Summary of FY 2005 Geosciences Research

May 2008

U.S. Department of Energy

TABLE OF CONTENTS

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

ARGONNE NATIONAL LABORATORY

Chemistry Division, Building 200
Argonne, IL 60439

CONTRACT: DE-AC02-06CH11357

PERSON IN CHARGE: P. Fenter

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

Paul Fenter (630)252-7053; fax (630)252-9570, Fenter@anl.gov

The objective of this program is to advance the basic understanding of rock-fluid and soil-fluid interactions through experimental studies on atomic-scale processes at the mineral-fluid interfaces. This is crucial to establishing the relation between atomic-scale processes and macroscopic geochemical transport in natural systems. The principle approach is to observe single-crystal mineral surfaces in situ during chemically controlled reactions with fluids using X-ray scattering, standing wave and absorption techniques with high brilliance synchrotron radiation. Phenomena of interest include mineral-water interface structure (including mineral surface structure and the perturbations of near-surface water structure induced by the mineral), adsorption/desorption of metal 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. Progress includes determination of the systematic variation of orthoclase dissolution kinetics with temperature and pH through in-situ and real-time measurements of dissolution at well-defined cleavage surfaces. Surface hydration structures of fluorapatite- and calcite-water interfaces were also determined. An extensive review of the current understanding of mineral-water interface structure as derived from X-ray scattering was published. The interaction of uranyl ions with calcite-water interfaces (both powder and single crystalline) was investigated revealing inner-sphere adsorption of uranyl ions coordinated to surface carbonates at edge sites or adjacent to Ca vacancies. Direct measurements were also performed to probe cation adsorption sites on muscovite. Technical advances in our understanding and application of X-ray scattering techniques were also developed. The ability to directly image ion site distributions on a mineral surface was demonstrated for the first time for ion adsorption at the rutile-water interface. A new understanding of the impact of mineral surface termination on X-ray diffraction data was developed, revealing the capability to determine mineral termination by inspection of X-ray reflectivity data. Initial proof-of-principle measurements established resonant anomalous X-ray reflectivity as a viable probe of ion adsorption at mineral-water interfaces, with both elemental- and interfacial-specificity.

IDAHO NATIONAL LABORATORY
Idaho Falls ID

CONTRACT: ID13727

PERSON IN CHARGE: P. Meakin

Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces

Paul Meakin, Paul.Meakin@inl.gov

Mineral surfaces in natural settings usually exhibit a significant degree of morphological heterogeneity. On scales from the molecular-scale to micron scales, surface roughness can be an important factor in growth, dissolution, and adsorption processes. Despite this fact, relationships between these processes and roughness have not lent themselves to easy quantification because of their inherent complexity. To address this complexity we are studying the dissolution behavior of various mineral surfaces at various length scales of observation accessible by atomic force microscopy (AFM). In FY05, we completed a study of the dissolution of prismatic and rhombohedral quartz surfaces by hydrothermal KOH/H_2O solutions. We characterized and explained the development of surface roughness in terms of multiple overlapping etch pit growth originating at various classes of crystalline defects. By determining rates of growth of individual features, the total dissolution rate of the surface could be estimated for the case where the features overlapped and the surface topography became complex (Yanina, Rosso, Meakin, 2006, Geochimica et Cosmochimica Acta, v. 70, pp. 1113-1127). The prismatic surface dissolves almost two orders of magnitude faster than the rhombohedral surface, mostly due to the difference in the number and the rate of dissolution of extended defects, such as dislocations. Our FY05 research activities also involved studying the reductive dissolution of hematite single crystals by Fe(II), ascorbate, citrate, and using oxalate as an Fe chelate. AFM, transmission electron microscopy, and X-ray photoelectron spectroscopy were used to examine the (001), (012), (113), and low-angle vicinal surfaces before and after dissolution. In this work, we discovered a unique coupling of surface reactivity involving charge transport through the bulk of the crystal. Nanopyramids of hematite grow on the (001) surface due to Fe(II) to Fe(III) conversion at this surface, electron equivalents are transported through the bulk crystal reducing Fe(III) at low-angle vicinal surfaces at which Fe(II) is released. The cycle is broken if either of the surface types is sealed. This novel finding contradicts the long-standing paradigm for iron oxide reductive dissolution developed over the past three decades from wet chemical observations.

LAWRENCE BERKELEY NATIONAL LABORATORY
Earth Sciences Division
Berkeley CA 94720

CONTRACT: CH11231

PERSON IN CHARGE: E. Majer

Center for Isotope Geochemistry

Donald J. DePaolo, 510-486-4975, 510-643-5064, Fax 510-642-9520, depaolo@eps.berkeley.edu or djdepaolo@lbl.gov

High-precision measurements of isotopic ratios in natural materials are combined with mathematical models to understand geochemical processes of interest for energy management. Natural isotopic tracers provide critical calibration of process models used in environmental management, radioactive waste management, geothermal technology development, global climate change, and energy exploration. Isotopic measurements are a means to interrogate complex natural fluid-rock-microbe systems to improve conceptual models of chemical and physical processes. The approach used involves modeling and systematic measurements of natural systems, supplemented by improvements in sampling methodology and measurement techniques. A major focus of the work involves using multi-collector ICP mass spectrometry to investigate natural isotopic variations of Fe, Ca, U, Th, Ra, Sr, Pb, and Cr. Recent results demonstrate that helium production by alpha decay of U and Th in olivine can be used for Quaternary geochronology of basalt lavas. Alpha-recoil effects on U isotopes in natural systems are being used to measure the rates of mineral dissolution in active low-temperature groundwater systems. The same recoil effects provide a means of measure the timescale of sediment transport from bedrock decomposition to deposition on the sea floor. Noble gas concentration measurements are being developed for continental paleotemperature studies, and as a global change monitor. Measurements suggest that Ca isotopes in marine carbonate record past climate and ocean chemistry changes, and that the equilibrium Ca isotopic fractionation factor for calcite - aqueous Ca is 1.0000 ± 0.0001. Modeling studies are aimed at relating isotopic variations to transport; matrix versus fracture flow in fluid-rock systems, atmospheric moisture transport versus surface fluxes, and drainage rates in deep soils of arid regions. Discrepancies between isotopically-measured natural mineral dissolution rates and theoretically predicted rates are being investigated with field studies and numerical models that account for pore scale transport effects.

Reactive Chemical Transport in Structured Porous Media

Tetsu K. Tokunaga, 510-486-7176, tktokunaga@lbl.gov

Transport of solutes through rocks and structured soils is controlled by two basic processes, advection along preferential flow paths, and diffusion from these flow paths into lower permeability matrices. At the larger scale, the evolution of flow path distributions is being analyzed in order to identify and explain statistically predictive behavior. At the smaller scale, this project is quantifying diffusion- and kinetically-controlled processes responsible for reactive transport between flow paths and their bounding

low permeability matrices. We hypothesized that unsaturated flow path distributions in unconsolidated rock deposits will be similar to those occurring in fractured rock formations under low infiltration rates. Our experiments showed that infiltration through rocks conforms to no previously reported behavior in soils, and that flow paths do not progressively converge into fewer flow paths. Instead, a fundamentally different hydraulic structure develops, having a Boltzmann (geometric) flux distribution, with the characteristic scale determined by the characteristic rock size. Although the phenomena are very different, the evolution of flow path distributions and local seepage rate distributions is predictable based on a statistical mechanical model for effectively random trajectories. Our findings are consistent with data on recharge flow paths in deep unsaturated fracture rocks at Yucca Mountain. Several diffusion- and kinetically-controlled characteristics of uranium (U) behavior in sediments were studied. These included transient U(VI) diffusion into bulk sediments, transient U(VI) diffusion within individual sand grains, quantifying U(VI) reduction to U(IV) in response to diffusively supplied organic carbon, and local redox disequilibrium between U(IVI)/U(IV) and Fe(III)/Fe(II). Micro-XANES spectroscopy (GSECARS) was used to quantify U concentrations and oxidation states in all of these studies. U(VI) diffusion into sediments occurs rapidly at nonneutral pH because of weak sorption. However, intragranular diffusion is highly heterogeneous, reflecting variability in mineralogy and micromorphology. U reduction zones can remain very shallow (mm to cm) when reduction is limited by organic carbon diffusion, microbial oxidation of organic carbon, and redox poising when nitrate is also present. Local redox disequilibrium between U(IVI)/U(IV) and Fe(III)/Fe(II) persists over relatively long times. These results collectively address some of the main rate controlling processes underlying U biogeochemical transformations.

Clay Mineral Surface Geochemistry

Garrison Sposito, (510) 643-8297, fax (510) 643-2940, gsposito@lbl.gov

High-precision measurements of isotopic ratios in natural materials are combined with mathematical models to understand the spatial and temporal scales of geochemical processes essential to energy management. Natural isotopic tracers provide critical calibration of process models used in radioactive waste management, geothermal technology development, global climate change analysis, and energy exploration. The kinetic fractionation of ionic and noble gas isotopes by diffusion in aqueous solution is an emerging area of research stimulated by recent advances in experimental technique that allow the measurement of very small isotopic mass dependence in diffusion coefficients. This breakthrough has important implications for improving the accuracy of measurements of the age and origin of pore waters in connection with the identification of sites for geothermal energy generation and for the subsurface sequestration of CO_2 or high-level radioactive wastes. To help interpret current experimental results, we use molecular dynamics (MD) simulations to investigate the influence of solute mass (m) on the self-diffusion coefficients (D) of ions and noble gases in liquid water. These simulations offer a powerful method to investigate mass dependence because solute-solvent interaction potentials are invariant under isotopic substitution, allowing the masses of diffusing atoms to be easily modified. Our simulations reveal the molecular-scale origins and mathematical form of the relation between D and m. For example, the self-diffusion coefficients of lithium, chloride, and magnesium ions were found to be inverse power-law functions of isotopic mass, with exponent b > 0 for lithium and chloride and b = 0 for magnesium, consistent with recent experimental results. Analysis of molecular trajectories in our simulations suggested that b-values are inversely related to collective solute-solvent interactions as represented by

the mean residence time of water molecules in the first ionic solvation shell. If this shell is stable on nanosecond timescales, as in the case of magnesium, isotopic mass affects only the frequency of the vibratory motion of the ion in its solvation-shell "cage", but not its self-diffusion coefficient.

Rate Controls in Chemical Weathering: A Reactive Transport Approach

Carl I. Steefel 510-486-7311; CISteefel@lbl.gov

The purpose 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.

A major focus of this project is to use the X-ray microtomography beamline at the Advanced Light Source (8.3.2) to create 3D images of the pore structure of weathered basalt at the 2-4 micron scale. This information is then used to establish the correlation between porosity and pore connectivity, which control the percolation and diffusion behavior of the material. The microtomography indicates that the chemical weathering process leads to the formation of sinuous channels or macro-pores with a connectivity that approaches 100% once a bulk porosity of about 25-30% is achieved as a result of weathering. Below bulk porosity values of about 16%, the pore network has essentially no connectivity, which severely limits the ability of reactive constituents in the pore fluid (principally dissolved CO_2 and O_2) to penetrate unaltered basalt. Combining conservative tracer experiments using micro-X-ray fluorescence as a mapping tool with the pore connectivity data has led to the development of a diffusion threshold model that captures the observed linear rather than parabolic growth rate of the weathering rinds.

A significant accomplishment of this project is the first measurement of clay (kaolinite) precipitation rates at ambient temperature and pressure (25°C and 1 bar). The results to date demonstrate that, at least at this pH value, kaolinite precipitation and dissolution are fully reversible. The kinetic experiments, by reversing the precipitation and dissolution reactions, also define the log Keq (the equilibrium constant) for this kaolinite as being 7.38. The data are best fitted with a square root dependence of the kaolinite rate on its saturation state (or affinity).

Prediction and Evaluation of Coupled Processes

Kartsten Pruess, k_pruess@lbl.gov

The purpose of the research proposed here is to develop a systematic, rational, and mechanistic understanding of the coupled physical and chemical phenomena that would be induced by injection of CO_2 into aquifers. This will be accomplished by means of conceptual, mathematical, and numerical models that are based on rigorous continuum theories of fluid dynamics, coupled with detailed rock

fracture mechanics and chemical speciation and reaction path analyses. By developing a mechanistic understanding of the relevant processes, this research will provide a sound basis for evaluating the feasibility of CO_2 disposal in different hydrogeologic environments, including fractured rock systems, and will provide engineering tools for the design, implementation, and monitoring of CO_2 disposal systems in aquifers.

The analysis demonstrates how a large-scale CO_2 injection operation results in a gradual increase of aquifer pressure, which could reach close to the lithostatic stress after years of injection. Such aquifer pressure increase will induce a number of hydromechanical interactions and geomechanical responses through changes in the effective stress field in both the injection aquifer and the overlying semi-permeable caprock. A general reduction in the vertical effective stress induces vertical expansion of the aquifer, which can be significant and can be monitored on the ground surface. A relatively slow increase of the aquifer pressure during a typical constant rate injection will induce poroelastic stresses in the caprock which prevent catastrophic mechanical rock failure in the form of hydraulic fracturing through a caprock. Instead, the principal rock mechanics effect will be shear-slip along pre-existing faults and fractures occurring in the lower part of the caprock near the injection aquifer. The analysis shows that although shear-slip would be induced in the lower part of the caprock, it is not likely to propagate a rock failure zone through the upper part of the cap if preventive operational actions are taken. Thus, monitoring of seismic events in the lower part of the cap together with monitoring of ground surface movement are essential for controlling the hydromechanical responses during a CO_2 injection operation.

Molecular-Level Studies of Fe-Al Oxyhydroxide Coating Formation on Quartz

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

High-precision measurements of isotopic ratios in natural materials are combined with mathematical models to understand the spatial and time scales of geochemical processes of interest for energy management. Natural isotopic tracers provide critical calibration of process models used in environmental management, radioactive waste management, geothermal technology development, global climate change, and energy exploration. Isotopic measurements represent a means to interrogate complex natural fluid-rock-microbe systems to improve conceptual models of the chemical and physical processes that affect their behavior. The aim is to advance the state of the art and to use these advances to investigate fundamental issues in geochemistry. Modeling and systematic measurements of natural systems are supplemented by efforts to improve sampling methodologies and measurement techniques. A major focus of the work involves using multi-collector ICP mass spectrometry to investigate natural isotopic variations of Fe, Ca, U, Th, Ra, Sr, Pb, and Cr. Recent results demonstrate that helium production by alpha decay of U and Th can be used to date volcanic eruptions over an age range from a few thousand years to several million years. Alpha-recoil effects on U isotopes in natural systems are being used to measure the rates of mineral dissolution in active low-temperature groundwater systems. The same recoil effects are being investigated as a means of measuring the timescale of sediment transport. Noble gas concentration measurements are being developed for continental paleotemperature studies, and as a global change monitor. Measurements suggest that there is systematic fractionation of Fe and Ca isotopes associated with weathering of silicate rock material. Modeling studies are aimed at relating isotopic variations to reservoir characteristics such as matrix versus fracture flow, to

atmospheric moisture transport and moisture sources, and drainage rates in deep soils of arid regions. Discrepancies between isotopically-measured natural mineral dissolution rates and theoretically predicted rates are being investigated with numerical models that account for pore scale transport effects.

Experimental, Theoretical, and Model-Based Studies of Crystallographically Controlled Self-Assembly During Nanocrystal Growth

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

The growth of ZnS nanoparticles in both water and mercaptoethanol was found to occur mainly by a crystallographically-specific oriented attachment (OA) mode. The growth mechanism determines particle morphology and microstructure. Twins and stacking faults form in the coarsened mercaptoethanol-capped ZnS, whereas more complex, closely spaced twins, stacking faults, and polytypic intergrowths form in coarsened water-ZnS. At long reaction times, diffusion-controlled growth removes surface irregularities arising from OA to yield rounded particles with complex internal structures. The character of the surface ligands affects both phase transition pathway and the temperature of phase transformation. Methanol desorption and rewetting, and water binding cause structural changes, reversible in the case of methanol ligands. Aggregation and disaggregation also cause reversible structural modifications. Dispersed nanoparticles in suspension have a more distorted internal structure than aggregated nanoparticles of the same size. The particles can be switched between these two structural states by changing the aggregation state at room temperature, implying a low activation energy. These results are believed to be the first observations of surface-driven room temperature transitions in nanoparticles. Detailed analysis of the structure of the ZnS nanoparticles via pair-distribution-function (PDF) analysis shows that in addition to a general contraction of the structure there is a type of inhomogeneous internal strain which causes considerable particle stiffening. This stiffening is further evidenced by an increase in the Einstein vibrational frequency for nanoparticle ZnS compared to the bulk. The growth and aggregation of goethite nanoparticles has been studied in the range of 3-200 nm, with both OA and irregular attachment mechanisms observed. Other work has measured the growth of goethite nanoparticles in real time using synchrotron-based wide angle and small angle x-ray scattering (WAXS and SAXS, respectively). OA appears to be the dominant process once particles reach 5 nm in size. At about 50 nm size a continuous classical growth process takes over. Nanoparticle goethite varies in sorption properties compared to bulk crystallites, with uptake less than predicted for a given surface area, and with sorption geometry for several types of ligands differing from the bulk.

Development of Isotope Techniques for Reservoirs

B. Mack Kennedy, 510-486-6451, bmkennedy@lbl.gov

This project develops 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) development of noble gases as phase-partitioning tracers to study water-CO_2 interaction during geologic sequestration and (2) the evaluation, verification, and application of new

isotopic techniques for placing time constraints on groundwater flow. Efficient and safe sequestration of large quantities of CO_2 will require reliable characterization of storage reservoirs and aquifers. Of particular interest is the amount of interstitial pore water, the extent of gas-water interaction, and the integrated gas/water volume ratio. Modeling suggests that gases of different solubility will exhibit chromatographic separation along a flow path with continued gas-water interaction and predicts that details of a chromatographic separation profile for a suite of gases with different solubility could constrain transport models and aqueous phase saturation. During a CO_2 sequestration experiment in the Frio Formation in the Gulf Coast South Liberty Field, Texas, a noble gas and SF_6 cocktail injected as a slug along with CO_2 was monitored and clearly demonstrated the utility of this approach. Differential arrival times for SF_6 and Kr translates to aqueous phase saturation along the flow path of ~22-51%. Groundwater recharge rates and residence times are relevant to water resource management, management of waste and contamination, paleoclimate studies and subsurface water-rock reaction and transport rates. In collaboration with Neil Sturchio, University of Illinois, Chicago and Dr. Zheng-Tian Lu, Argonne National Laboratory, radiochlorine (^{36}Cl) and radiogenic noble gases (^4He and ^{40}Ar) were compared to assess calculated residence ages of groundwater in the Nubian Aquifer, Egypt. The accumulation of radiogenic ^4He confirmed the age progression indicated by the $^{36}Cl/Cl$ ratios, but a flux of external ^4He that is equivalent to ~3.5 times the in situ production rate is required to reconcile the 4He accumulation ages with those determined from ^{36}Cl and a discrepancy between ^4He and ^{36}Cl ages in the oldest sample suggests that the external ^4He flux is not constant along the entire length of the flow path.

Kinetic Isotope Fractionation

John N. Christensen, 510-486-6735, jnchristensen@lbl.gov

Specifically designed experiments were used to measure the ratio of the diffusivities of ions dissolved in water and other solvents (e.g. D_{Li}/D_K, D_{7Li}/D_{6Li}, D_{25Mg}/D_{24Mg}, and D_{37Cl}/D_{35Cl} and D_{41K}/D_{39K}). Our first results have been published this year (1). The measured ratio of the diffusion coefficients for Li and K in water ($D_{Li}/D_K = 0.6$) is in good agreement with published data, verifying the experimental design we use to measure the relative mobility of ions, and by extension, to determine the fractionation of isotopes by diffusion in water. In the case of Li we found measurable isotopic fractionation associated with the diffusion of dissolved LiCl ($D_{7Li}/D_{6Li} = 0.99772 \pm 0.00026$). Our experiments involving Mg diffusion in water found no measurable isotopic fractionation ($D_{25Mg}/D_{24Mg} = 1.00003 \pm 0.00006$). Cl isotopes, though, were fractionated during diffusion in water ($D_{37Cl}/D_{35Cl} = 0.99857 \pm 0.00080$) whether or not isotopes of the co-diffuser (Li or Mg) were fractionated. Initial measurements suggest that Br or I as the co-diffuser with Li rather than Cl has little or no effect on the isotopic fractionation of Li. Preliminary experiments with K diffusion in water indicate measurable K isotopic fractionation, perhaps similar in magnitude to that observed for Cl. Experiments are underway to investigate Li and K diffusion in methanol, a less polar solvent than water. Other experiments are planned for the coming year to measure the relative diffusivities of the noble gasses (e.g. Ne, Kr, Xe) and their isotopes in water. The isotopic fractionation associated with the diffusion of ions in water is much smaller than values Richter found previously for the isotopic fractionation of Li and Ca isotopes by diffusion in molten silicate liquids. A major distinction between water and silicate liquids is that water surrounds dissolved ions with hydration shells, which very likely play an important but still poorly understood role in limiting the isotopic fractionation associated with diffusion. (1) Richter F.M., Mendybaev R.M, Christensen J.N., Hutcheon

I.D., Williams R.W., Sturchio N. C. and Beloso A.D. Jr (2006) Kinetic isotopic fractionation during diffusion of ionic species in water. *Geochimica et Cosmochimica Acta*, v.70(2), pp. 277-289.

Imaging Shear in Rocks

Seiji Nakagawa, 510-486-7894, snakagawa@lbl.gov

Rock is often permeated by fractures or faults that, depending on their permeability relative to the background, serve as either conduits for or barriers to subsurface fluid flow. Determining the permeability of these geological features is difficult using current geophysical techniques, because of the complex physics within the fluid-containing pore space of rocks. In this research, we investigate the seismic properties of fractures and faults to better determine their hydrological properties.

One logical tool for probing the permeability of fractures and faults is Biot's theory of poroelasticity, which describes the dynamic interactions of rock and fluid within the pore space. In recent years, many researchers have realized that heterogeneity in rock can intensify how fluid affects seismic wave propagation. In general, within heterogeneous rock, the stronger the contrast in both permeability and mechanical properties, the more significantly seismic properties are affected. Fractures and faults are a special case of such heterogeneity, exhibiting an extremely wide range of mechanical compliance and hydraulic permeability, even though they occupy a very small volume.

This research consists of (1) laboratory measurements of fracture seismic properties within a poroelastic background, (2) theoretical model development of seismic boundary conditions for poroelastic fractures, and (3) numerical modeling of wave propagation within a poroelastic medium containing single and multiple fractures. The laboratory measurements are conducted using a modified resonant-bar test device that allows us to measure small changes in fracture properties using wave frequencies near one kilohertz. We have developed a theory for seismic wave scattering by a fracture within a poroelastic medium, based upon a previously developed model for nonporoelastic media. By envisioning a fracture as a thin layer of poroelastic medium, the model provides a set of boundary conditions relating the velocity and stress across a fracture as a function of mechanical and hydraulic properties. This model will be used to interpret the experimental results, to examine wave scattering and guided wave propagation along a fracture, and to build numerical models by which to study wave propagation within a complex geological medium containing heterogeneous fractures and faults.

Scattering and Intrinsic Attenuation in Rock with Heterogeneous Multiphase Fluids

Lane R. Johnson, 510 486-4173, lrjohnson@lbl.gov

The computational framework and associated algorithms for performing 2D full-waveform inversion in an anisotropic viscoelastic medium have been developed. The gradient expressions required to update the viscoelastic moduli in a heterogeneous medium with transverse isotropy have been derived. These gradients were derived from the frequency-domain staggered grid finite difference equations. Using these gradients, the complex elastic constants can be updated with a nonlinear optimization method, such as conjugate gradients and Gauss-Newton inversion. By working in the frequency-domain, only the

magnitude and phase fields of the forward propagated strains and the back propagated stresses are required. This is in contrast to time-domain approaches that require storage of the forward propagated strains at all time steps. For realistic 2D and 3D models, storage of the forward propagated strains is not feasible given current computer memory limitations. The key to constructing these gradients is an efficient forward modeling code that computes the frequency response (i.e., magnitude and phase) of realistic 2D and 3D models. During the first two years of this project, we have developed a computationally efficient approach for computing the frequency response using a finite difference time domain (FDTD) code together with a phase sensitive detection (PSD) algorithm. This work, which has been submitted to Geophysical Journal International for publication, demonstrates that the FDTD+PSD approach has significantly lower memory requirements and operation counts for realistic 2D and 3D inversion problems.

Electromagnetic Inversion Project

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

Geophysical imaging of the subsurface continues to be an essential tool in the investigations of critical scientific problems relevant to the DOE's missions in energy and environment. With the advent of the latest generation of distributed computing platforms, geophysical imaging of the subsurface has begun to see critical advances, allowing for the capability to image the Earth at an unparallel level of accuracy and resolution. Even with these advances, both in imaging technology and distributed computing, much work remains in advancing these imaging methods. Of particular importance is the development of faster imaging schemes, and improvements in their efficiencies in analyzing high-density three-dimensional (3D) geophysical data sets; our focus continues to be on EM measurements. Such data sets arise in the exploration of hydrocarbons in complex geological terrains and the characterization of the subsurface to delineate pathways for contaminant transport. To address the efficiency problems we have added an additional level of parallelization in the imaging algorithms over the data space so imaging with multiple transmitters can be distributed over banks of processors, where within each bank, reside copies of the model discretization problem. This data decomposition is highly parallel and now allows for treatment of large-scale data volumes not previously possible and should greatly improve image fidelity. We have also analyzed a strategy to optimize the computational effort required for large-scale modeling within an inversion/imaging framework by separating the inversion grid from the simulation gird. Because we are interested in finely meshed earth models to image realistic structures, the inversion mesh must be designed accordingly. However, the forward modeling operator can act upon a coarser simulation mesh, or a subsection of the inversion mesh, thus providing a significant potential for computational speedup. Initial test results on mesh separation are very encouraging, approaching an order of magnitude reduction in computational time. Finally we continue to optimize the solution of the forward modeling problem using geometric multigrid methods. Our efforts thus far have been on speeding up 3D transient electromagnetic (TEM) field simulation problems, resulting is a factor of 5 reduction in solution time.

Permeability Dependence of Seismic Amplitudes

Steven R. Pride, (510) 495-2823, fax (510) 486-5686, srpride@lbl.gov

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 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.

Over the past year, emphasis was on performing numerical experiments that model/simulate the mesoscopic-flow mechanism. Synthetic rock samples are created on the computer that have spatially variable poroelastic moduli distributed over the pixels. The 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 give 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 is obtained using finite-difference approximations of Biot's poroelasticity equations. For the first time, rigorous stability conditions were obtained for Biot's equations. Depending on the property distribution in the synthetic sample, a wide range of seismic Q versus frequency f curves can be obtained, including constant Q. In particular, 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 $Q(f) = f^H$. Two articles were submitted for publication; one was accepted, and one is still under review.

Imaging Permeability and Fluid Mobility Using Time-Lapse Measurements

D. W. Vasco, (510) 486-5206, dwvasco@lbl.gov

We are 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.

In our second year we worked on imaging techniques for reservoir pressure measurements (Vasco and Karasaki 2006, Vasco 2006a), seismic waveforms (Amodei et al. 2006), and broadband electromagnetic data (Vasco 2006b). In addition, we developed a new approach to examine non-uniqueness associated with the geophysical imaging which we applied to seismic observations (Vasco 2006c). In addition, we investigated the possibility of utilizing both electromagnetic and seismic data to infer reservoir fluid saturations (Chen et al. 2006). We are currently generalizing the technique to include three-phase flow data, such as gas saturations and gas-oil ratios.

References: Amodei, D., Keers, H., Vasco, D., and Johnson, L., 2006. Computation of uniform wave forms using complex rays, Physical Review E, 73, 36704/1-14.

Chen, J., Hoversten, M., Vasco, D., Rubin, Y., and Hou, Z., 2006. A sampling-based Bayesian model for gas saturation estimation using seismic AVA and marine CSEM data, (submitted to Geophysics).

Vasco, D. W., 2006a. A low-frequency asymptotic method for modeling and inversion with an application to transient pressure measurements, (submitted to SIAM Journal on Applied Mathematics).

Vasco, D. W., 2006b. Trajectory-based modeling of broadband electromagnetic wavefields, (submitted to Geophysical Journal International).

Vasco, D. W., 2006c. Invariance, groups, and non-uniqueness: The discrete case, Geophysical Journal International (in press).

Vasco, D. W., and Karasaki, K., 2006. Interpretation and inversion of low-frequency head observations, Water Resources Research}, 42, W05408/1-18.

Air-Derived Noble Gases in Sediments

B.M. Kennedy, 510-486-6451, bmkennedy@lbl.gov

This project seeks to 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. 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. 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. We have also initiated a study of a variety of lab aggregated nanoparticles. We have found that aggregated FeOOH (alpha-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.

Nanoparticle Abundance, Stability, and Transport in the Subsurface

Jiamin Wan, (510) 486-6004, jmwan@lbl.gov

Interest in nanoscale phenomena in the geosciences has rapidly developed, such that we now need to know their impact on various macroscopic processes. The overall abundance of nanoparticles in typical subsurface soils and sediments is unknown. While the unusual properties including high reactivity are most pronounced when they occur as a dispersed phase, theories predict that nanoparticle have a strong tendency to flocculate and aggregate. Although much of their "nano" character is lost upon aggregating into large colloidal units, systematic studies of nanoparticle stability are needed. The importance of natural nanoparticles on facilitating chemical transport can only be evaluated based on knowledge of their inventories and mobility. For these reasons, this project is to understand nanoparticle abundance and stability under environmentally relevant conditions. We collected representative soils from different DOE sites cross the country. Sodium hexametaphosphate (HMP), a strong dispersing agent, was used to release aggregated clays and nanoparticles into suspension, providing an operationally defined maximum inventory of these fine size fractions in sediments. Diluted soil solutions (SS, 1:1 water/soil extraction), simulating chemical conditions in the subsurface, were used for other suspensions of their respective soils, and the released amounts of nanoparticles were regarded as the mobile inventories. Sedimentation by gravity followed by centrifugation was used to separate soil particles into the size ranges of < 2 μm, < 100 nm, $100 \sim 50$ nm, and < 50 nm (defined as nanoparticles). The results show that the inventory of < 50 nm size fraction was consistently at or below the detection limits (0.005 % mass). The 50 to 100 nm size fractions were quantifiable in most HMP dispersions, amounting 0 to 1.47 mass %, and the majority were measured at around 100 nm. The quantities of potentially mobile particles (released by SS) are strongly pH-dependent. Particles of < 100 nm were undetectable in the acidic suspensions (pH < 6.5). The common clay minerals montmorillonite and illite are the dominant crystalline phases in both size fractions (< 2 μm and < 100 nm), and organic carbon was found abundant in some sediment.

Workshop on Frequency-Dependent Geophysical Properties

Kurt Nihei, ktnihei@lbl.gov

A workshop entitled "Rainbow in the Earth: Frequency-dependent Geophysical Properties and their Relationships to Rock Properties at Multiple Scales" was held at Lawrence Berkeley National Laboratory on August 17-18, 2005. Over 60 scientists from universities, national laboratories, and the oil and gas industry attended. This workshop examined the nature and cause of the frequency-dependence of seismic and electromagnetic signals, and discussed approaches for utilizing frequency dependence in geophysical measurements to characterize and image the subsurface for energy and environmental applications. While it is widely appreciated that the seismic and electromagnetic signals that are used to probe the subsurface carry frequency-dependent information (i.e., color) about rock structure and properties over a range of scales, procedures for extracting this information from data are not routinely used in practice. Topics addressed in the workshop included measurements of frequency-dependent properties at the laboratory, borehole, and field scales, the rock physics basis for frequency-dependence, frequency-dependent anisotropy, the use of frequency-dependence in imaging, inversion,

and anisotropy, and estimation, scale information extraction, and active and passive monitoring. The oral and poster presentations were grouped into the following categories: (1) Structures and Scales, (2) Measurements, (3) Theoretical Basis, and (4) Applications.

LAWRENCE LIVERMORE NATIONAL LABORATORY

Energy and Environment Directorate
Chemistry, Materials, and Life Sciences Directorate
Livermore, CA 94550

CONTRACT: SFENG48

PERSON IN CHARGE: F. Ryerson

Investigation of the Physical Basis for Biomineralization

Jim DeYoreo, (925)423-4240, fax: 925-424-4820, deyoreo1@llnl.gov

Through biomineralization, living organisms utilize organic modifiers and molecular scaffolds to control nucleation and growth of both shaped single crystals and crystal composites. The purpose of this project is to explore the physical mechanisms, energetic factors, and stereochemical relationships that enable this process to proceed. Our approach is to apply scanned probe microscopy and molecular modeling to well-defined model systems in order to quantify the effects of growth modifiers on the energetic and thermodynamic parameters controlling crystallization. Our research has focused on calcite growth in the presence of simple amino acids, poly-amino acids, Mg, and Sr. Our work on pure calcite established the thermodynamic and kinetic parameters governing the advance of atomic steps. We found that introduction of simple amino acid enantiomers resulted in a chiral modification of growth morphology due to step-specific interactions altering the step edge energetics. The change in step shape was reflected in the macroscopic crystal habit. Molecular modeling confirmed the step-specific binding and provided a stereochemical basis for the interaction. Changing from simple to amino acids to poly-peptides strongly altered the effects on growth. While Asp(2) had little impact on calcite growth except at high concentrations, Asp(6) was a potent inhibitor even at sub-micromolar concentrations. Introduction of Mg also produced a step-specific modification due to its incorporation into the lattice, but we found that calcite inhibition by Mg was due to a simple shift in solubility rather than changes in step kinetics. Because Mg was incorporated at dramatically different levels at the two types of step edges on calcite, the resulting strain retarded growth near the corners of the calcite rhomb and led to elongation along the {001} axis. In contrast to Mg, Sr accelerated growth at low concentrations and then strongly inhibited it at high concentrations through a step pinning mechanism. These results argue for a model of growth modification in which step-specific interactions on existing crystal faces drives the modification of crystal shape. It contrasts with the accepted paradigm of stereochemical recognition in which the modifier binds to an otherwise unexpressed face of the crystal and stabilizes it thermodynamically.

Mineral Dissolution and Precipitation Kinetics

Kevin G. Knauss, knauss1@llnl.gov

Plug Flow Reactor (PFR) macroscale reactive transport experiments were completed to scale up from the Hydrothermal AFM (HAFM) experiments that we conducted previously. The experiments were designed to investigate the coupled dissolution of calcite and precipitation of strontianite under

conditions similar to those previously investigated over much shorter time and length scales using the HAFM. Fluid chemistry pH changes were dominated by the dissolution of calcite in the PFR run, but subsequent post-mortem of the reacted solids show that significant amounts of at least 2 distinct strontianite compositions were precipitated and coated the calcite grains. These results provide a vehicle for benchmarking our reactive transport simulators.

We also began designing a micro-bending jig and making modifications to the HAFM to permit us to make measurements of mineral dissolution and growth as a function of stress intensity, as well as follow subcritical crack growth in real time. We use an interferometer to measure radius of curvature in the stressed samples. We first built a 5x scale model to test performance and initial results using scaled glass samples suggest that the design functions as expected. We are able to span a range in stress intensity and rate space that overlaps and extends that currently available in the literature. Using the HAFM we will be able to investigate the effect of stress on mineral dissolution and growth and crack growth rates as a function of temperature, solution composition, pH, etc. We added a sample switching valve to the HAFM that permits us to quickly change solution compositions on the fly without restarting the runs.

Reactive Transport of CO$_2$ Rich Fluids

Russell Detwiler, 925-422-6229, fax: 925-423-1057, detwiler1@llnl.gov

Coupled reactive fluid flow and mechanical deformation of rock fractures leads to alteration in fracture transmissivities that are difficult to predict with existing models. Quantifying the impact of these processes on fracture transmissivities over a range of scales is critical to a range of problems including CO$_2$ sequestration and radioactive waste isolation. This project aims to develop scalable models of these coupled processes using an integrated computational and experimental approach.

We use a novel experimental approach to directly measure evolving fracture apertures during experiments. Fractures are fabricated by mating a rough, non-reactive glass surface with a smooth, transparent reactive surface (e.g., potassium dihydrogen phosphate). These 10 x 15 cm fractures allow us to systematically vary parameters such as flow rate and influent fluid chemistry in fractures with identical initial mineral composition and aperture fields. Well-established light transmission techniques provide unprecedented measurements of changing fracture apertures across the entire flow field at high spatial resolutions (80 x 80 micron pixels) during experiments. Recent modifications to the experimental system allow application of a steady confining stress to the transparent fracture surfaces. This leads to dissolution-induced closure of the fracture, which is measured using light transmission and LVDTs.

We have developed an efficient, parallelized, depth-averaged computational model of reactive fluid flow to simulate dissolution-induced aperture alteration. The model explicitly represents the small-scale flow, transport and reaction processes that control local dissolution rates. Using this model, which we have thoroughly evaluated through detailed comparison to experiments, we have simulated dissolution in meter-scale fractures over a broad range of flow rates and surface-reaction kinetics. Results of these computational studies demonstrate several distinct dissolution regimes that include uniform dissolution over the entire fracture (slow kinetics) the formation of complicated ramified channels (intermediate kinetics and flow rates) and single dominant dissolution channels (fast kinetics, slow flow). This

complex range of behaviors in fractures undergoing chemical alteration has potentially significant impacts for larger scale continuum models of these processes in fractured media.

CO$_2$ Sequestration: Measurement of Coupled Silicate Dissolution

Susan Carroll (925) 423-5694, fax (925) 422-0540, carroll6@llnl.gov

Objectives: The objective of this research is to measure dissolution and precipitation rates important to the mineralization of dissolved carbon at conditions relevant to CO$_2$ sequestration. Determination of mineral dissolution and precipitation kinetics is fundamental to the successful disposal of greenhouse CO$_2$-rich gases in aquifers, because reservoir storage capacity is directly related to the conversion rates of CO$_2$ to carbonate minerals. The reaction of CO$_2$ and water with unstable silicate minerals to produce more stable silicates (e.g. clays) and solid carbonates is the natural weathering process which is a dominant part of the long-term global geochemical cycling process. Our kinetic research will feed directly into promising reaction-transport codes that will evaluate aquifer storage of dissolved CO$_2$ and mineral carbonates, and resulting changes in porosity and permeability.

Project Description: Our approach is to conduct single and multi-mineral dissolution and precipitation experiments and reaction transport experiments in Ca-Al-Si-CO$_2$ and CaCO$_3$ systems as a function of pCO$_2$, pH and temperature. Supercritical CO$_2$ experiments simulate the reactive front of CO$_2$ plume and aquifer water and are designed to measure the available source of calcium for storage of CO$_2$ as carbonates and the source of aluminum and silica for the precipitation of secondary minerals that will effect aquifer porosity and permeability.

Results: We focused our work in FY03-FY05 on diopside dissolution experiments as a function of temperature and the extent of saturation as a function of solution composition and temperature. Steady-state dissolution rates of diopside are measured as a function of solution saturation state using a titanium flow-through reactor at pH 7.5 and temperature ranging from 125 to 175˚C. Diopside dissolved stoichiometrically under all experimental conditions and rates were not dependent on sample history. At each temperature, rates continuously decreased by two orders of magnitude as equilibrium was approached and did not exhibit a dissolution plateau of constant rates at high degrees of undersaturation. The variation of diopside dissolution rates with solution saturation can be described equally well with a ion exchange model based on transition state theory or pit nucleation model based on crystal growth/dissolution theory from 125 to 175˚C. At 175˚C, both models over predict dissolution rates by two orders of magnitude indicating that a secondary phase precipitated in the experiments.

The ion exchange model assumes the formation of a Si-rich, Mg-deficient precursor complex. Lack of dependence of rates on steady-state aqueous calcium concentration supports the formation of such a complex, which is formed by exchange of protons for magnesium ions at the surface. Fit to the experimental data yields

$$\text{Rate (mol diopside cm}^{-2}\text{ s}^{-1}) = k \times 10^{-E_a / 2.303RT} \left(\frac{a^2_{H^+}}{a_{Mg^{2+}}} \right)^n$$

where the Mg-H exchange coefficient, $n = 1.39$, the apparent activation energy, $E_a = 332$ kJ mol^{-1}, and the apparent rate constant, $k = 10^{41.2}$ mol diopside cm^{-2} s^{-1}.

Fits to the data with the pit nucleation model suggest that diopside dissolution proceeds through retreat of steps developed by nucleation of pits created homogeneously at the mineral surface or at defect sites, where homogeneous nucleation occurs at lower degrees of saturation than defect-assisted nucleation. Rate expressions for each mechanism (i) were fit to

$$R_i = cb_i \exp\left(\frac{-E_{b,i}}{kT}\right) K_{T,eq} \exp\left(-\frac{\pi \alpha_{T,i}^2 \omega h}{3(\mathbf{k}T)^2}\left|\frac{1}{\ln\Omega}\right|\right)$$

where the step edge energy (α) for homogeneously nucleated pits were higher (275 to 65 mJ m^{-2}) than the pits nucleated at defects (39 to 65 mJ m^{-2}) and the activation energy associated with the temperature dependence of site density and the kinetic coefficient for homogeneously nucleated pits ($E_{b\text{-homogeneous}}$ = 2.59 x 10^{-16} mJ K^{-1}) were lower than the pits nucleated at defects ($E_{b\text{-defect assisted}}$ = 8.44 x 10^{-16} mJ K^{-1}).

Kinetic Isotope Fractionation by Diffusion in Fluids

Ian Hutcheon, (925) 422-8841, fax: (925) 422-3160, hutcheon1@llnl.gov

The overall objective is to document and quantify kinetic isotope fractionations during chemical diffusion in a variety of liquids. One set of experiments was designed to measure the isotopic fractionation of Ca and Li in annealed diffusion couples juxtaposing molten basalt and rhyolite. The experiments confirmed and quantified our previous contention that chemical diffusion in silicate liquids can significantly fractionate isotopes in a mass-dependent way - in the case of ^{44}Ca/^{40}Ca by more than 6‰, and for ^{7}Li/^{6}Li by more than 40‰. Chemical and isotopic fractionation of dissolved species by diffusion in water was also studied using small spherical chambers filled with salt solutions (KCl, LiCl, MgCl$_2$) connected to a much larger water-filled reservoir by a cylindrical diffusion tube. If the dissolved species diffuse through the connecting tube at different rates, the residue of salt in the smaller chamber will become progressively enriched in the more slowly diffusing species. The validity of our experimental design was confirmed by reproducing the already known ratio of the diffusion of K to that of Li. In the case of MgCl$_2$ we found no measurable isotopic fractionation of Mg (<0.5‰ for ^{26}Mg/^{24}Mg) even when less than 5% of the original Mg remained in the inner chamber. If the mass–dependence of Mg isotope diffusion in water had been similar to that in molten silicate, we would have measured a fractionation of about 25‰. In the case of Li, we did measure a 5‰ fractionation of ^{7}Li/^{6}Li when 5% of the Li remained in the inner chamber, but again this is very significantly less than fractionation that would have occurred under similar circumstances in a molten silicate liquid. We interpret the much-diminished isotopic fractionation associated with diffusion in water relative to that in molten silicate liquids as being due to the dissolved ion plus its hydration sphere being the diffusion species in the water experiments. We are testing this suggestion by a new set of diffusion experiments involving dissolved noble gases in water.

Poroelasticity of Rocks and Rock/Fluid Mixture

James G. Berryman, berryman1@llnl.gov

The main thrust 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 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. 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 partially saturated cracks, and/or dry cracks can have a very strong effect on the seismic wave propagation speed and also on wave losses via 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 work in the last two 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 already stated) and some 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.

Electrical Properties of Rocks

Jeffery J. Roberts, (925) 422-7108, fax (925) 423-1057, roberts17@llnl.gov

The electrical properties of fluid-bearing materials are dependent on a number of factors including temperature, porosity, mineralogy, and clay content, as well as fluid content and pore fluid salinity. Electrical measurements are an important tool in probing the physical and chemical properties of rocks in the laboratory and in the field. Because electrical properties are sensitive to so many factors, and because many of these factors are parameters of geophysical interest, careful laboratory measurements are needed to improve the information available from field electrical measurements. The goal of this project is to measure the electrical properties of clay-bearing rocks as a function of confining and pore pressure, temperature, and pore saturant.

In FY05 the research has focused on experimental measurements of dielectric constant, electrical resistivity, and zeta potential of clay-water mixtures. We carried out electrical impedance measurements over the range of 1 Hz to 1 MHz on mixtures of swelling and non-swelling clay samples in NaCl solutions ranging from zero to 0.35 molar. The purpose of the measurements was to try to identify possible differences in the impedance response of the two clays under controlled conditions that could be exploited in the field. Results indicate that fluid salinity strongly affects surface conduction of swelling and non-swelling clays and the two types of clay respond very differently. For both clays, the d.c. conductivity follows Archie's Law down to very low brine concentrations [0.001 molar – 0.01 S/m for Na-montmorillonite (swelling) clay; 0.0001 molar – 0.001 S/m for kaolinite (non-swelling) clay]. At

lower NaCl concentrations the conductivity of the mixture is constant at a level consistent with the relative cation exchange capacity of each clay. For a dispersed clay mixture in brine, once the brine concentration exceeds the threshold conductivity, both the d.c. and complex conductivity is the same as that of a pure brine solution and the clay mixtures are indistinguishable.

Deposition of Carbons

Jeffery J. Roberts, (925) 422-7108, fax (925) 423-1057, roberts17@llnl.gov

An enduring question facing students of the Earth is what happens to rocks during the time leading up to catastrophic failure along a fault. The question has potentially enormous societal import for the obvious reason that an understanding of brittle failure may lead to better estimates of earthquake probabilities. This is a collaborative research project with investigators from Texas A&M (Kronenberg, Karner), The AMNH (Duba and Mathez), and LLNL (Roberts).

The basis of our project is that a systematic study of carbon deposition on fracture surfaces in rocks deformed through laboratory experiments may improve the understanding of processes in rocks that lead to electrical precursory phenomena. Accordingly, our interdisciplinary experimental study investigates the interaction between carbon-bearing fluids and mineral surfaces under crustal conditions. The key goals are to determine if carbonaceous films deposited on freshly generated surfaces affect rock deformation and to test the assertion of Roberts et al. (1999) that rapid deposition of carbon on new surfaces increases electrical conductivity.

Experimental development and building of the apparatus have been conducted at Texas A&M. The project has benefited from significant student involvement (TAMU). The experimental development has encountered a number of major challenges requiring changes of design including the switch to using jacketed hollow cylinders of quartzite under hydrostatic pressure. The new design has been very successful with recovered run products that display numerous well-developed sets of concentric and radial fractures.

We have successfully performed fracture experiments on 11 samples of Sioux quartzite in air, CO, and CO_2. Samples fractured in CO display significant amounts of carbon on new fracture surfaces. The control sample deformed in air contained very little carbon on new fractures produced during deformation. Additional experiments using methane are in progress and data analysis to determine the effect of pore gas composition on rock strength is underway.

The project has resulted in a number of outreach activities including a series of three public lectures held at The AMNH entitled "Earthquakes and Tsunamis."

Rheology of the Earth's Interior

William B. Durham, durham1@llnl.gov

The opportunity to deform minerals and rocks in the laboratory at pressures applicable to Earth's entire upper mantle and into the transition zone is now at hand. We exploit a high-pressure deformation

apparatus called the Deformation-DIA (D-DIA), designed to investigate the rheological properties of mantle materials to pressures of 15 GPa. Emphasis here is on olivine, the most abundant mineral in the upper mantle, and on quantifying the dependence of creep rate (viscosity) on pressure 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 will allow accurate modeling of the geodynamical behavior of Earth's interior. Several series of deformation experiments on olivine have been conducted using the D-DIA at synchrotron radiation facilities, mainly at NSLS, Brookhaven National Laboratory. In general, experiments were carried out at constant displacement rates of ~1×10^{-5} to 4×10^{-4} s^{-1} over shortening strains of $10-15\%$ at temperatures of $1273-1573$ K and pressures of $3-11$ GPa. In our latest experiment we reached 12 GPa at 1500 K, approaching the design limit of the D-DIA. Many of these experiments have been done for purposes of system characterization, calibration, and design, but based on our current measurements, the activation volume for olivine creep is about $6 \pm 2 \times 10^{-6}$ m^3/mol. This result is very preliminary since more analysis on sample microstructure as well as on sample water content is still in progress. Both the D-DIA and the x-ray diffraction techniques for measuring relatively low levels of deviatoric stress represent breakthrough technologies in deformation experiments. Much work to date has been dedicated to advancing the art. The operation of the D-DIA has been so successful that since the initiation of the project almost two years ago, at least three new instruments have been purchased by other earth science investigators, two of them installed at x-ray beamlines at APS (Argonne) and NSLS.

LOS ALAMOS NATIONAL LABORATORY

CONTRACT: NA25396

PERSON IN CHARGE: D. Janecky

High Resolution/High Fidelity Seismic Imaging

Michael Fehler, fehler@lanl.gov

Seismic migration imaging is used to determine the locations and geometric characteristics of structures in the Earth that may be of interest in resource identification, environmental remediation efforts, carbon sequestration, and for basic science applications. Due to the success in obtaining improved images of subsurface geometry from seismic migration imaging, there is now interest in obtaining additional information from images. Conventional Amplitude vs. Offset (AVO) analysis to obtain material properties does not yield good results in geologically complex regions. New methods of obtaining material property information have been proposed and tested. Some of these show promise for yielding valuable information about reservoir characteristics. There is also interest in better understanding the overall quality of images; e.g. what portions of an image derived from real data can be reliably interpreted. We are developing new, improved methods for wave equation migration imaging and in extending these methods for estimating impedance contrasts at boundaries. Our work during the past year has focused on developing a formalism and conducting numerical simulations for obtaining a better understanding of image resolution and how it is impacted by the migration velocity model and the accuracy of the migration operator used in the imaging.

Nonlinear Elasticity in Rocks

Paul Johnson, 505-667-8936, paj@lanl.gov

The 1992 Landers earthquake was a seminal event in earthquake studies. As seismic waves propagated northward from the epicenter, earthquakes occurred as far north as Yellowstone and into Montana coincident with the arrival time of seismic waves (or soon thereafter). The association in space and time of the events and seismic waves led many to speculate that the events were triggered by the seismic waves. Since this remarkable observation, there has been a concerted effort amongst researchers to determine if dynamic triggering of events actually takes place. Studies of the 1999 Hector Mine earthquake confirmed that dynamic wave excitation (seismic waves) triggered seismicity rate increases on the Landers, Hector Mine and Denali Faults, among others. These studies confirm that dynamic and static stress fields are important in triggering in the near field, and dynamic induced wave triggering dominates at larger distances. The physical origin of dynamic triggering remains one of the least understood aspects of earthquake nucleation. The dynamic strain amplitudes from a large earthquake are exceedingly small once the waves have propagated more than several fault radii, of order 10^{-7}-10^{-6}. The question is how do such small strains trigger earthquakes? In our work we hypothesize that the dynamic, elastic-nonlinear behavior of fault gouge perturbed by a seismic wave may be responsible. We base our hypothesis on recent laboratory dynamic experiments conducted in granular media, a fault gouge surrogate. From these we infer that, if the fault is already in a weakened state, seismic waves cause the

fault core modulus to abruptly decrease and weaken further. If the fault is already near failure, the process could induce fault slip. Supporting our hypothesis are recent stick-slip laboratory experiments where elastic wave excitation is applied. The experiments indicate that elastic waves of strains of order 5×10^{-5} can cause shear weakening. Recent seismic observations show that a "triggering threshold" exists at strain amplitudes just over 10^{-6}, corresponding to where we observe the onset of elastic nonlinear behavior in the laboratory. Long range goals include continued testing of the hypothesis with laboratory stick-slip experiments and seismic observations

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

Peter M. Roberts (505-667-1199, proberts@lanl.gov)

This project is investigating the effects of dynamic stress oscillations on the transport behavior of fluids and sub-pore-size particles (colloids) in porous media. Understanding this phenomenon is important because stress waves over a wide range of frequencies (1 Hz to 10 MHz) have been observed to influence porous fluid-flow behavior over a similarly wide range of scale lengths (nm to km). Potential field applications include enhanced oil production from depleted reservoirs, accelerated groundwater remediation, and controlling colloid transport at waste facilities. The project focus is on basic research to characterize the coupling of stress waves to colloidal forces in 2-phase (aqueous liquid plus solid) mass transport systems. The major goals are 1) to obtain improved experimental data for validating and quantifying proposed physical mechanisms, and 2) to define the hydrogeological, geophysical, and physicochemical conditions under which stress waves can alter colloid and fluid transport in porous media. Experimental laboratory studies are being performed at both microscopic and core scales, using two unique Los Alamos facilities. The Dynamic Stress Stimulation Laboratory (DSSL) is used to study low-frequency (1-1000 Hz) stress effects on fluid and colloid transport in porous core samples. The Automated Video Microscopic Imaging and Data Acquisition System (AVMIDAS) is used to visualize colloid behavior in parallel-plate glass cells and porous micro-models under the influence of high-frequency (10 kHz to 10 MHz) acoustic waves. Data from these two systems are compared to investigate possible scaling mechanisms for predicting similar behavior in the Earth's crust. Experimental results demonstrated that acoustics in the range of 500 kHz to 5 MHz and dynamic stress in the range of 10 to 100 Hz can cause changes in colloid detachment rates from solid surfaces, such as pore walls. The behavior of artificial colloid suspensions injected into sandstone cores and in the microscopic cell was observed to depend strongly on the ionic strength of the suspending fluid. Thus, the project is progressing towards understanding 1) the scale range over which colloid interactions can be affected by stress waves and 2) the physicochemical conditions under which stress-wave/colloid coupling is observed.

Summer of Applied Geophysical Experience (SAGE)

W. Scott Baldridge, (505) 667-4338, sbaldridge@lanl.gov

SAGE (Summer of Applied Geophysical Experience) is an ongoing, five-week long, field-based geophysical program for undergraduate- and graduate students, involving teaching and research on basic and applied geophysical problems. Approximately 30 students each year attend SAGE from a wide

range of large and small colleges and universities. The purpose is to enhance students' understanding of geophysics, introduce them to careers in the geophysical sciences and employment opportunities, and conduct leading edge research. Techniques include seismic reflection and refraction, gravity, ground-penetrating radar, electrical resistivity, magnetics, transient electromagnetics, and magnetotellurics.

SAGE 2005 successfully conducted coordinated geophysical surveys on both a small- and large-scale. A small-scale project, intended as a proxy for an environmental or security site, imaged meter-scale manmade excavations at an archaeological site using seismic refraction, ground-penetrating radar, magnetic, and electromagnetic techniques. Although the presence of such excavations was previously questioned by some archaeologists, SAGE 2005 was able robustly to demonstrate their existence, quantify their depths and dimensions, and model them using forward- and inverse techniques. Also imaged were collapsed adobe walls and room blocks. On a larger (kilometer) scale, participants used seismic, gravity, and electromagnetic surveys to investigate a continental rift basin. Seismic and gravity surveys were used to locate a buried, intrarift relay fault which plays an important role in transferring crustal strain between adjacent rift basins. Using geological information, the sense and amount of structural offset was determined, as well as the effect of the fault on the paleolandscape. Electromagnetic surveys, which are very sensitive to the presence of water and clay, were used to determine depth to groundwater and the quality of the water at several sites in the basin. All surveys were undertaken with the assistance of several geophysical companies, who contributed personnel, software, and equipment.

The work and training undertaken at SAGE apply to stratigraphy and structure of continental basins, environmental-restoration and waste-disposal issues, characterization of groundwater and economic resources, CO_2-sequestration, and defense-related methodologies. SAGE is leveraged by funding from the Los Alamos National Laboratory, from the U.S. National Science Foundation, and from a consortium of small and large companies.

Improved Sensitivity Uranium-Series Measurements

Michael T. Murrell, 505-667-4299, mmurrell@lanl.gov

Uranium-series disequilibria techniques are well-established and valuable tools for geochronology and geochemistry. Such measurements have historically been made by decay counting; however, there are considerable advantages in using mass spectrometric techniques for most applications. Our current emphasis is on methods that provide improved sensitivity for U-series studies that include in-situ spatial resolution for geologic materials. We are working towards this goal by combining the multiple collector ion counting of the Isoprobe ICPMS with laser ablation. We are moving from what is currently known about laser ablation MC-ICPS from studies of minerals, metal particles, coral, etc. into new areas such as U-series studies of young volcanics, fracture filling material, hominid fossils, and deep sea corals. This work provides information on the recent evolution of magmatic systems, human evolution, radionuclide transport, and the carbon cycle.

We continue to upgrade to the interface region of the Isoprobe to reduce backgrounds and increase sensitivity. The collimator cone before the hexipole analyzer has been replaced with a retarding lens system and the RF generator for the hexipole has been replaced by a wide amplitude system. We are now able to selectively tune the signal-to-noise within a mass region (e.g. U or Th) to further optimize

sensitivity. We have also installed the Cetac LSX-213 laser ablation system on this instrument to good effect. Our initial work focuses on U-series measurements in high U materials, including zircons from young volcanic rocks such as the Puy de Dôme trachyte. We will also use the laser to examine fracture materials obtained from the NOPAL I uranium ore deposit in Chihuahua, Mexico in order to better understand the extent and timing of radionuclide migration at this analog for Yucca Mtn. Finally, new U-series results from spring deposits in the Death Valley region have been used to reveal the timing and environment of past discharge. The work, done in collaboration with Reed Miner and Steve Nelson from BYU, demonstrates the exciting potential for fossil spring deposits to infer water sources and paleoflowpaths through trace elements, stable, and radiogenic isotopes.

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

Larry Hersman, hersman@lanl.gov

Microbial extracellular reductants produced by strict aerobes are so novel that little is known of 1) their structures, 2) their ability to reduce various Fe(III)(hydr)oxides, 3) the mechanism of reductant-facilitated Fe(III)(hydr)oxide dissolution, and 4) the broader implications and applications of extracellular reductants. We have shown that biologically relevant reducing agents, e.g. ascorbate, can reduce Fe(III) in Fe(III)(hydr)oxides, thereby facilitating dissolution. Our thermodynamic modeling shows that the formation of siderophore-Fe complex can significantly accelerate and influence the reduction-driven Fe(III)(hydr)oxide dissolution. During the proposed reduction-facilitated dissolution of Fe(III)(hydr)oxide, a siderophore binds Fe(II) liberated by a reductant from the Fe(III)(hydr)oxide. Although thought to bind only Fe(III), siderophores also bind Fe(II) tightly with overall stability constants of 1010-1023. Thermodynamic and kinetic factors favor the release of Fe(II) form the mineral surface. This combined with the siderophore's ability to bind Fe(II) will effectively result in the removal of end point inhibition and result in the enhancement of Fe dissolution. Preliminary experimental data from our laboratory strongly support the presence of an augmented effect of siderophore and reductant on the reductive dissolution. When dissolution of ferrihydrite is carried out with Tiron as a simple siderophore model, a pronounced synergistic effect of a reductive/ligand facilitated dissolution (Ascorbate + Tiron) is observed. This synergism mobilizes significantly more Fe than the sum of purely reductive (Ascorbate + Bathophenanthroline) and ligand facilitated (Tiron) dissolution. More importantly, the rate of dissolution is significantly enhanced and sustained overtime. A different biologically relevant reducing agent cysteine promoted dissolution has an identical dissolution profile as that seen for ascorbate promoted dissolution; however, the amount of Fe mobilized and the rate of dissolution both show a remarkable increase. Observed increase suggests that cysteine is possibly a better reducing agent than ascorbate. The presence of a previously undefined augmented effect on iron-oxide dissolution will significantly reshape the current thinking of microbial metabolism in general and more specifically microbial Fe acquisition. This will redefine fundamental research in biogeochemistry and environmental microbiology, and provide a novel foundation for application oriented research, including environmental remediation of toxic/radioactive metal ions and environmental mobilization of Fe as an essential nutrient for agriculture.

Energy Transport in Space Plasmas

S. Peter Gary, pgary@lanl.gov

The long-term goal of this research is to understand the flow of plasma and energy in the near-Earth space environment both from small- and large-scale points of view. The objective of this research is to use plasma theory, simulations, and data analysis to investigate the consequences of small scale fluctuations on the large-scale behavior of space plasmas, to further the understanding of the large-scale structure and evolution of the magnetosphere through theory and simulations, and to improve our understanding of the acceleration and transport of energetic particles within the magnetosphere. . Our most important accomplishment in 2005 was our use of plasma observations from Los Alamos instruments on the ACE spacecraft and hybrid computer simulations to show that four distinct signatures of ion heating by Alfven-cyclotron waves are observed in the solar wind. This agreement between theory and observations offers strong evidence that Alfven-cyclotron heating of protons and alpha particles takes place in the solar wind, and that this process also is likely to contribute to heating of ions in the solar corona.

OAK RIDGE NATIONAL LABORATORY

CONTRACT: OR22725

PERSON IN CHARGE: D. Cole

Nanoscale Complexity at the Oxide/Water Interface

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

This multi-institutional effort is focused on achieving a quantitative understanding of the interface between aqueous solutions and metal oxide nanoparticle and macrocrystal surfaces over a wide range of temperatures and solution chemistries. The pH- and temperature-dependent charging of oxide surfaces by reaction with water, and the association of solution counterions with the charged surface, form an interfacial domain termed the electrical double layer (EDL), which results from a complex interplay of electrostatic and van der Waals forces, quantum effects, lattice strain, ion hydration, hydrogen bonding, and specific binding of solute ions with the surface and one another. The experimental studies in this project are intended to quantify every aspect of the EDL for the selected solid phases and aqueous species, including degree of surface protonation and the total concentrations of counterions within the EDL, mineral surface structure, detailed geometrical information on ions and water molecules, and local bonding environments using non-perturbing, *in situ* measurements wherever possible. Principal investigators at Oak Ridge National Laboratory, Argonne National Laboratory, Penn State, Northwestern, Vanderbilt, Illinois State Water Survey, and their associates, employ a variety of unique approaches to elucidate the sub-angstrom-macroscopic structure and dynamics of the interfacial region, including: (1) surface pH titrations and ion adsorption studies to 300 degrees centigrade using oxide powder suspensions, coupled with temperature-dependent multisite complexation modeling; (2) electrophoresis measurements of oxide powder suspensions to 250 degrees centigrade; (3) synchrotron x-ray standing wave, absorption and reflection studies on single crystal surfaces into the hydrothermal regime; (4) *ab initio* and molecular mechanics calculations, and large-scale molecular dynamics simulations, integrating the results of all experimental approaches; and (5) neutron small angle and quasielastic scattering and reflection for probing the interfacial structure. This research impacts a broad range of DOE mission areas, including catalysis, nanoscience, waste migration, energy production, and biological processes.

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

J. Horita (865) 576-2750; Fax 865-574-4961; horitaj@ornl.gov

The purpose of this research is to conduct quantitative theoretical, experimental, and simulation studies of isotope partitioning of the most fundamental reactions and processes in geologic systems relevant to energy resource developments. Simple analogs for complex natural systems (gaseous molecules, aqueous fluids, and minerals) are studied in great detail to elevated temperatures and pressures with the most advanced and precise experimental techniques and theory-simulation methodologies available in

order to provide a solid foundation for the understanding and modeling of various geologic systems including sedimentary and geothermal systems. During the current funding period, our activities have been focused on the effect of pressure and fluid composition on isotope partitioning between brines, steam, and minerals at elevated temperatures, both experimental (neutron-scattering and laboratory experiments of the system brucite-water), and theoretical studies and molecular-based simulations of water and other simple geologic fluids.

Multi-Scale Studies of Fluid-Rock Interaction

D. R. Cole, 865-574-5473, Fax 865-574-4961, coledr@ornl.gov; Lee Riciputi, riciputilr@ornl.gov

We are utilizing secondary ion mass spectrometry capabilities for precise, high-spatial resolution analysis of light stable isotope ratios and trace element concentrations to investigate mass transport phenomena during fluid-solid interactions in both natural and experimental settings, seeking understanding of governing processes ranging in scale from the atomic to regional covering 10's to 1000's of km^3. Our work follows four major themes: (1) studies of fluid-rock interactions, particularly in lower temperature settings, with an emphasis on identifying potential fluid sources, fluid evolution, and flow patterns during regional fluid migration events; (2) experimental studies of isotope diffusion/kinetics and experiments of equilibrium mineral-fluid isotope partitioning; (3) collaborative efforts with academic and industrial partners on a variety of microscale studies of fluid-rock interactions; and (4) continued technical (instrumental) development in support of the previously outlined research areas. These efforts provide new insights concerning (1) the microscale mechanisms governing isotopic and elemental behavior during fluid-rock interaction and (2) how the microscale record preserves evidence of large-scale mass transfer processes in geologic systems. This project benefits from numerous collaborations with other FWP's at ORNL, academic, and industry partners.

Investigation of Mineral Reaction Zones and Associated Interfaces

D.R. Cole, 865-574-5473, Fax 865-574-4961, coledr@ornl.gov, L.R. Riciputi and J. Horita

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. The specific goals are three-fold: (a) to characterize the chemical, isotopic and textural features (e.g. porosity) of the reaction zone and its rate of formation, (b) to assess the nature of chemical and isotopic communication across the reaction zone as well as possible confinement effects on fluid properties and behavior, and (c) explore ways to determine the molecular and atomistic details of the interface between the product and parent phases. Wherever possible, we will examine the possible transport of elemental and isotopic species from the reaction zone into the unreacted parent. Two chemical systems are currently being examined: the conversion of periclase to brucite, 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. The ultimate desire is to obtain nanoscale observations that can be used to quantify molecular-level behavior. This effort benefits from collaborations with J. Larese, T. Labotka, C. Mora, L. Anovitz and M. Fayek (Univ. Tenn., Knoxville), P. Larson (Wash. State Univ.), and S. Utsunomiya (Univ. Michigan).

Experimental Studies of Hydrothermal Processes Employing In Situ pH Measurement

D.J. Wesolowski, (865) 574-6903, Fax (865) 574-4961, wesolowskid@ornl.gov

In this project, we investigate aqueous reactions of critical importance in modeling a variety of fluid-rock interaction 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 Oak Ridge National Laboratory'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, Mg, Ca, 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. We are also developing new pH sensors for oxidizing environments and temperatures above 300C, and initiating studies involving geobiological materials. This research involves extensive collaboration with visiting professors, graduate students and postdoctoral fellows who wish to take advantage of our unique capabilities and expertise.

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

J.G. Blencoe, 865-574-7041, Fax 865-574-4961, blencoejg@ornl.gov

Published thermophysical data for carbon dioxide-methane-hydrogen-water (CO_2-CH_4-H_2-H_2O) mixtures at 35-500°C, 0-100 MPa, are too sparse to permit formulation of accurate equations of state (EOSs) for these fluids. Reliable expressions could be used to solve many important petrologic, geochemical and societal problems. Applications of particular relevance to the energy and technological needs of the United States include: modeling the hydrodynamics of natural waters circulating through sedimentary basins, understanding how secondary porosity develops in oil and gas fields, modeling global cycling of greenhouse gases, and quantifying the phase behavior and chemical reactivity of CO_2 sequestered in geologic reservoirs.

To gain an improved understanding of the behavior of CO_2-CH_4-H_2-H_2O fluids in subsurface environments, more accurate thermophysical data are needed for these mixtures at elevated temperatures and pressures. Accordingly, we are using several unique experimental devices to measure, with unprecedented precision and accuracy, the densities, excess molar volumes and vapor-liquid equilibrium (VLE) relations of CO_2-CH_4-H_2-H_2O fluids at 35-500°C, 0-100 MPa. Coupled with suitable data from

the literature, the new experimental results will spur development of more comprehensive and reliable EOSs for predicting the thermodynamic excess properties of CO_2-CH_4-H_2-H_2O fluids over wide ranges of temperature, pressure and composition.

Isotopic Fractionation of Carbonate Systems

J. Horita, (865) 576-2750, Fax (865) 574-4961, horitaj@ornl.gov

Detailed, systematic laboratory experiments are proposed in order 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.). Such information is vital to our understanding of numerous dynamic geochemical processes involving CO_2 on a time-scale ranging from hours to thousands of years, ensuing from the injection of large volume of CO_2 into the subsurface. Our specific objective during the current period is to investigate the mechanisms, rates, and isotope fractionation during the formation of dolomite by (1) precipitation from a CO_2-bearing solution at low temperatures (25-90°C) and (2) replacement of calcite to dolomite in CO_2-rich fluids at moderately elevated temperatures (100-300°C). Novel neutron diffraction technique is also utilized to investigate nano- and intermediate-scale order-disorder of cations in dolomite formed under low- and high-temperature environments, both natural and experimental. The both isotopic and local-structural information obtained on sedimentary dolomite from this study will provide crucial information on the formation and transformation of calcite, dolomite, and other carbonate minerals in the subsurface.

PACIFIC NORTHWEST NATIONAL LABORATORY

CONTRACT: RL01830

PERSON IN CHARGE: A. Felmy

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

J.M. Zachara, (509) 376-3254, john.zachara@pnl.gov

Fe(III) oxides poise the oxidation/reduction potential of subsurface materials and act as electron acceptors for redox reactions. Dissimilatory metal reducing bacteria (DMRB) utilize these oxides as electron acceptors under anoxic conditions, and can transform them to other mineral phases. Past research has investigated the biomineralization of synthetic ferrihydrites in mineral suspensions inoculated with DMRB where mineral-microbe contact has been optimal. Important findings have been made on the nature and properties of biosynthetic Fe(II), Fe(II/III), and Fe(III) mineral phases, and their formation pathways driven primarily by biogenic Fe(II) flux. We have extended this research to natural ferrihydrites and to mineralogic configurations representative of *in-situ* Fe(III) oxide particle associations, including multi-mineral grain coatings and intragrain precipitates in lithic fragments. These characteristic microenvironments limit direct organism-Fe(III) oxide contact, and provide a unique physicochemical setting for biotransformation that has not been scientifically explored. Laboratory physical models involving the precipitation of nanoparticulate Fe(III) oxides in the internal pore space of porous silica, and the coating of quartz slides with mixtures of Fe(III) oxides and other relevant accessory phases are being used to study biotransformation reactions under controlled conditions that simulate lithic fragment interiors and grain coatings. Hypotheses will be evaluated in batch and flow systems incubated with Fe(II), bioreduced anthraquinone disulfonate, or DMRB that have been cultured anaerobically under controlled conditions. Physical model results are being used to interpret the biotransformation behavior of Fe(III) oxides in subsurface sediments containing particle coatings and intergrain precipitates. High resolution scanning and transmission electron microscopies, Mössbauer spectroscopy, conventional and synchrotron x-ray diffraction, XANES and EXAFS spectromicroscopy, and atomic force microscopy will be used to monitor reductant and microbe induced changes to the Fe(III) oxides.

Molecular Basis for Microbial Adhesion

Tjerk P. Straatsma, 509-376-4079, tps@pnl.gov

The goal of this project is the development of a theoretical modeling capability for the study of the interactions of lipopolysaccharides located on the outer membrane of gram-negative bacteria with mineral surfaces and the study of how such interactions affect metal uptake and mineral dissolution, and the application to better understand and predict 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. Outer membranes of Gram-negative bacteria have important structural, signaling, and transport functions that play a role in geochemical processes. Of particular interest to the US Department of

Energy are Gram-negative microbes such as *Pseudomonas aeruginosa* and *Shewanella oneidensis* because of the specific role that these bacteria play in the environment. The microbial outer membrane is believed to play a key role in processes that govern microbial metal binding, microbial adsorption to mineral surfaces, and microbe mediated oxidation/reduction reactions at the bacterial exterior surface. From complete and detailed composition information available for the lipopolysaccharide of P. aeruginosa, we have developed an accurate and consistent molecular model of this membrane, that has been validated against experimental data and its structural and for which its electrostatic properties have been characterized. Computer simulations have shown that the structurally asymmetric membranes display a resulting asymmetric charge distribution which has a significant effect on the transport properties of environmental ions as well as the adsorption to geochemical surfaces. We have developed a classical parameter set for uranyl and performed molecular dynamics simulations of uranyl and other ions binding to the LPS membrane. Using potential of mean force-driven free-energy calculations, we have been able to estimate the relative affinities of these environmentally contaminant ions to the LPS membrane.

Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces

Kevin M. Rosso, Kevin.Rosso@pnl.gov

Mineral surfaces in natural settings usually exhibit a significant degree of morphological heterogeneity. On scales from the molecular-scale to micron scales, surface roughness can be an important factor in growth, dissolution, and adsorption processes. Despite this fact, relationships between these processes and roughness have not lent themselves to easy quantification because of their inherent complexity. To address this complexity we are studying the dissolution behavior of various mineral surfaces at various length scales of observation accessible by atomic force microscopy (AFM). In FY05, we completed a study of the dissolution of prismatic and rhombohedral quartz surfaces by hydrothermal KOH/H_2O solutions. We characterized and explained the development of surface roughness in terms of multiple overlapping etch pit growth originating at various classes of crystalline defects. By determining rates of growth of individual features, the total dissolution rate of the surface could be estimated for the case where the features overlapped and the surface topography became complex (Yanina, Rosso, Meakin, 2006, Geochimica et Cosmochimica Acta, v. 70, pp. 1113-1127). The prismatic surface dissolves almost two orders of magnitude faster than the rhombohedral surface, mostly due to the difference in the number and the rate of dissolution of extended defects, such as dislocations. Our FY05 research activities also involved studying the reductive dissolution of hematite single crystals by Fe(II), ascorbate, citrate, and using oxalate as an Fe chelate. AFM, transmission electron microscopy, and X-ray photoelectron spectroscopy were used to examine the (001), (012), (113), and low-angle vicinal surfaces before and after dissolution. In this work, we discovered a unique coupling of surface reactivity involving charge transport through the bulk of the crystal. Nanopyramids of hematite grow on the (001) surface due to Fe(II) to Fe(III) conversion at this surface, electron equivalents are transported through the bulk crystal reducing Fe(III) at low-angle vicinal surfaces at which Fe(II) is released. The cycle is broken if either of the surface types is sealed. This novel finding contradicts the long-standing paradigm for iron oxide reductive dissolution developed over the past three decades from wet chemical observations.

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

Eugene S. Ilton, Eugene.Ilton@pnl.gov

This project concerns reactions between silicate minerals and toxic metal-bearing aqueous fluids. Specifically, we explore mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals and sorbed to mineral surfaces. Key techniques used are electron microscopy, x-ray photoemission spectroscopy, (XPS) and x-ray adsorption near edge spectroscopy. 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. Major questions surround the role of the intermediate U(V) in the heterogeneous reduction of U(VI) to U(IV). Initial results indicate that the ratio of structural Fe(II), the reductant, to U(VI) is an important parameter that determines the residence time of sorbed U(V). Future work will focus on whether U(IV) forms by two successive electron transfers or by disproportionation of U(V). Using theory to interpret XPS and XANES is an important part of this scientific program. We continue to make major advances in the interpretation and understanding of the XPS for transition metals (TMs) and actinides. We have demonstrated the importance of closed shell screening, a mechanism not normally discussed, for the XPS of MnO. Our prior study of the 4f XPS of U cations has been extended to take into account the final state relaxation of the U charge in the presence of the 4f-hole; this extension improves the agreement of our atomic theory with experiment for UO_2. It sets the stage for further calculations where the chemical environment of the cation will be taken into account. Applications of our theoretical capabilities to study XANES have been made for the Mn L-edge and the O K-edge in H_2O. For H_2O, we have definitively established the extents of valence anti-bonding and of Rydberg character in the excited states. This distinction is key to understanding the chemical significance of XANES measurements involving solvated metal cations. It is intended to further enhance our programs to allow a balanced, unified treatment of all important mechanisms for the XPS and XANES of metal cations.

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

Andrew R. Felmy, (509) 376-4079, ar.felmy@pnl.gov

This is a collaborative research project involving theoretical modeling studies at The University of California, Davis (J.R. Rustad), and at The University of Alabama (D.A. Dixon) in conjunction with experimental studies at PNNL (J.F. Boily and A.R. Felmy). The research emphasized detailed studies of the solvation of metal ions, polynuclear species, and mineral surface sites. The reactivity and the influence of carbonate at the both the surface and in the bulk of iron oxides is also being examined.

The UA group has been using *ab initio* electronic structure calculations to predict the behavior of aqueous inorganic systems focusing on predicting solvation properties, pKa's, and the behavior of aqueous metal binding energies. These calculations complement the molecular dynamics simulations (UCD group), and have been used to check and build potential functions These are the most accurate calculations of the solvation free energies of H^+, OH^-, the electron, and F^-.

The UCD group has been focused on unraveling the solvation and metal exchange rates of polynuclear clusters that can serve as models for mineral surface sites. Specifically, molecular dynamics simulations

were used to calculate activation barriers and rates of water exchange on a series of aqueous aluminum species of increasing complexity, including Al^{3+}, $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$, and $Al_{30}O_8(OH)_{56}(H_2O)_{26}{}^{18+}$. The results show widely varying water exchange rates of the different sites on the clusters which are in good agreement with the limited NMR data that is available.

The PNNL group has been focused on studying the solvation and protonation of hematite surfaces. The cryogenic XPS technique was used to show that hematite colloids with strongly-defined basal planes possess strong affinities for electrolyte ions, irrespective of the average surface charge/potential. These measurements also revealed very little proton uptake by the dominant ƒÝ-OH group. Combined electroacoustic/potentiometric measurements have revealed unusually low values of isoelectric points for hematite platelets dominated by the basal plane. These values are consistent with recent reports for low isoelectric points for the basal planes of corundum and hematite determined by Second Harmonic Generation spectroscopy.

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

Andrew R. Felmy, (509) 376-4079, ar.felmy@pnl.gov; J. Rustad

This work addresses two major areas: (i) molecular simulation of oxygen exchange processes in aqueous Keggin ions, which serve as well-characterized aqueous oxide surface surrogates, and (ii) ferric-ferrous electron transfer in hydrolyzing aqueous solutions, which is the first step towards looking at electron transfer reactions on mineral surfaces.

A new mechanism has been postulated to explain the reactivity trends for oxygen-isotope exchange reactions between sites in the aluminum polyoxocations of the ε-Keggin type and bulk solution. Experimentally, the molecules have four oxygens that differ considerably in reactivity both within a molecule, and between molecules in the series: Al_{13}, $GaAl_{12}$ and $GeAl_{12}$ $[MO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{n+}(aq);$ with M = Al(III) for Al_{13}, n = 7; M = Ga(III) for $GaAl_{12}$, n = 7; M = Ge(IV) for $GeAl_{12}$, n = 8]. A partly dissociated, metastable intermediate molecule of expanded volume is necessary for exchange of both sets of m_2-OH and that the steady-state concentration of this intermediate reflects the bond strengths between the central metal and the μ_4-O. This mechanism explains the reactivity trends for oxygen-isotope exchange in m_2-OH and h-OH_2 sites in the e-Keggin aluminum molecules, and also explains the observation that the reactivities of minerals tend to reflect the presence of highly coordinated oxygens, such as the μ_4-O in boehmite, α-, and γ-Al_2O_3 and their Fe(III) analogs. The partial dissociation of these highly coordinated oxygens, coupled with simultaneous activation and displacement of neighboring metal centers, may be a fundamental process by which metals atoms undergo ligand exchanges at mineral surfaces.

A molecular model has been developed for ferrous-ferric electron transfer in a hydrolyzing solution. The model predicts that increasing pH reduces the potential of mean force between the ferrous and ferric ions. The magnitudes of the calculated contributions from the barrier heights and the potential of mean force nearly cancel each other at the canonical transfer distance of 0.55 nm. There is a surprising amount of overlap in electron transfer reorganization energies for $Fe(H_2O)_6{}^{3+}$, $Fe(OH)(H_2O)_5{}^{2+}$, and

$Fe(OH)_2(H_2O)^+$, indicating that fluctuations in hydrolysis state can be viewed on a continuum with other solvent contributions to the reorganization energy.

First Principles Simulation of the Supercritical Behavior of Ore-Forming Fluids

Eric J. Bylaska, (509) 376-9114, fax (509) 376-3650, eric.bylaska@pnl.gov

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 between the 1st and 2nd hydration shell reflect the structure and dynamics in this region. These 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 use 1st principles dynamical simulations to investigate this behavior. In these simulations the interactions between ions are calculated directly from the electronic Schrödinger equation. This is required because the ion causes major changes in the solute-solvent and solvent-solvent interactions in the 1st and 2nd coordination shell. We have completed calculations for the Al^{3+} ion. These simulations include 128 waters and a total simulation time of 8ps. In the Al^{3+} system there is a very well structured 1st and 2nd coordination shell. For this ion the 1st hydration shell is very stable ($t_{1/2} \approx 1$sec). However, we have observed transitions between the structured 2nd hydration shell and the bulk region with a time scale of 10s of ps. The exchange reaction appears to follow a dissociative mechanism. However, the replacement of the 2nd shell water with a water from the bulk is 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. We believe that 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. The calculations reported here include both dynamical and hydrogen bonding effects of a large hydration region. This is a much more complete representation than has been used in prior quantum chemistry approaches.

SANDIA NATIONAL LABORATORY/ALBUQUERQUE

CONTRACT: AL85000

PERSON IN CHARGE: J. Merson

Molecular Simulations of Layered Minerals & Their Interactions with Hazardous Material

Randall T. Cygan, 505-844-7216; rtcygan@sandia.gov

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 and layered double hydroxide (LDH) phases.

Natural LDH clays are comprised of edge-sharing magnesium and aluminum octahedra that form layered structures with positive layer charge, and therefore can accommodate negatively-charged exchangeable species and water in the interlayer. These so-called inverse clays have structural, physical, and chemical properties that are quite similar to normal clays, except for structural differences in the charge distribution. We have developed molecular models of derivative LDH compounds with high (Mg:Al; 2:1) and low (Mg:Al; 3:1) charge density, in the presence and absence of water, and studied the orientation and hydrogen bonding behavior of the glycinate anion. We find the strongest interactions to be those involving the carboxylate group as hydrogen acceptor, and layer hydroxide or, to a smaller extent, water as hydrogen donors. We also completed molecular dynamics simulations of the naturally-occurring amino acids leucine and isoleucine, and, for comparison, of hexanoic acid and 2-aminohexanoic acid, as their anions incorporated into high charge density LDH. In all cases, the carboxylate group is hydrogen bonded to layer hydroxide. When water is present, it segregates into the region next to the hydroxide layer, and hydrogen bonds to carboxylate and hydroxide, as well as itself. We expect these facts will prove relevant to the condensation of amino acids and the uptake of peptides on LDH, as well as to protein folding in a more general context.

Metal-Anion Pairing at Oxide/Water Interfaces

Louise J. Criscenti, 505-284-4357, ljcrisc@sandia.gov

The main objective of this project is to investigate the possibility that divalent metals adsorb predominantly as metal electrolyte-anion ternary complexes on some oxide surfaces. At Sandia National Laboratories (SNL), classical molecular dynamics simulations of NaCl and MCl_2 (M = Mg^{2+}, Sr^{2+}, and Ba^{2+}) ion-pairs in solution and at the hydroxylated basal surface of gibbsite were performed to investigate the structure and relative stability of different aqueous and surface complexes. Calculated M-

O distances and coordination numbers in solution are consistent with experiment. In addition, calculated M-O and M-Al distances for metal adsorbed to the gibbsite surface match those found using X-ray absorption spectroscopy (XAS). However, these simulations suggest that alkaline-earth metals form inner-sphere complexes on the basal surface of gibbsite, rather than outer-sphere complexes as suggested by both bulk adsorption and XAS data on gibbsite powders. Exploratory research was performed to evaluate the capability of the force field CLAYFF to describe gibbsite edges and the quartz (001) and (101) surfaces. Preliminary results suggest that CLAYFF may require modification to describe the interaction of gibbsite edges with water; and that the flexible SPC water model with force field parameters for heavy metals like lead and cobalt, may be inadequate to calculate metal-anion complexation either in aqueous solution or at mineral surfaces. This project, directed by Criscenti at SNL, includes experimental components through Katz at University of Texas and Allen at Ohio State University who are, respectively, investigating metal binding to oxide surfaces using XAS, and establishing the presence of associated anions using vibrational sum frequency generation spectroscopy. At SNL, two manuscripts were completed that investigate the hydrolysis of Al-O and Si-O bonds at mineral surfaces, the role of solvation at mineral-water interfaces, and surface site acidities (Criscenti et al., Theoretical and ^{27}Al CPMAS NMR investigation of aluminum coordination changes during aluminosilicate dissolution, 2005, GCA 69, 2205-2220; Criscenti et al., Silicate glass and mineral dissolution: Calculated reaction paths and activation energies for hydrolysis of a Q3 Si by H_3O^+ using *ab initio* methods, submitted to JPC).

Interactions of Pore Fluid Pressure

William A. Olsson, waolsso@sandia.gov

Many porous materials, including some sandstones, exhibit non-uniform compaction into layers of differing porosity when subjected to non-hydrostatic, compressive stresses. We have reported the results of triaxial compression experiments done at a confining pressure of 45 MPa on Castlegate sandstone, while measuring simultaneously, stress, strain, acoustic emission locations, and permeability. A major result was that compaction localization produced up to a two-order-of-magnitude decrease in permeability. Correlation of local strain measurements and acoustic emission locations made on the same specimen showed that the compaction process proceeds as a propagating front approximately 20 mm thick. A model of the compaction process was developed that incorporates the moving boundary between compacted, low-permeability regions and un-compacted, higher-permeability regions, and compaction-induced fluid injection at the boundaries. Because of the inhomogeneous nature of compaction, and its temporal evolution, a number of phenomena related to fluid flow are predicted by the model: locally increased pore pressures and spatial changes in the effective permeability. Implications of the results for future experimentation and for reservoirs are, briefly, that the interaction between compaction-induced fluid pressure and compaction localization should lead to a phenomenon analogous to dilatancy hardening, impeding the propagation of compaction bands. New experiments have been initiated to answer important compaction localization questions. What are the differences in micromechanical properties that lead to inhomogeneous compaction in some sandstones versus homogeneous compaction in others? Also, field work suggests that natural compaction bands may have formed before the now-host rock was lithified. To gain some insight into these problems, samples of known, uniform, grain size distributions of St. Peter sand are being deformed in triaxial compression to search for conditions that may lead to compaction localization in sand, and furthermore to discover

whether grain size or grain size distribution play a role. Additionally, micro-seismic signatures from experiments on single-grain fracturing between hard platens are being investigated to learn more about the micro-mechanics of failure of quartz grains. Compaction localization and its effect on fluid movement in rock may have important consequences for extractive technologies applied to natural gas, oil, and water.

Micromechanical Processes in Porous Geomaterials

Joanne T. Fredrich, fredrich@sandia.gov

The objective is investigation of the microscale characteristics of geomaterials, and how these characteristics control the macroscopic behavior. The research focuses on porous earth materials that are central to geoscience applications, including geologic sequestration and hydrocarbon exploration and production.

A manuscript by Fredrich, DiGiovanni, and Noble that describes data collected during synchrotron computed microtomographic experiments performed at the APS GSECARS 13-BM beamline and lattice Boltzmann simulations of single phase flow was submitted to J. Geophys. Res. Permeabilities calculated from the simulations for sandstones with porosities from 5-35% agree with laboratory core-scale experiments over several orders of magnitude.

The pore-scale hydrodynamics were probed by visualizing the microscopic velocity field and analyzing the distribution of kinetic energy (White & Fredrich, 2005 Fall AGU). Velocity components not aligned with the macroscopic forcing provide a measure of flow tortuosity. Inefficient out-of-plane and recirculating flow consumes proportionally more energy as porosity is reduced. At low porosity, 48% of the energy is expended in this manner, dropping to 31% at high porosity. The distribution of kinetic energy as a function of nondimensional velocity reveals a unimodal distribution at high porosity, but bimodal distribution at low porosity, with the secondary peak corresponding to backward flow. To examine flow efficiency, we define a dead zone metric as the volume of pore space carrying <1% of the total kinetic energy. At low porosity, 74% of the pore space is dead zone, as compared to 55% and 35% at intermediate and high porosity, respectively.

In situ laser scanning confocal microscopy experiments provide insight into the effect of microscale roughness on fracture flow and colloid transport (Grasselli et al., 2005 Fall AGU). Fluorescent microspheres were used to simulate colloids with particle-image velocimetry used to track the particles. Data were input to a 2D coupled lattice-Boltzmann discrete element method simulator. Transport is dominated by the macroscopic parabolic velocity profile, although undulations in aperture increase the extent of low velocity zones that retard movement of microspheres, resulting in trapping. On a macroscopic scale this causes tailing of the breakthrough curve. Anisotropy in surface roughness causes anisotropy in breakthrough behavior for opposite flow directions.

Role of Fracture Intersections in the Flow and Transport Properties of Rocks

Harlan W. Stockman, hwstock@sandia.gov

This report describes lattice Boltzmann modeling efforts in the final phase of the study.

The stability of the lattice Boltzmann (LB) technique was improved, and the method was applied to oscillatory flow up to Peclet and Schmidt numbers > 1000. Under such conditions, recirculation zones and channeling greatly enhance mixing. Good agreement was found with benchmarks for oscillatory flow and dispersion in 3D geometries, and the uncertainty in the dispersion coefficient is estimated to be <12% under the achievable conditions. The model was used to explore the effects of slight oscillations in flow at fracture intersections. It was found these small oscillations could enhance the apparent mixing by a factor of 2 or more. Initial results of the high-Sc flow model were published in J. Biomech. Engg. (128(1), 106-114), and limits and improvements of the LB technique will be documented in an upcoming book chapter (In: Ho, C.K. and Webb, S.W. (eds.) Gas Transport in Porous Media, Springer, 400 pp. ISBN: 1-4020-3961-1).

The classic studies of Newhouse (Econ. Geol. 36, 612-629), for precipitation of solids in a flow field, were modeled by LB. It was found that the growth pattern of the precipitates was greatly dependent on the speed of diffusive transfer relative to the speed of crystal growth. Newhouse used crystalline materials with high solubilities and high growth rates. In geological systems, growth into the direction of flow may be much more limited, unless fluid speed is quite fast. Initial models of $CaSO_4$ growth in Hele-Shaw cells show a modest accumulation of precipitates on the upstream side of the initial seed.

PART II: OFF-SITE

AMERICAN SOCIETY FOR MICROBIOLOGY
1752 N Street, NW
Washington, DC 20036

Grant: DE-FG02-05ER64106

Funding Support for Students and Scientists Attending the Joint International Symposia for Subsurface Microbiology and Environmental Biogeochemistry

Rick Colwell, rcolwell@coas.oregonstate.edu

The joint international symposia on subsurface microbiology and environmental biogeochemistry were held at Jackson Hole, Wyoming, on August 14-19, 2005. This joint meeting had plenary sessions on carbon cycling, sequestration and energy, metal sequestration, methods and tools of biogeochemistry, field-scale biogeochemistry in the future, and extremophiles and exobiology. Other themes of geochemical interest that were addressed in concurrent oral sessions and poster sessions included biogeochemical cycling, redox geochemistry and microbiology, molecular scale science and subsurface microbiology, geophysics and microbiology, and bioremediation research and applications. The DOE grant was used to provide funding support to assist students and scientists to attend the joint symposia.

UNIVERSITY OF ARIZONA
Department of Agricultural and Biosystems Engineering
Tuscon, AZ 85721

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

Robert Roth, bobroth@ag.arizona.edu

The irrigation site located at the University of Arizona Maricopa Agricultural Center was designed to support controlled irrigation through the use of evenly spaced drip tubing under a heavy black plastic tarp. Soil solution samples (lysimeters) are placed at specific locations to collect water from 1.5 m, 3.0 m, and 10 m from the soil surface. Suction provided by a vacuum pump was applied to the lysimeters for 3 h prior to collection. After this time, the soil solution, if any, was collected and placed into 20 ml HDPE scintillation vials and stored at -15°C for later analysis. These samples were analyzed for pH and electrical conductivity (EC) was measured. High Performance Liquid Chromatography (HPLC) was employed in an attempt to determine the amount of biosurfactant present in each sample.

The field was irrigated for two weeks prior to sampling. Samples were collected at twenty dates from Nov. 2, 2004 to Feb. 5, 2005. A total of 316 samples were collected during this period. Not all of the suction lysimeters provided a soil solution sample, and in some cases, only a small amount (5 ml) was collected. A total of 600 analyses were conducted on these 316 samples for pH and EC. All 316 samples were analyzed for EC, but only 284 samples were analyzed for pH, due to the small volume of solution collected, as a minimum of 10 ml is required for pH analysis. There were differences in pH and EC of the various soil solutions at different depths and sample dates, but this is quite common for soil solutions. Samples of irrigation water with and without the biosurfactant were collected for comparison. There was no difference in pH or EC between untreated and treated irrigation water.

The biosurfactant was not detected in any soil solution sample. Numerous combinations of water, acetonitrile, methanol and chloroform were tested as the mobile phase in the HPLC procedure. There was no positive response in any results (peak-heights and areas) for any samples. The results of the samples corresponded to the results obtained by Dr. Harmut Spetzler. Evidently, there was no measureable surface tension difference between any of the samples he had tested with equipment at his facility in Colorado. It is apparent that the detection equipment doesn't have the required sensitivity to measure surface tension differences for these samples. All data collected from the Maricopa Agricultural Center were then forwarded to Dr. Spetzler for the final analysis of the study.

ARIZONA STATE UNIVERSITY
Department of Geological Sciences
Tempe, AZ 85287

Development of an Experimental Data Base and Theories for Prediction of Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures

Everett Shock, eshock@asu.edu

Reactions of aqueous solutions with rocks control the generation, migration, and accumulation of fossil fuels as well as many other geochemical processes. Analogous interactions determine the movement of metals, hydrocarbons and other toxic compounds in aquifers, tailings piles from mining landfills, nuclear waste repositories, and contaminated sites. This diversity of geochemical processes involving aqueous solutions is suited for study with theoretical models that employ thermodynamic data. The objective of this research is to combine new experimental measurements with theoretical equations of state and with first principles quantum mechanical predictions to supply the necessary thermodynamic data. Our use of experimental conductance measurements to get equilibrium association constants for a variety of aqueous electrolytes at high temperature has been going very well. We have measured association of the ions in the following salts: sodium acetate, sodium chloride, potassium chloride, sulfuric acid, hydrochloric acid, sodium sulfate, and sodium hydrogen sulfate. Methods for predicting second cross virial coefficients for interactions involving water have been developed. These predictions are needed in our new equation of state. Progress has been made in developing equations of state for salt solutions at high temperatures. We have collaborated in the construction of a new heat capacity calorimeter at the University Blaise Pascal in France so that measurements on this important property can be continued. In order to expand our thermodynamic database to cover temperatures and pressures where measurements are impossible, we have further developed our new method of predicting free energies of hydration. This method uses molecular dynamic simulation and *ab initio* quantum mechanics to make the predictions. The free energy of hydration of water at extremes of temperature and pressures has been predicted using this new method. We have also shown that our new method can predict hydration free energies of ions at high temperatures with good accuracy. It seems clear that using this new method we can now predict free energies of hydration with an accuracy of about 5 kJ/mole for any reasonably simple solute containing elements as heavy as chlorine at temperatures to about 3000 K and pressures to about 300,000 atmospheres.

ARIZONA STATE UNIVERSITY
Department of Geological Sciences
Tempe, AZ 85287

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

Lynda B. Williams, Lynda.Williams@asu.edu

The objective of this research program has been to use chemical and isotopic variations of diagenetic minerals and organic compounds in hydrocarbon bearing sedimentary basins in order to address the chemical dynamics (changes and movement over time) of fluids interacting with host rocks. We focus on trace elements and their isotopes as they are released from maturing hydrocarbon sources and fractionated during incorporation into authigenic clays and other mineral cements. In 2004 we studied Li isotopes as a monitor of hydrocarbon related fluids. We have 1) tested Li-isotope standards and SIMS protocol for Li-isotope ratio measurements, 2) conducted hydrothermal experiments to determine the equilibrium Li-isotope fractionation between illite and water and 3) tested the effect of crystal growth on isotope ratio measurements. Furthermore, in preparation for a comparison of experimental isotope fractionation results to field areas with different reaction kinetics, a variety of field areas were sampled. These include a contact metamorphosed bentonite, Salton Sea cores, the Geysers, and hydrothermal deposits from Yellowstone National Park. These samples are currently being prepared and analyzed for bulk and clay mineral composition. A select group of the samples will be used for our study of Li and B isotope variations in illlite formed in open and closed geologic systems at a various temperatures. The results of the hydrothermal reaction of clay mineral SWy-1 smectite to illite in sealed Au-capsules with water containing -67‰ delta ^{7}Li, 0‰ delta ^{11}B (300°C, 100 MPa) showed similar isotopic trends. This is important because it shows that tetrahedral (containing B) and octahedral (containing Li) sites of the illite re-equilibrate simultaneously. By separating the reaction products into fine (<0.2) medium (0.2 to 2.0) and coarse (>2.0) size fractions and studying the isotopic trends we have concluded that: 1) Small crystals reflect earliest precipitation in metastable equilibrium with fluid. 2) Larger illite crystals approach isotopic equilibrium faster than small crystals as smectite dissolves and illite grows. 3) Illite grows in equilibrium with the fluid in a matrix of smectite that is out of equilibrium. 4) The Li isotope fractionation between illite and water at 300°C is approximately -11‰.

BOSTON UNIVERSITY
Department of Physics and Center for Computational Science
Boston MA 02215

Grant: DE-FG02-95ER14498

Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes: Using Numerical Simulations of Complex Nonlinear Earth Systems

W. Klein, (617) 353-2188, klein@bu.edu

Research under this project is focused on the analysis of crustal deformation processes is strongly correlated complex nonlinear earth systems. The underlying rationale for the work has been the need to understand the hazards and risks that a variety of critical energy facilities face from several kinds of tectonic instabilities in the complex earth system, primarily earthquakes, but also including volcanic eruptions and landslides. Over the past three years, we have pioneered a large array of modeling and numerical simulation techniques to develop a deep understanding of the basic physical processes associated with space-time correlations. We have then showed how to apply these methods to observed data. Our approach is fundamentally based upon the novel application of methods of statistical and condensed matter physics to the understanding of nonlinear earthquake fault systems. We have discovered using simulations that the dynamics of real earthquake fault systems are an example of a phase dynamical system. This property can be exploited to formulate a means of detecting the systematic variations in seismic activity that occur prior to major earthquakes. In addition, one can formulate a class of forecast algorithms that are now being tested against real data and are being shown to be significantly more effective at forecasting observed large earthquakes than a corresponding random data set from which all the space-time structure has been removed by randomly re-shuffling the data in time. We are also applying these methods as well to the analysis of GPS and Synthetic Aperture Radar Interferometry data, which are other new types of crustal deformation data. In addition to these major results we have also determined that 1) There are several classes of earthquakes, each with a distinct set of scaling exponents; 2) the evolution of the earthquake seismicity patterns can be described with(surprisingly) a linear theory over short times, since the nonlinear clusters in the patterns have a very small amplitude; and 3) the non-equilibrium, driven, meanfield earthquake fault system in southern California has many characteristics(again, surprisingly) of equilibrium systems.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Division of Geological and Planetary Sciences
Pasadena CA 91125

Infrared Spectroscopy and Stable Isotope Geochemistry of Hydrous Silicate Glasses

E. Stolper, (626) 395-6504, fax (626) 568-0935, ems@expet.gps.caltech.edu

Objectives: This project focuses on applications of experimental petrology and stable isotope geochemistry to study of volatile components dissolved in silicate melts and glasses and CO_2 in the atmosphere.

Project Description: *Parts 1* and *3* involve equilibration of volatiles with silicate melts to determine fractionations and/or diffusion rates: CO_2 in *Part 1* and H_2O in *Part 3*. *Part 2* involves equilibrating olivine with basaltic liquid at 1 atm as a function of temperature to determine olivine-melt oxygen isotope fractionation factors for a wide range of melt compositions. *Part 4* is our study of CO_2 in air from the Los Angeles basin, especially as it relates to sources of pollution through time.

Results: *Part 1:* We published our work on Na-melilitic melt (*I Appora, et al. (2003) Experimental determination of oxygen isotope fractionations between CO_2 vapor and soda-melilite melt. Geochim. Cosmochim. Acta 67: 459-471*).

Part 2: We have found that homogeneous (in Fe/Mg, Ni, Ca) cores of olivine phenocrysts from Hawaii retain complex concentration profiles ("ghost" skeletal crystals, multiple oscillatory zones) in phosphorus, allowing visibility into a previously unknown stage in the history of these and other magmas.

Part 3: We have successfully used current understanding of melt structure and dissolved water speciation to model the strong dependence of water diffusivity on the concentration of water in basaltic to granitic melts. We found a correlation between water diffusivity and melt viscosity that could be useful for estimating water diffusion coefficients when no experimental data are available (S *Newman et al. (2005) Diffusion of water in silicate melts, Eos. Trans. AGU, Fall Meet. Suppl., Abstract MR13A-0070*).

A related paper is in press (*KA Kelley, et al. (2006) Mantle melting as a function of water content beneath back-arc basins (J. Geophys. Res. B)*).

Part 4: Our bi-daily analyses since 1998 continue. Carbon isotopic compositions of CO_2 reveal that a changing mix of imported petroleum has combined to produce a relatively constant composition for the pollutant endmember. (*S Epstein et al., in prep, Changes in concentration and isotopic ratios of CO_2 in air in the Los Angeles basin, California, between 1972 and 2003*).

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

Gerald J. Wasserburg, isotopes@gps.caltech.edu

The results obtained by Lemarchand, Wasserburg & Papanastassiou (GCA 2004) indicate that the observed Ca isotopic fractionation is plausibly due to an equilibrium fractionation between crystal & solution that is moderated by the non equilibrium precipitation of calcite/aragonite due to supersaturation conditions. Because of the general importance of the very small Ca isotopic shifts (<1,500 ppm) the refinement of Ca measurements has been undertaken. This has direct application to the ^{40}K-^{40}Ca isotopic system to early crustal evolution (>3 Gyr) and the evolution of sea water. The effects to be expected for this problem are less than 200 ppm in ^{40}Ca/^{44}Ca. We have developed reproducible procedures that now permit measurements with errors of 30 ppm (2 sigma). This is an improvement of over a factor of three from previous efforts. We are now applying this to trying to establish the Ca isotopic signature of Archean seawater through analysis of ancient carbonates and to investigating the mechanisms of Ca precipitation from solution.

UNIVERSITY OF CALIFORNIA, BERKELEY
Department of Earth and Planetary Science
Berkeley CA 94720

Grant: DE-FG03-01ER15163

Precipitation at the Microbe-Mineral Interface

Jill Banfield, 510 643 2155, jbanfield@berkeley.edu

Microbial biomineralization can dramatically modify the distribution of metals in the environment. The goals of this research are to determine the mechanisms by which cell surfaces, enzymatic activity, and microbial byproducts impact metal speciation and induce mineral precipitation. Our research focuses on biogeochemical processes in metal-contaminated environments associated with two abandoned mines. Field work was carried out at the Midnite Mine in Washington, where uranium contamination of soils and sediments has occurred, in a flooded underground mine tunnel in SW Wisconsin, where Zn, Pb, and U contaminants are cycled across a redox boundary, and in an acid mine drainage-impacted salt marsh on San Francisco Bay. We are analyzing how microbial activity in oxic and anoxic zones results in formation of metal oxide, metal sulfide, and phosphate biominerals in proximity to, and within, cells. Initially, we concentrated on uranium contaminated water and sediments, focusing on the mechanism of uranium reduction and determination of the organisms responsible. Recently, we analyzed metal sulfide and iron oxyhydroxide biomineralization processes and products, with emphasis on X-ray microscope-based detection of polymers that play roles in localizing precipitation and templating recrystallization of FeOOH.

UNIVERSITY OF CALIFORNIA, BERKELEY
Department of Earth and Planetary Science
Berkeley CA 94720

How Do Interfacial Phenomena Control Nanoparticle Structure?

Jill Banfield, 510 643 2155, jbanfield@berkeley.edu

The growth of ZnS nanoparticles with both water and mercaptoethanol was found to occur predominantly via crystallographically-specific oriented attachment (OA). The growth mechanism determines particle morphology and microstructure. Twins and stacking faults form in the coarsened mercaptoethanol-capped ZnS, whereas more complex, closely spaced twins, stacking faults, and polytypic intergrowths form in coarsened water-ZnS. At long reaction times, diffusion-controlled growth removes surface irregularities arising from OA to yield rounded particles with complex internal structures. The character of the surface ligands affects both phase transformation pathway and temperature of phase transformation. Methanol desorption and rewetting, and water binding cause structural changes, reversible in the case of methanol ligands. Aggregation and disaggregation also cause reversible structural modification. Dispersed nanoparticles in suspension have a more distorted internal structure than aggregated nanoparticles of the same size. Reversible switching between distorted and crystalline structures can be induced by changing the aggregation state at room temperature, implying a low activation energy for the transformation. The results are believed to be the first surface-driven room temperature transitions observed in nanoparticles. The results indicate that nanoparticle structure is not kinetically trapped, but responsive to environmental changes. The growth of goethite nanoparticles was explored with a variety of synthesis methods, including a flash annealing technique to create nanoparticles in the range from 5-80 nm with differing crystallinity, habit and surface properties. TEM characterization shows aggregation in the more equant particles that is suggestive of initial face-to-edge impingement. This mode of aggregation was further suggested in large scale 10,000 atom MD simulations that showed positive charge buildup at the edges of goethite nanoparticles and negative charge buildup in the centers of the faces. We thus infer a possible mechanism for OA in these nanoparticles that mitigates the problem of particle-particle electrostatic repulsion. Other work has measured the growth of goethite nanoparticles in real time via synchrotron-based wide and small angle x-ray scattering (WAXS and SAXS, respectively). As with ZnS there is evidence for a change of mechanism with nanoparticle size in the tens of nm regime, possibly from OA to diffusion-controlled growth.

UNIVERSITY OF CALIFORNIA, BERKELEY
Department of Earth and Planetary Science
Berkeley CA 94720

Diffusion/Dispersion Transport of Chemically Reacting Species

Harold C. Helgeson, brogie@berkeley.edu

A multitude of Gibbs free energy minimization computer experiments have been carried out in the 2005 fiscal year to explore comprehensively the consequences of incongruent melting of different hydrocarbon source-rock kerogens in the context of phase relations in the system CHO. These experiments, together with thermodynamic analysis of metastable equilibrium phase relations among petroleum, $CO_{2(g)}$, water, and kerogens with various (H/C)s along the U.S. Gulf Coast fluid-pressure (p_f) geotherm indicates that oil generation by melting of immature kerogen in hydrocarbon source rocks occurs at $p_{CO2(g)} = p_f$ over a narrow interval of log $f_{H2(g)}$, which decreases and becomes negligible with increasing depth, temperature, and log $f_{H2(g)}$. It follows that the corresponding phase assemblages constitute $f_{H2(g)}$ buffers in hydrocarbon source rocks. For example, at ~25 < T < 100ºC, incongruent melting of either a highly reduced immature type-I kerogen corresponding to $C_{171}H_{288}O_{9(c)}$ or a hydrogen-rich type II-kerogen represented by $C_{200}H_{260}O_{10(c)}$ produces petroleum + water + a kerogen with a lower H/C (in this case, $C_{292}H_{288}O_{12(c)}$). However, with increasing temperature from ~100 to ~ 150ºC, the metastable equilibrium phase assemblage generated by incongruent melting of either $C_{171}H_{288}O_{9(c)}$ or $C_{200}H_{260}O_{10(c)}$ no longer includes water, but instead generates petroleum + $C_{292}H_{288}O_{12(c)}$ + $CO_{2(g)}$. As temperature continues to increase above ~ 150ºC, a metastable highly oxidized mature kerogen ($C_{128}H_{68}O_{7(c)}$) is produced by incongruent melting of the $C_{171}H_{288}O_{9(c)}$, $C_{200}H_{260}O_{10(c)}$, or $C_{292}H_{288}O_{12(c)}$ kerogens, which results in metastable equilibrium at depth among $C_{128}H_{68}O_{7(c)}$, petroleum, and $CO_{2(g)}$. With further burial of the source rock at temperatures > ~ 225ºC, both $C_{171}H_{288}O_{9(c)}$ and $C_{200}H_{260}O_{10(c)}$ melt congruently to produce petroleum + $CO_{2(g)}$, but $C_{292}H_{288}O_{12(c)}$ continues to melt incongruently to form petroleum, $C_{128}H_{68}O_{7(c)}$, and $CO_{2(g)}$. However, in the latter case the volume of $C_{128}H_{68}O_{7(c)}$ produced in the process progressively decreases with increasing temperature to 300ºC as the volume of petroleum generated increases. Hence, with increasing temperature above 300ºC, $C_{292}H_{288}O_{12(c)}$ also melts congruently to produce petroleum + $CO_{2(g)}$.

UNIVERSITY OF CALIFORNIA, BERKELEY
Department of Earth and Planetary Science
Berkeley CA 94720

Grant: DE-FG02-05ER15637

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

H.-R. Wenk, (510) 642-7431, wenk@berkeley.edu

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.

UNIVERSITY OF CALIFORNIA, DAVIS
NEAT ORU
4440 Chemistry Annex
Davis CA 95616

Grant: DE-FG02-97ER14749

Thermodynamics of Minerals Stable Near the Earth's Surface

Alexandra Navrotsky, 530-752-3292, anavrotsky@ucdavis.edu

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, other phases related to acid mine drainage, phosphates, arsenates, and heavy metal containing minerals. New calorimetric approaches to the energetics of sulfide minerals are being developed.

UNIVERSITY OF CALIFORNIA, DAVIS
Department of Geology
Davis CA 95616

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

James R. Rustad, 530-754-6021, jrrustad@ucdavis.edu

The rates of water exchange with mineral surfaces and nanoparticles is a fundamental aspect of water-rock interaction. Water exchange rates on simple aquo ions vary by almost 20 orders of magnitude, depending on the chemical characteristics of the aquo ion at the exchange center. While aquo ion ligand exchange chemistry is a mature field, little is known even conceptually about how to extend these ideas to polynuclear complexes and, ultimately, to mineral surfaces and nanoparticles. To better understand how structural environments affect mineral surface reactivity, we have undertaken a series of molecular dynamics simulations to calculate activation barriers and rates for water exchange on a series of aqueous aluminum species of increasing complexity, including Al^{3+}, $Al_{13}O_4OH_{24}(H_2O)_{12}^{7+}$, and $Al_{30}O_8(OH)_{56}(H_2O)_{26}^{18+}$. We use the reactive flux method to calculate the rate of exchange of water at different sites on these complexes. The rate constant is taken as $k_{RF}=k_{plateau}k_{TST}$. k_{TST} is the transition state rate constant calculated from the potential of mean force $W(r)$. $k_{plateau}$ is the transmission coefficient extracted from the plateau value of the time-dependent transmission coefficient as calculated from the reactive flux method which takes into account transition state recrossings. For the molecular dynamics model, we use a slightly modified version of CLAYFF in conjunction with the SPC/E water model.

Our barrier calculations are in good agreement with NMR experiments for both hexaaquo Al^{3+} (90 kJ/mol, calc. vs 85 kJ/mol exp) and for the $Al_{13}O_4OH_{24}(H_2O)_{12}^{7+}$ ion (60 kJ/mol calc vs. 63 kJ/mol, exp.). We then used the model to make predictions for $Al_{30}O_8(OH)_{56}(H_2O)_{26}^{18+}$, which has six non-equivalent sites for water exchange. Precise rate parameters do not yet exist for $Al_{30}O_8(OH)_{56}(H_2O)_{26}^{18+}$, but NMR studies have shown that four of the 26 waters exchange much faster than the others. Our calculations are consistent with this observation, with a high exchange rate predicted for one set of waters with a symmetry multiplicity of four. 18 of the waters exchange at rates close to those observed on $Al_{13}O_4OH_{24}(H_2O)_{12}^{7+}$. Four are predicted to be slower than those observed for the $Al_{13}O_4OH_{24}(H_2O)_{12}^{7+}$ ion.

UNIVERSITY OF CALIFORNIA, DAVIS

Department of Chemistry, Department of Geology

Davis CA 95616

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

William H. Casey, 916-752-3211, whcasey@ucdavis.edu

The thesis of this research is that nanometer-sized metal-oxo molecules can serve as useful models for more complicated mineral structures and, by alternating between experiment and simulation, lead to knowledge of reaction dynamics in water. With these molecules we can probe reactions, such as isotope-exchange reactions at specific structural sites, that are also at the appropriate scale for treatment using sophisticated molecular-dynamic and electronic-structure methods. As an example, we showed that the kinetic data for exchange of waters around the $AlOH^{2+}$(aq) ion are most consistent with pentacoordination to oxygens, not hexacoordination as has been thought for decades. Simulation using Car-Parrinello methods confirmed the suspicion. This two-fold approach of experiment and simulation lends confidence to our ability to predict reactions for complicated materials in water.

To date, our research has focused on 1-2 nm size aluminum-hydroxide clusters although we are now branching into nanometer-sized transition-metal anions. Using the aluminum clusters, we constrained the time scales for proton and oxygen-exchange reactions between sites in the molecules and bulk solution. We showed that pathways for exchange of the hydroxyl bridges are sometimes enormously sensitive to small changes in structure whereas the rates of exchange of bound water molecules are robust and fall into a range that is familiar from studies of aqueous monomer ions. This similarity allows us to predict the rates of ligand-exchange reactions for more-complicated materials using well-understood models.

The nanometer-sized clusters are particularly useful because they are intermediate in scale between colloidal materials and simple monomer ions. The pathways for bridge ruptures in these clusters could not be uncovered with blind simulations. For example, oxygen-isotope exchange at hydroxyl bridges in the aluminum Keggin structures involves a metastable dimer-like moiety that forms at small concentrations. Similarly, using oxo-bridged clusters of Nb(V) and Ta(V), we find some evidence of oxygen-scrambling reactions within the molecules as they exchange oxygen isotopes with bulk solution, at least in early experiments.

UNIVERSITY OF CALIFORNIA, DAVIS
Department of Physics and Geology, and Center for Computational Science and Engineering
Davis CA 95616

Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes Using Numerical Simulations of Complex Nonlinear Earth Systems

John B. Rundle, (530) 752-6416, rundle@physics.cse.ucdavis.edu

Earthquakes represent a problem of significant interest to the US Department of Energy and its facilities, including nuclear power plants, research facilities and national laboratories, as well as other aspects of the energy infrastructure. The year 2006 marks the 100th anniversary of the San Francisco earthquake of April 18, 1906, still regarded as the greatest disaster to strike any US city. For these reasons, the development of techniques to understand and forecast damaging earthquakes is a critical need. Significant advances in our research program have come in the areas of 1) data analysis, as well as 2) models, the latter having suggested a number of new approaches to use in understanding the data; and in 3) approaching the goal of ensemble earthquake forecasting. In the area of data analysis, we have discovered a technique to determine when, within about a 2 year window, large-magnitude earthquakes are most likely to occur in an area the size of southern California. The technique makes use of data from standard seismic catalogs, and can be deployed in real time. Using numerical simulations, we have made considerable progress in understanding the basic physics of earthquake dynamics, allowing us to identify several classes of earthquakes. In addition, we have used these results to analyze the structure of fluctuations in such models, and to show that the fluctuations in mean field systems have a fundamentally different character as compared to systems that are not mean field. We have also extended and developed our topologically realistic models of earthquake faults at the system level, to include dipping faults having arbitrary rake angle. We used these new models to explore realistic simulations of earthquake histories, together with the resulting ground deformation, as well as the statistical physics of inter-earthquake time intervals. These types of models are being now used to construct an ensemble earthquake forecasting methodology, similar to that used in weather and climate prediction.

UNIVERSITY OF CALIFORNIA, LOS ANGELES

Department of Earth and Space Sciences
Los Angeles CA 90095

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

T. Mark Harrison, tmh@oro.ess.ucla.edu, (310) 825-7970

Our research is to assess the utility of thermochronologic and ion probe microscale isotope techniques in deriving fluid evolution and thermal histories in crustal environments that bear upon energy exploration, reservoir assessment, and paleoclimatology. We seek to characterize the timescales of transient heating in young geothermal systems, understand the temporal and spatial aspects of fluid/heat fractionation involved in the geothermal environment; and (3) develop high spatial and temporal resolution proxy climate records of modern and ancient speleothems. We have augmented our suite of zircon and sphene samples from 24 drillholes distributed through The Geysers geothermal field with a suite of samples from scientific drill hole SB-15-D from the Northwest Geysers field and are currently analyzing single crystals of sphene and zircon using (U-Th)-He methodology to evaluate competing models for the heat source of the Geysers plutonic complex. We have developed a model that simultaneously uses constraints from ^{40}Ar/^{39}Ar and (U-Th)-He dating to produce best-fit thermal history calculations for The Geysers and other areas. We have obtained a suite of samples from the 320 ka intrusive phase of the Medicine Lake geothermal field appropriate for thermochronological measurements. We are developing methods to obtain high spatial and temporal resolution proxy climate records from modern and ancient speleothems. Results from the 80 year record of Moondyne Cave, Australia, provides an excellent test of speleothem climate proxies because the regional climate and has experienced a 20% reduction of mean rainfall since 1964 and 0.8°C temperature rise since 1953. Inter-annual variations of oxygen and carbon isotopes were measured by conventional mass spectrometry whilst intra-annual δ^{18}O was measured by high spatial resolution ion microprobe. Both reveal surprising trends. δ^{18}O varies positively with temperature on both intra- and inter-annual timescales. On the inter-annual scale, δ^{18}O rises 0.3°C after 1974, 10 years after the regional rainfall decrease but synchronous with a delayed response seen in P and Mg, which otherwise vary strongly with rainfall, indicating that speleothem δ^{18}O is responding to rainfall δ^{18}O. Preservation of the annual rainfall δ^{18}O signal suggests that rainfall amount is recorded by speleothems in this region.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

Department of Earth Science
Santa Barbara CA 93106

Grant: DE-FG02-96ER14620

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

James R. Boles, (805)893-3719, boles@geol.ucsb.edu

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

Project Description: We have targeted active faults and young petroleum fields in southern California for study. Our most recent studies have been on the South Elwood fault in the Santa Barbara channel, the Refugio fault in the Transverse Ranges near Santa Barbara, and the Newport-Inglewood fault in the Los Angeles Basin. Subsurface core samples, outcrop samples, well logs, reservoir properties, pore pressures, and published structural-seismic sections are being collected to characterize the tectonic history and diagenetic evolution for the known fault networks. 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 geochemical signatures resulting from rapid CO_2 degassing. Our samples include calcite from well tubing scales, fault zones, and speleothems in man-made tunnels.

Results: Well tubing scales and speleothems show covarying carbon-oxygen isotopic signatures and may show considerable Mg substitution, both of which are attributed to rapid calcite crystallization. A manuscript by Perez & Boles has been published that describes the development of fractures that result from unloading of quartz cement in quartz sandstones. Using theoretical considerations and a natural analog from Venezuela, we show that thermoelastic contraction causes once deeply buried quartz cemented strata to develop fractures during uplift. On the hydrogeologic modeling front, Appold and others have a manuscript in review which 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 model links evolving fluid chemistry during mass transport to calcite precipitation.

UNIVERSITY OF CALIFORNIA, SANTA CRUZ

Institute of Geophysics and Planetary Physics
Santa Cruz CA 95064

Grant: DE-FG02-04ER15530

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

Ru-Shan Wu, 831-459-5135, wrs@pmc.ucsc.edu

The purpose of the current project is developing new methods for wave equation based imaging and extending these techniques for the estimation of subsurface model parameters. In the 2005/2006 project year, our research focuses on the following areas:

We improved the amplitude accuracy of the propagator in both $V(z)$ and more general $V(x, z)$ media. We derived the WKBJ solution from the principle of power flux conservation for an acoustic medium. With the advantage of the beamlet propagator, we applied the WKBJ correction within localized windows to form a true amplitude one-way propagator in a generally heterogeneous medium. This derivation can be extended to a general 2D or 3D model. Numerical results demonstrated that the one-way wave propagator with WKBJ correction provided amplitudes that agreed very well with those from the full-wave equation method in a smooth $V(z)$ medium. We used the one-way wave propagator and the local angle domain imaging condition to investigate the influence of acquisition aperture and propagator fidelity on the image amplitude. The results indicated that the propagator fidelity and acquisition aperture both influenced the imaging amplitude but the aperture had a much stronger effect than the accuracy of the propagator amplitude. In order to compare with other correction schemes used in literatures and implemented in the industry, we proposed a generalized amplitude gain control (AGC) factor to conduct amplitude correction. We applied these corrections to the SEG/EAGE 2D salt model and the Sigsbee2A model and compared the migrated images using different correction methods. The image quality of subsalt structures was greatly improved and the image amplitudes along subsalt faults were more balanced. The noises and migration artifacts were suppressed as well in certain degrees.

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 this way included both the effects of an acquisition system and the imaging (migration) process. This method could be applied to complex structures without smoothing the velocity model. It could also handle irregular acquisition geometry and finite frequency band.

UNIVERSITY OF CALIFORNIA, SAN DIEGO
Department of Chemistry and Biochemistry
San Diego CA 92093

First Principles Simulation of the Supercritical Behavior of Ore Forming Fluids

J.H. Weare, (858) 534-3286, fax (858) 534-7244, jweare@ucsd.edu

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 between the 1st and 2nd hydration shell reflect the structure and dynamics in this region. These rates vary over a very large range as a function of the properties of the ions (e.g. t1/2, 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 use 1st principles dynamical simulations to investigate this behavior. In these simulations the interactions between ions are calculated directly from the electronic Schrödinger equation. This is required because the ion causes major changes in the solute-solvent and solvent-solvent interactions in the 1st and 2nd coordination shell. We have completed calculations for the Al^{3+} ion. These simulations include 128 waters and a total simulation time of 8ps. In the Al^{3+} system there is a very well structured 1st and 2nd coordination shell. For this ion the 1st hydration shell is very stable (t1/2≈1sec). However, we have observed transitions between the structured 2nd hydration shell and the bulk region with a time scale of 10s of ps. The exchange reaction appears to follow a dissociative mechanism. However, the replacement of the 2nd shell water with a water from the bulk is 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. We believe that 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. The calculations reported here include both dynamical and hydrogen bonding effects of a large hydration region. This is a much more complete representation than has been used in prior quantum chemistry approaches.

UNIVERSITY OF CHICAGO
Center for Advanced Radiation Sources
5640 S. Ellis Avenue
Chicago IL 60637

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

Stephen R. Sutton, 630-252-0426, Fax 630-252-0436, sutton@cars.uchicago.edu

GeoSoilEnviroCARS is a national consortium of earth scientists whose goal is to operate, as a national user facility, synchrotron radiation beam lines at the Advanced Photon Source, Argonne National Laboratory. Instrumentation for the following techniques is open to the scientific community: (1) x-ray absorption fine structure spectroscopy; (2) fluorescence microprobe analysis; (3) microtomography; (4) powder, microcrystal and surface diffraction; (5) high-pressure crystallography with diamond anvil cells and multi-anvil presses, and (6) radiography at high pressure in the multi-anvil press. Research areas include phase transitions in mantle minerals, the properties of the Earth's core, migration and remediation of toxic metals and radionuclides in contaminated sediments, physical properties of porous media, redox chemistry of metals at the root-soil interface, chemical nature of hydrothermal fluids, and structures of and chemical reactions at mineral-water interfaces. In FY05, 234 beam time proposals were received, 192 unique users conducted experiments, and 89 papers were published. Published research included the following: (1) Iron-rich Silicates at the Core-mantle Boundary (W. Mao et al.); (2) Reconstruction of Deglacial Sea Surface Temperatures in the Tropical Pacific from Selective Analysis of Fossil Coral (N. Allison et al); (3) Uranium and Copper Speciation in Contaminated Sediments from a Hanford Process Pond (J. Catalano et al.); (4) Arsenic Speciation in Aquifer Sediments of Bangladesh (M. Polizzotto et al.); (5) Reoxidation of Bioreduced Uranium Under Reducing Conditions (J. Wan et al.); (6) Formation of Granular Jets (J. Royer et al.); (7) Microscale Properties of Multiphase Porous Media Systems (C. Willson et al.); (8) Pb(II) and As(V) Ion Partitioning at Polymer Film – Metal Oxide Interfaces (T. H. Yoon et al.).

UNIVERSITY OF CHICAGO
Center for Advanced Radiation Sources
5640 S. Ellis Avenue
Chicago IL 60637

Grant: DE-FG02-92ER14244

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

Stephen R. Sutton, 630-252-0426, FAX 630-252-0436, sutton@cars.uchicago.edu

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 2005, more than 20 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, phytoextraction mechanisms, and iron oxidation states in igneous petrogenesis. Examples of published work include the following: (1) Spatial distribution and speciation of Pb in soil surrounding corroding metallic Pb (Vantelon et al., 2005); (2) *In-situ* reduction of U(VI) to insoluble U(IV) via microbially mediated pathways (Tokunaga et al., 2005); (3) Aging effects on As retention mechanisms in former lead arsenate contaminated soils from Northeastern U.S. (Arai, et al., 2005); (4) Phytoextraction of [241]Am and other contaminants from soil by tobacco as influenced by several reagents (Fuhrmann and Lanzirotti, 2005); (5) Nematode response to, and uptake of, Pb contaminants to assess bioavailability (Jackson et al., 2005); (6) Alteration of catalyst composition during Fischer–Tropsch synthesis of clean hydrocarbon fuels from natural gas (Jones et al., 2005); (7) Mineralogy and oxidation state of As in roaster-derived iron oxides from the Giant gold mine, Yellowknife, Canada (Walker et al., 2005); (8) Chromate reduction within arid sediments from the Hanford, WA site (Ginder-Vogel et al., 2005); (9) Effects of fungal Mn oxidation in soil (Thompson et al., 2005).

UNIVERSITY OF CHICAGO
Department of the Geophysical Sciences
Chicago IL 60637

Kinetic Isotope Fractionation by Diffusion in Liquids

Frank M. Richter, 773-702-8118, Fax 773-915-9505, richter@geosci.uchicago.edu

The overall objective is to document and quantify kinetic isotope fractionations during chemical diffusion in a variety of liquids. One set of experiments was designed to measure the isotopic fractionation of Ca and Li in annealed diffusion couples juxtaposing molten basalt and rhyolite. The experiments confirmed and quantified our previous contention that chemical diffusion in silicate liquids can significantly fractionate isotopes in a mass-dependent way - in the case of $^{44}Ca/^{40}Ca$ by more than 6 per mil, and for $^{7}Li/^{6}Li$ by more than 40 per mil. Chemical and isotopic fractionation of dissolved species by diffusion in water was also studied using small spherical chambers filled with salt solutions (KCl, LiCl, $MgCl_2$) connected to a much larger water-filled reservoir by a cylindrical diffusion tube. If the dissolved species diffuse through the connecting tube at different rates, the residue of salt in the smaller chamber will become progressively enriched in the more slowly diffusing species. The validity of our experimental design was confirmed by reproducing the already known ratio of the diffusion of K to that of Li. In the case of $MgCl_2$ we found no measurable isotopic fractionation of Mg (<0.5 per mil for $^{26}Mg/^{24}Mg$) even when less than 5% of the original Mg remained in the inner chamber. If the mass–dependence of Mg isotope diffusion in water had been similar to that in molten silicate, we would have measured a fractionation of about 25 per mil. In the case of Li, we did measure a 5 per mil fractionation of $^{7}Li/^{6}Li$ when 5% of the Li remained in the inner chamber, but again this is very significantly less than the fractionation that would have occurred under similar circumstances in a molten silicate liquid. Our interpretation that the much-diminished isotopic fractionation associated with diffusion in water is due to the mass of dissolved ion plus its hydration sphere is being tested by molecular level calculations that suggest that the residence time of water in the inner hydration sphere may be more important than the number of waters in the inner sphere.

CLARK UNIVERSITY
Department of Physics
Worcester MA 01610

Physics of Channelization: Theory, Experiment, and Observation

Arshad Kudrolli, (508) 793 7752, akudrolli@clarku.edu

We study the physical processes that create eroded channels and drainage networks. We specifically address the problem of erosion driven by subsurface "seepage" flows. Whereas the flow of water through the subsurface is well characterized by Darcy's law, seepage flows out of a sloping surface can result in a channelization instability that is relatively poorly understood. We seek a better understanding of this erosive process, not only because of its importance to fluvial erosion, but also because it raises fundamental questions concerning the continuum mechanics of wet sand.

Our approach combines physical reasoning, mathematical theory, simple laboratory experiments, and low-cost field observations. We focus on the development of continuum models for the channelization process along with studies of the microscopic (i.e., granular) basis of these models.

In Fiscal Year 2005 we found that aspects of single-channel dynamics in our laboratory experiments could be well characterized by an effective equation for the evolution of transects across the channels. The erosion rate in the model is composed of diffusive and advective components as well as a simple driving term due to seeping water. Under steady driving conditions, the model predicts an asymptotically self-similar growing shape for the channel transects. A preliminary investigation of a system of ravines incised into unconsolidated sand on the Florida Panhandle suggests that our model is applicable to the field scale (i.e., channel widths of approximately one hundred meters). In particular, our model fits observed channel shapes and appears to offer a method for the estimation of erosive transport coefficients.

COLORADO SCHOOL OF MINES

Center for Wave Phenomena
Green Center
Golden CO 80401

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

Ilya Tsvankin, 303-988-0461, fax 303-273-3478, ilya@mines.edu

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 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 travel time 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.

Project results: The project only began in September 2005. The research plan for the first project year includes development of the anisotropic geometrical-spreading correction for multiazimuth PP-wave data in layered orthorhombic media and application of this technique to field data. We are also investigating the amplitude response of an effective triclinic medium formed by two orthogonal vertical sets of micro-corrugated fractures embedded in isotropic host rock.

COLORADO SCHOOL OF MINES
Department of Geophysics
Golden CO 80401

Optical Measurement of Seismic-Frequency Attenuation and Velocity Dispersion at In-Situ Conditions

Michael Batzle, mbatzle@mines.edu

We have developed a fiber-optic strainmeter to estimate moduli and seismic wave attenuation at low frequencies (10-3000 Hz) in a stress-strain experiment. The system follows a Mach-Zehnder interferometer setup from which phase lags (attenuation) and deformations (moduli) are estimated from the fringe pattern. By using interferometry high sensitivity to deformations (picometers) and phase lags (microradians) is achieved. Stress-strain measurements using strain gages or ultrasonic wave propagation sample only part of the core sample, the fiber-optic strainmeter would analyze the rock sample response to an applied stress as a whole. The first experiment on a Plexiglas sample showed that attenuation estimates are more robust that deformation estimates based on difficulties on the light intensity and sensitivity to the fiber length that is glued to the sample. For Plexiglas, Young's attenuation varies from 0.04 to 0.1 for frequencies between 70 and 1100 Hz. These attenuation estimates are in good agreement with measurements done on Plexiglas using strain gages and also from independent measurement through a resonant bar experiment. Currently we are working on improving the system's performance (e.g. light intensity, fiber of different length, glue sensitivity, phase estimation), as well as preparing a rock sample to be measured.

UNIVERSITY OF COLORADO

CIRES/Geological Sciences
Boulder CO 80309

Grant: DE-FG02-04ER15589

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

Hartmut Spetzler, spetzler@colorado.edu, 303-492-6715

We have been exploring a new technology that is based on using low-frequency seismic attenuation data to monitor changes in fluid saturation conditions in two-fluid phase porous materials. The seismic attenuation mechanism is related to the loss of energy due to the hysteresis of resistance to 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. We have concluded a three year field study at the Maricopa Agricultural Center site of the University of Arizona. Three sets of instruments were installed along an East-West line perpendicular to the 50 m by 50 m 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. Installation of instruments commenced in late summer of 2002. The instruments operated nearly continuously until April 2005. During the fall of 2003 the site was irrigated with water and one year later with water containing 150 ppm of a biosurfactant additive. This biodegradable additive served to mimic a class of contaminants that change the surface tension of the irrigation fluid. Tilt data clearly show tidal tilts superimposed on local tilts due to agricultural irrigation and field work. When the observed signals were correlated with site specific theoretical tilt signals we saw no anomalies for the water irrigation in 2003, but large anomalies on two stations for the surfactant irrigation in 2004. Occasional failures of seismometers as well as data acquisition systems contributed to less than continuous coverage. These data are noisier than the tilt data, but do also show possible anomalies for the irrigation with the surfactant. The quantity of data is large and deserves careful analysis. Detailed analyses of the two data sets are ongoing.

UNIVERSITY OF COLORADO
Department of Civil, Environmental, and Architectural Engineering
Boulder CO 80309

The Physics of Two-Phase Immiscible Fluid Flow in Single Fractures and Fractured Rock

Harihar Rajaram, hari@colorado.edu

This project aims to develop quantitative understanding of the critical processes controlling two-phase flow and transport in fractures. Our previous work identified the importance of geometry, or structure, of the two fluid phases in controlling system behavior. We have developed unique experimental systems to create and measure a wide range of phase structures. Flow and transport experiments through these structures have facilitated concurrent model development.

Highlights:

1. Solute transport in partially saturated fractures: In this research, we have carried out large-scale simulations to improve understanding of the influence of an entrapped phase on solute transport. There are several interesting results - (i) for the satiated state corresponding to capillary-dominated entrapment, modified invasion percolation dictates an invariant entrapped phase saturation regardless of domain size. Thus, transport is controlled by the blob size distribution (which scales with domain size) rather than aperture variability and Fickian transport regimes are never encountered. (ii) There are few qualitative similarities between behavior in different realizations, even when the entrapped phase saturation is the same. This behavior is in contrast to that observed for relative permeability, which shows surprising robustness across a range of complex phase distributions. 2. Reactive two-phase flows: We have carried out preliminary experiments to quantify the behavior of aperture-altering flows under partially saturated conditions. Chaotic behavior and flow-path switching occurs followed by a dramatic transition to film-dominated flow as the aperture is substantially enlarged due to dissolution. 3. Anisotropic properties of shear fractures: The directionality associated with shear suggests anisotropy in fracture aperture correlation and transmissivity, which appears to have been overlooked in the literature. In several papers, directionally averaged results are presented for aperture correlation. We derived theoretical expressions for the aperture correlation function, highlighting longer persistence and a larger integral scale normal to the shear than parallel to it, and an effective transmissivity tensor with higher transmissivity normal to shear. The hydraulic anisotropy depends on the coefficient of variation of the aperture field and the Hurst exponent, incorporating contributions from both the aperture correlation structure and anisotropic geometry of contact areas.

UNIVERSITY OF CONNECTICUT

Department of Marine Sciences
1080 Shennecossett Road
Groton CT 06340

Air-Derived Noble Gases in Sediments: Implications for Basin Scale Hydrology

Thomas Torgersen, 860 405 9094, thomas.torgersen@uconn.edu

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. 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. 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. We have also initiated a study of a variety of lab aggregated nanoparticles. We have found that aggregated FeOOH (α-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.

UNIVERSITY OF FLORIDA
Chemical Engineering Department
PO Box 116005
Gainesville FL 32611

Pore-Scale Simulations of Dissolution Breakthrough in Rough Fractures

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

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. The aim of this work is to develop pore-scale numerical simulations of chemical erosion in fractured rocks, to validate the methods by comparison with simple model systems, and to elucidate the mechanisms involved in acid erosion of a rough fracture. 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 (33:L05401, 2006). It was also selected as a highlight by the editors of GRL.

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

A Comparative Study of Dissolution Processes on Growth/Cleavage Surfaces and at Near/Far-from Equilibrium Conditions

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

It is widely agreed that surface pitting is one of the key controls for mineral dissolution. Extensive studies have documented pit observation on weathered or dissolved minerals, the relationship between pit formation and mineral dissolution rates, and the characteristic conditions for surface pitting development. Still, more questions emerge and need to be addressed, and one of them relates to dissolution kinetics and pit geometry. For example, different minerals or the same minerals dissolving at different conditions reveal pits with different size and depth. In this study, we attempt to develop a geometric-kinetic model to illustrate the relationship between pit geometry and the dissolution rate at different directions.

Consider the formation of an etch pit on a flat surface F that has a vertical dissolution rate of v_f. Assuming the vertical pit nucleation rate at a linear dislocation is v_{pit} and the vertical (to F) dissolution rate of the pit slope surface, S, is v_s. The following conditions hold for the pit formation: $v_{pit} > v_f$, $v_{pit} > v_s$, and $\tan q = v_{pit}/v_h$ where v_h is the horizontal dissolution rate of monolayer F, and q is the acute angle shared by F and S. Furthermore, the depth and width of the pit will be controlled by the relative magnitude of individual rate: when $v_{pit} \gg v_f$, deep and wide pits develop if $v_s > v_f$, otherwise deep and narrow pits form if $v_s < v_f$; when $v_{pit} > \sim v_f$, shallow and wide pits dominate if $v_s > v_f$, or shallow and narrow pits occur if $v_s < v_f$. Geometric constrains finally lead to the following relationships: $v_{f} = v_h \tan q - 1/\cot q(dD/dt)$, and $v_s = (dw/dt – v_h)\cot q$, where D and w are the radius of the pit measured on F and the terrace width measured on S, respectively, and t is the time. Since v_h, q, D, and w are experimental measurables, these expressions allow us to determine the surface retreat rate v_f and v_s during dissolution. We are currently testing this model on gypsum and calcite, two sparsely dissolving salt minerals but with very different characteristics of surface pitting.

GEORGIA STATE UNIVERSITY

Department of Geosciences
Atlanta, GA 30303

Grant: DE-FG02-02ER15365

Development and Application of a Paleomagnetic/Geochemical Method for Constraining the Timing of Burial Diagenetic Events

W. Crawford Elliott, wcelliot@gsu.edu

The proposed work tests a hypothesis that chemical remanent magnetization (CRM) is formed as a result of the smectite to illite conversion. This hypothesis is tested by comparing the timing of chemical remnant magnetization (CRM) recorded by authigenic magnetic minerals to the measured K-Ar dates of diagenetic illite in the Disturbed Belt, Montana.

In the Disturbed Belt, Montana, the clay mineralogy data and K-Ar ages of I-S were studied in the Cretaceous Marias River Shale and in adjacent Cretaceous and Jurassic rocks. The percentages of I-S were > 70% illite layers in I-S separated from thick bentonites and bentonitic shales. The absence of the $2M_1$ illite polytype in most bentonitic shales does not permit the derivation of the age of diagenetic I-S by Illite Age Analysis and yet constrains the upper estimate of maximum burial temperature to $< 250^{\circ}C$. The average age of concordant clay sub-fractions separated from three thick bentonites of Cretaceous and Jurassic depositional age increases from southeast (53.6 Ma) to northwest (56.7 Ma) along strike of the Disturbed Belt. The measured K-Ar ages of I-S and percentages of illite layers in I-S support previous interpretation by Hoffman (1976) that diagenetic illite formed in response to thrust sheet burial. This northwestward increase of mean ages of I-S is consistent with a thrust sheet emplacement model for the Disturbed Belt (Mudge, 1980). These data will be integrated with paleomagnetic data being measured by Prof. R.D. Elmore to test the hypothesis that CRM resulted from the smectite to illite conversion.

Diagenetic settings (such as thrust sheet burial, burial metamorphism, maturation of hydrocarbons and the movement of fluids and heat due to contact metamorphism) provide information about the formation of authigenic magnetic minerals and diagenetic illite in relation to prominent geologic processes and, in turn, increase our knowledge of the diagenetic processes marking the time-temperature window for the generation of oil and gas.

HARVARD UNIVERSITY
School of Engineering and Applied Sciences
Cambridge MA 02138

Dissolution Mechanisms of the Carbonate Minerals

Scot T. Martin, scot_martin@harvard.edu, (617) 495-7620

Calcium carbonate minerals in soils, biomaterials, stone structures, and atmospheric particles undergo cycles of wetting and drying. Changes in the molecular and the physical features of the surface and hence in surface reactivity accompany the cycling of the layer thickness of adsorbed water during drying and rewetting. Under humid air a cleaved calcite surface reconstructs through pit dissolution and film growth. After 7 to 9 hours at 80% relative humidity (RH), 50% to 80% of the surface is covered by a film that is flat-topped, 1 nm high and oriented relative to the substrate. The local dielectric constant of the film is less than that of the substrate. As a result, when film coverage approaches a maximum, surface ion mobility and density decreases and the surface is less polarizable. Furthermore, an observed dependence of the contact mode film height on RH suggests that loosely bound water is part of the film, which may be a hydrated calcium carbonate phase. Hydrated calcium carbonate is widely understood to require the co-presence of organic materials, such as lipids and proteins, to inhibit rapid recrystallization. The results of this work, however, suggest that hydrated calcium carbonate could also be kinetically stable in inorganic systems having a favorable match to the underlying calcite substrate. Transformation of the metastable hydrated calcium carbonate film to a more thermodynamically stable phase often occurs with time. Possible phases for the $CaCO_3$-H_2O system of this study include metastable calcite polymorphs such as aragonite and calcite. In more complex, multicomponent environmental systems, phase transformations during aging could provide pathways for the incorporation of foreign divalent metals, such as Mg^{2+} and Cd^{2+}. The foreign ions could diffuse into the labile hydrate structure and could become locked in place upon an abrupt phase transition. This proposed pathway could circumvent energetically unfavorable and slow solid-state diffusion.

UNIVERSITY OF HOUSTON
Department of Physics
University of Houston
Houston TX 77204

Grant: DE-FG02-05ER15697

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

Arthur B. Weglein, (713) 743-3848, aweglein@central.uh.edu

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.

UNIVERSITY OF ILLINOIS
Department of Geology
1301 W. Green St.
Urbana IL 61801

Grant: DE-FG02-00ER15028

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

R. James Kirkpatrick, kirkpat@uiuc.edu

With the overall objectives to advance molecular-scale understanding of the properties of aqueous solutions at mineral surfaces, in interlayer galleries and in nano-confinement, our 2005 research was focused on three topics:

Combined NMR, XRD and MD computer modeling studies of organic-inorganic nano-composites. Mg/Al layered double hydroxides, containing formate, acetate, propionate, citrate, and glutamate, were investigated by MD simulations for wide ranges of water contents to complement X-ray and NMR measurements for the same systems under variable relative humidity conditions. Computed hydration energies suggest high water affinity of the system leading to enhanced swelling of the LDHs in agreement with the large interlayer spacing observed by XRD under high RH conditions. This organo-LDHs behavior contrasts sharply with LDHs containing inorganic species.

Combined NMR and MD modeling studies of Cs^+ and Cl^- interaction with natural organic matter. NMR measurements of CsCl solutions containing Suwannee River NOM at pHs from 3.4 to 9.0 and comparable neat CsCl solutions show that the NOM presence has little effect on the ^{133}Cs chemical shifts, demonstrating that its local coordination environment does not change significantly due to interaction with NOM. MD simulations support these results and show that Cs^+-NOM association occurs principally as outer-sphere complexation and does not reduce the Cs^+ mobility sufficiently to cause NMR line broadening. The ^{35}Cl NMR and the MD results both demonstrate no significant Cl^--NOM complexation in the pH range investigated, consistent with negative charge on the NOM.

MD simulation of the quartz-water interface. MD simulations of the hydrated and fully hydroxylated quartz (001) surface show that interfacial H_2O molecules both donate and accept H-bonds to/from surface OHs and that the interfacial water structure is very similar to those at other hydroxylated surfaces, such as $Ca(OH)_2$. Interfacial H_2O and surface Si-OHs together form a stable well-interconnected H-bonding network. On average, the H-bonds involving Si-OH are stronger than those among water molecules. However, the higher ordering of interfacial water (compared to bulk liquid) can not be adequately described as simply "ice-like", it rather resembles the behavior of supercooled water.

Published papers based on this research can be accessed from:
http://www.geology.uiuc.edu/~kirkpat/papers.htm and
http://www.geology.uiuc.edu/~kalinich/publications.html

UNIVERSITY OF ILLINOIS
Department of Geology
1301 W. Green St.
Urbana IL 61801

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

Craig Bethke, (217) 333-3369, bethke@uiuc.edu

We use quantitative modeling techniques to better understand how physical transport, chemical reaction, and microbiological activity work together to control the chemical composition of groundwater in the Middendorf aquifer, a mostly confined aquifer of the Atlantic Coastal Plain province, in South Carolina. Historically, geochemists called first on equilibrium thermodynamics and then geochemical kinetics to explain how groundwater evolves in composition as it flows through the subsurface. These attempts have fallen short, however, and there is a general consensus currently that microbial life exerts a dominant influence on groundwater chemistry, although an influence that has proved difficult to quantify. We are sampling groundwater from an array of wells across the aquifer and analyzing it chemically and microbiologically. The chemical analyses include assays of the oxidized and reduced species that serve as electron-donating and electron-accepting species for respiring organisms. We are analyzing biomass filtered from the water in various ways, including MPN, T-RFLP, MPN-PCR, and real-time PCR. We will integrate the results of these analyses into a reactive transport model to attempt to explain the distribution of chemical reaction and microbial activity in the aquifer.

UNIVERSITY OF ILLINOIS AT CHICAGO
Department of Earth and Environmental Sciences
Chicago IL 60607

Grant: DE-FG0203ER15381

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

Neil C. Sturchio, 312-355-1182, fax 312-413-2279, sturchio@uic.edu

In this collaborative program with Paul Fenter (Argonne National Laboratory) and others, we continue the development and application of synchrotron X-ray scattering techniques for in situ studies of mineral-fluid interfaces, taking advantage of the major increases in temporal and spatial resolution afforded by the high X-ray brilliance and energy available at the Advanced Photon Source (APS). These experiments will help bridge the gap between real-space and reciprocal-space techniques, will further define kinetics and reaction mechanisms at the atomic scale in key mineral-fluid systems, and will constrain the continued development of theory pertinent to processes at mineral-fluid interfaces. Advances in these fundamental areas will yield significant benefits in terms of DOE mission-related applications, such as energy resource exploration and utilization, environmental restoration and waste management, and materials Structure and bonding at the mineral-fluid interface are just beginning to be understood for the most simple minerals, and further progress is limited by the development of new experimental and computational techniques capable of elucidating the atomic realm. A particularly powerful set of techniques for studying surfaces, thin films, and interfaces arises from X-ray scattering effects. This set of techniques, which become practical only at high-intensity synchrotron radiation sources, includes X-ray reflectivity, surface and thin-film diffraction, crystal truncation rods (CTR), and X-ray standing waves (XSW). These experiments demonstrated the first uses of X-ray reflectivity, thin-film diffraction, XSW, and CTR measurements for in situ studies of mineral-fluid interfaces in static and dynamic mineral-fluid systems. We are focusing our efforts in several experimental thrusts, each corresponding to a major area of scientific need in mineral-fluid interface studies. Progress during the past year included further investigations of a broad range of mineral-water interface structures, processes (molecular adsorption and mineral dissolution), and reaction kinetics, for a broad range of mineral-water systems (carbonates, silicates, and oxides). We have emphasized applications of resonant anomalous x-ray reflectivity (RAXR). These are the first applications of RAXR to mineral-fluid interfaces, and they have revealed a new level of complexity in our understanding of ion adsorption behavior at such interfaces.

UNIVERSITY OF ILLINOIS AT CHICAGO

Department of Earth and Environmental Sciences
845 W. Taylor St., MC-186
Chicago IL 60607

Grant: DE-FG02-02ER15364

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

Kathryn Nagy, klnagy@uic.edu, (312) 355-3276

We seek to acquire mechanistic understanding of processes at the mineral-water interface that explain macroscopic observations and that can be applied to problems such as the distribution and reactivity of environmental contaminants as well as the chemically-reactive behavior of ground water flow in porous media. We are addressing two specific questions regarding rates and mechanisms of sorption, dissolution, and growth. First, what is the nanoscale/molecular scale structure of the interface between micas or clays (phyllosilicate minerals) with aqueous solutions and how does that structure relate to the processes of sorption and secondary mineral nucleation and growth? Second, what systematics control the aging kinetics of nanoparticles of iron-oxides and the simultaneous incorporation of chemical components such as contaminant ions and organic molecules?

The basal surface of phyllosilicates is a primary sorbent of environmental contaminants, natural organic matter, and life-sustaining nutrients. Micas are also superb atomically-flat substrates used in materials science and surface physics applications. Despite the interdisciplinary importance of phyllosilicate basal surfaces, a full molecular-scale description of the crystal-solution interface structure is not yet available. Our recent application of X-ray scattering techniques using high brilliance synchrotron radiation coupled with atomic force microscopy (AFM) has revealed molecular-scale details of the interface structure such as relaxation of atoms in the crystal, surface roughness, and properties of the electrical double layer in the contacting aqueous solution (containing water, monovalent and divalent cations, anions, and natural organic molecules). Parameterization of the data provides subnanometer-scale resolution of the relaxation of the solid, structure of the overlying solution including positions of sorbed ions, and structure of the sorbed organic films.

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 have aged Fe-oxides in the presence of perrhenate anion under oxidizing conditions. Results indicate that uptake is controlled by pH-dependent sorption onto nanoparticles of ferrihydrite that recrystallize to more stable iron-oxide phases.

INDIANA UNIVERSITY
Department of Geological Sciences
Bloomington IN 47405

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

Arndt Schimmelmann, (812) 855-7645, aschimme@indiana.edu

Changes in the ^{2}H/^{1}H (or D/H) ratio of sedimentary organic matter (SOM) during thermal maturation have been difficult to interpret because the effects of hydrogen exchange and kinetic fractionations are confounded in natural samples. Isotopically labile organic hydrogen in fossil fuels occupies chemical positions that participate in isotopic exchange and in chemical reactions. During last year, we monitored changes in the H-isotopic exchangeability and stable isotope D/H ratio in oil and maturing kerogens in source rocks to evaluate paleoenvironmental and diagenetic influences. The influence of thermal maturity on D/H stable isotope ratios of non-exchangeable organic hydrogen and on hydrogen isotopic exchangeability (expressed as H_{ex}, in % of total organic hydrogen) was investigated in two suites of type-II kerogens (the insoluble fraction of organic matter in marine sediments). In both kerogen suites, D/H ratios increase with maturity up to an R_o ~1.5 %, then level out. Increasing D/H ratios suggest (i) isotopic transfer of ^{2}H-enriched hydrogen from water into the pool of organic non-exchangeable hydrogen, and/or (ii) preferential loss of ^{1}H-enriched organic moieties from kerogen during maturation. More extensive ^{2}H-enrichment with increasing maturity in New Albany Shale kerogens relative to Exshaw Formation kerogens is apparently driven by a higher ^{2}H-abundance in New Albany Shale formation waters and a larger water-kerogen isotopic difference. To date, this is the strongest evidence for hydrogen isotopic transfer between naturally maturing kerogen and water hydrogen (published in *Organic Geochemistry*, http://dx.doi.org/10.1016/j.orggeochem.2005.10.006). In 2005, we finalized an invited review article "Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation" for the prestigious *Annual Review of Earth and Planetary Sciences,* (http://dx.doi.org/10.1146/annurev.earth.34.031405.125011). In this paper, we review experimental and field data that document a progressive increase in the D/H ratio of most organic hydrogen at the bulk and molecular levels, and suggest that the transfer of hydrogen from water to organic matter is the most important mechanism leading to those changes. SOM and water in natural petroleum systems approach a pseudoequilibrium D/H fractionation of about −80 to −110‰. D/H ratios of organic hydrogen can preserve quantitative information about paleoclimate throughout diagenesis, and some qualitative information through catagenesis.

JOHNS HOPKINS UNIVERSITY
Department of Earth and Planetary Sciences
Baltimore MD 21218

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

Grant Garven, garven@jhu.edu

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

Project Description: We have targeted active faults and young petroleum fields in southern California for study. Our most recent studies have been on the South Elwood fault in the Santa Barbara channel, the Refugio Fault in the Transverse Ranges near Santa Barbara, and the Newport-Inglewood Fault in the Los Angeles Basin. Subsurface core samples, outcrop samples, well logs, reservoir properties, pore pressures, and published structural-seismic sections are being collected to characterize the tectonic history and diagenetic evolution for the known fault networks. These data provide constraints for finite element models that are being developed to predict fluid pressures, flow patterns, rates of deformation, temperatures, and diagenetic mineralization/dissolution patterns associated with large fault systems. We are also seeking to identify geochemical signatures resulting from rapid CO_2 degassing. Our samples include calcite from well tubing scales, fault zones, and speleothems in man-made tunnels.

Results: Well tubing scales and speleothems show covarying carbon-oxygen isotopic signatures and may show considerable Mg substitution, both of which are attributed to rapid calcite crystallization. A manuscript by Perez & Boles has been published that describes the development of fractures that result from unloading of quartz cement in quartz sandstones. Using theoretical considerations and a natural analog from Venezuela, we show that thermoelastic contraction causes once deeply buried quartz cemented strata to develop fractures during uplift. On the hydrogeologic modeling front, Appold and others developed a manuscript (in press) that mathematically models the observations on the Refugio Fault with different reactive flow 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 model links evolving fluid chemistry during aqueous mass transport, fluid mixing, and calcite precipitation.

JOHNS HOPKINS UNIVERSITY
Department of Earth and Planetary Sciences
Baltimore MD 21218

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

David R. Veblen, (410) 516-5049, dveblen@jhu.edu

This project is an investigation of reactions between silicate minerals and toxic metal-bearing aqueous fluids. We are specifically exploring mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals and sorbed to mineral surfaces. The project has three main components: experimental investigation of U reduction and sorption by phyllosilicates; transmission electron microscopy (TEM) characterization of reaction products; and development of new characterization techniques. Technique development includes X-ray photoelectron spectroscopy (XPS) and atomistic-scale TEM methodologies to probe sorption behavior and redox reactions. Experiment design and sample characterization is aimed at elucidating crystallographic and solution controls on heterogeneous electron transfer between phyllosilicates and multivalent metals in the environment. Most recently, we have integrated hydrothermal synthesis of phyllosilicates with varied layer-charge distribution into our experimental strategy.

The research has focused on heterogeneous reduction of uranyl by Fe(II)-bearing micas. Valence state of uranium strongly influences its solubility and sorption behavior thereby determining its mobility in environmental systems. Recent results include: differentiation of reactivity of basal surfaces, edges, and interlayer regions; identification of effects of alkali cations in solution on heterogeneous reduction of uranyl by micas; and discovery that heterogeneous reduction of uranyl on Fe(II)-mica surfaces produces pentavalent uranium as a major sorbed species. Our research suggests that pentavalent U may play an important, but hitherto unrecognized, role in the U geochemical cycles.

TEM work has emphasized development and application of energy-filtered techniques. This has included compositional imaging at the sub-nanometer scale, valence imaging for transition metals at the nanometer scale, and investigation of chemical segregation at grain boundaries. Electron energy-loss spectroscopy (EELS) of U phases and sorption products currently centers on utilization of novel-edge fine structure. X-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) have been used to determine the valence state and location of metals sorbed to phyllosilicates. This work includes development of ab initio theoretical models to better interpret fine structure in the XPS of transition metals. Our long-range goals are to understand the electron transfer mechanisms of heterogeneous redox reactions in phyllosilicates and simulate complex bonding environments that represent sorption at surfaces and nanosized particles.

JOHNS HOPKINS UNIVERSITY
Department of Earth and Planetary Sciences
Baltimore MD 21218

Predictive Single-Site Protonation and Cation Adsorption Modeling

Dimitri A. Sverjensky, 410-516-8568, sver@jhu.edu

During this period my research has finalized a predictive surface chemical model for oxide mineral surfaces in both 1:1 and 2:1 electrolyte solutions. Predictive correlations for the adsorption of the monovalent alkalis (Geochim. Cosmochim. Acta, 69, 225-257) and the divalent alkaline earths (in review) consistent with crystal chemical and solvation theory have been developed which enable predictions of proton surface charge as functions of pH, ionic strength and electrolyte type for many minerals in an internally consistent manner. A new approach to oxyanion adsorption is being developed which will enable the addition of sulphate, carbonate, silicate, and oxalate surface complexation. In combination with the above results for 1:1 and 2:1 electrolytes, this will enable the prediction of surface charge and speciation on minerals in model natural waters including rivers, soil waters, groundwaters, and seawater. Furthermore, using this new approach, metals and semimetals that form oxyanions, such as chromium, arsenic, and selenium can be incorporated using surface species on the oxide minerals that are in agreement with those demonstrated by independent X-ray and infrared studies. The overall objective is prediction of the role of adsorption reactions on the acquisition of metals by fluids circulating through aquifers in the earth's crust.

LOUISIANA STATE UNIVERSITY
Department of Geology and Geophysics
Baton Rouge, LA 70803

Grant: DE-FG02-01ER15167

3D Sedimentological and Geophysical Studies of Clastic Reservoir Analogs: Facies Architecture, Reservoir Properties, and Flow Behavior within Delta Front Facies Elements of the Cretaceous Wall Creek Member, Frontier Formation, Wyoming

Christopher White, cdwhite@lsu.edu

The first year of this project focused on methods to prepare fluid flow models from geophysical responses and evaluate the sensitivity of these flow models to uncertainty in geophysical and geological variables. Research used the now-complete Corbula Gulch (distributary channel) data set to develop algorithms because the Wall Creek (deltaic) data set is not yet ready.

Some fluid flow models included heterogeneous sandstone permeability estimated via correlation with ground-penetrating radar attributes. However, most flow models neglected the relatively small variance in sandstone permeability and focused on geostatistical models for the distribution of shales draping inclined, accretionary bedding. Shale models were inferred from outcrop data and via correlation to instantaneous amplitude of radar responses. Both approaches yielded approximately isotropic variograms with integral ranges of 5-8 m. Stochastic images of shales were generated on the accretion surfaces using sequential Gaussian simulation. Suites of flow simulations demonstrate that for the moderate shale coverage fraction (*circa* 30 percent), large surface spacing (about 1 m or more), and low correlation range observed at Corbula Gulch, these shale drapes have a small effect on flow behavior except for decreasing vertical permeability. Two journal articles (Mathematical Geology and AAPG Bulletin) describe this work.

Current work focuses on object models and radar responses for calcite concretions in the Wall Creek Member. The improved object models include sophisticated bias corrections based on Abel transforms and Markov chain models.

A stratigraphic grid will be constructed as interpreted radar surveys become available.

UNIVERSITY OF MARYLAND
Department of Chemistry and Biochemistry
College Park MD 20742

Grant: DE-FG02-94ER14467

Theoretical Studies on Heavy Metal Species in Solution

J. A. Tossell, 301-405-1868, Fax 301-314-9121, tossell@chem.umd.edu

Our research group utilizes the techniques of computational quantum chemistry to study the structures, energetics and properties of various species in solution, as components of mineral glasses, or absorbed on mineral surfaces. The focus in Fiscal Year 2005 has been on obtaining experimental values for the fractionation of ^{11}B and ^{10}B between $B(OH)_3$ and $B(OH)_4^-$ by accurate determination of the difference of pKa's of 99 % enriched ^{11}B and ^{10}B $B(OH)_3$. This work has been done in collaboration with Prof. Robert Byrne (U. of South Florida) and Prof. J. Kaufman (UMCP) and his graduate student Kateryna Klochko. We have also calculated the ^{11}B NMR and the ^{11}B,^{10}B isotopic fractionation for a number of species formed by the adsorption of $B(OH)_3$ or $B(OH)_4^-$ onto humic acids, suggested by the analogous experimental study of Lemarchand, et al. (2005). An extensive study has also been done at high quantum chemical levels on the structure, stability and spectral properties of oligomers of the unstable species H_2CO_3. This is the first study to quantitatively match the vibrational spectra obtained experimentally for an incompletely characterized H_2CO_3 solid. A species $B(OH)_2CO_3^-$ has been identified as a possible product of the incorporation of $B(OH)_3$ into calcite. Improved methods for calculating interaction energies of solution species have allowed us to determine free energies for a number of reactions of As compounds, including acid dissociation, sulfidation and changes in As coordination and water incorporation. Previous calculations of energetics for $HgCl_n$, n=1 - 4, have been refined and we have extended such calculations to the study of bisulfide and polysulfide complexes.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Department of Earth, Atmospheric, and Planetary Sciences
Cambridge MA 02139

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

J. Brian Evans, brievans@mit.edu

Temporal and spatial variations of permeability, common in the Earth, are driven by a complex set of processes including fracturing, diagenesis, brittle pore collapse, pressure solution, creep flow, and crack healing. 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. 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 work fell 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. For example, we investigated changes in transport properties during triaxial compressive loading and purely isostatic compressive loads in sandstone, marble, limestone, granular aggregates of quartz and mica or illite and also studied thermal cracking in Sioux quartzite, Carrara marble, and a reservoir rock from Awibengkok, Indonesia. The exact evolution of permeability as a function of changes in porosity depends of the process(es) by which the pore geometry is changed, including, for example, pressure solution, cataclastic fracturing, and creep processes. By making measurements of some synthetic material with differing mineral phase contents, we obtained insight into the effect of mineral heterogeneities on the transport properties. We also ran experiments designed to understand the effect of changing pore geometry on permeability and on electro-kinetic properties. Finally, because we often measure the permeability of the laboratory samples using the oscillating pore pressure method, we conducted an analysis of the relative uncertainties of the measurement of storativity and permeability by this technique. This study confirmed a frequency effect noticed previously by other workers. The results show that the permeability measurements are robust and accurate, but that storativity measurements are quite sensitive to details of the apparatus.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Earth, Atmospheric, and Planetary Sciences
Cambridge MA 02139

Physics of Channelization: Theory, Experiment, and Observation

Daniel H. Rothman, (617) 253-7861, dhr@mit.edu

We study the physical processes that create eroded channels and drainage networks. We specifically address the problem of erosion driven by subsurface "seepage" flows. Whereas the flow of water through the subsurface is well characterized by Darcy's law, seepage flows out of a sloping surface can result in a channelization instability that is relatively poorly understood. We seek a better understanding of this erosive process, not only because of its importance to fluvial erosion, but also because it raises fundamental questions concerning the continuum mechanics of wet sand.

Our approach combines physical reasoning, mathematical theory, simple laboratory experiments, and low-cost field observations. We focus on the development of continuum models for the channelization process along with studies of the microscopic (i.e., granular) basis of these models.

In Fiscal Year 2005 we found that aspects of single-channel dynamics in our laboratory experiments could be well characterized by an effective equation for the evolution of transects across the channels. The erosion rate in the model is composed of diffusive and advective components as well as a simple driving term due to seeping water. Under steady driving conditions, the model predicts an asymptotically self-similar growing shape for the channel transects. A preliminary investigation of a system of ravines incised into unconsolidated sand on the Florida Panhandle suggests that our model is applicable to the field scale (i.e., channel widths of approximately one hundred meters). In particular, our model fits observed channel shapes and appears to offer a method for the estimation of erosive transport coefficients.

MICHIGAN TECHNOLOGICAL UNIVERSITY
Department of Geological and Mining Engineering and Sciences
1400 Townsend Drive
Houghton MI, 49931-1295

Grant: DE-FG02-05ER15674

Permeability Dependence of Seismic Amplitudes - Data Acquisition Program - Phase 1, Design Study

Roger Turpening, roger@mtu.edu

Objective: The objective of this research is to provide the high-frequency, wide-bandwidth, field-scale, data acquisition segment of a major, investigation into seismic attenuation. Theoretical and laboratory investigations in seismic attenuation are taking place at several places in the seismic community.

Project Description: Rigorous attenuation research requires:

• Separate, dedicated boreholes for the seismic sources
• Wide bandwidth (six to eight octaves), high-frequency (10Hz - 3kHz) data
• Long distances, i.e. many wavelengths between receiver boreholes
• Many wavelengths of propagation in a porous and permeable reservoir
• Time-lapse measurements while changing the fluids in the reservoir—i.e. intrinsic attenuation separated from scattering
• Both compressional and shear wave measurements.

The goal of this design phase is to determine the location of the source holes such that drilling can proceed immediately at the onset of Phase II. The limiting factor is the propagation distance for compressional waves from the relatively weak, high-frequency (piezoelectric) source. Shear waves will be generated by the very strong downhole, axial, vibrator.

Results: In early July 2005 Z-Seis. Inc., funded by DOE-Fossil Energy, acquired a cross well reflection image of the hydrocarbon reservoir (reef) at the MTU test site using a piezoelectric source. During program special efforts were made to acquire data at very large source to receiver offsets.

Whereas the crosswell reflection data was acquired with a sweep length of 0.35 seconds we used a sweep ten times longer (3.3 seconds) and we doubled (16) and quadrupled (32) the number of sweeps in a stack. With these parameters we were able to achieve ray path lengths of 3,900 ft. and still observe the entire sweep (100 Hz.-3,000Hz). Signals were "seen" at ray path lengths of 4,900 ft. and they would be usable at this distance using deviated source boreholes. In addition these ray paths passed through the porous and permeable reef, which attenuates high-frequency energy, just as they would in the full-scale experiment.

MINERALOGICAL SOCIETY OF AMERICA

3635 Concorde Pkwy Ste 500
Chantilly VA 20151

Grant: DE-FG02-01ER15127

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

J. Alex Speer, (703) 652-9950, fax: (703) 652-9951, j_a_speer@minsocam.org

The project was for the support of two Mineralogical Society of America and Geochemical Society short courses and companion Reviews volumes in 2005:

[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. . Convenors were Peter Reiners (Yale University) and Todd Ehlers (University of Michigan). Registrations were taken by the Mineralogical Society of America and 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. Convenors were Jillian F. Banfield, Javiera Cervini-Silva, and Kenneth H. Nealson. Registrations were taken by the Mineralogical Society of America and 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.

UNIVERSITY OF MINNESOTA
Department of Geology and Geophysics
Pillsbury Hall
Minneapolis MN 55455

Rheology of Earth's Interior

D.L. Kohlstedt (612) 624-7311, fax (612) 625-3819, dlkohl@umn.edu

The overall scope of this research is to determine the high-temperature, high-pressure flow law for olivine, an essential step in understanding the dynamics of Earth's deep interior. A series of twenty deformation experiments have been conducted using the D-DIA apparatus at synchrotron radiation facilities. Polycrystalline samples were hot-pressed from powders of olivine plus 5% enstatite. Experiments were carried out at constant displacement rates of 1×10^{-5} to 4×10^{-4} /s to shortening strains of ~15% with temperatures between 1273 and 1573 K and pressures of 3 to 10 GPa. The chemical environment of the olivine samples is fixed; the oxygen fugacity is buffered by the existence of both Ni and NiO, and silica activity is set by the presence of enstatite.

Precise measurements at high pressure of stress, strain, strain rate, pressure, and temperature are a distinct feature of this study. During a deformation experiment, x-ray radiographs taken periodically of the sample column yield the change in length of the sample as a function of time, from which strain and strain rate are calculated. Pressure is determined based on the spacing of x-ray diffraction peaks from a small amount of well-characterized proxy material, MgO, inserted into the deformation column, while differential stress is obtained from the strain of various lattice planes in the sample measured as a function of orientation with respect to the stress field.

Analyses of our data yield an activation volume for creep of 6×10^{-6} m^3/mol. Additional analyses of the microstructures as well as the water contents of our samples are still in progress. Nonetheless, these results indicate that previously reported values are a factor of two to three too large. Our new results are very exciting, as they indicate that the D-DIA experiments have adequate resolution to determine important flow parameters such as activation volume.

The techniques used for both D-DIA experiments and x-ray diffraction measurements are breakthrough technologies compared to conventional deformation experiments. Significant effort on cell design now permits experiments to 12 GPa at 1500 K. Our software package greatly simplifies data reduction, reducing the time by a factor of ten.

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

Grant: DE-AT01-04ER15569

Board on Earth Sciences and Resources

Anthony R. de Souza, 202-334-2744, adesouza@nas.edu

The Board on Earth Sciences and Resources is the focal point of earth science activities at the National Academies. Founded in 1988, the Board provides objective advice through its mandated, requested, and self-initiated studies. Many of the Board's activities are conducted through its six standing committees. Theses committees are Earth Resources, Seismology and Geodynamics, Geological and Geotechnical Engineering, Geophysical and Environmental Data, Mapping Sciences, and Geographical Sciences.

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

Grant: DE-FG02-05ER15664

Grand Research Questions in Solid-Earth Sciences

Anne M. Linn, 202-334-2744, alinn@nas.edu

Progress in the solid-Earth sciences has been remarkable over the last few decades, driven by the availability of new instruments and improved modeling capabilities, reduced barriers to cooperation with scientists in other countries, and increased coordination with other disciplines, such as astronomy and biology. With research advancing on such a wide front, it can be difficult to define the frontiers of scientific inquiry and to convey that information in a way that captures the imaginations of Congress, federal agencies, the broader scientific community, and the general public.

A committee of the National Academies has been charged to identify the grand research questions driving the solid-Earth sciences. Although other reports have identified research priorities in the solid-Earth sciences, few have cast them mainly as compelling, fundamental science questions. Such "big picture" questions may require decades to answer and research support from many agencies and organizations. The answers to these questions could profoundly affect our understanding of the planet on which we live.

The research questions chosen in this study 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. A preliminary set of questions was posted for community comment in professional society newsletters and the National Academies website in early 2006. The committee is now refining the questions and describing them in short, plain language that will be understandable by agency managers, scientists in other disciplines, members of Congress, and the general public. The report is expected to be released by the end of 2006.

NEW ENGLAND RESEARCH
White River Junction, VT 05001

Grant: DE-FG02-98ER14906

Evolution of Fracture Permeability

Stephen Brown, sbrown@ner.com

We are investigating the complex active chemical interaction between pore fluid and fractures that causes the fluid composition and fracture surface topography to change over time.

Our experimental model consists of $CaSO_4$ samples pressed with a constant force against an inert textured fracture surface. Pore fluids ranging from unsaturated to supersaturated are introduced to one end of the sample in order to actively alter the fracture surface topography. We analyze features on the evolving fracture surfaces including high-flow dissolution channels, dissolution-resistant plateaus, and caverns formed from precipitate. We use finite difference and lattice Boltzmann (LB) methods to calculate pore fluid flow direction and magnitude over the entire sample surface.

The flow channel networks evolve from a homogeneous system to one more (self) organized and complex. LB methods predict the formation of major dissolution features seen in the experiments, such as long undissolved "stringers" in the lee of obstacles.

LB predicts that dendrites may grow along fracture surfaces under saturated conditions. This form of growth can be the major cause of decreasing permeability, even when the added solid fraction is small. LB predicts dendrites will grow toward time-varying regions of fast flow. Based on this idea, some larger-scale numerical models of permeability evolution in actively dissolving or infilling fracture are being developed. The models studied so far show a self-organization of flow channel structure and nearly linear changes in fluid permeability with time.

We substantiate these findings by obtaining quantitative observations from fractures and veins in drill core obtained from Awibengkok, Indonesia. Images of veins are analyzed for geometrical properties including variations in vein width, the roughness of vein walls, and the minimum aperture distribution. Most veins developed by episodic fracturing, fluid flow, and mineralization, implying that void space and permeability varied markedly over the life of the vein. Using our observations from the veins split core and thin sections we present a series of four qualitative permeability models that differ depending upon the history of fracturing and mineralization.

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

Fluid and Particulate Transport in Self-Affine Fractures

Joel Koplik, (212) 650-8162, fax: (212) 650-6835, koplik@sci.ccny.cuny.edu

1. We studied the fluctuations in the shape of a high-Peclet number dispersion front expanding radially in a self-affine fracture, and found that the front itself developed a self-affine structure with the same Hurst exponent as the fracture surface. In effect, a self-affine fractal surface is able to "impose itself" on a flexible object moving through it. We used both numerical simulations and direct experimental observations as data, and analyzed the front using an average wavelet analysis which is more suitable than box-counting for self-affine structures. The range of length scales over which the front was self-affine was bounded below by the mean fracture aperture and above, remarkably, by the entire width of the front rather than the surface correlation length.

2. The permeability anisotropy resulting from shear displacement of the complementary self-affine walls of a rough fracture was investigated using experiments and lattice Boltzmann calculations. In the laboratory, a clear anisotropy in a dispersion front is observed in the presence of shear displacements, and allowed us to estimate the ratio of the permeabilities for flow parallel and perpendicular to the shift. Numerical simulations allowed us to explore the parameter space in more detail. A simple model was proposed which accounts for the development of channels perpendicular to the shift, and which qualitatively explains these results and in particular predicts a permeability decreasing (increasing) linearly with the variance of the aperture field for flow parallel (perpendicular) to the shear displacement.

3. As an first step in considering the dynamics of non-Newtonian fluids in fractures, we developed and tested a numerical code based on a modified version of the lattice-Boltzmann method. The basic idea is due to Aharonov and Rothman and involves adjusting the relaxation time parameter in the BGK approximation to the Boltzmann equation locally, so that the viscosity has the correct (power-law) dependence on the strain rate. The code was tested on a non-trivial reentrant corner flow, which contains nearly-singular corner regions of high stress as well as channel-flow regions with mild linear stress variation, and the results agreed well with a finite element continuum calculation.

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

Contract: DE-FG02-03ER15458

Stress-Dependent Acoustic Propagation and Dissipation in Granular Materials

Hernan A. Makse, (212) 650-6847, fax (212) 650-6835,
hmakse@levdec.engr.ccny.cuny.edu

This project is a collaboration between CCNY and Schlumberger. The goal of the project is to combine experiments, theory and simulations to develop an understanding of the elastic and viscoelastic properties of granular materials.

(i) Nonlinear elasticity and acoustics of granular materials. We attempt to understand the elastic response of a granular assembly under loading. Our experiments reveals that elasticity theory fails to describe the elastic properties of granular assemblies. We show that a correct treatment should include the collective relaxation mechanisms related to structural disorder and nonaffine motion of grains. A theoretical investigation in collaboration with Cornell University allows the incorporation of additional degrees of freedom resulting in predictions which are in far better agreement than previously. We also investigate the Green (response) function of random packings of grains.

(ii) Compaction and stress relaxation. The relaxation and dissipative properties of cohesionless granular assemblies under compression are being studied both experimentally and numerically. We investigate the system's exploration of the static configurations through a novel compaction procedure at varying confining pressures. Once the system is fully compactified we study the slow relaxation dynamics under an applied strain. The computer simulations show that the main process responsible for the logarithmic stress relaxation is the collective particle motion and rearrangements of grains predominantly via sliding.

We characterize an analogous ``glass transition'' for packed granular systems, below which the system shows aging in time dependent sliding correlation functions.

(iii) Dissipation in granular matter. An important goal of this project is to elucidate the origin of the dissipation mechanisms in granular materials. To this end we performed a series of experiments, simulations and theory to calculate the effective mass of a rigid cavity filled with loose granular particles. Our results show that the dominant features of the response are a sharp resonance and a broad background. These features are taken to understand the effects of the vast parameter space contributing to acoustic damping. This includes studies on compaction, temperature tests, effects of humidity, and surrounding fluids (air, water), effects of filling fractions, friction and coefficients of restitution and different particle characteristics.

STATE UNIVERSITY OF NEW YORK, STONY BROOK
Department of Geosciences
Stony Brook NY 11794

Grant: DE-FG02-96ER14633

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

Martin A.A. Schoonen, 516-632-8007, mschoonen@notes.cc.sunysb.edu

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. The program integrates observations at the macroscopic level with those at the microscopic scale. It is this integration that has proven to be very useful and productive. The objective of the research has been to understand important fundamental aspects of the surface chemistry of pyrite, such as charge development, reactivity, surface stoichiometry, surface structure, and interaction with dissolved constituents (sorption). Our ultimate goal is to provide insight into the role of pyrite as reactant, sorbent, and (photo)catalyst in environmentally and geologically relevant environments. This research has recently brought forth to the scientific forefront the importance of non-stoichiometric sites or defects in controlling the reactivity of pyrite. Many fundamental questions regarding the origin, presence, electronic structure, and reactivity of these defects remain unanswered and are being addressed in our studies. We believe that we need to answer these questions in order to provide the basic science needed for the development of the next generation of techniques in the abatement of acid mine drainage, one of the most important environmental problems we face (about 1 million dollars is spent per day on this problem). We argue that by understanding the reactivity of pyrite at the molecular scale strategies can be developed that target one or more of the elementary reactions in the oxidation of pyrite. While our research is primarily motivated by a desire to understand pyrite oxidation at the molecular level, our work is also of importance to several technical problems where the surface chemistry of pyrite plays a role, such as flotation of pyrite in the mining industry, acidification of hydrocarbon reservoirs (a problem relevant to terrestrial CO_2 sequestration), and sorbent of radionuclides and other constituents (e.g. gold).

STATE UNIVERSITY OF NEW YORK, STONY BROOK
Department of Geosciences
Stony Brook NY 11794

Grant: DE-FG02-99ER14996

Microscale Processes and Macroscopic Behavior of Porous Geomaterials

Teng-fong Wong, (631) 632-8212, Teng-fong.Wong@stonybrook.edu

The objective of this project is 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, as well as theoretical and numerical analyses. The overall goal of the research program is to enhance the fundamental understanding of failure and transport, and thereby strengthen the scientific basis for the application of laboratory results to various technological efforts of current societal concern and impact. Progress to date includes (1) systematic investigation of the micromechanics of failure in three porous limestones, and constitutive modeling of shear-enhanced compaction in clastic and carbonate rocks, (2) laboratory investigation and theoretical modeling of the influence of heterogeneity and anisotropy on the development of compaction localization in porous sandstone and permeability evolution, (3) CT-imaging of damage development and strain localization in porous sandstones, and (4) finite-element and discrete element modeling of brittle failure and compaction localization in carbonate and clastic rocks. List of publications in the current funding period: (1) Baud, P., L. Louis, C. David, G.C. Rawling, and T.-f. Wong, Effects of bedding and foliation on mechanical anisotropy, damage evolution and failure mode, in High-Strain Zones: Structure and Physical Properties, ed. D. Bruhn and L. Burlini, Geological Society London Special Publication No. 245, 223-249, 2005. (2) Tembe, S., V. Vajdova, T.-f. Wong, and W. Zhu, Initiation and propagation of strain localization in circumferentially notched samples of two porous sandstones, J. Geophys. Res., 111, B02409, doi:10.1029/2005JB003611, 2006b. (3) Wong, T.-f., R.H.C. Wong, K.T. Chau, and C.A. Tang, Microcrack statistics, Weibull distribution and micromechanical modeling of compressive failure in rock, Mech. Mat., 38, 664-681, 2006.

STATE UNIVERSITY OF NEW YORK, **STONY BROOK**
Department of Applied Mathematics and Statistics
Stony Brook NY 11794

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

W. Brent Lindquist, (631) 632-8361, lindquis@ams.sunysb.edu

This joint project, between Princeton (Peters and Celia) and Stony Brook (Lindquist) is in its first year. The goal is to bridge the gap between our knowledge of small-scale geochemical reaction rates and reaction rates meaningful for modeling transport at macroscopic ("core") scales. This will be accomplished by: (1) characterizing sedimentary rocks using a variety of imaging methods including CT scanning (to provide geometric microstructure information) and electron microprobe analysis (to provide mineral content information); and (2) developing a new pore-scale network model that combines information about rock pore structure, mineralogical characteristics, and flow properties to simulate flow and reactive transport in porous media. The model will be used as a computational tool to examine the scaling properties of geochemical reaction rates in porous media and predict changes in rock properties (e.g. porosity).

The first year component of the Stony Brook project consisted of an extensive microstructure characterization, based upon three dimensional, synchrotron X-ray CT imagery, of 12 core samples taken from abandoned and active wells in the Viking sedimentary basin in Alberta. This basin is an archetype of a field that might be used for carbon sequestration. The core characterizations will provide the network realizations used in the flow simulations. The characterized networks will be used directly in the flow models, as well as statistically characterized to create stochastically equivalent networks.

UNIVERSITY OF NORTH TEXAS

Department of Chemistry
P.O. Box 305070
Denton TX 76203

Contract: DE-FG02-04ER15508

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

Paul S. Bagus, bagus@unt.edu

This project concerns reactions between silicate minerals and toxic metal-bearing aqueous fluids. Specifically, we explore mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals and sorbed to mineral surfaces. Key techniques used are electron microscopy, x-ray photoemission spectroscopy, (XPS) and x-ray adsorption near edge spectroscopy. (XANES) The XPS and XANES are used to identify the chemical environment of metal cations including their oxidation state. 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.

We continue to make major advances in the interpretation and understanding of the XPS for transition metals (TMs) and actinides. We have demonstrated the importance of closed shell screening, a mechanism not normally discussed, for the XPS of MnO. (Bagus and Ilton, 2006) This screening induces contraction of the energetic separation of XPS features because of the covalent character of the screened orbitals; it provides a fundamental justification for the practice of scaling the atomic interaction integrals. Our prior study of the 4f XPS of U cations (Ilton and Bagus, 2005) has been extended to take into account the final state relaxation of the U charge in the presence of the 4f-hole; this extension improves the agreement of our atomic theory with experiment for UO_2. It sets the stage for further calculations where the chemical environment of the cation will be taken into account. Applications of our theoretical capabilities to study XANES have been made for the Mn L-edge and the O K-edge in H_2O. For H_2O, we have definitively established the extents of valence anti-bonding and of Rydberg character in the excited states. (Bagus *et al.*, 2006) This distinction is key to understanding the chemical significance of XANES measurements involving solvated metal cations.

Without our development of new functionality for our numerically intensive programs to study electronic structure in metal complexes, this progress would not have been possible. It is intended to further enhance our programs to allow a balanced, unified treatment of all important mechanisms for the XPS and XANES of metal cations.

NORTHWESTERN UNIVERSITY
Department of Civil and Environmental Engineering
Evanston IL 60208

Interactions of Propagating Compaction Fronts and Pore Fluids in Porous Rock

J.W. Rudnicki, 847-491-3411; FAX 847-491-4011, jwrudn@northwestern.edu

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 one or more 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 CO_2. 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.

A theory that treats the formation of these bands as an alternative solution to uniform compression shows that such localization is possible for inelastic compacting materials and, in agreement with laboratory observations, for stress states on a "cap" yield surface, for which the shear stress needed for further inelastic deformation decreases with increasing compressive hydrostatic stress. Although predictions are roughly consistent with laboratory observations, quantitative comparison with results for several sandstones is poor, perhaps, because of the simplicity of the constitutive formulation.

Conditions governing the extension of compaction to tens of meters in length, as observed in the field, have been addressed by analyzing the stress in front of a compaction band, modeled as a flat ellipsoidal inclusion with elastic properties different from those of the surroundings and subject to an inelastic compactive strain. Inelastic compaction in the band increases the compressive stress, but the full stress state is three-dimensional and the stress path depends on the mismatch of elastic properties. A second calculation identifies the energy released in steady state propagation of a band in a plane layer as approximately equal to the remote compressive stress times the inelastic compaction, with a correction for the elastic mismatch. Using representative values inferred from field data yields an energy release rate of 40 kJ/m², which is roughly comparable with compaction energies inferred from axisymmetric compression tests on notched sandstone samples.

UNIVERSITY OF NOTRE DAME

Department of Civil Engineering and Geological Sciences
Notre Dame, IN 46556

Grant: DE-FG02-02ER15323

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

Patricia Maurice, pmaurice@kant.helios.nd.edu

The interactions of bacteria with metals and environmental nanoparticles can play an important role in the mobility of metals through porous media. In this first year of the study, we made significant progress on several aspects of our study. First, we made significant progress on a study of the effects of siderophores on metal adsorption to kaolinite. Siderophores are metal-complexing ligands with high affinities for Fe(III), produced by many microorganisms in Fe-deficient environments. Siderophores can also form strong complexes with other metals such as Pb and Cd; hence, siderophores may play an important role in controlling metal mobility in porous media. This study compared the effects of siderophores desferrioxamine-B (DFO-B), desferrioxamine-D (DFO-D1), desferrioxamine-E (DFO-E), as well as siderophore-like ligand acetohydroxamic acid (aHA) on Pb and Cd adsorption to kaolinite (KGa-1b) at pH 4.5 to 9, in 0.1 M $NaClO_4$, at 22°C, in the dark. At pH > 6.5 all of the siderophores plus aHA, inhibited Pb adsorption, with inhibition increasing in the order aHA < DFO-D1 < DFO-B.

THE OHIO STATE UNIVERSITY
Department of Chemistry
100 W. 18th Ave.
Columbus OH 43210

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

Heather C. Allen, (614) 292-4707, allen@chemistry.ohio-state.edu

One of the primary goals of this collaborative (Criscenti, Katz, and Allen) research is to develop an approach for predicting the types of metal surface complexes that form on mineral surfaces, specifically focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models (SCMs) to predict adsorption behavior. Our collaborative research program probes the question of the formation of ternary metal-anion surface complexes on oxide surfaces using several techniques that provide adsorption data at the angstrom, nanometer, and macroscale. In the Allen Lab, surface vibrational sum frequency generation (SFG) in addition to Raman and infrared spectroscopies are used to better understand adsorption of surface complexes at the air-oxide and water-oxide interfaces.

The initial collaborative investigations focused on metal adsorption onto alumina and silica surfaces from different electrolyte solutions. These surfaces were selected for several reasons: (1) for the molecular modeling efforts, force field parameters for crystalline gibbsite ($Al(OH)_3$) were already well established, (2) for vibrational sum frequency generation (VSFG) spectroscopy, the structure of water is most easily deconvoluted from spectra of water adsorption on fused silica, and (3) less macroscopic adsorption and X-ray absorption spectral data has been collected for these solids.

The Allen lab has published several manuscripts describing the role of water on the adsorption of an array of organic compounds to the amorphous silica and corundum surfaces. We have elucidated the hydrophilic nature of corundum and in other cases, elucidated the lack of hydrophilicity of the amorphous silica surfaces. Organic adsorption as a function of relative humidity (at ambient pressures) is facilitated by the island-like water behavior on these oxide surfaces, likely forming hydrated oxide islands in addition to isolated water islands. Clearly, water plays a pivotal role for the adsorption mechanism. We have also shown that molecules that contain amine and methylene groups will preferentially adsorb with the amine nitrogen where the amorphous silica surface donates a single hydrogen from a silanol surface group. Acidity constants (pKas) were also shown to be within a narrow range based on the direct observation of the adsorbed complex.

THE OHIO STATE UNIVERSITY
Department of Geological Sciences
Columbus OH 43210

Nanobiogeochemistry of Microbe/Mineral Interactions: A Force Microscopy and Bioinformatics Approach

Steven Lower, lower9@osu.edu

Atomic force microscopy (AFM) was combined with two-dimensional gel electrophoresis and mass spectrometry to search for evidence of putative mineral-specific outer membrane proteins (OM) synthesized by *Shewanella oneidensis* for Fe-oxide binding and/or anaerobic Fe(III) reduction. AFM shows that *S. oneidensis* possess an affinity towards goethite (FeOOH) but not diaspore (AlOOH) under anaerobic conditions, despite the fact that diaspore is isostructural with goethite and has essentially the same surface charge. The worm-like chain model was used to identify force-signatures indicative of putative OM polypeptides that bind to goethite. Two-dimensional protein expression patterns show that over 100 OM proteins are differentially expressed under aerobic versus anaerobic Fe(III) reducing conditions. Peptide mass fingerprinting and tandem mass spectrometry were used to identify several of the protein spots predominately detected when Fe(III) was the terminal electron acceptor. Among those identified were proteins involved in metal reduction, protein transport and secretion, polysaccharide biosynthesis and export, and hypothetical proteins with unknown functions. A comparison of the AFM and proteomic data suggest that a few specific OM-proteins are synthesized by *S. oneidensis* under anaerobic conditions to function in iron oxide binding and/or Fe(III) reduction. This suggests the intriguing possibility that metal reducing bacteria contain the genetic repertoire to make proteins directed at specific inorganic phases.

THE UNIVERSITY OF OKLAHOMA
School of Geology and Geophysics
100 East Boyd Street
Norman, OK 73019

Development and Application of a Paleomagnetic/Geochemical Method for Constraining the Timing of Burial Diagenetic Events

R. Douglas Elmore, delmore@ou.edu

Studies of diagenesis caused by fluid migration or other events are commonly hindered by a lack of temporal control. Our results to date demonstrate that a paleomagnetic/geochemical approach can be used to date fluid migration as well as burial diagenetic events. Our principal working hypothesis is that burial diagenetic processes (e.g., maturation of organic-rich sediments and clay diagenesis) and the migration of fluids can trigger the authigenesis of magnetic mineral phases. The ages of these events can be constrained by comparing chemical remanent magnetizations (CRMs) to independently established Apparent Polar Wander Paths. Whilst geochemical (e.g. stable isotope and organic analyses) and petrographic studies provide important clues for establishing these relationships, the ultimate test of this hypothesis requires the application of independent dating methods to verify the paleomagnetic ages. Towards this end, we have used K-Ar dating of illitization as an alternative method for constraining the ages of magnetic mineral phases in our field areas. We have made significant progress toward understanding the origin and timing of chemical remagnetization related to burial diagenetic processes. For example, a recently completed field study documents a relationship between remagnetization and the maturation of organic matter (Blumstein et al., 2004). We have tested the hypothesized connection between clay diagenesis and remagnetization by conducting K-Ar dating of authigenic illites in units in Scotland and Montana with CRMs (e.g., Elliott et al., 2006). We have also developed a fluid related model for alteration and remagnetization of Appalachian red beds that involves reduction and mobilization of iron phases by hydrocarbons and precipitation of authigenic hematite as a result of the introduction of meteoric fluid recharge (Cox et al., 2005). In addition, our recent studies of fluid-related CRMs along faults in Scotland provide information on the timing and origin of fluid flow events along the Moine and Great Glen faults (Parnell et al., 2004; Blumstein et al., 2005; Elmore et al., 2006).

OREGON STATE UNIVERSITY
College of Oceanic and Atmospheric Sciences
Oceanography Admin Bldg 104
Corvallis OR 97331

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

Gary D. Egbert, 541-737-2941, egbert@coas.oregonstate.edu

This research project is focused on improving efficiency and practicality of three dimensional inversion of multi-frequency and multi-source electromagnetic (EM) data. Our approach is based on the observation that for each search step a straightforward application of an iterative linearized optimization algorithm such as conjugate gradients (CG), requires the equivalent of at least two forward model solutions for each frequency/source pair. These calculations potentially provide multi-dimensional information about data sensitivity that is mostly discarded in a standard CG-type scheme, where they are used to define only a single additional search direction in the model space. We have developed and tested one specific algorithm that uses more of the computed data sensitivity information to yield much more rapid convergence than previously used approaches. Iterative minimization of data misfit is pursued for each frequency separately using a CG approach, and all search directions are saved. These are then merged over all frequencies in a reduced data space CG inversion. In the second (multi-frequency) phase of the inversion an OCCAM type scheme is used, with the regularization parameter varied to optimize data misfit (and then model norm). In tests on 2D MT problems of realistic size and complexity this new algorithm converged with 5-10 times fewer forward modeling steps compared to both full data sensitivity OCCAM schemes, and CG. Memory requirements were similarly reduced by a factor of 5-10 relative to the most efficient (data space) methods based on calculation of the full sensitivity matrix. In addition to the increased efficiency relative to CG, the scheme allows true norm minimizing solutions to be sought, as solution of the inverse problem for multiple values of the damping parameter remains practical. The algorithm is directly applicable to 3D inverse problems, where comparable gains in efficiency are expected. To more readily explore variants on this scheme, and to allow the algorithms developed to be applied to a wider range of EM geophysical field techniques, we have developed our test inversion system in modules, using an object oriented computer programming paradigm.

PENNSYLVANIA STATE UNIVERSITY
Department of Geosciences
University Park PA 16802

Grant: DE-FG02-05ER15675

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

Susan L. Brantley, brantley@essc.psu.edu, 814-865-1619

Despite the importance of processes by which water-induced chemical reaction turns bedrock into saprolite and soil, no quantitative methods exist to explain the process of physicochemical disaggregation of bedrock. We are testing the hypothesis that the rates and mechanisms of transformation of cohesive bedrock to disaggregated saprolite are determined by coupling between chemical, physical, and possibly microbial processes driven by water fluxes into bedrock. This hypothesis stems from observations documenting that rates of mineral reaction in the field are slower than rates in the laboratory. Weathering rates are at least partially determined by the formation of reactive surface area at the bedrock-saprolite interface. To understand weathering rates in laboratory and field, the coupling of (bio)physicochemical reactions, important in many natural and engineered systems, must be modeled quantitatively. We are developing a model for water influx and reaction at the bedrock/saprolite interface and testing the model on quartz diorite weathering in Puerto Rico. Weathering of quartz diorite occurs by spheroidal weathering, a process which often defines the transition of bedrock to saprolite on many rock types in many climate settings. We are investigating whether spheroidal weathering occurs because of (bio)geochemical reactions controlling components such as Fe and O at the bedrock-saprolite interface. We are using biogeochemical mass balance, transport and kinetics, and fracture mechanics to calculate intensity of weathering, rates of fracture formation due to chemical reaction, and rates of water influx. The Puerto Rican diorite, perhaps one of the best studied weathering sites in the world, allows well-constrained model testing that can be extended to other settings. Our interdisciplinary team collaborates within a broader framework of scientists and engineers within the Penn State Center for Environmental Kinetics Analysis (CEKA). CEKA is an NSF- and DOE-funded Environmental Molecular Science Institute whose goal is to investigate scaling in environmental kinetics. CEKA DOE funding supports four DOE collaborators at national laboratories; no DOE funding supports PSU PIs. In the context of CEKA, no investigations of physicochemical coupling such as that described in this proposal have been planned: here, we propose complementary work to enhance and amplify the overall CEKA effort.

PRINCETON UNIVERSITY
Department of Civil and Environmental Engineering
Princeton NJ 08544

Grant: DE-FG02-05ER15636

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

Catherine A. Peters, (609) 258-5645, cap@princeton.edu

Geologic sequestration of carbon dioxide in deep saline aquifers is under consideration as one of the primary strategies for solving the problem of elevated atmospheric CO_2 concentrations. This project focuses on CO_2/mineral reactions and the problem of up-scaling geochemical reaction rates. These reactions are important in understanding the long-term viability of carbon sequestration because they influence (i) pH buffering of formation acidity, (ii) changes in porosity and permeability, and (iii) sequestration capacity. The extents to which these reactions are expected to occur in the time-scales relevant for carbon sequestration are poorly understood because of uncertainties regarding reaction kinetics in porous media. We are developing a pore-scale network model that combines information about rock pore structure, mineralogical characteristics, and flow properties to simulate flow and reactive transport in porous media. The model is being used as a computational tool to examine the scaling properties of geochemical reaction rates in porous media and to predict changes in rock properties such as porosity. This work seeks to bridge the gap between our knowledge of small-scale geochemical reaction rates and reaction rates meaningful for modeling porous medium flow at macroscopic scales. Specifically we are focusing on pore-to-core up-scaling. This is an innovative and new application of pore-scale network models. A multidisciplinary team of investigators has been assembled, representing expertise in environmental geochemistry, hydrogeology, and mathematics. Rock samples come from the Alberta Basin, a representative North American sedimentary basin, and are being characterized using CT scanning, image analysis, X-ray diffraction, electron microprobe analysis, mercury porosimetry, and gas adsorption. While we focus on applications to carbon sequestration, the approach applied here will have broad applicability to reactive transport problems.

PRINCETON UNIVERSITY
Department of Geosciences
Princeton NJ 08544

Grant: DE-FG02-02ER15063

In-Situ Evaluation of Soil Organic Molecules: Functional Group Chemistry Aggregate Structure, and Metal and Mineral Surface Complexation Using Soft X-Ray Synchrotron Methods

Satish C.B. Myneni, smyneni@princeton.edu

Organic molecules (humic substances) derived from the decomposition of plant and other biological material are ubiquitous in soil and sediment systems, and play a central role in mediating a variety of biogeochemical reactions and cycling of elements. While their role in different environmental processes is well established, underlying molecular mechanisms are not understood. Using direct X-ray spectroscopy and spectromicroscopy and conventional laboratory methods, we are correlating the structural chemistry of humics and their role in various environmental processes.

Our previous investigations indicated that element-specific functional group information of humics in soils and sediments could be probed directly using X-ray spectroscopy. Studies conducted on the functional group chemistry of halogens (specifically brominated compounds) associated with soils, and coastal and deep sea sediments in the past year indicated that stable natural organohalogens are widely distributed, and that their concentrations are much greater than previously assumed. Their distribution is not correlated with any of the associated common major and trace elements. Studies are in progress to identify the process responsible for their formation.

We are also investigating humic-mineral interactions, and how they modify the functional group chemistry of sorbed humic substances and mineral-water interfacial reactions. Our studies indicate that humic molecules are fractionated upon reaction with different minerals, and the C-, N-, and S-functional groups of sorbed humics are significantly different from that of bulk humics. While previous investigations have shown that the molecular sizes are affected because of mineral interactions, this is the first time chemical fractionation of humics is documented. Once sorbed on mineral surfaces, humics significantly altered the contaminant sorption (e.g. Ni^{2+}) by minerals. A detailed examination of undisturbed soil profiles also showed that the functional group chemistry of natural organic molecules changed significantly with different horizons in soil, indicating that fractionation takes place in soil systems, and that the laboratory models mimic the natural processes closely. These studies suggest that organo-mineral interactions significantly influence the types of organic molecules stored, and the fate of pollutants in soils and sediments.

PURDUE UNIVERSITY
Department of Physics
West Lafayette IN 47907

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

Laura J. Pyrak-Nolte, 765-494-3027, Fax: 765-494-0706, ljpn@physics.purdue.edu

The objective of this research is to investigate the effects of time-varying length-scales on seismic wave propagation through fractured rock. The seismic response of a fracture is affected by intrinsic length scales associated with the fracture as well as lengths scales associated with the seismic measurement. In this study, we focus on the effect of the scale of observation on monitoring alteration of a fracture caused by reactive flow. 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.

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.

Future work includes additional measurements of local and global seismic parameters for fractured samples subjected to two-phase flow and biomimetic growth. 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.

RENSSELAER POLYTECHNIC INSTITUTE

Department of Earth and Environmental Sciences
Troy, NY 12180

Grant: DE-FG02-94ER14432

Transport Properties of Fluid-Bearing Rocks

E. B. Watson, (518) 276-8838, fax (518) 276-2012, watsoe@rpi.edu

The research supported by this grant addresses "fluid-assisted" chemical transport in the Earth's lithosphere through systematic experimental investigations at appropriate temperatures and pressures (500-900°C; 1-1.5 GPa) and can be broadly categorized into three related efforts: (1) evaluating the permeability of faceted grain-scale pores; (2) constraining the transport rates and morphology of carbon along grain boundaries; (3) measuring the 3-D geometry of individual pores by atomic force microscopy (AFM).

Many naturally occurring materials exhibit pores bounded by rational faces (facets) instead of the curved surfaces predicted in theoretical treatments and exhibited in rocks like quartzite. Recent analyses of materials exhibiting variable degrees of faceting, from moderately faceted quartzite to highly faceted amphibolite, show that permeability is only significantly affected when pore walls are highly faceted. Highly faceted pores remain disconnected at low fluid fractions, much like pores with high dihedral angles. The transport and morphology of elemental carbon along grain boundaries may significantly affect electrical conductivity of Earth materials. All experiments indicate that diffusion of carbon along grain boundaries is sluggish; movement may only be accelerated when grains coarsen (through diffusion of silica in the case of quartz). The results suggest that films may only exist provided that the carbon is produced as a film from another C-bearing phase, and that the grain boundaries are stable. Grain boundary migration causes isolation of discrete grains of carbon that are connected only at high volume fractions.

The 3-D pore geometry of individual pores can be measured through a new experimental technique in which fluids are introduced along synthetic grain boundaries produced by juxtaposing oriented and polished slabs of a mineral(s) in a piston-cylinder. After the experiment, grain boundaries are separated to expose half of each fluid-filled pore on complementary slabs. Two advantages of this technique are that the: (1) 3-D pore geometry can be directly measured using AFM, and (2) solid-solid interfacial energy can be controlled by varying the amount of crystal lattice mismatch (determined by electron backscatter diffraction) between juxtaposed crystals, and thus complementary dihedral angles can be measured as a function of lattice coincidence using AFM.

RENSSELAER POLYTECHNIC INSTITUTE
Department of Earth and Environmental Sciences
Troy, NY 12180

Application of Geophysical Tomographic Imagery to the Development of Subsurface Flow and Transport Models

Jonathan Newell, newelj@rpi.edu

Objectives: This project seeks to refine the technology for forming and interpreting electrical resistance tomographic (ERT) images and electrical impedance tomographic (EIT) images of the subsurface zone. We seek to establish the extent of the advantage of using multiple current sources over a single source in such a multiple-electrode system. We also seek to assess the added information available in the reactive component of impedance above that available with only the resistance component.

Project Description: We have built four arrays of electrodes, each having eight electrodes arranged at intervals along a straight rod 15 mm in diameter. Each electrode extends 15 mm along the rod, and the spacing between electrodes is also 15 mm. Each electrode is connected to a current source and voltmeter, allowing patterns of current to be applied, and both real and quadrature voltages to be measured simultaneously on all electrodes. The four arrays were placed vertically in a saline tank at the four corners of a square, and the ability of these data to distinguish the presence of a small conductive target placed in the tank at different sites among these electrode arrays was assessed.

We then buried this electrode array in a bed of Ottawa F-35 sand. Saline was added to the sand in varying amounts to assess the ability to find saturation or unsaturated sand, and to detect a plume of fluid in an unsaturated bed.

Results: Distinguishability of a conductive target was lowest at the midpoint of an edge of the array square. It increased slightly at the center of the square, and increased substantially near the electrodes. At all distances, distinguishability was about three times higher using multiple current sources, compared to using only one source. In sand, the resistance at all electrodes was similar and low when the bed was saturated. A strong gradient of resistance was seen from the top to the bottom of the bed after it had drained for five days. When a plume of fluid was introduced at the middle of one side of the array, it produced a large resistance decrease within two minutes.

UNIVERSITY OF SOUTH CAROLINA
Department of Geological Sciences
Columbia SC 29208

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

Alicia Wilson, awilson@sc.edu, (803) 777-1240

Knowledge of the residence time of fluids in sedimentary basins is necessary for understanding such processes as sedimentary diagenesis, ore formation, petroleum migration and carbon sequestration. Previous estimates of residence time in huge foreland basin settings vary widely, however. In the Alberta Basin, previous geochemical studies have indicated that deep brines are derived from ancient, evaporatively-concentrated seawater, implying a residence time of hundreds of millions of years. Previous hydrogeologic simulations of flow through foreland basins have instead calculated residence times of only a few million years. This project is designed to reconcile these conflicting results by creating new hydrogeologic models of the Alberta Basin. Models will incorporate variable-density fluid flow, heat transport, solute transport, sediment compaction, and simple geochemical reactions, including dissolution of halite, Br-Cl ratios, and stable isotope systematics. These hydrogeologic models will be the first to use multi-component geochemical data to constrain simulations of brine migration and residence time.

Numerical simulations will begin at ~100 Ma, at approximately the onset of Laramide uplift. Simulations will therefore capture the potential impact of rapid sedimentation, including compaction-driven flow, followed by the onset of topography-driven flushing ~60 Ma and erosion of kilometers of sediment. An important question in this work is whether the low permeability of Cretaceous shales is sufficient to shelter brines for 100s of millions of years, or whether local flow patterns associated with shale compressibility during loading and unloading may have limited large-scale brine transport. Salt dissolution capabilities have been added to the code. Preliminary modeling and additional code development are underway.

STANFORD UNIVERSITY
Department of Civil and Environmental Engineering
Stanford CA 94305

Grant: DE-FG02-03ER15454

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

Ronaldo I. Borja, (650)723-3664, borja@stanford.edu

We investigate strain localization phenomena in granular rocks using theory of plasticity and finite element simulations. Our goals are to accurately predict the onset of strain localization and continue the numerical simulation beyond the localization point. There are four main tasks identified in the project: formulation and implementation of a three-invariant elastoplastic constitutive model, introduction of non-coaxial plasticity into the constitutive framework, implementation of a well-known phenomenological friction law in the framework of the strong discontinuity model, and analysis of test data for different rocks. A three-invariant elastoplastic constitutive law is appropriate for rocks since these materials exhibit lower yield stress in tension than compression. Lately it also has come to light that the inclusion of the third invariant can enhance the onset of strain localization. Non-coaxial plasticity is often used to represent vertex-like structure in brittle rock masses, and so we also investigate its impact on the localization properties of rocks. Once a deformation band forms in an intact rock, its overall mechanical behavior is dominated by the softening plasticity occurring inside the band. We capture the mechanical properties inside the band using a state- and slip speed-dependent friction law.

A significant component of the research involves the development of a computational model, based on nonlinear finite element method, for capturing the mechanical response of rocks prior to and beyond the onset of localization. We investigate the effects of the third invariant and non-coaxial plasticity by casting these models in conventional nonlinear finite element framework. Further, we model the evolution of the ensuing deformation band, including its propagation through the material, using a non-conventional finite element technique based on embedded strong discontinuity. The latter technique allows an accurate representation of both small-scale (deformation inside the band) and large-scale (overall deformation of rocks) phenomena without severe mesh refinement. Finally, we use the developed multi-scale modeling approach to analyze a host of test data involving strain localization in granular rocks in axisymmetric and plane strain compression. Our analysis involves prediction of the initiation of deformation bands using classical bifurcation theory, and a geometric characterization of how they advance through the material.

STANFORD UNIVERSITY
Department of Geophysics
Stanford CA 94305

Geochemical Controls on Nuclear Magnetic Resonance Measurements

Rosemary Knight, 650-736-1487, rknight@pangea.stanford.edu

Proton nuclear magnetic resonance (NMR) has the potential to provide a wealth of information about the physical, chemical, and biological properties of geological materials. The goal of our research is to advance the fundamental understanding of the link between the NMR response and the geochemical 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 the effects of the specific mineralogic form of the iron and the distribution of the iron on NMR relaxation mechanisms. In addition the current models of NMR relaxation times 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 conducting a three-year laboratory-based study of NMR relaxation time measurements in water-saturated porous materials where sample composition, pore structure and geochemical conditions are carefully controlled or determined. NMR samples are prepared by coating pure quartz sand with minerals containing both Fe(III) and Fe(II). The surface area and porosity of each sample is determined, and the distribution of the iron-bearing mineral examined using scanning electron microscopy. We measure the NMR time constants T1 and T2 of samples at chemical equilibrium and as the chemistry of the system changes due to changing redox conditions and ongoing biological activity. We are working initially with systems that can be described as spatially homogeneous and will then investigate the role of pore-scale variability in geochemical properties in determining NMR relaxation times.

To date we have completed NMR measurements on iron-coated quartz sands saturated with deionized water and on iron-coated quartz sands under changing redox conditions. The results have shown that NMR relaxation times are strongly influenced by the mineralogy of the iron coatings. Measurements of the NMR relaxation time of iron-coated sands under changing redox conditions revealed that temporal changes in mineralogy result in changes in the measured NMR relaxation time. These measurements have allowed us to start to understand the fundamental geochemical controls on the NMR response of geological materials.

STANFORD UNIVERSITY
Department of Geophysics
Stanford CA 94305

Porous Reservoir Rocks with Fluid: Seismic and Transport Properties

Amos Nur, (650) 723-9526, Amos.Nur@stanford.edu

The objective of this project is to develop methodologies for numerically simulating mechanical and transport properties of sediment. This contributes to our goal of discovering and understanding links between geophysical measurements and the underlying rock and pore-fluid properties as well as toward better reservoir detection, description, and mapping, and of physical and chemical processes in the crust.

1. Modeling rock properties: Compaction bands (CB) form pervasive arrays that exert substantial fluid-flow effects at scales relevant to production and storage. The CB porosity and permeability are difficult to measure directly. Reliable estimates can be obtained by conducting numerical flow simulations on 3-D realizations of the pore structure generated from thin-section images. 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).

2. Gas flow in digital pore geometry: We have 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, to calculate the gas surface area 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.

3. Improving Quantification of Pore Geometry: We explore links among local internal magnetic field from NMR simulation, local fluid velocity distribution from Lattice-Boltzmann flow simulation, and the distance transform map of the pore geometry. 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. We find that the gradient of local internal magnetic field is closely related 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.

STANFORD UNIVERSITY
Department of Geological and Environmental Sciences
Stanford CA 94305

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

D. D. Pollard, dpollard@pangea.stanford.edu; A. Aydin, aydin@pangea.stanford.edu

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.

TEMPLE UNIVERSITY
Department of Chemistry
Philadelphia PA 19122

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

Daniel R. Strongin, 215-204-7119, Fax 215-204-1532, dstrongi@temple.edu

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. The program integrates observations at the macroscopic level with those at the microscopic scale. It is this integration that has proven to be very useful and productive. The objective of the research has been to understand important fundamental aspects of the surface chemistry of pyrite, such as charge development, reactivity, surface stoichiometry, surface structure, and interaction with dissolved constituents (sorption). Our ultimate goal is to provide insight into the role of pyrite as reactant, sorbent, and (photo)catalyst in environmentally and geologically relevant environments. This research has recently brought forth to the scientific forefront the importance of non-stoichiometric sites or defects in controlling the reactivity of pyrite. Many fundamental questions regarding the origin, presence, electronic structure, and reactivity of these defects remain unanswered and are being addressed in our studies. We believe that we need to answer these questions in order to provide the basic science needed for the development of the next generation of techniques in the abatement of acid mine drainage, one of the most important environmental problems we face (about 1 million dollars is spent per day on this problem. We argue that by understanding the reactivity of pyrite at the molecular scale strategies can be developed that target one or more of the elementary reactions in the oxidation of pyrite. While our research is primarily motivated by a desire to understand pyrite oxidation at the molecular level, our work is also of importance to several technical problems where the surface chemistry of pyrite plays a role, such as flotation of pyrite in the mining industry, acidification of hydrocarbon reservoirs (a problem relevant to terrestrial CO_2 sequestration), and sorbent of radionuclides and other constituents (e.g. gold).

TEXAS A&M UNIVERSITY
Texas Engineering Experiment Station
College Station TX

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

John W. Morse, (979) 845-9630; fax (979) 845-9631, morse@ocean.tamu.edu

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. Little is known regarding the kinetics of calcite dissolution, diffusion of carbon dioxide in natural gas, and displacement of natural gas by carbon dioxide under conditions to be encountered in these reservoirs. 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. The requisite data will be used to develop a model for mass transport and reaction kinetics for the injection and storage of carbon dioxide in carbonate or carbonate-bearing depleted gas reservoirs. The dissolution rate of calcite was measured in geologically relevant Na-Ca-Mg-Cl synthetic brines. Rate dependency on brine composition, pCO_2, and temperature was modeled. Additional experiments were designed to measure the solubility of calcite in these complex systems. Calculations based on the findings of this research demonstrated that the reaction fronts in calcium-rich, high pCO_2 brines can be expected to be very sharp as a consequence of the small carbonate carrying capacities and relatively fast kinetics. Even at high flow rates (3 m/d) that might be expected in the vicinity of an injection well, the solutions achieve equilibrium in a matter of only a few tens of millimeters. Two types of flue gas were used in displacement experiments: dehydrated flue gas with 13.574 mole % CO_2 (Gas A), and treated flue gas with 99.433 mole % CO_2 (Gas B). The dispersion coefficient of pure CO_2 at 70°C and 1,500 psig is approximately 0.15 cm^2/min. This value is in good agreement with the dispersion coefficient of Gas B, 0.13 to 0.15 cm^2/min, which contains 99.433 mole % CO_2. Displacement efficiency of Gas B and pure CO_2 are also very similar. Second, the dispersion coefficients for Gas A, 0.18 to 0.25 cm^2/min, is consistently higher than that for pure CO_2 and for Gas B.

TEXAS A&M UNIVERSITY
Texas Engineering Experiment Station
College Station TX

Grant: DE-FG02-00ER15034

Time-Lapse Seismic Monitoring and Performance Assessment of CO$_2$ Sequestration in Hydrocarbon Reservoirs

Akhil Datta-Gupta, 979-847-9030, datta-gupta@tamu.edu

The goal of this project is to assess the feasibility of time-lapse seismic monitoring of CO$_2$ sequestration using coupled fluid flow and seismic modeling in fractured reservoirs. Concurrently we want to develop a formalism for the assimilation of static and dynamic data sources in the reservoir and quantification of uncertainty in performance predictions of CO$_2$ sequestration, particularly for fractured hydrocarbon reservoirs. We use a dual-porosity streamline model for fluid flow simulation in fractured reservoirs by treating the fracture and matrix as separate continua that are connected through a transfer function (Al-Hutheli and Datta-Gupta, 2004). We analytically compute the sensitivities that define the relationship between the reservoir properties and the fluid production response in fractured reservoirs. Production data integration into geologic models is carried out via a generalized travel time inversion (Al-Harbi, Cheng, and Datta-Gupta, 2005). The generalized travel time inversion shows clear potential for resolving the general trends of fracture distributions in synthetic and field data. We examine the viability of time-lapse seismic monitoring using an integrated modeling of fluid flow, including chemical reactions, and seismic response. Our results also show that for accurate time-lapse response, it is important to model the precipitation and dissolution reactions that occur during CO$_2$ injection. Specifically, the CO$_2$ dissolution and the acidification of the brine trigger a variety of geochemical reactions that can significantly alter the rock-fluid properties. The gas-liquid dissolution and the intra-aqueous phase reactions are relatively fast and their effects on time-lapse seismic response can be seen at the end of CO$_2$ injection. The mineral reactions are typically very slow and their effects are detectable only after hundreds of years. Salinity change, which is of order of 10% in this study, changes the brine phase properties significantly. The combination of physical and chemical changes in the sequestration reservoir lead to changes in AVO attributes on the order of 15%, suggesting that these parameters can be very useful tools for monitoring changes in reservoir conditions in a sequestration site (Kumar, Shekhar, Datta-Gupta and Gibson, 2006).

UNIVERSITY OF TEXAS

Department of Civil Engineering
Austin TX 78712

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

Lynn E. Katz, 512-471-4244, lynnkatz@mail.utexas.edu.

One of the primary goals of this collaborative (Criscenti, Katz, and Allen) research is to develop an approach for predicting the types of metal surface complexes that form on minerals surfaces, specifically focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models to predict adsorption behavior. Katz' group is focusing on investigating metal sorption behavior on quartz, ferrihydrite, and gibbsite surfaces using both macroscopic (batch sorption experiments) and microscopic (spectroscopic analysis) studies as well as predicting sorption behavior using surface complexation modeling.

Katz's group has investigated metal ion sorption behavior over a wider range of background electrolyte concentrations and an extensive range of surface coverages of sorbed metals using substrates including quartz, gibbsite, and iron oxides. The results showing that the removal of Sr(II) from the aqueous phase in quartz and gibbsite systems was reduced with increasing ionic strength agreed with the spectroscopic measurements taken in concentrated systems showing that Sr(II) forms outer-sphere complex on solid surfaces. Different electrolyte anions in concentrations between 0.01 to 0.5 M did not affect Co sorption behavior providing that the solution conditions were below those required for formation of Co(II) precipitates. At higher Co(II) concentration (10^{-5}M), the removal of Co in the quartz system decreased with increasing ionic strength due to the formation of Co-kerolite as confirmed by EXAFS analysis. Pb^{2+} uptake by quartz or gibbsite were not affected by the type or concentrations of background electrolytes of $NaNO_3$ and $NaClO_4$ for concentrations up to 0.5 M. Conversely, changes in background NaCl concentrations resulted in a significant change in Pb^{2+} uptake onto both quartz and gibbsite for Cl^- concentrations ranging from 0.01 to 1M due to the formation of complexes with Pb in aqueous phase. The results from studies of these extended systems suggest that solution composition as well as the substrate affects metal ion sorption behavior. We have also initiated modeling studies using spectroscopy to guide the selection of surface complexation reactions. We have successfully predicted Cd(II) and Pb(II) single solute and bi-solute sorption onto iron oxide using various versions of the surface complexation models.

UNIVERSITY OF TEXAS
Bureau of Economic Geology
University Station Box X
Austin TX 78713

Grant: DE-FG02-03ER15430

Predicting Fracture Porosity Evolution in Sandstone

S.E. Laubach, 512-471-6303, steve.laubach@beg.utexas.edu

The goal of this research is understand how fracture growth and diagenetic alteration interact to systematically create and destroy fracture porosity. We are studying a key link between mechanical and chemical processes in opening fractures. Specifically, we have tested a new theory of quartz cementation that postulates that the rate-limiting step for cementation is precipitation, with supply and transport being of secondary importance. We are testing the hypotheses that this cementation process governs evolution of (1) fracture porosity and (2) fracture growth (through diagenetic effects on the subcritical crack index). Interactions of fracture growth and sealing and evolving rock properties in turn control many aspects of fracture pattern development. High temperatures and reactive fluids in sedimentary basins dictate that interplay and feedback between mechanical and geochemical processes significantly influence evolving rock and fracture properties. In addition to the new diagenesis and fracture model, our study of mechanical and diagenetic feedback loops involves new approaches to high-resolution microstructure quantification over large sample areas, improved measurement methods of key mechanical properties, advanced fracture-mechanics-based fracture growth modeling, and new approaches to quantifying fracture size and spatial arrangement. This cross-disciplinary research is resulting in a fundamental advance in our understanding of how the diversity of natural fracture patterns evolves and better predictions of fracture pattern attributes in the subsurface where sparse sampling is the rule. Mechanical models typically neglect cementation in fractures and the rock mass, tacitly assuming that cementation rates are slow relative to fracture and that fracture and fracture filling are decoupled. We show that this assumption is not justified. Neglecting the well-documented chemical reactions (diagenesis) that pervade sedimentary rocks may result in missing important mechanical and chemical feedbacks that could govern fracture patterning. This is a central but little explored topic in fracture characterization and prediction. Tests of our models in the Piceance Basin, Colorado, where extensive core samples of subsurface fractures are available, and in two outcrop studies show that our approach results in a significant improvement in prediction of fracture attributes. Our work marks a paradigm shift in fracture and diagenesis research.

UNIVERSITY OF TEXAS AT DALLAS
Department of Geosciences
800 West Campbell Road
Richardson, TX 75080-3021

3-D Sedimentological and Geophysical Studies of Clastic Reservoir Analogs: Facies Architecture, Reservoir Properties, and Flow Behavior within Delta Front Facies Elements of the Cretaceous Wall Creek Member, Frontier Formation, Wyoming

Janok Bhattacharya, jpbhattacharya@uh.edu

Ground Penetrating Radar (GPR) has been used to image the 3-D internal structure (and thus the 3-D facies architecture) of a top-truncated delta front in the topmost parasequence in the Wall Creek Member of the Frontier Formation in Wyoming, and to estimate the distribution of low permeability concretions throughout the 3-D GPR volume. The interpretation of the GPR data is based both on correlations with outcrop and on calibration with core data from holes within the survey grid. From the 3-D GPR volume, two main radar facies (RF) are identified between a pro-delta mud layer and a transgressive erosional boundary. RF1 corresponds to tide-influenced mouth bars formed by a unidirectional flow during delta progradation or bidirectional flow during tides, whereas RF2 is correlated with laterally migrating channels developed on the pro-delta muddy layer or on previous bar deposits. The delta-front foreset beds dip in the same direction as the dominant paleocurrent indicators. The GPR interpretation is consistent with the outcrop interpretation that, following a regressive period, nine bodies consisting of three facies architectural elements were developed at the Raptor Ridge site before subsequent transgressive ravinement. The individual 3-D deltaic facies architecture was reconstructed from the 3-D GPR volume and indicate that the depositional units are larger than the survey grid.

Cluster analysis of the GPR attributes (instantaneous amplitudes and wavenumbers) calibrated with the cores and the outcrop was used to predict the distribution of near-zero permeability baffles throughout the 3-D GPR volume; criteria were defined and applied separately in the bars and channels. The predicted concretions in the bars and the channels are 14.8% and 10.7% by volume, respectively, which is consistent with those observed in the cores (14.70% and 10.54%, respectively). The estimated concretions are distributed in an aggregate pattern with irregularly oriented branches within the 3-D GPR volume, indicating that the cementation does not follow a traditional center-to-margin pattern. The concretions are integrated into a 3-D digital geological solid model to provide a 3-D structural framework for 3-D reservoir modeling.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
Department of Geosciences
Blacksburg VA 24061

Contract: DE-FG02-00ER15112

Investigation of the Physical Basis for Biomineralization

Patricia Dove, dove@vt.edu, (540) 231-2444

Through biomineralization, living organisms utilize organic modifiers and molecular scaffolds to control nucleation and growth of both shaped single crystals and crystal composites. This project explores the physical mechanisms, energetic factors, and stereochemical relationships that enable this process to proceed. Our approach is to apply scanned probe microscopy and molecular modeling to well-defined model systems in order to quantify the effects of growth modifiers on the energetic and thermodynamic parameters controlling calcite crystallization.

The composition of molecules isolated from biominerals has long-suggested that control of mineral growth is linked to the chemical features of biologic molecules. In one study, we reported the role of Asp-n (n=1-6) peptides in modulating step-solvation to induce an unusual crossover in step specific interactions and affect calcite growth morphology (Elhadj et al., 2006, CGD).

More recently, we have found a systematic relationship of promotion of the growth of calcite ($CaCO_3$) by very low concentrations of aspartic acid-rich peptides that is proportional to their net negative molecular charge and hydrophilicity. The degree of enhancement is dependent on peptide composition, but not on peptide sequence. Data analysis shows that this rate enhancement arises from an increase in the kinetic coefficient. We interpret the mechanism of growth enhancement to be a catalytic process whereby biomolecules reduce the magnitude of the diffusive barrier, Ek, by perturbations that displace water molecules. The result is a decrease in the repulsive barrier for attachment of solutes to the solid phase. This previously unrecognized relationship also prevailed in recently reported data showing acceleration of calcite growth rates over rates measured in the pure system by nanomolar levels of abalone nacre proteins. These findings show that an insight derived from data for small model peptides can be scaled up to analyze biomineralization mediated by more complex proteins. We suggest that enhancement of calcite growth may now be predicted *a priori* from the composition of peptide sequences and the calculation of values for hydrophilicity and net molecular charge. This insight may also contribute to an improved understanding of diverse systems of biomineralization and design of new synthetic modulators.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
Department of Geosciences
Blacksburg VA 24061

Contract: DE-FG02-02ER15326

Nanobiogeochemistry of Microbe/Mineral Interactions: A Force Microscopy and Bioinformatics Approach

Michael F. Hochella, Jr., (540) 231-6227, hochella@vt.edu

Atomic force microscopy (AFM) was combined with two-dimensional gel electrophoresis and mass spectrometry to search for evidence of putative mineral-specific outer membrane proteins (OM) synthesized by *Shewanella oneidensis* for Fe-oxide binding and/or anaerobic Fe(III) reduction. AFM shows that *S. oneidensis* possess an affinity towards goethite (FeOOH) but not diaspore (AlOOH) under anaerobic conditions, despite the fact that diaspore is isostructural with goethite and has essentially the same surface charge. The worm-like chain model was used to identify force-signatures indicative of putative OM polypeptides that bind to goethite. Two-dimensional protein expression patterns show that over 100 OM proteins are differentially expressed under aerobic versus anaerobic Fe(III) reducing conditions. Peptide mass fingerprinting and tandem mass spectrometry were used to identify several of the protein spots predominately detected when Fe(III) was the terminal electron acceptor. Among those identified were proteins involved in metal reduction, protein transport and secretion, polysaccharide biosynthesis and export, and hypothetical proteins with unknown functions. A comparison of the AFM and proteomic data suggest that a few specific OM-proteins are synthesized by *S. oneidensis* under anaerobic conditions to function in iron oxide binding and/or Fe(III) reduction. This suggests the intriguing possibility that metal reducing bacteria contain the genetic repertoire to make proteins directed at specific inorganic phases.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
Department of Geosciences
Blacksburg VA 24061

Electron Density Distributions as a Guide for Understanding the Reactivity of Silicate Earth Materials

Donald J. Rimstidt, jdr02@vt.edu

This research project used *ab initio* periodic and molecular orbital calculations to generate electron density distributions, ρ, for reagents and silicate structures. As shown by Bader and his co-workers, the Laplacian of the electron density distribution provides a unique opportunity to establish an electron density model of reactivity. By evaluating the critical point properties of the electron density distribution, a spatial mapping of sites of potential electrophilic and nucleophilic attack at the surfaces and in the bulk of important silicate minerals were identified for the first time, providing mechanistic insight into how Lewis acids mount electrophilic attacks and how Lewis bases mount nucleophilic attacks on specific SiOSi and SiOAl bonds. These results are being tested using high-resolution rate measurements, an approach that has proven to be highly successful in organic and inorganic chemistry. We anticipate that this coupling of knowledge of the electron density distribution with kinetic measurements will provide a significant advance in the field of geochemistry. A model for the precursor steps in the dissolution of forsterite was created by Yun Liu, a postdoctoral researcher who joined this project in 2004. In addition Dr. Liu has produced a series of models that show that olivine series mineral dissolution rates are proportional to the length of the M-OH bond in the M-OH-Si(OH)$_3$ surface species that is formed by a series of precursor reactions. Experiments performed by Amanda Olsen, a Ph.D. candidate working on this project, show that the silica release step requires both H$^+$ and a ligand to be present in the activated complex and that breaking the M-OH bond appears to be the rate-determining step in the dissolution of olivine series minerals. Thus, we have used a combination of ab initio quantum mechanical models and an experiment to identify the reaction pathway for the dissolution of the olivine series of minerals in acidic solutions. Similarities with the pH dependence of the dissolution rate of other silicate minerals suggest that the ligand exchange reaction proposed here as the rate determining step for the dissolution of the olivine series minerals is common to many other silicate materials.

UNIVERSITY OF WISCONSIN
Department of Geology and Geophysics
Madison WI 53706

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

John W. Valley, (608) 263-5659, fax (608) 262-0693, valley@geology.wisc.edu

We installed the first CAMECA 1280 ion microprobe in March 2005, followed by 9 months of testing and repair before acceptance. We have concentrated development on high precision analysis of oxygen isotopes and now routinely obtain precision of 0.1-0.2‰ (1sd) for delta(18-O) from a 10 micron spot using the multicollector, the new NMR magnet control system, and new software. This greatly improved performance has permitted us to begin a range of previously impossible projects. We have developed new oxygen isotope standards for quartz, calcite, dolomite, hematite, pyroxenes, olivines, feldspars, and glasses. Testing and development are under way for other isotope systems including carbon, iron, and sulfur.

We have completed a study of quartz overgrowths in St. Peter sandstone (Jacque Kelly MS 2006). Approximately 500 analyses of overgrowths as thin as 10 microns reveal remarkable homogeneity for all diagenetic quartz cements within a single sample and for all samples of St. Peter sandstone from across SW Wisconsin; values of delta(18-O)(overgrowth) average 29.6 ±1‰. Detrital quartz grains range from 6 to >10‰. When compared to the groundwater flow model of Arnold et al. (1997), these results show that quartz cements were not precipitated by circulating brines related to the SW Wisconsin MVT-type Pb-Zn district. We propose that overgrowths formed as silcretes at low temperatures, 20-40°C, from surface fluids. To our knowledge, this is the first evidence that coarsely crystalline optically continuous cements can form at such low temperatures.

Other ion microprobe studies of hydrothermal processes include analysis of delta(18-O) in:

• 1-4 mm quartz-calcite strain fringes on pyrite from greenschist facies schists in Vermont and the Pyrenees to constrain metamorphic temperatures and fluid conditions during deformation.
• Zoned olivine phenocrysts from Mauna Kea to test magmatic assimilation of weathered basalts vs. exotic mantle reservoirs.
• Zoned 100 micron zircons from rhyolites (Yellowstone, Timber Mtn., Yucca Mtn.) to evaluate mechanisms and time scales of hydrothermal alteration.
• Heterogeneously altered calcite from the periclase zone, Alta contact aureole to study the cycling of fluid pressure from lithostatic to hydrostatic.

UNIVERSITY OF WISCONSIN
Department of Civil and Environmental Engineering
Madison WI 53706

A 3D Numerical Analysis of the Grounded Electric Source, Transient Electromagnetic Geophysical Method

David Alumbaugh, alumbaugh@engr.wisc.edu

A numerical study was conducted to investigate the governing physics of galvanic source electromagnetic (EM) methods for marine exploration scenarios. The marine exploration scenario investigates the physics of marine frequency-domain controlled source EM (FDCSEM) and time-domain controlled source EM (TDCSEM) methods to explore resistive hydrocarbon reservoirs in marine environments. Unlike the marine MT (MMT) method, these two methods are very sensitive to a thin hydrocarbon reservoir at depth because their sources generate vertical as well as horizontal currents. As for the FDCSEM method, the normalized EM peak response occurs where the airwave starts to dominate the seafloor EM response in the background model. This point is a function of source frequency, seawater depth and seafloor resistivity. The peak magnitude of the normalized EM response depends on whether the high concentration of vertical currents can reach and interact with the reservoir effectively. Noise levels of the EM receivers are important factors for successful FDCSEM and TDCSEM survey design. The major benefit of using magnetic field responses over electric ones is that the noise level of magnetic receiver theoretically allows for greater surface coverage compared to that of the electric receiver. Like the GESTEM method, the TDCSEM method also requires the use of a proper transient EM pulse such that the relatively high frequencies are produced. The impulse response of the TDCSEM method is characterized by two-path diffusion of the EM signal. The initial response is caused by faster signal diffusion through the less conductive seafloor, while the later arrivals result from slower diffusion through the more conductive seawater. Therefore, at larger separations, the effects of the seafloor and seawater are separable. This can be useful in reducing the airwave problem associated with the FDCSEM method in shallow marine environments.

WOODS HOLE OCEANOGRAPHIC INSTITUTION
Department of Geology and Geophysics
Woods Hole MA 02543

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

Wenlu Zhu, wzhu@whoi.edu

Triaxial hydromechanical tests indicate that permeability and porosity evolution during shear-enhanced compaction is primarily controlled by stress. Furthermore, the influences of the mean effective stress and deviatoric stress can be decoupled. The drastic permeability reduction during shear-enhanced compaction is sensitive to the loading path, which indicates that the stress-induced permeability anisotropy may be significant in the cataclastic flow regime. Based on microstructural observations, we developed a cumulative damage model to quantify the stress-induced anisotropic permeability development during the shear-enhanced compaction. Using this model, we are able to link the transient permeability anisotropy to the influence of stress state and loading path on the yield stress and microscopic stress heterogeneities. The good agreement between our modeling results and experimental data implies that the cumulative damage model captures the key micromechanical processes operating during cataclastic flow. While the development of permeability in lithified rocks is primarily controlled by microcracking and pore collapse, the permeability evolution in unconsolidated materials, such as sediments and fault gouge, is primarily controlled by the development of fabric and shear localization via accumulation of shear strain. The fundamental differences in evolution of permeability anisotropy should be accounted for in crustal models that couple mechanical deformation and fluid transport. Localization develops in compacting porous sandstones under relatively high confining pressure, both in the field and laboratory. The compaction bands that result are morphologically different from shear bands produced under low confinement; the former are arrays of discrete bands or diffuse zones sub-perpendicular to maximum compression. We found that with the 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. The development of compaction bands is associated with permeability reduction and the formation of hydraulic barriers, which may allow elevated pore pressures.

WOODS HOLE OCEANOGRAPHIC INSTITUTION

Department of Marine Chemistry and Geochemistry

Woods Hole MA 02543

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

Jeffrey Seewald, (508) 289-2966, jseewald@whoi.edu

Factors that regulate the generation and composition of natural gas during the thermal maturation of petroleum are poorly understood. The origin of natural gas is being investigated by conducting a series of laboratory heating experiments to constrain the stability of petroleum and its degradation products in the presence of water and minerals at elevated temperatures and pressures. Experiments reacting whole oils dissolved in water with Fe-bearing minerals and anhydrite have been conducted at 325-350°C. Experimental results indicate that the stability of oil and reaction pathways responsible for its degradation is strongly dependent on redox. In the presence of mineral oxidants, stepwise oxidation of C_{2+} hydrocarbons causes rapid decomposition to produce a CH_4- and CO_2-rich gas. Similar results are obtained regardless of whether the mineral oxidant is anhydrite or Fe-bearing sulfides and oxides. Aqueous sulfur species in intermediate oxidation states are catalytically active during oxidation reactions. Under reducing conditions, thermal cracking reactions dominate and decreased rates of oil degradation are observed. Except for the production of copious CO_2 and organic acids, the chemical and isotopic composition of gaseous products generated by stepwise oxidation are indistinguishable from those produced during thermal cracking. These results suggest that oxidative degradation may represent a previously unrecognized process responsible for the generation of dry natural gas. Additional experiments investigating specific reactions responsible for the decomposition of aqueous organic acids and anions have been conducted at 225 to 325°C. Results indicate that the relative rates of acetic acid oxidation and decarboxylation are strongly influenced by the presence of catalytically active Fe-bearing minerals. Decomposition of longer chain acids proceeds through deformylation to produce alkenes and formic acid that rapidly react with water to form alkanes and CO_2. Aqueous formic acid is highly reactive at temperatures typical of petroleum producing sedimentary basins and rapidly attains a state of thermodynamic equilibrium with CO and CO_2. The experimental results are consistent with concentrations of organic acids observed in basinal brines and can be used to constrain their roles during sediment alteration and the generation of natural gas.

WOODS HOLE OCEANOGRAPHIC INSTITUTION
Department of Marine Chemistry and Geochemistry
Woods Hole MA 02543

Organic Geochemistry of Continental Margin and Deep Ocean Sediments

Jean Whelan, jwhelan@whoi.edu

The objective of this program has been to develop a better understanding of processes of hydrocarbon generation and migration in coastal and offshore sedimentary basins as an aid in predicting favorable exploration areas for oil and gas. Research focused on utilization of organic compounds in elucidating mechanisms, rates, and consequences of subsurface fluid flow. These processes have a strong effect on the economics of oil production, particularly with respect to where, how much, and the quality of petroleum which can be produced in a particular area. Our particular long term interest was to better understand the role of migrating gas in these reservoirs. Past research, in collaboration with scientists at Cornell, Louisiana State University and Texas A&M, has shown that the oil gas system throughout a 200 mile north to south transect across the northern Gulf of Mexico continental shelf and slope has been very dynamic with as much as 30 volumes of gas having passed through and altered oils to the north of the transect. Modeling together with our previous geochemical data showed the source, maturity, and the degree of alteration of these oils and also that the reservoirs have only recently been charged. Furthermore, the Cornell modeling results suggested that earlier oil which entered these reservoirs was probably very efficiently flushed upward and out into the overlying water column. The total volume of gas which has been involved in gas washing decreases in moving southward along our transect so that oils in the southern-most Green Canyon wells showed little or no alteration attributable to gas washing. Work this year focused on the best way to utilize a new technique, GCxGC, as a powerful visual correlation tool, for showing changes in all the important diagnostic compounds and the processes affecting them in a single oil at one time. The new GCxGC results compare favorably with more labor intensive and less intuitively obvious ion extraction fragmentogram procedures used previously. Work was initiated on similar studies in shallower gas and oil seeps in the Santa Barbara channel and offshore California.

WRIGHT STATE UNIVERSITY
Department of Chemistry
Dayton OH 45435

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

Steven R. Higgins, 937-775-2479, steven.higgins@wright.edu

This project has focused on experimental investigations on the nanoscale chemistry and dynamics of carbonate mineral surfaces exposed to aqueous solutions. Mineral growth research of carbonates emphasized image formation mechanisms during the mineralization process at the nanometer scale through Lateral Force Microscopy (LFM) and the relationship between the LFM signal and the surface composition through synchrotron x-ray reflectivity experiments performed at Argonne National Laboratory. Earlier work on dolomite surface chemistry revealed self-limiting film growth behavior, via *in-situ* atomic force microscopy (AFM) investigations, that was attributed to strain-limited epitaxial growth of a non-dolomitic phase. X-ray reflectivity investigations lead to a detailed model for the dolomite/film/aqueous solution interfacial region. This model reveals significant calcium surface enrichment (~200% excess over magnesium) in supersaturated solutions containing comparable magnesium and calcium concentration. Furthermore, the model showed significant film strain, confirming the predictions from the AFM investigations. In the LFM investigations, the Ca/Mg composition of the film was found to influence the friction between the AFM tip and sample surface, consistent with a compositional correlation with film strain. The results showed that Mg-rich films generally displayed lower friction than Ca-rich films, leading to the hypothesis that cation size correlates with the observed friction force. The hypothesis was further tested using calcite substrates as a template for film growth of impure calcite containing Cd and Sr ions. In both of these investigations, the friction signal was generally higher on the impure phase than the pure calcite, showing that the incorporation of the smaller Cd ion into calcite does not decrease friction as proposed. The current working hypothesis is directed toward testing a film strain base mechanism for friction contrast. The outcomes of these investigations will provide a more detailed model for carbonate-water interfaces, particularly in supersaturated solutions, and will also advance the science of surface imaging at nanometer distance scales with improved understanding of the relationships between interface composition and tip-surface interaction forces.

UNIVERSITY OF WYOMING
Department of Geology and Geophysics
Laramie WY 82071

Multiscale Reactive Transport in Processes Related to CO$_2$ Sequestration: Nanoscale Dynamics, Upscaling, and Non-Steady State Kinetics

Carrick M. Eggleston, 307-766-6769; Fax: 307-766-6679, carrick@uwyo.edu

Previously, we described progress on the mineral hematite and its dissolution characteristics because it represents a material that is chemically simpler than multicomponent oxide minerals such as feldspars. Although the potential for redox activity introduces complications, the fact that hematite can be doped as (most commonly) an n-type semiconductor means that processes at the hematite surface can be addressed electrochemically, to the extent of probing surface potentials and capacitances that are inaccessible with other (insulating) minerals. Thus, we have emphasized the use of hematite as an electrode. Work with hematite has also continued because of its importance as a photocatalyst in solar water splitting. Appropriately doped hematite has the ability to photolyze water and, coupled to another photocatalyst, participate in the production of hydrogen fuels. We have completed a set of studies designed to locate the flatband potential of hematite films grown by ultrasonic spray pyrolysis and chemical vapor deposition. In one set of experiments, we used the scan-rate dependence of capacitive currents in cyclic voltammetry to quantify space-charge layer capacitance as a function of potential and thus form a Mott-Schottky plot. We confirmed these results using both transient and steady-state photocurrent onset potential. Because the hematite photocatalysts are frequently operated at extremely high pH, we have investigated the dissolution characteristics of hematite at high pH. Finally, we have measured anisotropy in photocurrents – and found that, in keeping with the known antiferromagnetic structure of hematite and low conductivity parallel to the [001] direction, photocurrent densities were much high on crystal planes parallel to the [001] direction. Photocurrent densities were as high as 1 mA cm^{-2} on (110) in AM 1.5 simulated sunlight (Xe lamp), suggesting that nanocrystalline films with high surface area could produce several mA cm^{-2}. These findings have both energy-technology implications in solar energy utilization, and implications for the geochemistry of the early Earth. We are starting to investigate ways to couple a hematite photocatalyst to a suitable photocatalyst for carbonate reduction, such as MnS, for a novel carbon sequestration approach.

YALE UNIVERSITY
Department of Geology and Geophysics
New Haven CT 06520

Grant: DE-FG02-01ER15173

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

Robert A. Berner, 203-432-3183, Fax 203-432-3134, robert.berner@yale.edu

During the year 2004-2005 we worked on the following topics:

1. A field study of the effects of angiosperms vs gymnosperms on silicate weathering is being conducted at the Yale Myers Forest in Connecticut. Petrographic and electron microprobe analyses have revealed weathering along fractures, especially along those inhabited by roots.

2. An experimental plant-weathering system has been constructed in the laboratory to complement the field studies. Gymnosperm and angiosperm seedlings/saplings are grown in deep soil-filled clear Plexiglas containers which can be sampled via ports along the sides. The "soil" is a mixture of clear plastic spheres in clear phytagel mixed with Hoagland's nutrient solution. This arrangement allows for viewing of root development and contact with minerals. Selected granitic and basaltic minerals are mixed into the "soil" for later study for incipient etching as a result of plant-induced weathering.

3. We continued computer modeling of the oxidation of organic matter and pyrite in black shales. To aid the modeling measurements were made on an organic-rich Devonian shale. This included SEM photomicrographs of the organic matter texture, permeability and porosity measurements, BET surface area, and determinations of the concentrations of organic carbon and nitrogen, and sulfur and their changes with depth. We are now concentrating on the inclusion of the kinetics of pyrite oxidation, as it relates to organic matter oxidation, in the modeling.

4. A theoretical model (Berner and Beerling, 2005) was constructed to try to explain why there is a relative lack of calcium carbonate deposition at the Triassic-Jurassic extinction boundary. The hypothesis, that degassing of vast amounts of CO_2 and SO_2 by volcanism could have made the ocean sufficiently acidic to inhibit carbonate formation, was tested.

YALE UNIVERSITY
Department of Geology and Geophysics
New Haven CT 06520

Grant: DE-FG02-01ER15216

Integrated Studies of Coupled Flow, Reaction, and Diffusion in Earth's Crust

Danny Rye, danny.rye@yale.edu

Objectives:
To improve our understanding of crustal processes of fluid / rock interaction through an integration of modeling, field observations, and laboratory analysis; to develop new conceptual and computational models of coupled fluid flow and chemical reactions of geologic environments; to collect and interpret stable isotopic and geochemical field data at many spatial scales.

Project Description:
We combined field, modeling, and laboratory isotopic and chemical measurements to quantify flow, diffusion, and reaction in Earth's crust, with a focus on fractures and flow in low-permeability rocks.

Results:
Field-based and modeling studies of the interaction of fluids and crustal rocks provide important new constraints on crustal mass transfer and reaction kinetics within low permeability rocks. Morphological variations in metamorphic garnets indicate substantial deviations from chemical equilibrium during mineral nucleation and growth. Field and modeling studies of metamorphosed carbonate rocks, Connecticut, show that crustal fluids mobilize a wide variety of elements, including the rare earths. In these rocks, lithologic contacts and fractures were primary flow conduits, consistent with field-modeling results for the subduction complex on Tinos, Greece. Oxygen and carbon isotopic results from interbedded carbonates and shales from shallow-crustal rocks of the Conasauga Group indicate, during deformation, fracture flow and local derivation of fluids in shales and introduction of fluids from shales into the fracture network of the carbonates. Halogen ratios from fluid inclusions indicate that ore fluids in the Irish Zn-Pb deposits were derived from deeply circulated seawater. A new online technique to measure oxygen isotopes in silicates is under development, using Teflon tape or CF in a TC-EA, with encouraging initial results. Modeling of kinetically controlled metamorphic reactions in siliceous carbonate rocks in two dimensions shows that kinetics can cause significant deviation from traditionally accepted reaction pathways. Kinetic effects due to mineral surface areas can lead to the selection of either reaction or buoyancy driven fluid flow styles. Diffusion modeling of high-temperature metamorphic and igneous sequences indicates significant kinetic effects on trace element distribution. Modeling of weathering and erosion of black shales shows little feedback between atmospheric oxygen levels and oxidation of organic matter and pyrite.

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

ON-SITE INSTITUTION	FY01	FY02	FY03	FY04	FY05
Argonne National Laboratory	552	530	445	480	535
Idaho National Laboratory				50	50
Los Alamos National Laboratory	1235	1189	1353	1409	1320
Lawrence Berkeley National Laboratory	2367	2570	2045	2758	3240
Lawrence Livermore National Laboratory	1784	1644	1523	1598	1335
Oak Ridge Institute for Science and Education	30				
Oak Ridge National Laboratory	1293	1340	1190	1250	2075
Pacific Northwest Laboratory	727	822	875	920	860
Sandia National Laboratory	1367	1470	1355	1274	980
total, on-site published	9624	9565	8786	9739	10395
total, off-site published	10393	10487	10513	10410	10492
total, operating published	20017	20052	19299	20149	20887
total, equipment	1402	1200	1023		
Total GEOSCIENCES-published	21419	21252	20322	20149	20877
OFF-SITE INSTITUTION					
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)	102	105	108	133	132
Boston Univ. (Klein)	122	127	132	126	130
Caltech (Stolper)	150	150	156	162	

Caltech (Wasserburg)	225		225	215	200
Calif., Univ. of Berkeley (Banfield)					200
Calif., Univ. of Berkeley (Banfield)	178			150	153
Calif., Univ. of Berkeley (Helgeson)	179	182	164	163	167
Calif., Univ. of Berkeley (Wenk)					150
Calif., Univ. of Berkeley (Nishiizumi)	144				
Calif., Univ. of Berkeley (Sposito)	74				
Calif., Univ. of Davis (Rock)	161	163	171		
Calif., Univ. of Davis (Navrotsky)	166	166	198	202	194
Calif., Univ. of Davis (Rustad)					78
Calif., Univ. of Davis (Rustad)				97	136
Calif., Univ. of Davis (Casey)	72	178	109	113	319
Calif., Univ. of Davis (Rundle)			141	135	143
Calif., Univ. of Los Angeles (Harrison/McKeegan)	130	132	135	148	79
Calif., Univ. of Santa Barbara (Meiburg)		68	66		
Calif., Univ. of Santa Barbara (Boles)	79	71	78	86	79
Calif., Univ. of Santa Cruz (Wu)	299	308	388	306	318
Calif., Univ. of San Diego (Weare)		125	125	125	
Chicago, Univ. of (Sutton/Rivers)	500	525	550	575	600
Chicago, Univ. of (Sutton)	148	129		143	125
Chicago, Univ. of (Richter)	96		99	102	138
Clark Univ. (Kudrolli)		45	45	47	
Colorado School of Mines (Klusman)		161			
Colorado School of Mines (Batzle)			140	117	114
Colorado School of Mines (Tsvankin)	230		239	249	150
Colorado, Univ. of (Rajaram)	54	106	70	72	
Colorado, Univ. of (Rundle)	130	136			

Colorado, Univ. of (Spetzler)	185	153	143	155	55
Colorado, Univ. of (Ge)	94				
Colorado, Univ. of (Nagy)	62				
Connecticut, Univ. of (Torgersen)		27	35	33	
Delaware, Univ. of (Wood)	141		138	142	
Florida, Univ. of (Ladd)	83	111	89		155
George Washington Univ. (Teng)		143			98
George Washington Univ. (IPA Lesmes)				225	150
Georgia State Univ. (Elliott)		26	21		22
Gordon Res. Conf. (Kronenberg, Jessell)		10		10	
GSY-Inc. (Mackie)	46				
Harvard Univ. (Martin)			85	83	81
Hawaii, Univ. of (Martel)	108				
Houston, Univ. of (Weglein)					101
Idaho, Univ. of (Nicholl)	36	54			
Idaho, Univ. of (Wood)			10	10	10
Idaho State Univ. (Magnuson)					
Illinois, Univ. of (Kirkpatrick)		209	233	241	248
Illinois, Univ. of (Bethke)		117	214	92	270
Illinois, Univ. of Chicago (Sturchio)			59	60	62
Illinois, Univ. of Chicago (Nagy)		150		148	145
Indiana, Univ. of (Ortoleva)	117	120	124		
Indiana, Univ. of (Schimmelman)	78	84	119	112	119
Institute for Scientific Information (Zamojcin)		10			
Johns Hopkins Univ. (Garven)	78	75	89	80	88
Johns Hopkins Univ. (Veblen)	150	155	160	289	205
Johns Hopkins Univ. (Sverjensky)	90	140	140	137	153

	C1	C2	C3	C4	C5
Lehigh Univ. (Ilton)	115	115			
Louisiana State Univ. (White)	41		40	46	
Louisiana State Univ. (Dutrow)			9	9	9
Maryland, Univ. of (Lower)		20	67		
Maryland, Univ. of (Tossell)	59	63	79	99	99
Mass. Inst. Tech. (Harvey)	37	38			
Mass. Inst. Tech. (Toksoz)	240	240			
Mass. Inst. Tech. (Evans)	194	205	209	222	235
Mass. Inst. Tech. (Rothman)	133	152	158	160	
Massachusetts, Univ. of (Boutt)					145
Michigan Tech Univ. (Turpening)	165	11	114		144
Mineralogical Society of America (Speer)	62	40	30	20	
Minnesota, Univ. of (Yuen)	90	90			
Minnesota, Univ. of (Kohlstedt)				38	39
NAS/NRC (Schiffries/DeSouza)	90	90		90	90
NAS (Wessner)		114			
NAS (Linn)					200
Nevada, Univ. of (EPSCOR - McCall)	8	9	6		
New England Res. (Brown)		204	199	206	100
New Mexico Inst. Min. Tech. (Wilson)	65	94	101	108	
New Mexico, Univ. of (Ingber)	71	71			
NY, City Univ. of CC (Koplik)	90	95	98	102	
NY, City Univ. of CC (Makse)			85	85	
NY, State Univ. of Stony Brook (Schoonen)	60	102	65	66	
NY, State Univ. of Stony Brook (Wong)	95		120	124	128
NY, State Univ. of Stony Brook (Lindquist)	67	64	64		64
North Texas, Univ. of (Bagus)				35	35

Northwestern Univ. (Rudnicki)	88	91	120	118	123
Northwestern Univ. (Geiger)					3
Notre Dame, Univ. of (Maurice)	70	121	174	178	
Notre Dame, Univ. of (Maurice)				6	
Ohio State Univ. (Lower)				71	
Ohio State Univ. (Allen)				41	42
Oklahoma, Univ. of (Elmore)	124	102	103		47
Oregon State Univ. (Haggerty)	68	75			
Oregon State Univ. (Egbert)		80	89	86	
Penn State Univ. (Elsworth)		99	98		
Penn State Univ. (Brantley)	147	160	145		174
Penn State Univ. (Brantley)				9	
Princeton Univ. (Myneni)	102	102			
Princeton Univ. (Peters)					114
Purdue Univ. (Pyrak-Nolte)	85	102	105	109	
Renesselaer Polytech. Inst. (Newell)		44	45	47	
Renesselaer Polytech. Inst. (Watson)	198	199	199	247	208
San Diego State Univ. (Jiracek)		5			
South Carolina, Univ. of (Wilson)				50	54
Southern California, Univ. of (Maxworthy)		82	84		
Stanford Univ. (Mavko)	104	151	149	150	
Stanford Univ. (Borja)			99		99
Stanford Univ (Knight)			143	139	146
Stanford Univ. (Nur)	200	200	200	208	217
Stanford Univ. (Pollard/Aydin)	260	257	267	261	261
Stanford Univ. (Segall)	100				
Temple Univ. (Strongin)	60	83	87	91	

Tennessee, Univ. of (Thonnard)	122	129	146		
Texas A&M Univ. (Kronenberg)		65			
Texas A&M Univ. (Morse)		128	130	133	135
Texas A&M Univ. (Datta-Gupta)		111	130	138	140
Texas, Univ. of (Katz)				71	75
Texas, Univ. of (Laubach)			196		227
Texas, Univ. of Dallas (McMechan/Bhattacharya)	262		95	96	
Texas Tech Univ. (Graham)	90	90	9		
Utah, Univ. of (Forster)	50	50			
Utah, Univ. of (Tripp)	77				
Utah State Univ. (Evans)	85	85			
Virginia Tech (Rimstidt)			114	118	124
Virginia Tech (Dove)		121	126		178
Virginia Tech (Hochella)	66	88		104	98
Washington, Univ. of (Unsworth/Booker)	95				
Washington Univ., St. Louis (Shock)	196				
Wisconsin, Univ. of (Alumbaugh)	52		101	96	
Wisconsin, Univ. of (Haimson)	107	110	106		
Wisconsin, Univ. of (Goodwin)					108
Wisconsin, Univ. of (Valley)		168		204	210
Woods Hole OI (Whelan)	180	197	206	204	
Woods Hole OI (Zhu)	43	44	46	48	50
Woods Hole OI (Seewald)	120			179	177
Wright State Univ. (Higgins)			70	71	73
Wyoming, Univ. of (Eggleston)	85	85	52	45	46
Yale Univ. (Rye/Bolton/Ague)	300	326	327		157
Yale Univ. (Wettlaufer)					115

Yale Univ. (Berner)	109	110	110	130	130
Other	559	124			
OFF-SITE TOTALS	10393	10487	10513	10410	10492