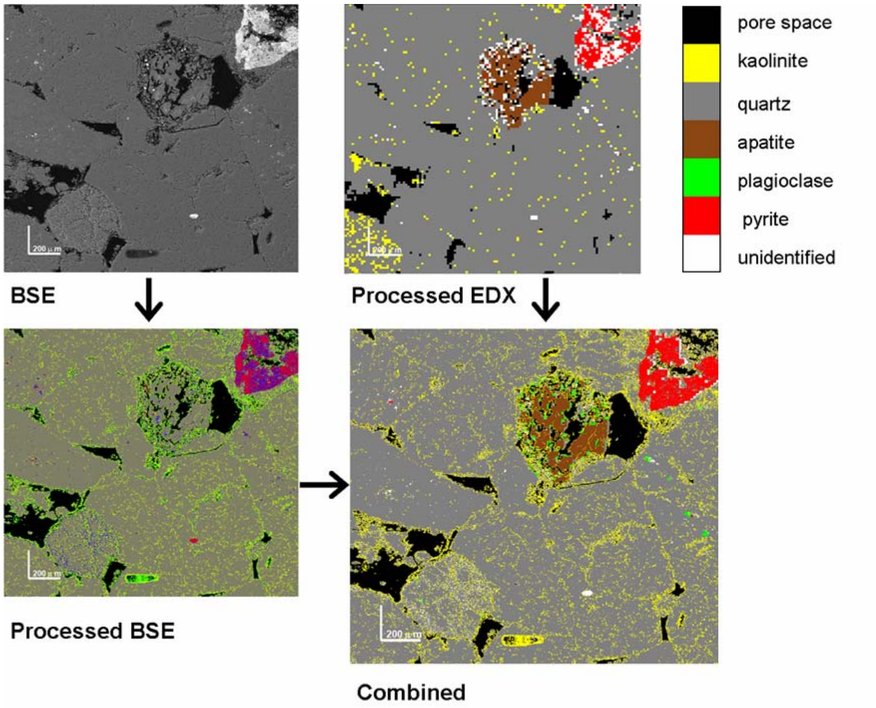

Figure caption: Imaging and interpretation of the mineralogy of a 2D thin section of a Viking sandstone. The image captured from BSE microscopy (upper left) is interpreted with respect to pore space, quartz, kaolinite and other minerals (lower left). The mineral map determined from EDX spectroscopy (upper right) provides information about specific minerals that cannot be easily distinguished using BSE. The combined BSE/EDX image (lower right) successfully resolved kaolinite from quartz, as well as other minerals from each other.

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Contract: DE-FG02-04ER15508

Reaction and Transport of Toxic Metals in Rock-Forming Silicates at 25°C

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Objectives: To better understand electron transfer reactions between Fe(II) in silicates and sorbed 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 silicate 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: Important contributions in FY06 included a careful analysis of a series of U4f spectra that showed varying degrees of reduction. Using factor analysis and both constrained and unconstrained fitting of spectral features we were able to convincingly demonstrate that the satellite features normally associated with monovalent U(IV) and U(V) oxides are also robust indicators of U oxidation states in mixed valence U oxides. In other work we showed that even Fe(II) poor micas, under both oxidizing and reducing conditions, can reduce minor to trace amounts of U(VI) that have diffused into the interlayer region and that electron transfer must occur across the tetrahedral layer. Diffusion modeling coupled with XANES indicated that the reduced species was immobile and that only the oxidized species diffuses. Further, once reduced in the interlayer, reoxidation to U(VI) is kinetically hindered. With respect to ab initio modeling of XPS and XANES spectra of actinides, much of the year was spent writing code and adapting codes for use on parallel computer systems in order to take into account environmental effects. The actinides pose a significant challenge due to the number of electrons in the system and the need to consider relativistic effects even for the valence level. We are now positioned to calculate the XANES and XPS of small embedded cluster models such as UO_8 to simulate the effect of covalency on the multiplet structure of UO_2 and to implement charge transfer configurations and higher order excitations.

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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: The most detailed field study of compaction bands to date indicates that they have a roughly elliptical profile. This observation suggests a model of a band as a narrow ellipsoidal inclusion with elastic properties different from those of the surroundings and subjected to an inelastic compactive strain. For this model the compactive displacement of the boundary is proportional to the width of the band and supports the use of the width as proxy for the band displacement, as done in field studies. A detailed parameter study of this model indicates that for the aspect ratios observed in the field, 10^{-3} to 10^{-4}, the stress states within and near the edge of the band are well-approximated by the limiting case of zero aspect ratio. In addition, for parameters representative of the field site, the elevation of compressive stress near the tip of the band is dominated by the inelastic compaction and relatively insensitive to elastic mismatch of the band and surrounding material, so long as it is not too large. The stress state ahead of the band is, however, fully three dimensional and the stress path depends on the mismatch of elastic properties.

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Grant: DE-FG02-06ER15787

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

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

Project Description: We are generating – using rigorous synthetic organic chemistry – a wide variety of geochemically important organic functional groups at various mineral/water interfaces and to spectroscopically characterize them in the infrared using broadband vibrational sum frequency generation (BB-VSFG). We determine their interfacial charge densities, interfacial potentials and energy densities with the goal of assessing their affinity towards ionic and neutral aqueous pollutants using second harmonic generation (SHG). Furthermore, we track changes in the molecular structure of the organic adlayers and in the absolute orientation of the interfacial water molecules both with SHG and BB-VSFG while working at environmentally relevant pH, ionic strength and temperature. Our results will be important for improving surface complexation models and chemical transport models by incorporating heterogeneous parameters derived from interface-specific kinetic, thermodynamic, spectroscopic and structural data into computer models for simulating contaminant transport in the presence and absence of interfacial

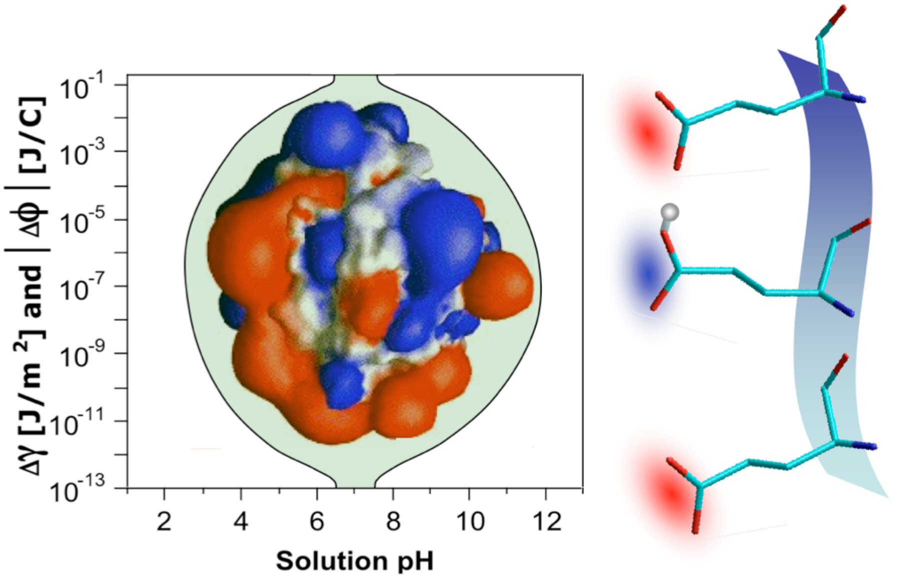

Figure 1. Molecular level view of protonation states for carboxylic acid side chains on amino acids that are part of natural organic matter agglomerates or NOM coatings on mineral oxide soil particles. Clearly, for a given bulk pH, the local pH can span multiple pH units and is controlled by molecular proximity of the organic functional groups. *Red*: deprotonated, or *charged*, at bulk pH 7, *Blue*: protonated, or *neutral*, at bulk pH 7.

processes.

Results: This program has focused on three activities: 1) the synthesis of meaningful organic and inorganic heterogeneous acid-base systems that are important in biogeochemistry; 2) the measurements of their full thermodynamic state information, including their interfacial pKa values, their interfacial potentials and charge densities, and their energy densities; and 3) the tracking of the interaction of these interfaces with inorganic and organic ground water contaminants. We apply chi(2) and chi(3) nonlinear optical spectroscopies and use homo- and heterodyne-like detection schemes to extract the otherwise exceedingly small signals. Figure 1 shows that our molecular-level measurements result in surface-specific thermodynamic parameters that are useful for assessing how interfacial acid-base systems will respond to various geochemically representative bulk pH values. For a bulk pH of seven, the local pH at the interface between bulk ground water and colloids coated with humic or related organic acids can span up to nine orders of magnitude in proton concentration. This clearly indicates that bulk thermodynamic parameters are not applicable to geochemical models that predict ground water pollutant transport if that prediction involves heterogeneous acid-base chemistry. We have applied these measurements and demonstrated our findings for oxide/water interfaces, amino acids at oxide/water interfaces, aromatic and aliphatic acids at oxide/water interfaces, and for DNA oligonucleotides at oxide/water interfaces. We then tracked the interaction of veterinary antibiotics (morantel, oxytetracycline) as well as small inorganic anions (chromate, nitrate) and inorganic cations (barium, strontium, cadmium, and manganese) with these interfaces. Very recently, we carried out nonlinear optical measurements in which the protonation state of fused silica/water interfaces and those functionalized with amino acids is tracked as a function time, bulk solution pH, and electrolyte concentration. While the bulk pH and the interfacial protonation state change simultaneously at low electrolyte concentrations, Debye-Hückel lengths approaching one nanometer lead to delays in the interfacial response that last for hours. Once the interface does undergo acid-base chemistry, the system rapidly cascades into steady state. Surface titration experiments show massive hysteresis, shifting interfacial acidities by a record eight orders of magnitude for multiple hours.

The dynamic and steady state experiments presented in this work are consistent with the notion that hysteresis shifts the interfacial acid-base equilibria of surface-bound inorganic and organic acids and bases much further away from their corresponding bulk values than what had been known previously about these systems under steady-state conditions. Given the environmentally and biologically relevant electrolyte concentrations and flow rates that promote this effect, the long time scales during which the systems stay jammed have direct implications for interfacial acid-base chemistry wherever surfaces and interfaces are routinely subjected to changing bulk solution pH conditions. These applications include acid-base chemistry involving heterogeneous contaminant processing and transport in geochemistry as well as pollutant remediation.

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Grant: DE-FG02-04ER15495

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

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Objectives: The 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: The VSFG data from Ohio State has led our team research into the area of ion pairing in the bulk aqueous solution and at interfaces. We have been focusing on nitrate interfacial segregation and ion pairing characteristics with the dications of interest here. 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. We have confirmed earlier ion pairing work in the aqueous phase, mainly pointing to the strong hydration shell of Mg^{2+} and how this inhibits ion pairing characteristics of $Mg(NO_3)_2$ in aqueous solution. However, most interesting is that at the air-aqueous interface, Mg^{2+} does not approach the interface easily and thereby allows nitrate anions to approach the interface where the nitrate frequency is indicative of an unperturbed nitrate, meaning that nitrate is free of interaction of its counterion. Magnesium is unique in this context. All other cations investigated at the air-aqueous interface showed ion pairing characteristics similar to their bulk behavior. Modeling studies have shed light on the energetics of this observed phenomenon.

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Grant: DE-FG02-02ER15318

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 the 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 we have developed a full set of modules for the 3D MT inverse problem. This rather different inverse problem has been considered as we have developed the modular inversion system, although we have not yet tested 3D inversion capabilities. One specific feature of the system is that the model parameter is treated as a purely abstract data type—i.e., data objects taken to 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 model parameterization module. This greatly simplifies modification of the specific model parameterization, since we can guarantee that no modules depend on details of the model parameter representation, or details of our 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: During FY2006 we completed initial development and testing of a hybrid a hybrid algorithm combining elements of the standard CG and "Occam" minimum structure inversions, which adjusts the regularization parameter for step-length control. Rather than calculate the full Jacobian, the scheme uses the Lanczos bidiagonalization of the Jacobian, separately for each frequency, to generate (and save) a series of linear data contrasts, and the corresponding data sensitivities. The bidiagonalization procedure is truncated after a small number of steps, and the saved sensitivities, and corresponding linear combinations of data (for each frequency separately) are then used in a reduced data space Occam inversion. Tests on synthetic data for a two-dimensional magnetotelluric problem show the method provides essentially the same solutions as those obtained using a GN method requiring full calculation of the Jacobian, but at a fraction of the computational cost. The new approach is also 3-5 times more efficient than the standard CG approach.

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Grant: DE-FG02-05ER15675

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

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Objectives: We hypothesize that the rates and mechanisms describing the reactions that control the transformation of cohesive bedrock to disaggregated saprolite are determined by coupling between chemical, physical, and microbial processes driven by water and reactant fluxes into bedrock.

Project description: We are developing a model for water influx and reaction at the bedrock/saprolite interface and testing it on 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 hence the rate of production of saprolite from intact bedrock in this setting. 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 completed on advanced 1-D models of reaction and 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.

We have also developed a weathering conveyor belt model (Figure 1) which uses approximate first-order descriptions of weathering rate and chemistry within the weathering profile to study the evolution of a random distribution of initial joint-bound block sizes to residual corestones at the erosional surface. This model will be used to help systematize the interpretation and organization of field data. 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.

The first visible weathering reactions are the dissolution of plagioclase and the oxidation of biotite. Microscopic and spectroscopic results reveal that hornblende does not dissolve or oxidize within the ~45-cm thick rindlet zone, but dissolves completely within the 7 cm spanning the rindlet-saprolite interface. The dissolution of hornblende was found to be the dominant contributor of aqueous iron to the deep saprolite and the source of Fe(II) for deep saprolite microorganisms. Oxidation of Fe(II) within biotite crystals in the rindlets was observed using optical microscopy and inferred from microprobe analysis, which showed a loss of K^+ that increased with distance from the corestone. Biotite loses K^+ ions from the interlayer to maintain charge balance during Fe(II) oxidation. The loss of interlayer K^+ permits adsorption of water expanding the lattice, inferred to cause spheroidal fracturing. The synchrotron X-ray microprobe at SSRL was employed to determine if this reaction occurs within the corestone. The X-ray microprobe results documented Fe(III)-rich zones within individual biotite grains. These data were fit to XANES spectra taken from the Fe(III)-rich zones and compared to XANES spectra for known phases. The fits demonstrated that the Fe(III)-rich zones are oxidized biotite and not precipitated Fe(III)-(hydr)oxides or other Fe(III) phases. X-ray microprobe results also document decreased K content that corresponds to the zones with higher Fe(III), supportive of our hypothesis that oxidation of biotite Fe(II) within the corestone is responsible for initiating bedrock fracturing.

Biological iron oxidation has been shown to be coupled to bedrock weathering five meters below the soil surface of the Luquillo Forest. As bedrock weathers, ferrous iron is released from silicate minerals, providing substrate for iron-oxidizing bacteria. In turn, autotrophic iron-oxidizing bacteria fix CO_2, providing organic carbon substrate for other organisms in the ecosystem. At the base of the soil profile directly above the quartz diorite corestones, direct counts by standard epifluorescence microscopy revealed that total microorganisms, including iron-oxidizing bacteria, increased in abundance relative to numbers found throughout the overlying mineral matrix. These observed increases in total and culturable cells and DNA yields at lower depths were correlated with moisture and HCl-extractable iron. Confocal laser scanning microscopy (CLSM) demonstrates bacterial distribution in material from the saprolite-bedrock interface zone. The CLSM images of saprolite grains demonstrate consistent physical association between bacterial cells and amorphous secondary minerals but not with quartz particles. Iron oxidizing bacteria have been cultured from saprolite, and PCR primers have been developed for functional genes involved in the Fe-oxidation pathway. These primers will be used on DNA extracted from saprolite to indicate the presence of these genes in the community DNA.

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) and where autotrophic iron-oxidizing bacteria support the heterotrophic population and contribute to bedrock disaggregation and saprolite formation.

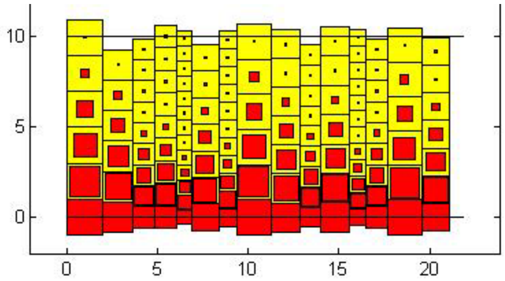

Figure 1. Random corestone blocks are weathered as they approach the erosional surface 10 meters above the level of inception of weathering. A limiting corestone diameter condition has been applied. Red = corestone (unaltered bedrock), yellow = saprolite formed from corestones.

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Grant: DE-FG02-05ER15636

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

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

Project Description: This study focuses on reaction rate laws describing acid-driven mineral dissolution. 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 come from the Viking Formation in the Alberta Sedimentary Basin, provided by the Alberta Geological Survey. Imaging methods include X-ray computed microtomography and subsequent analysis for 3D void space characterization. We also employ a combination of backscatter electron microscopy (BSE) and energy dispersive X-ray (EDX) spectroscopy for statistical characterization of reactive mineral patterns. One important goal of the spectroscopic imaging and interpretation is to characterize pore contact with individual minerals thereby quantifying meaningful surface areas for use in reactive transport models.

Results: Analysis of the void space of nine rock specimens has provided a wealth of data on connectivity of pore networks as well as distributions of pore volumes, surface areas, and throat areas. All the specimens are sandstones of comparable porosity, and yet order of magnitude variation is found in pore properties across them. Furthermore, there is order of magnitude variation of pore properties within specimens. To characterize the mineralogy and its relation to pore space, we developed an innovative procedure which combines EDX spectroscopy and BSE imagery of 2D thin sections (see figure). Multiple element maps from EDX are interpreted to generate a single mineral map. The EDX map is combined with a BSE map, which has high resolution plus some information that cannot be obtained from EDX. Then the amount of each mineral present and adjacent to the pore space is calculated. As an example, in the image shown below, only 9% of the mineral matter is kaolinite, but it coats as much as 80% of the pore perimeter, obscuring the minerals that would be reactive under acidic conditions. The EDX/BSE image analysis method shows great potential for determining reactive mineral availability and better surface area estimations. Incorporation of these results into reactive transport models will allow for more accurate representation of formation reactivity with injected CO_2. New pore-network models were developed based on these void-space and mineralogical characterizations, and we have begun to develop models for reactive flow simulations. These simulations are designed to examine up-scaling of reaction rates, thereby quantifying the extent to which reactions rates measured in laboratory settings are applicable for larger-scale modeling. Simulation conditions represent inflow of acidic CO_2-rich brine under high-pressure conditions relevant to carbon geosequestration. We have found that approximating the distributed pore-scale network with a “bulk” continuum model becomes progressively inaccurate as the acidity of the system is increased. Simple corrections to reactive surface areas may work, but require generalization to other flow regimes and pH conditions.

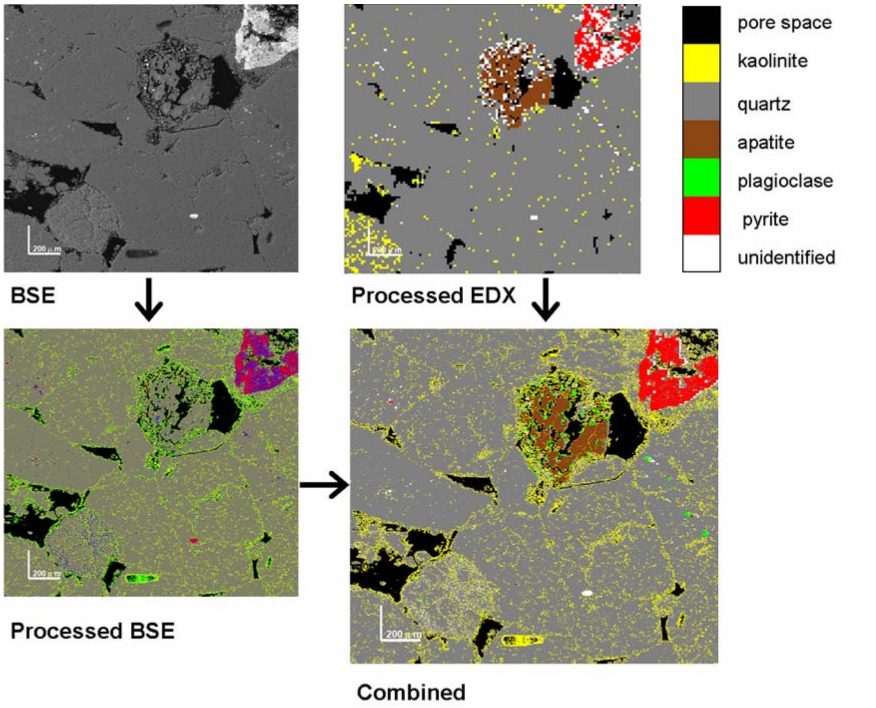

Figure caption: Imaging and interpretation of the mineralogy of a 2D thin section of a Viking sandstone. The image captured from BSE microscopy (upper left) is interpreted with respect to pore space, quartz, kaolinite and other minerals (lower left). The mineral map determined from EDX spectroscopy (upper right) provides information about specific minerals that cannot be easily distinguished using BSE. The combined BSE/EDX image (lower right) successfully resolved kaolinite from quartz, as well as other minerals from each other.

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Grant: DE-FG02-97ER14785

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: The focus of the research was the development of an acoustic lens system to determine the effect of the scale of observation (field-of-view) on monitoring alteration of a fracture caused by reactive flow and/or particle transport/deposition. The investigation was performed on fractured carbonate rock and on a standard sample made of acrylic with approximately the same dimensions. To control the scale of observation, an acoustic lens system was used to produce pseudo-collimated acoustic beams with known diameters. Seismic measurements and volumetric flow rates were made on the fractured sample prior to and after reactive flow with an HCl solution. High resolution two-dimensional acoustic maps of the fracture were obtained through diffraction-limited acoustic mapping without the use of the lenses

Results: Statistical analysis showed that prior to reactive flow, multiple measurements on the local scale can be averaged to obtain the same seismic response of a fracture as on the global scale. However, after reactive flow, averaging of local scale measurements did not result in the same interpretation of fracture properties as those made on larger scales. This corresponds to the alteration of the spatial correlation length of the fracture geometry caused by the reactive flow. A two-point correlation analysis of the high resolution seismic maps showed that the spatial correlation length of the fracture was roughly isotropic prior to reactive flow but became anisotropic after reactive flow. Changes in the flow rates from chemical etching of the fracture can only be detected/interpreted from multiple local scale measurements made below the scale of the spatial correlations within the fracture. Work is progressing measuring measurements of local and global seismic parameters for fractured samples subjected to grain/particle (microsphere) transport. The data will enable the determination of the link between the seismic response and fluid flow, as well as the scaling behavior of these properties.

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Grant: DE-FG02-94ER14432

Properties of Interfaces in Fluid-Bearing and Fluid-Absent Rocks

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Objective: To further advance our understanding of fluid flow in deep seated regions of the Earth through investigations into the role of grain boundary energetics on the geometry of solid/fluid interfaces.

Project Description: A multi-faceted experimental research program was used to investigate how C-O-H fluid transport in the Earth is affected by grain boundary (interfacial) energetics. In the upper portion of the Earth's crust transport of fluid is accommodated via a network of fractures and open porosity. At depths exceeding ~15 km ductile deformation dominates and fluid transport occurs through an interconnected network of pores whose shapes are determined by minimization of energy along grain interfaces. Our research efforts have focused on the physical and chemical properties of grain boundaries that control interfacial energetics, which govern intergranular pore geometry and long-range permeability. Small changes in interfacial energetics may exert strong control on the geometry of fluid-filled pores in texturally equilibrated rocks. We designed experiments so that changes in grain boundary energy are reflected in observable grain boundary microstructures. The objectives were pursued using solid-media, high pressure-temperature techniques that have been in continuous development since the project began in 1994.

Results: During the last year we pursued four specific research initiatives:

1) We examined the *permeability of rocks containing small fractions of platy minerals*. We found that minor platy minerals principally resided in open pores and their presence had little effect on permeability.
2) The *permeability of rocks with faceted pore walls* is significantly decreased when a large proportion of crystal/fluid interfaces are faceted. Faceting of pore walls was most prevalent in pores adjacent to platy minerals such as pyroxene, amphibole, mica, etc. and at high fluid fractions. Rocks that contain platy minerals are likely to be poor conductors of fluids, and rocks that do not tend to facet are likely to focus the transmission of fluids.
3) The *fraction of grain boundaries wetted by a fluid* was evaluated for several fluid/rock systems with varying degrees of pore wall faceting as a function of fluid volume. The wetness parameter was shown on theoretical grounds to be important to the seismic and rheological properties of fluid bearing rocks.
4) *Interfacial energy anisotropy* was gauged by differences in the dihedral (wetting) angle formed by supercritical H_2O in contact with grain boundaries representing different degrees and types of lattice misorientation (tilt vs. twist, etc.). An atomic force microscope (AFM) was used to quantify the three-dimensional geometry of individual pores (Figure). The fluid-filled pores

formed along grain boundaries between slabs of quartz with known lattice orientations. Anisotropy was shown to be generally small in the case of quartz: twist boundaries show angles of 55 ± 4° and tilt boundaries 45 ± 3.5°. The results confirmed that the simpler, more traditional (but less accurate) ways of measuring dihedral angles do produce results that can be used with confidence to assess long-range connectivity of fluids.

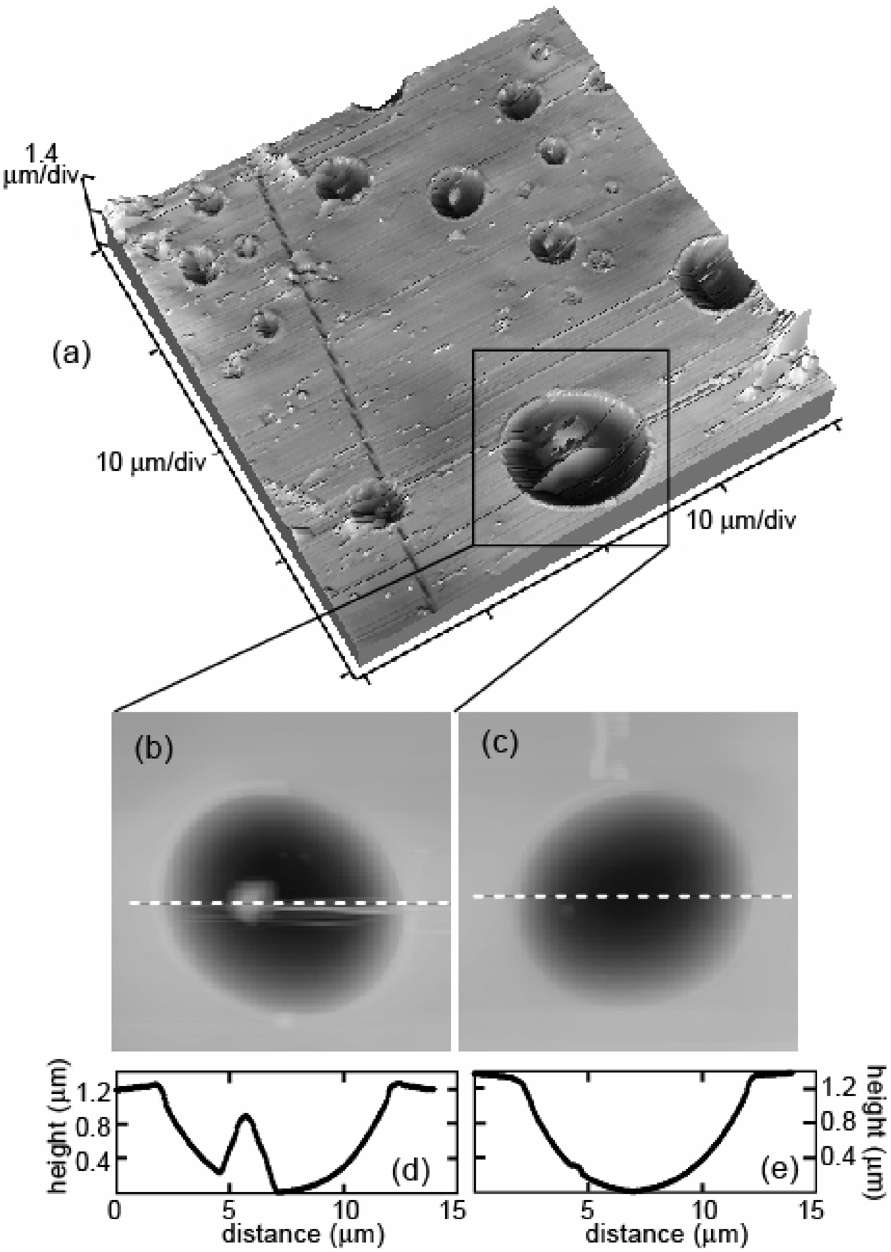

Figure. (a) Three-dimensional AFM image of the lower half of a synthetic grain boundary formed between two quartz slabs showing lenticular-shaped pores that were filled with fluid during the experiment. The pore denoted in the inset is shown in (b) along with its topographic profile (d). The mirror image of this pore that formed on the upper half of the grain boundary is shown in (c) along with its topographic profile (e).

SOCIETY OF EXPLORATION GEOPHYSICISTS

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Grant: DE-FG02-06ER15759

Society of Exploration Geophysicists' Annual Meeting Workshop

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Objectives: The Society of Exploration Geophysicists' (SEG) Development and Production (D & P) Committee holds a half day workshop each year at the Annual Meeting. It is traditional for the topic of this workshop to be "The Best of the D & P Forum". The D & P Forum is a major SEG function comprised of three or four days of scientific papers on a narrow subject of interest to society members. The workshop is comprised of seven or eight papers from this three or four day event.

Project Description: In May of 2005 the D & P Forum topic was "What's to be Gained from Seismic Loss?" This was an excellent three and a half days focused on the nature of seismic attenuation and the information that can be extracted from attenuation—a parameter little used today. The 2005 D & P Workshop was held on Thursday, Nov. 10, 2005 at the SEG Annual Meeting in Houston, Texas using seven papers from the Forum.

Results: Stepping back to look at intrinsic attenuation itself we find that one of the parameters that influences its behaviour is permeability. This property is vital to all tasks that society demands from the earth—CO_2 sequestration, nuclear waste storage, hydrocarbon extraction, and environmental management, to name a few. To date no one has found a way to extract permeability from intrinsic attenuation, first we must understand the role played by permeability, amongst the several other variables, in seismic attenuation. This has been of some interest to the Office of Science. For this reason the Geoscience Program lent its support to the D & P Workshop at the SEG Annual Meeting in 2005. This support allowed the society, a non-profit organization, to admit students free of charge. Roger Turpening and Sven Treitel were co-chairmen and the attendance was overwhelming—standing room only.

The agenda was filled, as mentioned above, with the best papers from the 2005 Forum—papers by Steve Pride, Tapan Mukerji, Richard Gibson, Jerry Harris, James Rickett, Ronny Hofmann, and J.P. Blangy. The subjects ranged from the measurement of intrinsic attenuation at low frequencies in the lab to modeling and interpretation of attenuation. Most important were two papers that examined fluid mobility and velocity dispersion (a property demanded of elastic media when attenuation is present) and the common features of fluid related attenuation-dispersion mechanisms. All papers focused only compressional wave attenuation.

In fact it is important to note the topics that were not addressed at this workshop or the underlying three and a half day forum. Neither meeting contained any papers that addressed the separation of intrinsic seismic attenuation from scattering nor shear wave intrinsic attenuation. These may be related phenomena, i.e., given both compressional and shear wave apparent attenuation, one might be able to isolate the media perturbations causing scattering.
The support from the Office of Science's Geoscience Program made the workshop the "standing room only" success that it was.

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Grant: DE-FG02-04ER15515

Understanding Long-Term Solute Transport in Sedimentary Basins: Simulating Brine Migration in the Alberta Basin, Canada

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Objectives: Develop quantitative estimates of mass transport and fluid residence time in a resource-rich sedimentary basin where previous geochemical and hydrogeologic estimates of residence time have contrasted sharply.

Project Description: Mass transport in deep sedimentary basins strongly affects CO_2 sequestration, ore formation, petroleum migration, and geochemical reactions that affect petroleum reservoir quality, but mass transport in this type of setting is currently poorly understood. This lack of knowledge is highlighted in the resource-rich Alberta Basin, where geochemical studies estimate the residence time of brines in this basin to be hundreds of millions of years, whereas past hydrogeologic models have predicted that these brines could be flushed out less than 5 My. This project will reconcile these two very different estimates through the use of new hydrogeologic models that account for variable-density fluid flow, heat transport, solute transport, dissolution of salt deposits, and sediment compaction. Including brine migration and such geochemical tracers as oxygen isotopes and Cl/Br ratios will allow these models to be calibrated to a significantly greater body of data than previous models.

Results: A large amount of geologic data was assimilated to create the input files necessary for this work, including basin-wide sediment stratigraphy, sediment properties, sedimentation rates, and erosion rates over the last 100 My. The computer code COMPACT was modified to account for dissolution of salt deposits, and modifications allowing sediment decompaction during erosion were initiated. Preliminary models of early basin evolution (sediment deposition and compaction) were constructed and run.

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Grant: DE-FG02-03ER15454

Three-Invariant Non-Coaxial Elastoplastic Constitutive Modeling and Its Implications on the Localization Properties of Rocks

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Objectives: This project investigates the role of the third stress invariant on the localization properties of rocks. The project also investigates the post-localization response of rocks through finite element simulation employing an embedded strong discontinuity enhancement technique.

Project Description: Strain localization is an instability problem commonly observed in rocks undergoing nonhomogeneous deformation. To model this phenomenon the rock is assumed to deform homogeneously until the constitutive relation allows a bifurcation from a smoothly varying deformation field into a highly concentrated deformation band mode. Mathematical theory of plasticity is often employed to characterize the pre-localization constitutive response. Unfortunately, most elastoplastic constitutive models for rocks define yielding in terms of the first two stress invariants only. The third stress invariant accounts for the difference in the yield strength in tension and compression, and for rocks the effect of the third stress invariant on the constitutive response could be significant. This project employs a three-invariant formulation along with nonlinear finite element modeling to define the pre-localization constitutive relation for rocks. Upon detection of deformation band-type bifurcation, the finite element description is enhanced with a strong discontinuity to resolve steep gradients on the deformation band.

Results: Numerical simulations conducted during Year 3 have focused on capturing the effects of the third stress invariant and large deformation on the localization properties of rocks. To make the analysis meaningful, we have chosen the problem of folding of sedimentary rocks and the accompanying damage as a prototype boundary-value problem. Figure 1 shows deformed finite element meshes induced by a horizontal contraction of sedimentary rock strata, producing an asymmetric anticline. Strain localization is detected on the forelimb side of the anticline, consistent with observed fracture density patterns on many anticlines. Since damage zones are important conduits for fluid flow, our ability to identify such zones of damage from numerical simulation represents an important advance in physics-based modeling of rock behavior.

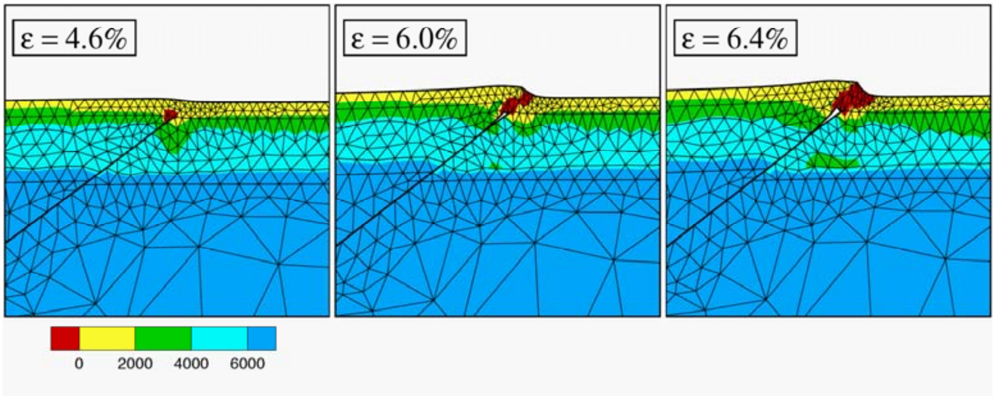

Figure 1. Horizontal contraction and folding of sedimentary rock. The fault is modeled using nonlinear contact mechanics; bifurcation is predicted using a three-invariant Matsuoka-Nakai elastoplastic constitutive model. Reproduced from Sanz et al. (2007), Acta Geotechnica 2(1).

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Grant: DE-FG02-03ER15382

Geochemical Controls on Nuclear Magnetic Resonance Measurements

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Objectives: The objective of our research is to advance the fundamental understanding of the link between the nuclear magnetic resonance (NMR) response and geochemical properties of geological materials.

Project Description: Proton NMR has the potential to provide a wealth of information about the physical, chemical, and biological properties of geological materials. While it is well established that the presence of iron is a dominant factor in determining the NMR response of rocks and soils, we lack an understanding of how the specific mineralogic form and surface distribution of iron affects NMR relaxation mechanisms. In addition, the current models of NMR relaxation in porous materials greatly oversimplify both the geometry of the pore system and the related interaction between the water protons and the paramagnetic iron. We are currently conducting a laboratory-based study of NMR relaxation measurements in water-saturated porous materials in which sample composition, pore structure and geochemical conditions are carefully controlled and determined.

Results: To date we have completed NMR measurements on iron-coated quartz sands with six different mineralogies and have collected NMR measurements of iron-coated quartz sands under changing redox conditions. We measured the NMR time constant, T_2, of samples at chemical equilibrium and as the chemistry of the system changed. In FY 2006 we focused on identifying the minerals formed in samples with changing chemistry and related the NMR measurements from these samples to the NMR measurements of corresponding iron-coated quartz sands in chemical equilibrium. The mineralogy was determined using a variety of spectroscopic techniques including x-ray diffraction spectroscopy and extended x-ray adsorption fine-edge spectroscopy.

Our results show that NMR relaxation times are strongly influenced by the mineralogy of iron present on the pore surface. Measurements of the NMR relaxation time of iron-coated sands under changing redox conditions demonstrate that temporal changes in redox state result in a clear change in NMR relaxation time. Spectroscopic analysis of the samples reveals that these changes in relaxation times correspond directly with changes in mineralogy. These measurements provide a basis for exploring the fundamental geochemical controls on the NMR response of geological materials.

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Grant: DE-FG02-03ER15423

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

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Objectives: The overall objective of this project is to develop rock physics methodologies for numerically simulating mechanical and transport properties of sediment. This will contribute to our long-term goal of discovering and understanding links between geophysical measurements and the underlying rock and pore-fluid properties. We expect that this work will contribute toward better reservoir detection, description, and mapping, as well as better understanding of physical and chemical processes in the crust.

Project Description: A key element of our computational approach is to incorporate realistic grain and pore micro-geometries into the rock models. For many decades, rock models were limited to extreme geometric idealizations that yielded equations that could be solved analytically. For example, elastic rock models consisted of spherical grains or elastic frames filled with ellipsoidal cavities; similarly, transport properties were modeled using networks of round pipes, linked at nodes. In the current project, we are instead using actual micro-geometries taken from thin sections, scanning electron micrographs, and 3D X-ray CT scans; high-performance algorithms are replacing oversimplified analytical solutions of the past. These models better represent actual rock properties and allow us to explore how changes to the microstructure, resulting from processes such as compaction and diagenesis, impact the mechanical and transport properties.

Results: One application is to compaction bands (CB), which are thin, tabular structures of decreased porosity and permeability in sandstone that form pervasive arrays that exert substantial fluid-flow effects at scales relevant to production and storage. To accurately model these effects requires knowing CB porosity and permeability, which are difficult to measure directly owing to the thinness (~1 cm) of the bands. Reliable estimates can be obtained, however, by conducting numerical flow simulations on 3-D realizations of the pore structure generated from thin-section images. We demonstrate the efficacy of this computational rock physics approach for CBs exposed in the Aztec Sandstone of southeastern Nevada—an exhumed analog for aeolian aquifers and reservoirs. Calibrated estimates of porosity and permeability from the method match well the available measurements for both the CBs (<10% and <10 mD) and matrix (~25% and ~1,500 mD).

Another application is modeled gas flow at the pore scale, aiming at understanding and simulating geological CO_2 sequestration. We have used 3D digital sandstone samples, initially brine saturated. Partial dissolution of the gas in the aqueous phase and chemical reaction between rock and CO_2 were not included. However, we have calculated the gas surface area which can be used to estimate the dissolution rate of CO_2. We have used our two-phase Lattice-Boltzmann flow simulation. We then calculated the surface area of gas phase during flow. The gas surface area strongly depends on grain sorting. The relation between gas surface area and volume of gas shows very different trends for well-sorted rocks and poorly sorted rocks.

We also explore links among local internal magnetic field from NMR simulation, local fluid velocity distribution from Lattice-Boltzmann flow simulation and the distance transform map (or erosional length) of the pore geometry. The distance function is a geometrical property of the pore space. The motivation is to find systematic relationships between this purely geometrical property and the different internal fields (magnetic field, fluid velocity) that govern the macroscopic NMR and flow transport properties of the rock. Such relationships would help us to improve permeability predictions from the NMR responses. We found that the gradient of local internal magnetic field is closely interrelated to the distance function; however, the local fluid velocity field does not provide any obvious relation to the distance function. The relation depends on the connectedness of the distance function along the backbone of the flow channels within the pore space. We then used the skeleton of the pore geometry, which can be calculated from the distance function field, since the skeleton of pore geometry is the area where the fluid velocity higher. The three local fields (distance function, fluid velocity, and internal field) at the skeleton have possible interrelations. The work so far has been exploratory with applications of different morphological transforms on the pore-space.

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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.

Project Description: We are conducting a broad-based research project to map and characterize structural heterogeneities 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 research comprises three complementary sub-projects: (1) realistic representation in flow simulations of the fundamental structural elements within and between fault zones, with a special focus on capturing continuity and intersections between structures; (2) understanding the impact of compactive deformation bands on background permeability and fluid flow; and (3) development of 2D mechanical models for faults and damage zone structures. 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) Characterization of fault structure, linkage and fluid-flow effects

We are developing methodologies for the geometrical and statistical characterization of fault networks associated with both large (seismic-scale) faults and small (non-seismic-scale) faults. The ultimate objectives of this work are (1) to establish rationales for the assessment of the properties of fracture patterns related to faults (as a function of the fault slip and architecture) and (2) to use these rationales together with field and statistical data to develop realistic fracture patterns to be implemented into generic flow simulators.

The results already obtained include: (1) a comprehensive database for the length and angular relationships between faults and their splays; and (2) detailed field and statistical characterizations of fault damage zones and fault networks that allowed us to propose a new conceptual model for damage zone evolution with fault growth.

We have also investigated the impact of various degrees of fillings of slip surfaces on the upscaled permeability of fault zones in sandstone. The results for open slip surfaces versus partially filled slip bands show 2 orders of magnitude variation in scaled up fault zone permeability in the fault-normal direction and a factor of 2 variation in the fault-parallel direction, models with open slip surfaces corresponding to higher effective permeabilities.

(2) Structural geology and fluid-flow effects of compaction bands

We used a detailed, air photo-based map of compaction bands of an area of more than 30 acres to demonstrate the significance of their effects at scales relevant to reservoir and aquifer production. One telling result is that optimal alignment of an injector-producer well array with the dominant band orientation can increase production efficiency by more than a third. Significant impacts related to the presence of the bands and their dominant trend are apparent: the average pressure drop required to drive flow between wells exceeds that for band-free sandstone by a factor of three and is 10% to 50% higher across the bands versus along them; reservoir production efficiency varies up to 56% for a typical five-spot well array, depending on its orientation relative to the dominant band trend; and contaminant transport away from a point source within an aquifer tends to channel along the bands, regardless of the regional gradient direction. We conclude that accounting for the flow effects of similar compaction-band arrays would prove essential for optimal management of those sandstone aquifers and reservoirs in which they occur. We also tested a new method for permeability estimation from thin section in collaboration with the Stanford Rock Physics group. This research provides independent confirmation of the porosity and permeability reductions that render compaction bands effective baffles to fluid flow.

(3) Mechanical models of faults and damage zone structures

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 stress concentrations can produce secondary opening fractures, deformation bands, and other structures in the fault damage zone. These structures emanate from the sides of faults or slipping interfaces such as pre-existing joints and sedimentary bedding planes. We have investigated different algorithms that address the inherent non-linearity of contact problems and problems with propagating flaws and cracks. The complementarity algorithm provides an efficient alternative because it increases accuracy, enforces the contact constraints strictly, avoids user-defined parameters, reduces the computational time significantly, and significantly improves the convergence of the models. Matlab codes have been written to implement this algorithm and the displacement discontinuity method for solving elastic boundary value problems relevant to faults and their damage zones.

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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 FY2006 was into three areas: (A) micro- and macroscopic studies of the affect of bacteria (those common to AMD environments) on pyrite with and without adsorbed phosphocholine lipid; (B) spectroscopic studies of the pyrite (and isostructural disulfides) oxidation in both the abiotic and biotic environments; and (C) pyrite oxidation when commingled with other common sulfides.

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 research from our laboratory has shown that the adsorption of two-tail lipids of phosphocholine lipids, such as L-α-Phosphatidylcholine, Hydrogenated lipid and 1,2-bis(10,12-tricosadiynoyl)-*sn*-Glycero-3-Phosphocholine on pyrite resulted in a marked decrease in oxidation rate.

All of our prior studies were done in an abiotic environment. We have initiated research to investigate the behavior of these organic overlayers in the presence of bacteria common to AMD environments. Experiments are showing that the organic layers are not only stable in the biotic environment (using both autotrophic and heterotrophic bacteria) and suppress pyrite oxidation, but in addition the adsorbates modify the binding of the bacteria on the pyrite surface. In particular, recent results are suggesting that the application of lipid to a pyrite surface with attached bacteria, results in the displacement of the microbe. These results suggest that the application of phosphocholine lipid to pyrite in the environment may prove to be a future remediation technique. Atomic force microscopy and attenuated total reflection Fourier transform infrared spectroscopy are the primary techniques in this research area.

Vibrational Spectroscopic Study of the Oxidation of Pyrite and Vaesite in Oxidizing Gaseous and Aqueous Environments

The reaction of FeS_2 (pyrite) and NiS_2 (vaesite) gaseous and aqueous oxidizing condition was investigated using Horizontal Attenuated Total Reflection Fourier-Transform Infrared spectroscopy (HATR-FTIR). Vaesite adopts the pyrite structure and a comparison of the oxidation mechanism and reactivity of these isostructural minerals is allowing us to develop a relationship between reactivity and disulfide electronic structure. Isotopic labeling experiments were used to compare the reaction mechanism of pyrite and vaesite oxidation. These experiments have shown for example that while sulfate product is largely derived from water reactant, but the microscopic controls of the reactivity of the two minerals are quite different. Differences in the influence of defects (dominated by the presence of Fe^{III} on pyrite) and in electrical conductivity are being investigated as reasons for these differences.

Study of the Nature and Reactivity of Defects on the Pyrite Surface

A question that is being asked in the present research, is how does the commingling of pyrite with other metal sulfides affect oxidation rates and mechanism? This has profound implications on the rate of pyrite under real environmental conditions. Mine waste and natural occurrences of pyrite often contain an assemblage of sulfide minerals, non-sulfide minerals, and organic material (e.g., coal). To address the influence of the complexity of the waste or natural material, we are investigating the interaction between coexisting sulfide minerals. Few studies have addressed the interaction and possible synergistic interplay that may occur as two or more sulfides are present in the same system. Our working hypothesis is twofold. (1) Hydrogen peroxide and hydroxyl radical formed in the oxidation of pyrite may accelerate the oxidation of other sulfides. (2) Electron transfer between pyrite and other metal sulfides (i.e., galvanic contact) will alter the oxidation rate of the two phases, when compared to the individual and electrically separated phases. Recent experiments have shown that having galena (PbS) in contact with pyrite in a oxidizing aqueous environment, there is a significant reduction in the pyrite oxidation rate. Scanning electron microscopy (SEM) images show that when galena is present the dissolution pits that characterize pyrite oxidization are reduced. Aqueous batch reaction data shows that the amount of Fe released into solution also is reduced under these same conditions consistent with the SEM observation. The galena however oxidizes readily (Pb secondary phases resulting from this process appear on the pyrite). Galena does not oxidize readily under these conditions if it appears alone. Hence, there is a synergistic effect when pyrite and galena are present together. Understanding this process will have great implications on understanding the oxidation of sulfides in important environmental processes, such as acid mine drainage.

TEXAS A&M UNIVERSITY
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Grant: DE-FG02-00ER15033

Experimental and Analytical Studies to Model Reaction Kinetics and Mass Transport of Carbon Dioxide Sequestration in Depleted Carbonate Reservoirs

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Objectives: 1) To determine and model the reaction kinetics of dissolution of carbonate minerals in saline waters under temperature and pressure conditions approximating those in gas-bearing carbonate reservoirs; 2) Study the displacement of natural gas by supercritical carbon dioxide, and 3) Develop appropriate models for application to the sequestration of carbon dioxide in carbonate gas reservoirs.

Project Description: Sequestration of carbon dioxide in depleted gas reservoirs appears to be a viable option, with a possible economic spin-off from the recovery of significant gas reserves. At the elevated temperatures and pressures encountered in reservoirs, carbon dioxide behaves as a supercritical fluid. Under these conditions, little is known regarding the kinetics of calcite dissolution by carbon dioxide, diffusion of carbon dioxide in natural gas, and displacement of natural gas by carbon dioxide. This project is conducting research to better understand these phenomena through experimental determination of the reaction kinetics for calcite dissolution, coefficient of dispersion, and displacement mechanisms in respect to supercritical carbon dioxide at temperatures and pressures typically found in reservoirs. Results will be presented in a manner that can be used in site specific models.

Results: Calcite Solubility in Brines: This study investigated calcite solubility approached from under-saturation in geologically relevant Na-Ca-Mg-Cl synthetic brines (35 to 200 g L^{-1} TDS) at CO_2 partial pressures of ~0.1, 0.5 and 1.0 bar at 25 °C. Stoichiometric (pK^*_{sp}) equilibrium constants ranged from 6.4 to 4.8, decreasing with increasing brine TDS. In general, good agreement was found between measured and predicted solubility data. Evaluation of the Ca^{2+} and CO_3^{2-} activity coefficients with EQPITZER in brines < 100 g L^{-1} TDS yields a mean value of the thermodynamic $pK_{sp} = 8.41 \pm 0.12$ in good agreement with literature data (8.48 ±0.02). However, in more concentrated brines the pK_{sp} values systematically decreased to 8.11 ± 0.02 in the most calcium-rich brines. The deviation was strongly correlated with calcium ion activity and was also observed in magnesium-free solutions. The error can be interpreted as the result of an uncertainty in the calculated activity of the carbonate ion, which occurs in exceedingly low concentrations in these calcium-rich, high $p\mathrm{CO}_2$ brines. As a result, calculated calcite saturation states may erroneously suggest in excess of a 2-fold supersaturation in the most concentrated brines. This should be a consideration in kinetic studies where precise knowledge of near-equilibrium saturation states is critical in evaluating reaction rate constants and reaction orders.

Dissolution Kinetics: This study measured calcite dissolution rates in geologically relevant Na-Ca-Mg-Cl synthetic brines (50 to 200 g L^{-1} TDS). The dissolution rate dependency on brine composition, $p\mathrm{CO}_2$ (0.1 to 1 bar), and temperature (25.0 to 82.5°C) was modeled using the empirical rate equation

$R = k(1-\Omega)^n$ where R is the rate, k and n are empirical fitting terms, and 1-Ω the degree of disequilibrium with respect to calcite. When Ω is defined relative to an apparent kinetic solubility, *n* can be assumed first-order over the range of Ω investigated (Ω = 0.2 to 1.0). Rates increased with increasing $p\mathrm{CO_2}$ as did the sensitivity to brine concentration. At 0.1 bar, rates were nearly independent of concentration (k = 13.0 ±2.0 x 10^{-3} moles $\mathrm{m^{-1}}$ $\mathrm{hr^{-1}}$). However, at higher $\mathrm{CO_2}$ partial pressures rates became composition dependent and the rate constant, *k*, was shown to be a function of temperature, $p\mathrm{CO_2}$, ionic strength, and calcium and magnesium activity. The rate constant (*k*) can be estimated from a multiple regression (MR) model of the form $k = \beta_0 + \beta_1(T) + \beta_2(pCO_2) + \beta_3(I) + \beta_4(a_{Ca^{2+}}) + \beta_5(a_{Mg^{2+}})$. A relatively high activation energy (E_a = 20 kJ $\mathrm{mol^{-1}}$) was measured, along with a stirring rate independence suggesting the dissolution is dominated by surface controlled processes at saturation states Ω > 0.2 in these calcium-rich brines. The addition of 1 g $\mathrm{L^{-1}}$ $\mathrm{SO_4^{2-}}$ resulted in a rate inhibition that was highly sensitive to increasing concentrations of calcium and magnesium. Consequently, even though sulfate concentrations in subsurface formation waters are generally less than that in seawater, at TDS concentrations greater than 200 g $\mathrm{L^{-1}}$, its effect on the rate may be of similar magnitude. These findings provide an opportunity to improve reaction-transport models in carbonate-bearing saline reservoirs, where $p\mathrm{CO_2}$ is >0.1 atm (pH <~6.5), by adding considerably more realistic reaction kinetics.

Gas Displacement Experiments: Experiments were performed to simulate the dissolution of Austin chalk by $\mathrm{CO_2}$ injection. A total of 2.587 moles of carbon dioxide was cycled through the core sample, approximately equal to 30 days of injection in the field. Core porosity was measured using the CT scanner. Results indicate porosity was increased by as much as 2.5%. UCS was reduced by approximately 30% of its original value for specimens subject to dissolution. Displacement experiments were conducted at cell pressures of 1500 psig and temperature of 60°C using a 1 foot long and 1 inch diameter Berea sandstone cores. Pure $\mathrm{CO_2}$ and treated flue gas (99.433 % mole $\mathrm{CO_2}$) were injected into the Berea sandstone core initially saturated with methane at a pressure of 1500 psig and 800 psig respectively. Results from these experiments show that the dispersion coefficient for both pure $\mathrm{CO_2}$ and treated flue gas are relatively small ranging from 0.18-0.225 $\mathrm{cm^2}$/min and 0.28-0.30 $\mathrm{cm^2}$/min respectively. The recovery factor of methane at break-through is relatively high, ranging from 71%-80% of original gas-in-place for pure $\mathrm{CO_2}$ and 90% to 92% OGIP for treated flue gas, the difference resulting from different cell pressures used. Therefore it would appear that, in practice, injection of treated flue gas is a cheaper option compared to pure $\mathrm{CO_2}$ injection.

For the unconfined compressive strength tests, corefloods were first conducted at high flowrates ranging from 5 ml/min to 20 ml/ min, pressures of 1700-1900 psig and a temperature of 65°C. These conditions simulate injecting $\mathrm{CO_2}$ originating from an electric power generation plant into a depleted gas reservoir and model the near well bore situation. Results from these experiments show a 1% increase in porosity and changes in injectivity due to permeability impairment. The cores are then subjected to an unconfined compressive strength test. Results from these tests do not show any form of weakening of the rock due to $\mathrm{CO_2}$ injection.

TEXAS A&M UNIVERSITY
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Grant: DE-FG02-00ER15034

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

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Objectives: Our work focuses on fully integrating fluid flow and seismic data for monitoring injected CO_2 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. The resulting algorithms will be suitable for large-scale field applications.

Project Description: Carbon dioxide sequestration remains a compelling topic as a potential approach for mitigating the effects of greenhouse gases on global warming. One of the most mature and promising technologies is sequestration of CO_2 in known hydrocarbon reservoirs, using modern seismic imaging to monitor CO_2 movement. However, challenges remain, especially over long time scales when geochemical processes have significant influence on both fluid flow and seismic waves. Our work aims to broaden the applicability of seismic monitoring of sequestration by accounting for additional physical and chemical processes affecting CO_2. Effective field applications also require careful, quantitative measures of uncertainty for which we are applying an efficient Bayesian framework for data integration and a novel two-stage Markov Chain Monte Carlo (MCMC) method for uncertainty assessment. These will be incorporated into a systematic workflow that we will validate by analyzing field data from an ongoing enhanced oil recovery pilot project.

Results: Our work to date has focused on two areas: (1) a fast and rigorous compositional streamline formulation of CO_2 injection for modeling subsurface flow and transport, and (2) the improvement of existing seismic models of fractured reservoirs by incorporating pressure changes.

In the streamline work, we have developed a compositional formulation for fast modeling of CO_2 injection with rigorous treatment of compressibility effects (Osako and Datta-Gupta, 2007). Our approach accounts for compressibility effects during both pressure calculations and transport of overall composition/saturation along streamlines. This is done by introducing an ‘effective density’ that accounts for volume changes along streamlines (Cheng et. al., 2006). Fig. 1 shows that these effects are important. In addition, to accelerate calculations, we introduced an ‘optimal’ coarsening algorithm that allows significant time savings.

Our second area of emphasis also aims to provide more efficient algorithms for large scale reservoir models. Specifically, most recently developed theoretical models for the seismic properties of fractured media do not include the influence of pressure and often require the specification of many unknown parameters. We developed a simpler model that allows more straightforward model generation and new insights into rock properties by accurately predicting changes in seismic velocity with pressure.

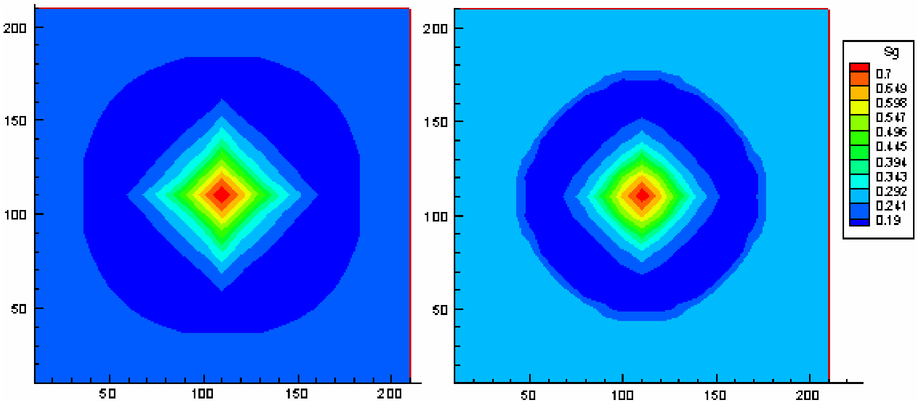

Fig. 1. Spatial distribution of gas saturation with (left) and without (right) compressibility effects (simulation time *t* = 5 days). The difference in these solutions is important for applications such as predicting seismic reflection amplitudes.

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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 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 macroscopic adsorption experiments, X-ray absorption and vibrational sum frequency spectroscopies (XAS, VSGS), and molecular modeling to investigate adsorption at mineral surfaces in different solution compositions. The spectroscopic data identifies types of surface complexes formed. Molecular modeling will support this data 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: Macroscopic experiments and XAS have been completed for adsorption of Sr^{2+}, Co^{2+}, and Pb^{2+} on quartz and gibbsite from the three different electrolytes. Except for Pb^{2+}, the metal adsorption edges in NaCl, $NaNO_3$, and $NaClO_4$ solutions overlapped, suggesting that adsorption is independent of electrolyte-type. Decreasing Pb^{2+} adsorption with increasing ionic strength was attributed to the formation of aqueous lead-chloride complexes. Cobalt sorption at high surface coverage was attributed to surface precipitation of Co-kerolite or Co hydrotalcite. XAS data suggest that Sr^{2+} forms outer-sphere complexes on both surfaces and both Co^{2+} and Pb^{2+} form inner-sphere complexes. At high surface coverage, Co surface precipitates were observed. The data also suggest that Pb^{2+} adsorption to gibbsite is dependent on the electrolyte. In one case, Pb^{2+} adsorbs to one type of surface site; in another, Pb^{2+} adsorbs to two different site types.

Molecular modeling results from the Criscenti group for alkaline earth metals (Mg^{2+}, Sr^{2+}, and Ba^{2+}) in chloride solutions successfully describe metal hydration shells as a function of ionic radii and M-O bond lengths, both in aqueous solution and on the (001) gibbsite surface. Molecular modeling data also suggests that at higher temperature, inner-sphere coordination of alkaline earth metals may be significant. However, macroscopic sorption results for strontium sorption to gibbsite showed an ionic strength effect on sorption at temperatures as high as 90°C suggesting that outer-sphere sorption is still dominant. Thermodynamic calculations suggest that Sr^{2+} sorption is strongly dependent on the change in the ion product of water with temperature.

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Grant: DE-FG02-03ER15430

Predicting Fracture Porosity Evolution in Sandstone

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Objectives: Our goal is to understand how fracture growth and diagenetic alteration interact to create and destroy fracture porosity. We are testing the hypothesis that records of fracture opening can be recovered from fractures formed in the subsurface and that along with fluid-inclusion data and diagenetic and geomechanical models these records can help recover the duration and rates at which fractures open and rock properties change. We use a diagenetically sensitive geomechanical model to investigate how diagenesis affects development of fracture aperture, length, and spatial arrangement.

Project Description: Fluid flow in fractured rock is an increasingly central issue in recovering water and hydrocarbon supplies and geothermal energy, in predicting flow of pollutants underground, in engineering structures, and in understanding large-scale crustal behavior. Yet mechanical models typically neglect cementation in fractures and the rock mass, tacitly assuming that cementation rates are slow relative to fracturing and that fracture growth and fracture filling are decoupled. Our studies show that this assumption is not justified and 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 exploring three topics. Each involves cross-disciplinary efforts in rigorous fracture and diagenesis characterization and geomechanical and diagenetic modeling.

1. 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. Core-based studies are underway in the Piceance basin, Colorado and East Texas basin and outcrop studies in two units. The outcrops allow us to study aspects of fracture size and spatial arrangement that cannot be measured in core.

2. 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.

3. Our research shows that heterogeneous sealing of large, static fractures by carbonate cementation is a widespread phenomenon that blocks fractures that grow concurrently with quartz cementation. 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. Our observations of core and an outcrop analog show that diverse suites of carbonate cements show regional and local variations in composition, distribution, and timing. We delineate these patterns to guide reaction path modeling. These observations also provide a constraint on fracture timing and duration estimates derived from quartz cementation models and observations.

Results: Reconstructions of fracture aperture development tied to burial history analysis indicate fractures grow episodically during long duration loading of the rock mass. We are in the midst of linking reconstructed opening histories to rigorous fluid inclusion and isotopic analysis of cement deposits recording opening histories. Geomechanical models that incorporate diagenesis produce fracture size and spatial arrangement patterns that cannot be accounted for when diagenesis or mechanics are treated as separate, isolated processes. Excellent progress is being made in testing the structural diagenetic model, including completion of two dissertations and two master's theses in 2006 with an additional dissertation and two master theses due to finish in early 2007. Fracture and diagenesis characterization, experiment results and geomechanical and diagenetic modeling explain how fracture aperture (and related porosity) develops through time and is preserved. Crystallographic analysis of bridge structures using electron backscatter diffraction methods is producing interesting results useful for testing the fracture diagenetic model. We developed a new hybrid mechanical fracture growth model that compliments our geomechanical model. This new model successfully explains how fracture size distributions arise in a diagenetic environment. We are also exploring whether fracture aperture increase, as evidenced by multiple cracking events often observed in mineral bridges, is linked with fracture propagation (i.e., is the tip propagating as the fracture gets wider), or if fracture length and height reach their ultimate values early in the deformation history and aperture accumulation is a reflection of increasing remote extension without further fracture propagation.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

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Contract: DE-FG02-00ER15112

Investigation of the Physical Basis for Biomineralization

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Objectives: This project pursues an understanding of the physical mechanisms by which inorganic and organic additives modify the thermodynamics and kinetics of calcite nucleation and growth. The purpose of this project is to: 1) complete work on polypeptides; 2) extend the understanding obtained with these "simple" systems to real protein fractions found in certain marine organisms, and 3) launch a major effort to understand thermodynamic and kinetic controls on nucleation that allow organisms and other biomediated processes to deterministically produce mineral components with specific location, crystallographic orientation, and phase.

Project Description: The research is focused on advancing a fundamental understanding of chemical factors that modify the rate and shape of how minerals form. Our methodology consists primarily of *in situ* force microscopy investigations of growth on calcite surfaces under controlled conditions of temperature and supersaturation. Concomitantly, we are performing molecular modeling to elucidate the stereochemical relationships between additives and crystal surfaces that lead to growth modification. For all of these modifiers, our results have provided significant advances in our quantitative understanding of controls on calcite growth kinetics, morphology, and habit. These new (and forthcoming) insights have numerous applications to both basic and applied scientific needs.

Results: During FY06, we made findings in three research areas: 1) Biomolecular and impurity controls on growth; 2) Inorganic modifiers of growth; 3) Fundamentals of crystal growth and dissolution.

Peptide controls on calcite mineralization: Polyaspartate chain length affects growth kinetics and acts as a stereochemical switch on morphology (Elhadj et al., 2006a, Crystal Growth Design). Polyaspartate domains are a prominent feature of proteins associated with biogenic carbonates and have been implicated in modifying crystal morphology through specific interactions with step edges. Here we show that the morphology and growth kinetics of calcite are modified in a systematic way when a series of poly-L-aspartates, Asp_{1-6}, are introduced into solution. *In-situ* measurements of step propagation rates by atomic force microscopy show these effects are specific to the crystallographically distinct step types— Asp_1 and Asp_2 have stronger interactions with acute step edges, a crossover occurs for the longer $\mathrm{Asp}_{4,5,6}$ biomolecules that favor stronger interactions with obtuse steps. Independent analysis of Asp_n-step edge interactions by semi-empirical quantum mechanical modeling show the switch occurs because, Asp_n binding, the energy required to dehydrate acute steps is greater than that at the obtuse steps when n = 3-6. Step velocity measurements show that the concentration of Asp_n needed to stop growth scales exponentially and inversely with the calculated binding energies allowing a simple model of Asp_n adsorption to the steps. The findings suggest a process by which small fluctuations in primary structure and solvent interactions near proteins influence calcite shape.

Effects of temperature and transport conditions on calcite growth in the presence of Mg^{2+} (Wasylenki et al., 2005a, GCA). Nanoscale effects of strontium on calcite growth: AFM study in absence of vital effects (Wasylenki et al., 2005b, GCA). These experimental study linked *in situ* measurements of step migration rates for layer growth of calcite at various levels of supersaturation and fluid Sr or Mg concentrations with high spatial resolution analyses of Mg or Sr contents in experimental crystals. Our results show that Sr and Mg have complex and very different behaviors as impurities. Results of these investigations demonstrate the importance of understanding impurity-specific interactions with calcite growth surfaces and transport conditions at the microscopic scale. Despite similar chemical behavior in some systems, Mg and Sr have very different effects on calcite growth.

Mechanisms of classical crystal growth theory explain quartz and silicate dissolution behavior (Dove et al., 2005, PNAS). A complete physical picture that explains widely observed variations in dissolution behavior is lacking and some data show apparent inconsistencies that cannot be explained by the largely empirical kinetic 'laws'. Here we found that mineral *dissolution* can be understood through the same mechanistic theory of nucleation developed for mineral *growth*. In principle, this theory should describe dissolution but has never been tested. By generalizing nucleation rate equations to include dissolution, we arrive at a model that predicts how quartz dissolution processes change with undersaturation from step retreat, to defect-driven and homogeneous etch pit formation. The theory also explains the dissolution kinetics of major aluminosilicates— kaolinite and K-feldspar. In doing so, it provides a sensible origin of discrepancies reported for the dependence of kaolinite dissolution *and* growth rates on saturation state by invoking a temperature-activated transition in the nucleation process (**Fig. 1**). Though dissolution by nucleation was previously unknown for oxides or silicates, our mechanism-based findings are consistent with recent observations of dissolution (i.e. demineralization) in biological minerals. Nucleation theory may be the missing link to unifying mineral growth and dissolution into a mechanistic and quantitative framework across the continuum of driving force.

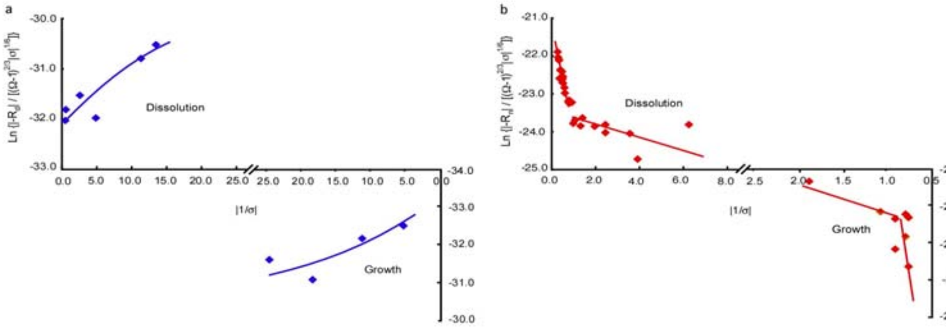

Fig. 1. Theoretical model resolves discrepancy between kaolinite data collected at 80°C (left) and 150°C (right) for both growth and dissolution.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
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Contract: DE-FG02-06ER15786

Frontiers In Biogeochemistry And Nanomineralogy: Studies In Quorum Sensing And Nanosulfide Dissolution Rates

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Objectives: This DOE project is concentrating on two research areas of geochemical importance: mineral-microbe interaction and nanomineralogy. In the field of mineral-microbe interaction, we are examining how bacterial cell-cell communication (quorum sensing) may be involved in geochemical processes. In the field of nanomineralogy, we are conducting a comprehensive study of the dissolution and solubility of nanosulfides as a function of crystal size.

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 is 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 their environment, abiotic or biotic.

Dissolution reactions of galena (PbS) and sphalerite (ZnS) are responsible for a number of environmental problems, such as Zn and Pb releases which result in the incorporation of toxic metals into surface water and groundwater. A detailed understanding of the dissolution of galena and sphalerite 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 these minerals has never been studied experimentally.

Results: In numerous bacteria, *luxS* catalyzes the formation of a quorum sensing signal called AI-2 (furanosyl borate diester). To evaluate the role of *luxS* in *S. oneidensis*, a full gene deletion was constructed. The mutant, DLΔls13, was verified genetically via DNA sequencing and by testing its ability to produce AI-2. Compared to the wild type (WT), the mutant showed a marked reduction of AI-2 production. The mutant showed similar AI-2 production as *Escherichia coli* DH5α, a strain known to produce background levels of AI-2. AI-2 production was restored in the mutant upon complementation via a plasmid encoded *luxS*. With our collaborators at Montana State University, we have started to conduct aerobic and anaerobic biofilm experiments via a flow through system. Whether our biofilm is grown aerobically on a glass surface or anaerobically on a hematite surface, our preliminary results show that DLΔls13's ability to form a biofilm was inhibited compared to wild type after 48 hours.

Preparation of high quality galena nanocrystals of various sizes is a prerequisite to investigate size-dependent dissolution. We have synthesized galena nanoparticles via a Sol-Gel method originally reported by Joo et al. [J. Am. Chem. Soc. 125 (2003) 11100], in which $PbCl_2$ and S are used as the lead and sulfur precursors, respectively, and oleylamine is used as both a surfactant and a solvent. We have synthesized separate and nearly-monodispersed galena nanoparticles in two sizes, ~5nm and ~12nm, have been synthesized, as shown in Figure 1 below. High Resolution Transmission Electron Microscopy (HRTEM) images indicate that the nanocrystals are single crystals with a nearly perfect lattice. The HRTEM investigations also confirm that the galena nanoparticles are truncated by {100}, {110}, and {111} facets. This result is consistent with the growth theory of halite-structured crystals like galena, i.e., relatively fast growth can happen along [111], [100], and [110] directions because of the high intrinsic surface energy of the faces perpendicular to these directions. Preliminary dissolution experiments of the 5nm galena shows that the dissolution rate is much slower than bulk galena. This has important implications in lead transport and bioavailability in ground and surface waters.

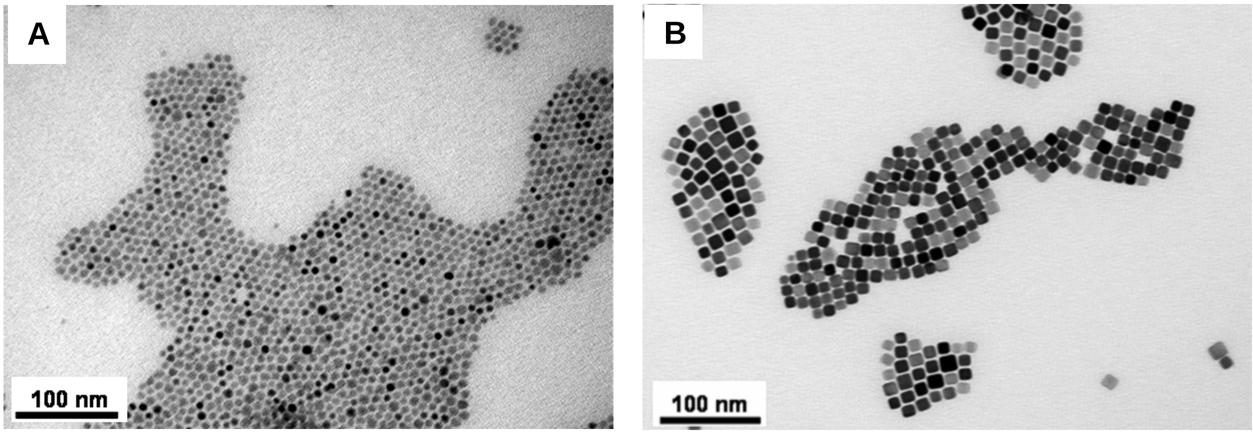

Figure 1. TEM overview images of galena (A) ~5nm and (B) ~12nm nanoparticles.

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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, composition, and location 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 *synthetic* and *natural* grain-cement systems using novel approaches that provide insight into grain-scale mechanics. We will:

1) Develop methods for fabrication of synthetic assemblages of soda-lime silicate beads and both sodium silicate and calcium carbonate cements, and approaches to isolating similar elements from natural systems.

2) Design apparatus to test mechanical properties of synthetic grain-cement assemblages. Use nanoindentation to probe properties such as elastic modulus, hardness, and plasticity of grains and cements in both natural and synthetic systems.

3) Conduct microstructural analysis to relate physical elements of synthetic and natural systems to their structural response to stress in both elastic and inelastic deformation.

4) Develop quantitative relationships describing the stress-strain response of cemented granular systems and incorporation of microscale material response into a DEM.

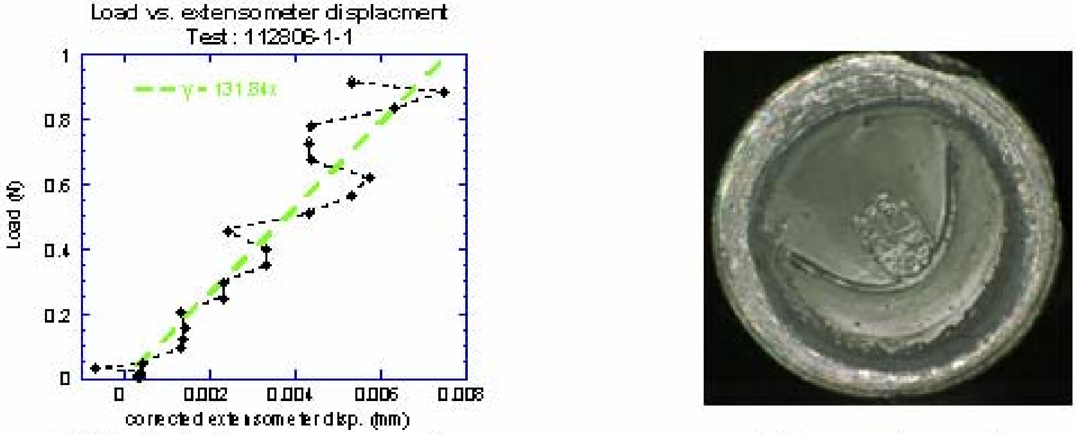
Results: We cemented pairs of 1.0 and 1.5mm diameter soda lime beads together at one contact point with various volumes of three sodium silicate cements (Figure 1a). The formation of cracks and air bubbles as the sodium silicate cements cured was a major challenge, overcome by sonicating assemblages during initial curing.
Fixturing for shear and tensile testing of the bead assemblies was designed, fabricated and tested (Figure 1). Although bubbles and cracks within the cement certainly influenced the first tests, the experiments demonstrate that tensile and shear stiffness and strength of the bonded assemblies can be measured using

both test configurations. *These initial tests show that, even with defects, the cement bonds are surprisingly strong*.

Using instrumented indentation, we measured variations in hardness, modulus, and fracture toughness within quartz grains in a natural sandstone. We had some success correlating inter- and intragranular variations in measured indentation response with crystallographic orientation and internal microstructure. However, we determined that we cannot easily test grain-cement boundaries. Relevant physical parameters therefore will be determined on selected sandstones and related to grain contact strength through measurement of P and S wave velocities. Ultrasonic velocities, and related elastic moduli, vary with grain contact strength.

(a) synthetic bonded sample

(b) tensile test experiment



(c) load-displacement trace from tensile test experiment

(d) fractured sample

Figure 1 – Images and plots associated with synthetic two particle grain-cement sample preparation and testing.

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Grant: DE-FG02-93ER14389

Micro-Analysis of Oxygen Isotope Ratios in Quartz Overgrowths: Cooling Basin Brines and Genesis of MVT Lead-Zinc Deposits

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Objectives:

1. To improve microanalytical techniques for stable isotope analysis.
2. Development of procedures for oxygen isotope analysis by Cameca 1280 ion microprobe.
3. To decipher the complex history of continent-scale migration of hydrothermal brines.
4. To evaluate oxygen isotope thermometry in quartz-overgrowths as a guide to genesis of base metal deposits.

Project Description: This study focuses on microanalysis of quartz overgrowths in the St. Peter sandstone. New techniques employing ion microprobe analysis permit study of oxygen isotope ratio in ultra-small samples. We have contoured $\delta^{18}O$ across single crystals and within individual overgrowths. Mineral zonation patterns provide new insights into processes of water/rock interaction and the local vs. continent-scale migration of basin brines through sandstone aquifers.

Our study centers on sandstone aquifers that carried upwelling heated basin brines responsible for Mississippi Valley Type (MVT) Pb-Zn ore deposits, migration of oil and gas, and widespread K-metasomatism. These processes are linked throughout the Midwestern US with tectonically-controlled gravity-driven flow extending for 100's of kilometers onto the craton. We have focused on the Upper Mississippi Valley district of SW Wisconsin. We are using ion microprobe analysis and oxygen isotope thermometry to test two hypotheses: 1) quartz cements formed from far-traveled brines from the Illinois Basin and 2) cements formed by locally derived fluids of pedogenic origin. Temperatures will be correlated to the regional groundwater flow model of Arnold et al. (1997). While the local distribution of ores is well known, the larger regional picture of fluid flow in sandstone is difficult to trace because the clean sandstone aquifers are not reactive. Our work shows that quartz overgrowths are a trace, but common occurrence in shallowly buried St. Peter sandstones of Wisconsin and that oxygen isotope compositions can be measured with high accuracy by ion microprobe.

Results: The first CAMECA ims-1280, a large radius multicollector ion microprobe/ secondary ion mass spectrometer, was delivered to our lab, Wisc-SIMS, at the University of Wisconsin in 2005. 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 $\delta^{18}O$ (quartz or zircon) of 0.1 to 0.2‰ for sample volumes that are 100 times smaller (<1 ng) than by single collector ion probe and 10^6 to 10^9 times smaller than possible by laser fluorination/ mass-spectrometry.

Cathodoluminescence imaging is important to identify fine-scale quartz cements for analysis by ion microprobe. In 2006, we installed a new Hitachi SEM and dedicated high sensitivity CL detector (plus EDA, BSE, EBSD). This $375K instrument was funded by NSF (70%) and UW (30%), and is located in Geology, near the ion microprobe and electron microprobe labs.

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; microcrystalline or opaline silica are not observed. Cores of DQ grains were separated from 53 rocks and analyzed by laser fluorination, resulting in an average δ^{18}O of 10.0±0.2‰ (1SD, n=108). Twelve thin sections analyzed by CAMECA 1280 ion microprobe have identical average δ^{18}O(DQ) of 10.0±1.4‰ (1SD, n=90), but range by ~6‰ revealing the true variability (from ~7.2 to 12.8‰), which is 10 times greater than analytical precision of the ion probe. This variability is masked by bulk laser fluorination analysis. Whole rock samples from the same 53 rocks were analyzed by laser fluorination, giving δ^{18}O between 9.8 and 16.7‰ (n=110). Quartz overgrowths in thin sections from 12 rocks were analyzed by ion microprobe and have an average δ^{18}O of 29.3±1.0‰ (Fig. 1, 1SD, n=161). Samples with more cement have higher δ^{18}O(WR). The volume percent of quartz cement, calculated by mass balance, varies from <1 to 21 vol.%. Eolian sandstones average 11 vol.% cement compared to 4% for marine samples.

We investigated two models for quartz cementation. Model 1 hypothesized that quartz overgrowths formed from hydrothermal precipitation by ore-forming brines related to Mississippi Valley Type (MVT) mineralization and that temperatures varied regionally from 110 to 50ºC as cooling brines migrated northward from the Illinois basin onto the Wisconsin arch. Model 2 proposes that quartz overgrowths formed at low temperature as silcretes or during early diagenesis in the vadose zone. The small variability of δ^{18}O(Qt overgrowth) values (Fig. 1) rules out a systematic 60° regional temperature variation that is predicted by groundwater flow modeling for MVT brines in SW Wisconsin (Arnold et al. 1997) and suggests that these syntaxial quartz overgrowths formed as groundwater silcretes at 10-40ºC with δ^{18}O(meteoric water) = -2 and -9‰. The higher % cement in eolian samples is consistent with dissolution of fine grains and abraded grain boundaries, and from increased groundwater pH in a desert environment. These results suggest that δ^{18}O of overgrowths may be a proxy for δ^{18}O(meteoric water) and paleoclimate.

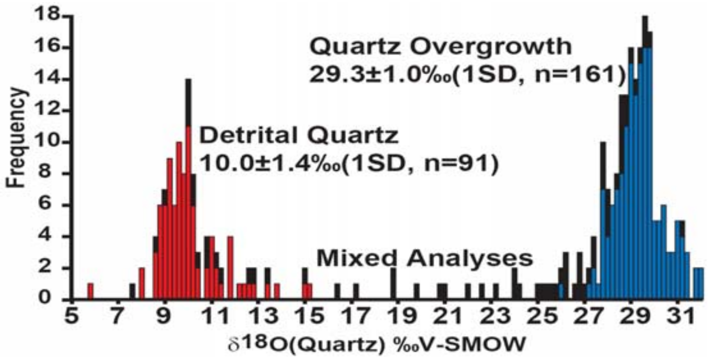

Figure 1. Ion microprobe analyses of detrital quartz and quartz overgrowths, St. Peter sandstone, SW Wisconsin (Kelly et al. 2007).

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Grant: DE-FG02-00ER15058

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: *Effect of shear localization on initiation and growth of compaction bands*
We continue to investigate the interaction between different failure modes in porous sedimentary rocks, and how does it affect fluid flow. Compaction in porous sedimentary rocks involves Hertzian fracture facilitated grain crushing and pore collapse as well as intergranular pressure solution. Recent field and laboratory studies have demonstrated that different modes of strain localization occur in porous sandstones at different stress conditions and that each deformation mode induces significant permeability changes. In particular, shear localization generally provide conduits for pore fluid discharge, whereas compaction bands generally induces significant permeability reduction and provides hydraulic barriers, enabling the development of pore pressure excess.

In many geological settings, different modes of strain localization coexist. Because most natural environments include preexisting heterogeneities that are reactivated during basin evolution or tectonic loading, it is important to determine the type of dynamic hydromechanical behavior expected in a rock that includes a pre-existing fault and is loaded at conditions where an intact porous rock would fail by compaction localization. To address this question, we performed a set of two-step experiments. First, samples of porous Bentheim sandstone samples were deformed at an effective pressure of 5 MPa until shear localization developed in each. Second, each sample was reloaded and deformed at effective pressures of 5-200 MPa. Under 5 MPa confining pressure, the samples showed stable sliding along the pre-existing shear-band. With increasing confining pressure, compaction localization occurred in the pre-faulted rocks. The compaction bands generally initiated at the pre-existing fault and gradually developed into a series of bands that intersect the fault (Figure 1). The experimental data also indicate that the presence of a preexisting shear fault can be very effective in enhancing the local stress and activating various failure modes. The interaction between shear localization and compaction localization significantly alters the pore structure and thus plays an important role in pore pressure excess and earthquake generations in seismogenic zone.

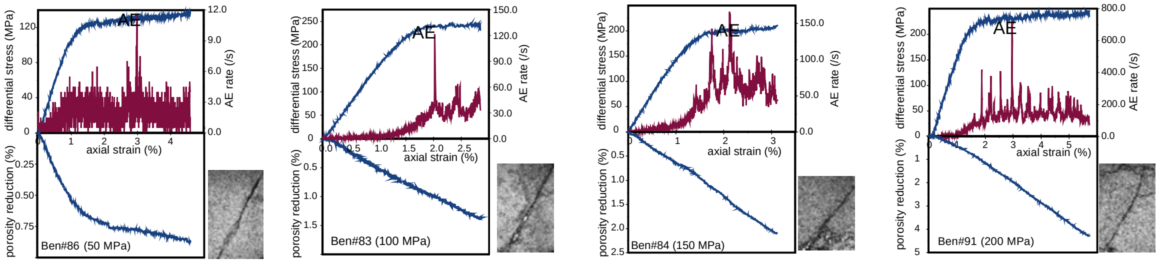

Figure 1 Differential stress (top) and porosity reduction (bottom) versus axial strain for pre-faulted Bentheim sandstone samples deformed at effective pressure of 50, 100, 150 and 200 MPa (from left to right), respectively. Acoustic emission (AE) activity was also measured during deformation (curves in magenta). Micrographs of deformed samples indicate that with increasing confining pressure, multiple compaction localization bands are developed across the pre-existing shear band.

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Laboratory Constraints on the Stability of Petroleum at Elevated Temperatures: Implications for the Origin of Natural Gas

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Objectives: Laboratory experiments are being conducted to constrain geochemical processes that regulate the hydrogen and carbon isotope composition of low molecular weight organic compounds in natural gas and associated aqueous fluids at elevated temperatures and pressures. This information is being used in conjunction with results from field based studies aimed at characterizing microbial ecosystems in co-produced fluids from the Potato Hills gas field in southeastern Oklahoma to assess the role of microbes in the generation of natural gas.

Project Description: Numerous laboratory and field studies have demonstrated the participation of sedimentary minerals and water as reactants and catalysts in chemical transformations associated with the degradation of oil and the formation of low molecular weight organic compounds that constitute natural gas. The occurrence of such processes in natural environments, however, can be difficult to recognize because the composition of organic alteration products may not be substantially different than those produced by thermal cracking. Our research has focused on the use of laboratory experiments to develop diagnostic tools based on hydrogen and carbon isotopes that can identify specific geochemical and biological processes responsible for the formation of natural gas. We have expanded our approach to include an assessment of microbial activity in relatively low temperature (<70°C) natural gas reservoirs in southeastern Oklahoma because microbial activity may represent a key process regulating the chemical and isotopic composition of natural gas. In general, microbial activity under anaerobic conditions at substantial depth within sedimentary basins has not been considered as factor in petroleum degradation and the formation of natural gas, despite the enormous amounts of chemical energy and temperature conditions compatible with life.

Results: Recent results of laboratory experiments have unequivocally demonstrated that carboxyl carbons in aqueous organic acids exchange carbon with aqueous carbonate and may subsequently be reduced to their corresponding alkanes at the relatively reducing conditions that characterize subsurface environments. Accordingly, inorganic carbonate species may contribute to the carbon isotope composition of thermogenic hydrocarbons. Preliminary data from additional experiments have demonstrated that the hydrogen isotope composition C_2-C_5 *n*-alkanes and water at 325°C and 350 bar approach values controlled by equilibrium fractionation. A key implication of this result is that the isotopic composition of natural gas in subsurface environments at elevated temperatures may attain a state of temperature dependent isotopic equilibrium with coexisting aqueous fluids and can be used as an indicator of subsurface temperature conditions.

Phylogenetic analysis of microbial populations in co-produced fluids from the Potato Hills gas field reveals putative syntrophic communities dominated by heterotrophic bacteria and methanogenic Archaea. The bacterial communities consist predominantly of members of the *Clostridiales* and

Thermoanaerobacteriales. Archaeal sequences belong to the *Methanosarcinales* and the *Methanomicrobiales*. Based on sequence similarity, resident microbes are likely thermophiles, with optimum growth at 60-80˚C, which is in line with the optimum growth temperature of the obtained isolates and *in situ* production temperatures of the wells. The data are indicative of a microbial community that is involved with syntrophic fermentation of organic acids, possibly resulting in the production of C_{2+} hydrocarbons in natural gas.

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Grant: DE-FG02-06ER15775

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

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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 focus on geochemical processes occurring at the Santa Barbara oil seeps, we used GC × GC to examine differences in samples from subsurface reservoirs, a proximal seep at the sea floor, and the sea surface overlying the same seep. The chromatograms (Figure 1) revealed that biodegradation controlled compositional changes of reservoir oil during transport to the sea floor, and physical processes controlled compositional changes during transport from the sea floor to the sea surface. The compound classes displaying the highest levels of biodegradation between the subsurface and sea floor include many of the components present at high concentration, such as *n*-alkanes, branched/isoprenoid alkanes, alkyl mono-cyclic alkanes, alkyl benzenes, and alkyl naphthalenes. These losses are attributed to the action of anaerobic prokaryotes in the subsurface. However, sea surface samples showed that a significant portion of the low molecular weight compounds were rapidly removed via evaporation at the sea surface and not dissolution in the water column. The changes described here provide previously unattainable patterns of metabolic preference and were able to disentangle signals for evaporation versus dissolution. These results highlight a better means to quantify the rates and extent of weathering processes for complex hydrocarbon mixtures.

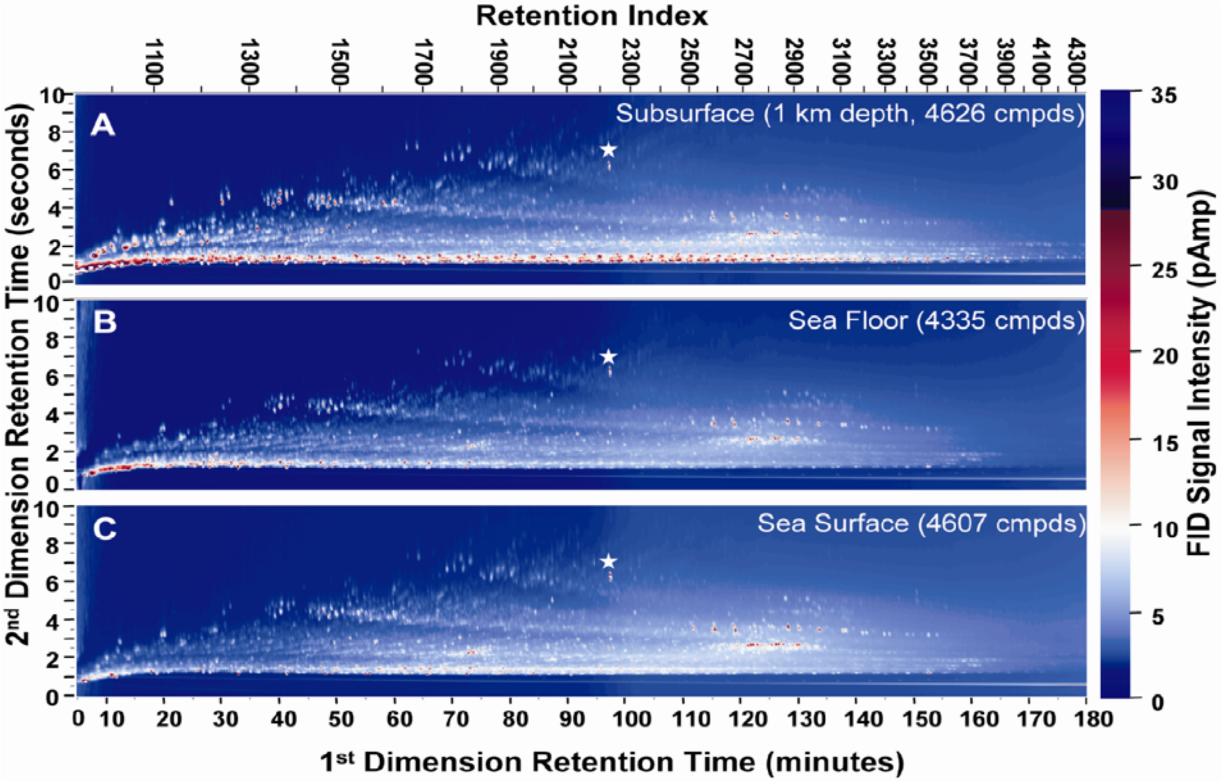

Figure 1. GC×GC-FID chromatograms of (**A**) crude oil from Platform Holly (Well #2342-15; 34°23.370 N by 119° 53.258 W), (**B**) oil collected as it was emerging from the sea floor at Jackpot Seep, and (**C**) a droplet of oil collected as it was spreading on the sea surface above Jackpot Seep. Blue corresponds to the base-plane; individual white markings correspond to small peaks (compounds at low concentrations); red corresponds to large peaks (compounds at high concentrations). The star shown in the middle of the chromatogram denotes the elution position of the internal standard, dodecadihydrotriphenylene.

WRIGHT STATE UNIVERSITY
Department of Chemistry
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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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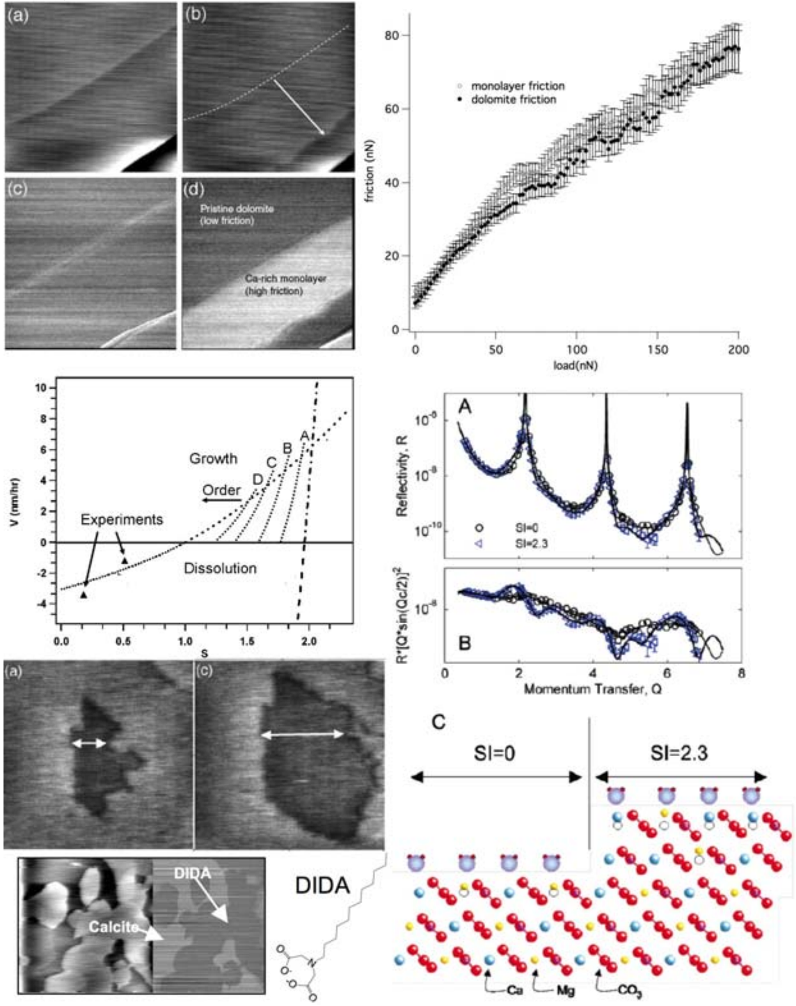
Website: www.chm.wright.edu/higgins/research.html

Objectives: The project objectives at WSU are centered around two major hypotheses: (1) That the surface chemistry of minerals has a direct influence on the sliding resistance (i.e., friction) between a scanning probe microscope tip and mineral surfaces and (2) that the surface chemistry "signal" in friction force microscopy (FFM) may be amplified through adsorption of chelating surfactants to specific metal sites on mineral surfaces.

Project Description: The project at WSU 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 ligand/surfactant synthesis for application in chemical enhancement of surface properties. 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) and force modulation microscopy (FMM). 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 and FMM 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. The results from this project will improve our understanding of the surface chemistry of carbonate minerals relevant to surface and subsurface aquifer systems and on a distance scale (nanometers) that can be computationally modeled at the semi-empirical level.

Results: Monolayer films grown on dolomite from supersaturated aqueous solutions (Ca:Mg = 1 in solution) displayed a distinctly higher friction force, in solution, under the load of an AFM probe when compared with native dolomite surfaces (Fig. 1, top-left). The actual difference in friction was small and only occurred at loads of 50-100 nN, suggesting that the film was more compliant than the dolomite surface under the load of the probe (Fig. 1, top-right). X-ray reflectivity measurements (Fig. 1, middle-right) revealed that the film was significantly strained with Ca and Mg ions displaced vertically from their ideal locations in the surface layer (Fig. 1, bottom-right). The film was also found to be enriched in Ca ($Ca_{0.75}Mg_{0.25}CO_3$) and consisted of two layers (e.g., a bilayer film instead of a monolayer film). AFM dissolution kinetics measurements on this film in comparison with the dolomite substrate revealed that the film solubility (dot-dash line in Fig. 1, middle-left) was considerably higher than dolomite (dotted line in Fig. 1, middle-left), consistent with the observed strain in the film. We predict that as the conditions of film growth are gradually made less favorable (e.g., closer to equilibrium growth solutions), the degree of strain and disorder in the film will decrease as will the film's solubility (A-D lines in Fig. 1, middle-left).



Initial syntheses and testing of alkyliminodiacetates (i.e., chelating surfactants) were carried out to begin evaluation of sorptive properties of these ionic species. Dodecyliminodiacetate (DIDA, structure shown in Fig. 1, bottom-left) was dissolved in alkaline aqueous solution (0.05 mM) and a calcite surface was exposed to this solution. AFM topographic and friction force images (Fig. 1, bottom-left) revealed that the binding of these surfactant molecules to calcite was highly favorable, producing surfactant islands of 1.8 nm height (left image) and that these islands had distinctly lower friction than the native calcite (right image). With future developments of this methodology, it may be possible to map surface chemistry on mineral surfaces using AFM as a nanometer-scale chemical probe. This work is an important step in advancing the state-of-the-art in *in-situ* analytical mineral surface science through the synergistic combination of synthetic chemistry, complexation and surfactant chemistry, and *in-situ* probe microscopy.

UNIVERSITY OF WYOMING
Department of Geology and Geophysics
Laramie WY 82071

Grant: DE-FG02-06ER15825

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

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

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

Results: We have 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, soon to expand to 4 fume hoods as a second laboratory room becomes available. We have produced conductive and photosensitive hematite films, and can now move toware the manufacture of photosensitive tips for the proposed Waveguide Scanning Photocurrent Microscopy (WaSPM). We have apparatus ready to test for light outscattering by these and other tips, and to detect outscattered light. We anticipate that these outscattering and light detection experiments will take place over the summer during the first full year of the project. Figure 1 shows dark current, photocurrent, and chopped-light results for one of our films. This demonstrated the ability of the doped hematite films to generate photocurrents.

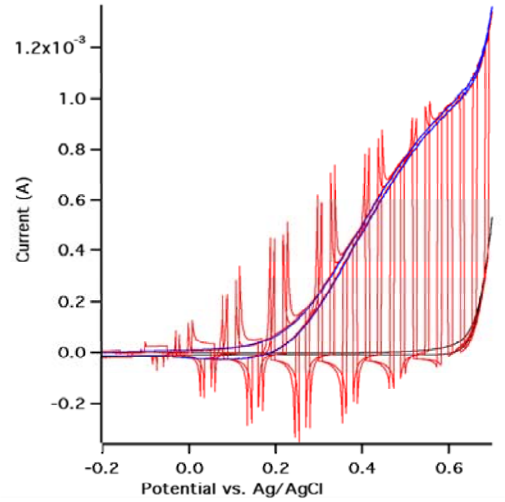

Figure 1: Currents as a function of electrochemical potential at pH 13.6. Dark current, photocurrent, and current transients in chopped light are plotted.

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 has the overall goal of showing that outer-membrane cytochromes from dissimilatory metal-reducing bacteria undergo conformation change due to redox reactions, adsorption, and interaction with other proteins. We compare the electrochemical behavior of isolated proteins with that of whole-cell suspensions. We focus on MtrC and OmcA, two well-characterized outer-membrane cytochromes from *Shewanella oneidensis* MR-1 because these proteins are directly implicated in electron transfer to minerals for an organism that is 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, and optical waveguide lightmode spectroscopy (OWLS), and quartz crystal microbalance (QCM) techniques detect structural changes in adsorbed cytochromes.

Results: Progress so far includes:

1) A series of cyclic voltammetry experiments with films of the outer-membrane cytochromes OmcA and MtrC (protein provided by Liang Shi and Brian Lower, PNNL). Results show that electrons can be exchanged between cytochromes and iron oxide electrodes.
2) A series of cyclic voltammetry experiments with wild-type *Shewanella oneidensis* MR-1 under aerobic and anaerobic conditions, using cultures grown both aerobically and anaerobically.
3) A set of OWLS adsorption experiments for OmcA, showing peak adsorption at between pH 6.5 and 7.0. Adsorption densities are similar for iron oxide (hematite) as compared to aluminum oxide.
4) A set of OWLS adsorption experiments for MtrC, showing peak adsorption at pH 8.5. This is quite different from the results for OmcA, and unexpected given that MtrC and OmcA have isoelectric points that do not differ greatly.

A set of QCM adsorption experiments for MtrC, comparable to the OWLS experiments. QCM includes water bound with the protein in the total adsorbed mass, whereas the OWLS results exclude water in the adsorbed mass. Thus, we find that 78% of the total adsorbed mass at pH 7 is water associated with the protein.

YALE UNIVERSITY
Department of Geology and Geophysics
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Contract: 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 the 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, produce 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 Adanced 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.

Results: We have performed two sets of experiments at the Advanced Photon Source. In the first suite of experiments, we froze model solutions of monodisperse silica spheres (radius, R = 0.14 μm) and deionized water at concentrations of about 0.30 and 0.20 particle volume fraction. We also used one bisdisperse sample with 0.30 total volume fraction composed of equal volumes of silica spheres with R = 0.14 μm and $R = 0.40 μm radius, in order to frustrate colloidal crystallization. We chose silica particles because the density of silica is significantly different from that of water, 2.21g/cm^3 versus 1

g/cm^3 at 0°C. The density difference is important in XPCS because x-rays scatter from electrons, so a difference in density indicates a difference in electron density and therefore stronger scattering. We used deionized water in an attempt to rule out effects due to dissolved impurities. We chose high volume fractions based upon the conclusion of previous studies that most premelting is due to the high-curvature regions. However, we could not attain volume fractions as high as the ones in their study because our solutions had to flow into the sample cell. We found that the premelted layer is probably too thin, even at temperatures very near T_m, to allow a detectable amount of diffusion during experimentally accessible times. Even at very long times no decay is evident. We could not extend our measurements to longer times due to the loss of stability in the CCD detector, which could introduce false decay of the correlation function.

The second suite of experiments was dramatically different. We again froze model solutions of monodisperse silica spheres (R = 0.14 μm) but added salt to the water and lowered the particle concentrations to 0.05 and 0.07 particle volume fraction. Guided by our previous work we added the salt (with a minor colligative effect of 0.016°C) to enhance the thickness of the premelted liquid and this, in concert with reduction of the particle concentration we hypothesized would suppress colloidal crystallization. The results are striking and, to our knowledge, entirely novel. We are observing the restricted brownian motion of particles in ``solid'' ice facilitated by the presence of premelted liquid. Clearly, at very low temperatures the dynamics will vanish.

Finally, it is notable that the system coarsens in time at a given temperature, an example of such is shown in last figure where we see that the dynamics slow down over a period of about an hour. We hypothesize that the particles find themselves in larger volumes of included liquid, such as in veins, nodes and trijunctions and that, due to the freezing process, the Debye length decreases and hence flocculation or colloidal crystallization is facilitated. Thus, the effective particle size increases in time and hence the diffusivity decreases in time.

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Grant: DE-FG02-01ER15173

Plants, Weathering, and the Evolution of Atmospheric Carbon Dioxide and Oxygen

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Objectives:

1. The effect of plants on CO_2 uptake via weathering.
2. Major factors affecting the weathering of organic matter and pyrite in black shales
3. The evolution of CO_2 and O_2 over the past 540 million years
4. Changes in O_2 across the Permian-Triassic boundary (250 Ma).

Project description: Field work in the Cascades Mountains of Washington State was completed to examine the weathering of silicate rocks by conifer vs deciduous trees. This included collection of soils and intrusive and extrusive rocks in direct contact with tree roots of varying ages. Rock surface morphology is being examined and geochemical and petrological analysis of the rocks and cores is ongoing. Long-term laboratory experiments that parallel this fieldwork have been set up successfully.

Examination of major factors that affect the oxidative weathering of organic matter and pyrite in black shales has been done using a diffusion, advection and chemical reaction computer model.

Steady state computer modeling of the evolution of CO_2 and O_2 over Phanerozoic time (past 540 million years) continued with the construction of a combined interactive model for CO_2 and O_2 that emphasizes the rapid recycling of these substances via deposition, uplift and erosion.

A time–dependent model for O_2 was constructed to track changes in atmospheric O_2 across the Permian-Triassic boundary. This spans the time of the greatest extinction of life.

Results: Bulk soil chemistry suggests that the weathering of granitic rocks by conifers may be more rapid than that by maple and aspen trees. This has major bearing on the evolution of atmospheric CO_2 because the rise of angiosperms between 130 and 80 million years ago may or may not have had an important effect on atmospheric CO_2 and its uptake during silicate weathering. However, our continuing studies of the rock-root interface and laboratory experiments are needed to check this very preliminary result.

The results of our black shale weathering model indicate that the major factor affecting the uptake of atmospheric O_2 during weathering of reduced carbon and sulfur is the uplift and exposure to the atmosphere of the rocks, and not changes in atmospheric oxygen.

Use of new carbon isotopic data and consideration of rapid recycling leads to the conclusion that a secondary maximum of atmospheric O_2 occurred near the Silurian/Devonian boundary. This coincided with the first invasion of the land by organisms, chiefly arthropods, and may be a contributing cause for this major evolutionary event.

The major biological extinction at the Permian-Triassic boundary was accompanied by a large but temporally extended drop in atmospheric oxygen. The drop in O_2 was caused primarily by the lack of burial of terrestrially derived organic matter due to the decimation of trees by yet unknown processes.

DOE/OBES Geosciences Research: Historical Budget Summary

(Thousands of dollars)

ON-SITE INSTITUTION	FY02	FY03	FY04	FY05	FY06
Argonne National Laboratory	530	445	480	535	758
Idaho National Laboratory			50	50	50
Los Alamos National Laboratory	1189	1353	1409	1320	963
Lawrence Berkeley National Laboratory	2570	2045	2758	3240	2939
Lawrence Livermore National Laboratory	1644	1523	1598	1335	1141
Oak Ridge Institute for Science and Education					105
Oak Ridge National Laboratory	1340	1190	1250	2075	1750
Pacific Northwest Laboratory	822	875	920	860	910
Sandia National Laboratory	1470	1355	1274	980	975
total, on-site published	9565	8786	9739	10395	9591
total, off-site published	10487	10513	10410	10492	9544
total, operating published	20052	19299	20149	20887	19135
total, equipment	1200	1023			
Total GEOSCIENCES-published	21252	20322	20149	20877	19135
OFF-SITE INSTITUTION					
Alabama, Univ. of (Dixon)					47
American Chemical Society (Brandes)			5		
American Society for Microbiology (Colwell)				5	
Arizona, Univ. of (Roth)			25		
Arizona State Univ. (Shock)	225		239	101	
Arizona State Univ. (Hervig/Williams)	105	108	133	132	135
Boston Univ. (Klein)	127	132	126	130	134
Caltech (Stolper)	150	156	162		167

Caltech (Wasserburg)		225	215	200	
Calif., Univ. of Berkeley (Banfield)				200	200
Calif., Univ. of Berkeley (Banfield)			150	153	123
Calif., Univ. of Berkeley (Helgeson)	182	164	163	167	
Calif., Univ. of Berkeley (Wenk)				150	150
Calif., Univ. of Davis (Rock)	163	171			
Calif., Univ. of Davis (Navrotsky)	166	198	202	194	197
Calif., Univ. of Davis (Rustad)			97	78	82
Calif., Univ. of Davis (Rustad)				136	137
Calif., Univ. of Davis (Casey)	178	109	113	319	
Calif., Univ. of Davis (Rundle)		141	135	143	151
Calif., Univ. of Los Angeles (Harrison/McKeegan)	132	135	148	79	
Calif., Univ. of Santa Barbara (Meiburg)	68	66			
Calif., Univ. of Santa Barbara (Boles)	71	78	86	79	95
Calif., Univ. of Santa Cruz (Wu)	308	388	306	318	327
Calif., Univ. of San Diego (Weare)	125	125	125		269
Chicago, Univ. of (Sutton/Rivers)	525	550	575	600	697
Chicago, Univ. of (Sutton)	129		143	125	148
Chicago, Univ. of (Richter)		99	102	138	143
Clark Univ. (Kudrolli)	45	45	47		59
Colorado School of Mines (Klusman)	161				
Colorado School of Mines (Batzle)		140	117	114	
Colorado School of Mines (Tsvankin)		239	249	150	
Colorado School of Mines (Snieder)					97
Colorado, Univ. of (Rajaram)	106	70	72		
Colorado, Univ. of (Rundle)	136				
Colorado, Univ. of (Spetzler)	153	143	155	55	58

Connecticut, Univ. of (Torgersen)	27	35	33		32
Delaware, Univ. of (Wood)		138	142		
Florida, Univ. of (Ladd)	111	89		155	108
George Washington Univ. (Teng)	143			98	
George Washington Univ. (IPA Lesmes)			225	150	6
Georgia State Univ. (Elliott)	26	21		22	
Gordon Res. Conf. (Kronenberg, Jessell)	10		10		
Gordon Res. Conf. (Hirth)					10
Harvard Univ. (Martin)		85	83	81	96
Houston, Univ. of (Weglein)				101	
Idaho, Univ. of (Nicholl)	54				
Idaho, Univ. of (Wood)		10	10	10	
Idaho State Univ. (Magnuson)					88
Illinois, Univ. of (Kirkpatrick)	209	233	241	248	216
Illinois, Univ. of (Bethke)	117	214	92	270	
Illinois, Univ. of Chicago (Sturchio)		59	60	62	51
Illinois, Univ. of Chicago (Nagy)	150		148	145	
Indiana, Univ. of (Ortoleva)	120	124			
Indiana, Univ. of (Schimmelman)	84	119	112	119	141
Institute for Scientific Information (Zamojcin)	10				
Johns Hopkins Univ. (Garven)	75	89	80	88	124
Johns Hopkins Univ. (Veblen)	155	160	289	205	205
Johns Hopkins Univ. (Sverjensky)	140	140	137	153	158
Johns Hopkins Univ. (Jahren)					101
Lehigh Univ. (Ilton)	115				
Louisiana State Univ. (White)		40	46		
Louisiana State Univ. (Dutrow)		9	9	9	

Maryland, Univ. of (Lower)	20	67			
Maryland, Univ. of (Tossell)	63	79	99	99	
Mass. Inst. Tech. (Harvey)	38				
Mass. Inst. Tech. (Toksoz)	240				
Mass. Inst. Tech. (Evans)	205	209	222	235	304
Mass. Inst. Tech. (Rothman)	152	158	160		160
Massachusetts, Univ. of (Boutt)				145	
Michigan Tech Univ. (Turpening)	11	114		144	
Mineralogical Society of America (Speer)	40	30	20		35
Mineralogical Society of America (Speer)					5
Minnesota, Univ. of (Yuen)	90				
Minnesota, Univ. of (Kohlstedt)			38	39	176
NAS/NRC (Schiffries/DeSouza)	90		90	90	90
NAS (Wessner)	114				
NAS (Linn)					200
Nevada, Univ. of (EPSCOR - McCall)	9	6			
New England Res. (Brown)	204	199	206	100	
New Mexico Inst. Min. Tech. (Wilson)	94	101	108		
New Mexico, Univ. of (Ingber)	71				
NY, City Univ. of CC (Koplik)	95	98	102		107
NY, City Univ. of CC (Makse)		85	85		85
NY, State Univ. of Stony Brook (Schoonen)	102	65	66		87
NY, State Univ. of Stony Brook (Wong)		120	124	128	125
NY, State Univ. of Stony Brook (Lindquist)	64	64		64	87
North Texas, Univ. of (Bagus)			35	35	35
Northwestern Univ. (Rudnicki)	91	120	118	123	113
Northwestern Univ. (Geiger)				3	49

Notre Dame, Univ. of (Maurice)	121	174	178		
Notre Dame, Univ. of (Maurice)			6		
Ohio State Univ. (Lower)			71		
Ohio State Univ. (Allen)			41	42	44
Oklahoma, Univ. of (Elmore)	102	103		47	
Oregon State Univ. (Haggerty)	75				
Oregon State Univ. (Egbert)	80	89	86		98
Penn State Univ. (Elsworth)	99	98			
Penn State Univ. (Brantley)	160	145		174	176
Penn State Univ. (Brantley)			9		
Princeton Univ. (Myneni)	102				
Princeton Univ. (Peters)				114	160
Purdue Univ. (Pyrak-Nolte)	102	105	109		288
Renesselaer Polytech. Inst. (Newell)	44	45	47		
Renesselaer Polytech. Inst. (Watson)	199	199	247	208	215
San Diego State Univ. (Jiracek)	5				
Society of Exploration Geophysics (Smith)					5
South Carolina, Univ. of (Wilson)			50	54	54
Southern California, Univ. of (Maxworthy)	82	84			
Stanford Univ. (Mavko)	151	149	150		
Stanford Univ. (Borja)		99		99	102
Stanford Univ (Knight)		143	139	146	
Stanford Univ. (Nur)	200	200	208	217	
Stanford Univ. (Pollard/Aydin)	257	267	261	261	
Temple Univ. (Strongin)	83	87	91		91
Tennessee, Univ. of (Thonnard)	129	146			
Texas A&M Univ. (Kronenberg)	65				

Texas A&M Univ. (Morse)	128	130	133	135	157
Texas A&M Univ. (Datta-Gupta)	111	130	138	140	143
Texas, Univ. of (Katz)			71	75	78
Texas, Univ. of (Laubach)		196		227	197
Texas, Univ. of Dallas (McMechan/Bhattacharya)		95	96		
Texas Tech Univ. (Graham)	90	9			
Utah, Univ. of (Forster)	50				
Utah State Univ. (Evans)	85				
Virginia Tech (Rimstidt)		114	118	124	
Virginia Tech (Dove)	121	126		178	226
Virginia Tech (Hochella)	88		104	98	122
Wisconsin, Univ. of (Alumbaugh)		101	96		
Wisconsin, Univ. of (Haimson)	110	106			
Wisconsin, Univ. of (Goodwin)				108	
Wisconsin, Univ. of (Valley)	168		204	210	217
Woods Hole OI (Whelan)	197	206	204		
Woods Hole OI (Zhu)	44	46	48	50	61
Woods Hole OI (Seewald)			179	177	184
Woods Hole OI (Reddy)					157
Wright State Univ. (Higgins)		70	71	73	98
Wyoming, Univ. of (Eggleston)	85	52	45	46	
Wyoming, Univ. of (Eggleston)					154
Wyoming, Univ. of (Eggleston)					100
Yale Univ. (Rye/Bolton/Ague)	326	327		157	
Yale Univ. (Wettlaufer)				115	100
Yale Univ. (Berner)	110	110	130	130	130
Other	124				1

OFF-SITE TOTALS	10487	10513	10410	10492	9544